PROCEEDINGS SERIES

THERMODYNAMICS

PROCEEDINGS OF THE SYMPOSIUM ON THERMODYNAMICS WITH EMPHASIS ON NUCLEAR MATERIALS AND ATOMIC TRANSPORT IN SOLIDS ORGANIZED BY THE INTERNATIONAL ATOMIC ENERGY AGENCY IN CO-OPERATION WITH THE COMMISSION ON THERMODYNAMICS AND THERMOCHEMISTRY OF THE INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY AND HELD IN VIENNA, 22-27 JULY 1965

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Knowledge of the thermodynamics of nuclear materials is vital to the design of reactor fuels and moderating and cooling systems, in fact all facets of nuclear plant operation that involve mixtures of, or contact between, two or more elements in single- or multi-phase systems. The steep thermal gradients and the high temperatures involved in nuclear technology pose special problems for engineers and thermodynamicists, who have found that extrapolation of low-temperature data to high temperatures very often proves invalid. For this reason, standard thermodynamic techniques such as calorimetry and EMF-methods have been extended into high-temperature regions.

Since the Agency's last conference on this subject, also held in Vienna (Thermodynamics of Nuclear Materials, 1962), there have been notable advances in calorimetry performed at temperatures greater than 1000°C, and in the use of EMF cells with solid electrolytes operated at similar temperatures. Significant advances have also been made in measuring diffusion parameters at the higher temperatures.

An important field covered in this Symposium was the correlation of such atomic transport data with thermodynamic data, a prerequisite if the nuclear engineer is to incorporate diffusion results into his normal process-assessment techniques.

Finally the Symposium suggested the requirements for good critical tables. The mere compiling of such data is no longer sufficient; the compiler must have free access to all the data of a particular experiment, he must have an intimate knowledge of experimental work in this field and he must weight every figure quoted in the light of his experience. As a step in this direction, the Agency has called on the services of many well-known experts and is preparing a number of monographs giving critical assessments of thermodynamic data and phase-diagrams for many of the elements of interest in reactor design.

Most of the countries engaged in research in thermodynamics were represented at the meeting, which was held in co-operation with the Commission on Thermodynamics and Thermochemistry of the International Union of Pure and Applied Chemistry.
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INTRODUCTORY LECTURE
Introductory comment.

I should like to make one comment on Dr. Roberts' paper. For many years thermochemists have felt that it is necessary to get accurate data on single compounds, on the elements and their compounds. In spite of this, there are still vast gaps in the information that thermodynamics and thermochemistry have provided on single compounds, and now Dr. Roberts has convinced me that this is not even the starting point for the problems of real technology. We must move into the field of mixtures, binary mixtures, ternary mixtures, and solid solutions, for example. We have in fact only barely begun the work which must be done.
THERMOCHEMISTRY AND NUCLEAR ENGINEERING

M.H. RAND AND L.E.J. ROBERTS

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, BERKS., ENGLAND

Abstract — Résumé — Аннотация — Resumen

THERMOCHEMISTRY AND NUCLEAR ENGINEERING. Thermochemical data is of value to the nuclear engineer engaged in the preparation of special materials, the design and operation of reactors or the processing of irradiated fuels, both as a tool for the prediction of behaviour and as a framework within which results can be correlated. Most of the present reactor types involve the use of solid fissile and fertile metals, compounds or alloys. These may be in the form of rods or plates surrounded by a metal can, or dispersed in a cermet or coated with an impermeable skin. Accurate phase diagrams are required as well as a complete knowledge of equilibria at high temperatures; this task is complicated by the wide ranges of stoichiometry that occur in some of the phase diagrams at high temperatures, and by the profound effects of comparatively small amounts of impurity on the phase stability. Examples are drawn from recent work on the oxides and carbides and hydrides, and the gaps in our knowledge of these and other systems are assessed.

The lifetime of a fuel is often limited by the chemical and physical changes that occur on irradiation. The direct effects due to irradiation anneal out at high temperatures, but the composition of the fuel changes due to fission. The migration and distribution of fission products depend on their chemical nature and on their behaviour in a steep temperature gradient. A start has been made on the analysis of this situation by thermochemical arguments but much more data is required. The use of fluid fuels - either liquid metals or fused salts - requires a very complete knowledge of their thermochemistry. Again, the effects of temperature gradients and of the change in composition as fission proceeds have to be taken into account. Equilibria in liquid metal and fused salt systems also form the basis for a number of methods of separating fissile elements and fission products by rapid processes carried out at high temperatures.

Compatibility problems between structural materials, moderators, control rods and coolants also have to be considered. Many of the components of a reactor core have to last throughout the life of a reactor, 20 years or more. Problems may arise due to the precipitation of impurity phases and of mass transfer down temperature gradients; these may be assessed by thermochemical calculations. The temperatures of operation of these materials are often low enough for considerable radiation damage to occur, and transmutation effects may be appreciable over long periods. The effects of such changes on thermochemical properties is another challenging field.

THERMOCHEMIE ET GENIE NUCLEAIRE. Les constantes thermochimiques sont importantes pour l'ingénieur spécialisé dans la préparation de matériaux spéciaux pour l'industrie nucléaire, l'étude et le fonctionnement des réacteurs ou le traitement des combustibles irradiés; elles fournissent à la fois le moyen de prévoir le comportement des diverses matières et le cadre nécessaire pour la comparaison des résultats obtenus. La plupart des filières actuelles comportent l'emploi de métaux, composés ou alliages, fissiles et fertiles, solides. Ces matériaux peuvent se présenter sous la forme de barreaux ou de plaques gainés de métal, ou de dispersions dans un cermet; ils peuvent aussi être revêtus d'une couche imperméable. Il est indispensable d'établir des diagrammes de phases précis et d'acquérir une connaissance complète des équilibres à haute température; cette tâche est rendue complexe par les grands intervalles stœchiométriques qui apparaissent dans certains diagrammes de phases à haute température, et par les effets profonds que des quantités d'impuretés relativement faibles exercent sur la stabilité des phases. Les auteurs donnent des exemples empruntés à des études récentes sur les oxydes, les carbures et les hydrures; ils évaluent les lacunes que comportent nos connaissances sur ces systèmes et sur d'autres systèmes.

La durée de vie utile d'un combustible est souvent limitée par les modifications chimiques et physiques dues à l'irradiation. Les effets directs de l'irradiation disparaissent à haute température, mais la fission fait varier la composition du combustible. La migration et la distribution des produits de fission dépendent de la nature chimique de ces produits et de leur comportement en présence d'un fort gradient de température. On a fait une première tentative pour analyser cet état de choses par des raisonnements thermochimiques, mais il
faudrait disposer de valeurs numériques bien plus nombreuses. L’emploi de combustibles fluides, métaux liquides ou sels fondus, exige une connaissance très complète des valeurs de leurs constantes thermochimiques. À encore il faut tenir compte des effets des gradients de température et des changements de composition dus au détournement du processus de fission. Les équilibrages des systèmes de métal liquide et de sel fondu constituent également la base de plusieurs méthodes de séparation des éléments fissiles et des produits de fission par des traitements rapides à haute température.

Il convient également d’examiner les questions de compatibilité entre matériaux de construction, talienséteurs, barres de commande et fluide de refroidissement. De nombreuses parties constitutives d’un cœur doivent subir pendant toute la durée de vie du réacteur, soit une vingtaine d’années ou davantage. Des difficultés peuvent surgir du fait de la précipitation de phases d’impuretés ou d’un transfert de masse selon des gradients de température décroissants; il est possible de les évaluer par des calculs thermochimiques. Les températures de travail de ces matériaux sont souvent suffisamment basses pour qu’il se produise de graves dommages radioinduits et les effets de transmutation à long terme peuvent être appréciables. Les effets de ces modifications sur les propriétés thermochimiques sont un autre domaine ouvert à la sagacité des chercheurs.

**TERMOXHIMIA Y YEĐERNA TÉHNIKA.** Termoхимические данные представляют ценность для инженера - ядерника, занимающегося изготовлением специальных материалов, конструированием и эксплуатацией реакторов или переработкой облученного топлива, как основа для предсказания поведения этих материалов и как пределы, в которых может быть установлена корреляция результатов. Большинство существующих типов реакторов связано с использованием твердых расширяющихся и воспроизводящихся металлов, соединений или сплавов. Они могут быть в виде стержней или пластин с металлическим покрытием, могут быть диспергированы в кермете или покрыты герметической оболочкой. Необходимо иметь точные фазовые диаграммы, а также все данные о равновесиях при высоких температурах; эта задача усложняется существованием широких диапазонов стехиометрии в некоторых фазовых диаграммах при высоких температурах и сильным влиянием сравнительно небольших количеств примесей на фазовую устойчивость. Приводятся примеры из последней работы с окислами, карбидами и гидридами и указываются пробелы в наших знаниях в отношении этих и других систем.

Продолжительность службы топлива зависит часто от химических и физических изменений, происходящих при облучении. Непосредственные эффекты как результат облучения отживаются при высоких температурах, однако состав топлива меняется в результате деления. Миграция и распределение продуктов деления зависят от их химической природы и их поведения при крутых температурных градиентах. Положено начало анализу этого с позиций термохимии, но для этого требуется значительно больше данных. Использование жидкого топлива, жидких металлов или расплавленных солей, требует знания их подробных термических характеристик. Кроме того, необходимо учитывать влияние температурных градиентов и изменений состава при делении. Равновесия в системах жидких металлов и расплавленных солей также лежат в основе ряда методов разделения расщепляющихся элементов и продуктов деления с помощью быстрых процессов, осуществляемых при высоких температурах.

Следует также рассмотреть проблемы совместимости конструкционных материалов, замедлителей, регулирующих стержней и теплоносителей. Многие из компонентов активной зоны реактора должны работать в течение всего срока службы реактора, т.е. в течение 20 лет или более. Могут возникнуть проблемы в связи с осаждением примесных фаз и переносом массы ниже температурных градиентов. Они могут быть решены с помощью термомеханических расчетов. Температуры, при которых используются эти материалы, часто довольно низки, чтобы вызывать значительные радиационные повреждения. Эффекты трансмутации могут быть ощутимыми в течение длительного периода времени. Другой областью, требующей к себе внимания, является влияние таких изменений на термохимические свойства.

**TERMOQUIMICA E INGENIERIA NUCLEAR.** Los datos termoquímicos presentan un valor para el ingeniero nuclear dedicado a la preparación de materiales especiales, al proyecto y manejo de reactores o al tratamiento de combustibles irradiados, tanto como herramienta para predecir comportamientos cuanto como marco que permita correlacionar los resultados. La mayoría de los tipos actuales de reactor implican el uso de metales, compuestos o aleaciones sólidas, fisionables y fétiles. Estos materiales pueden tener la forma de barras o placas rodeadas de una vaina metálica, estar dispuestos en un ceramet o recubiertos con una envoltura impermeable. Se necesita contar con diagramas de fase precisos y también con un conocimiento completo de los equilibrios a altas temperaturas; complican esta tarea los amplios intervalos estequiométricos que aparecen en alguno de los diagramas de fase a altas temperaturas y los profundos efectos que sobre la estabilidad de las fases ejercen cantidades relativamente pequeñas de impurezas. La memoria presenta ejemplos tomados de
trabajos recientes sobre óxidos, carburos e híbridos, y evalúa las soluciones de continuidad existentes en nuestro conocimiento sobre estos y otros sistemas.

Los cambios químicos y físicos debidos a la irradiación limitan a menudo la vida útil del combustible. Los efectos directos de la irradiación se compensan a altas temperaturas, pero la composición del combustible cambia como resultado de la fisión. La migración y distribución de los productos de fisión depende de su naturaleza química y de su comportamiento en un gradiente de temperatura muy empinado. Se ha iniciado el análisis de esta situación mediante razonamientos termodinámicos, pero se necesita aún mayor cantidad de datos. El uso de combustibles líquidos, ya sea metales líquidos o sales fundidas, exige un conocimiento muy completo de sus propiedades termoquímicas. Asimismo, es necesario tener en cuenta los efectos de los gradientes de temperatura y de los cambios de composición debidos al avance de la fisión. Los equilibrios en sistemas de metal líquido y de sales fundidas constituyen también la base para una serie de métodos de separación de elementos fisionables y productos de fisión mediante procesos rápidos desarrollados a altas temperaturas.

También es necesario considerar problemas de compatibilidad entre materiales estructurales, moderadores, barras de control y refrigerantes. Muchos componentes del núcleo de un reactor deben durar toda la vida de éste, es decir, 20 años o aún más. Pueden surgir problemas debidos a la precipitación de fases de impurezas y a las transferencias de masas según los gradientes de temperatura; estos fenómenos pueden evaluarse mediante cálculos termodinámicos. Las temperaturas de trabajo de estos materiales son a menudo suficientemente bajas para que se produzcan considerables daños por radiación, y los efectos de transmutación pueden ser apreciables durante periodos prolongados. Los efectos de estos cambios sobre las propiedades termoquímicas constituyen otro campo que se abre al investigador.

We attempt to summarize in this paper the application of thermochemical data and concepts to the various practical problems that arise in the development of nuclear power for civilian uses. The most valuable application is to the prediction of the stability of phases in temperature gradients and on temperature cycling, and of the compatibility of materials; it is frequently possible to choose the combination of materials most likely to be stable on the basis of thermochemical arguments and to concentrate experimental work on those areas likely to be profitable or of key importance. Even where the data are not complete enough to allow of confident prediction, the analysis of experimental data by the application of thermodynamic concepts is often a valuable step in assessing the reliability of extrapolation to practical conditions.

The chemist in the nuclear power industry is concerned with (i) the chemical stability and compatibility of materials used in the various designs of nuclear reactors, (ii) the specification and production of these materials and (iii) the separation of valuable fissile and fertile materials from fission products. The behaviour of materials in reactors is complicated by radiation and transmutation effects and it is always necessary to remember the steep temperature gradients which are an inescapable feature of reactor design. Since it is often necessary to guarantee the behaviour of materials over long periods, owing to the limited possibilities of inspection and maintenance of nuclear plants, the effects of minor constituents present as impurities or as transmutation products are very important.

The range of materials problems in the nuclear energy industry as a whole is very wide. The most common materials used or under study in the various types of nuclear reactor are shown in the list below.

Solid Fuels
- Uranium metal and alloys
- High melting compounds - UO₂, UC, UN, US, UP
- Pu enrichment - ~2% for thermal reactors
- ~20% for fast reactors
Fuel cladding: Mg, Al, Be, Zr alloys, stainless steels
Fuel coatings: C, SiC, Al₂O₃
Dispersed Fuels: Cermets – UO₂ in steels; UO₂ in W, etc.
                – UC₂ in C; UO₂ in BeO; UC in SiC
Coolant: H₂O, D₂O, CO₂, He, Na, Na-K, Pb
Fertile Materials: ThO₂, ThC₂ – often in solid solutions
Liquid Fuels: UF₄ in LiF–BeF₂ (ThF₄ in LiF–BeF₂ as fertile material)
              PuCl₃ in NaCl–KCl
Control Materials: Boron alloys and B₄C; cadmium alloys; rare earth alloys and oxides
Structural Materials: Austenitic and ferritic steels; graphite; special alloys
Moderators: Graphite, BeO, H₂O, D₂O

Uranium fuels, either natural or enriched with a few percent of ²³⁵U
or ²³⁹Pu, are used in most types of thermal reactor and the other materials
are chosen so as to minimize parasitic neutron absorption. The use of thin
stainless-steel cladding is permissible in gas-cooled thermal reactors;
zirconium or Zr-alloys have to be used in water-cooled reactors because of
better corrosion resistance. The range of choice of materials for use in
fast reactors is far broader because of the more uniform values of neutron
absorption cross-sections at high energies. The use of dispersed fuels is
common in highly rated reactors, where it is usual to use highly enriched
fuel, but to mix fertile and fissile material in order to achieve reasonably
long periods of fuel irradiation; thus a HTR reactor of the 'Dragon' type uses
particles of (U, Th)C₂ dispersed in the graphite moderator, each particle
being coated with pyrocarbon to limit the spread of fission products.

It is quite impossible in a short survey to deal with all the individual
problems; many of them are discussed in other papers to this Symposium.
We shall concentrate on a few examples that have attracted a lot of attention,
or which seem to us to be typical of the type of thermochemical work which
is required. First of all, it is necessary to have fairly complete knowledge
of the thermochemistry of the major compounds of elements of particular
relevance to the industry — we may include U, Pu, Th, Be, Zr and refractory
metals in this list. Gaps in our knowledge of uranium and plutonium thermo-
chemistry have been pointed out by one of us [M.H. Rand] in other papers.¹

Phase Diagrams

A very large effort has been expended in determining accurate phase
diagrams for all classes of compounds; such information is vital for pre-
dicting the limits between which different materials can be used, and for

¹ RAND, M.H., KUBASCHEWSKI, O., The Thermochemical Properties of Uranium Compounds,
   RAND, M.H., "Some inconsistencies in the thermodynamic data for uranium compounds", Thermodynamics
   of Nuclear Materials, IAEA, Vienna (1962) 71-81.
   RAND, M.H., "Thermochemical properties", Plutonium; Physico-Chemical Properties of its
production control. The determinations of phase diagrams and solubilities have received the major portion of the thermochemical effort expended on the solid alloy systems.

Much of this research has been stimulated by the search for phases which are stable under irradiation conditions. The effects of irradiation may be divided into two types:

(i) Radiation damage results from the passage through a crystal lattice of highly charged particles moving at high speeds, causing local ionization and the displacement of atoms or ions from their normal lattice sites. The residual permanent damage depends on the rate at which the displaced atoms can return to their original sites, which is a function of the type of lattice and of the temperature. This type of damage tends to a saturation limit at a certain dose level.

(ii) Transmutation effects arise because of the introduction into the crystal lattice of foreign atoms; the most important of these are the rare gases, which are insoluble in almost all solids. Atoms of krypton and xenon are produced during fission and tend to congregate into bubbles, if the temperature is high enough to permit migration, causing distortion and swelling of the matrix material. These effects are cumulative, increasing as the irradiation dose increases.

Both uranium and plutonium exist in a number of crystallographic forms, with the ranges of stability summarized below:

<table>
<thead>
<tr>
<th>Uranium</th>
<th>Plutonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) R.T. – 668°C</td>
<td>( \alpha ) R.T. – 122°C</td>
</tr>
<tr>
<td>( \beta ) 668 – 775°C</td>
<td>( \beta ) 122 – 205°C</td>
</tr>
<tr>
<td>( \gamma ) 775 – 1132°C</td>
<td>( \gamma ) 205 – 318°C</td>
</tr>
<tr>
<td>( \delta ) 318 – 452°C</td>
<td>( \delta' ) 452 – 476°C</td>
</tr>
<tr>
<td>( \epsilon ) 476 – 640°C</td>
<td></td>
</tr>
</tbody>
</table>

The occurrence of the \( \alpha \rightarrow \beta \) transformation in uranium at 668°C, with a considerable decrease in density, is a major limitation on the use of uranium metal as a nuclear fuel. A further complication is the anisotropic swelling suffered by \( \alpha \)-uranium during irradiation. The crystal structure of \( \alpha \)-uranium is unique and highly anisotropic, approximating to a layer structure, and the coefficient of thermal expansion depends strongly on the crystallographic direction. In common with other crystals with these properties, a crystal of \( \alpha \)-uranium expands more in one direction than another as atoms are displaced into interstitial positions during irradiation at temperatures below about 500°C [1].

\( \gamma \)-uranium has a simple cubic structure which can be quenched to room temperature by alloying with molybdenum. This is not the thermodynamically stable state of U-Mo alloys at temperatures below 570°C, as may be seen from a portion of the phase diagram reproduced in Fig. 1 [2], and these alloys undergo a phase transformation to the stable \( \alpha + \delta \) configuration on irradiation at temperatures between 480°C and 570°C at low fission rates. At high fission rates and low temperatures, however, the \( \alpha + \delta \) structure reverts to the \( \gamma \)-phase, and the fuel is relatively stable [3]. We see here one example
FIG. 1. The system uranium-molybdenum

of a common result of irradiation — the formation, at low nominal temperatures, of a structure that is thermodynamically stable only at high temperatures.

The preferred method of minimizing the effects of irradiation damage in uranium metal fuels is to control the grain size and grain orientation of uranium metal by appropriate annealing and quenching treatment. There remains the cumulative damage due to transmutation — the rising concen-
tration of xenon and krypton gases as fission proceeds. At reactor operating temperatures, the atoms tend to precipitate to form bubbles and these cause irradiation swelling. The mechanism of movement of helium bubbles in copper has been shown by Barnes and Mazey [4] to be due to the surface diffusion of metal atoms around the surface of a gas bubble under the influence of a strong temperature gradient. It is possible that some driving force exists in uranium fuels which causes small gas bubbles to migrate and eventually coalesce; it is an experimental fact that serious swelling occurs when the gas bubbles increase in size. The fuel designer therefore has to try to retain the rare gases in the maximum number of bubbles of the minimum size, to restrict their migration and prevent grain growth by recrystallization.

Solubility and phase diagram data have been exploited to these ends. The unique crystal structures of α and β-uranium result in the formation of very few solid solution ranges, but a variety of intermetallic compounds are formed. This seems to be the reason for the marked effect of certain impurities on the irradiation swelling properties. The single element which has the greatest effect of a number that were tried was aluminium, and the effect was slightly enhanced by iron and carbon [5]. The heat treatment was important: it was necessary to quench from the beta phase and anneal in the alpha phase; the aluminium and iron dissolve in the β-phase but are re-precipitated during alpha-annealing as $\text{UAl}_2$ and $\text{U}_6\text{Fe}$, finely dispersed on the grain boundaries and within the grains. These precipitates act as nucleation centres and prevent bubble migration by "anchoring" a proportion of them.

We may note that little is known about the thermodynamics of the solid alloy systems, except the phase diagrams, although a considerable amount of data exists on the activities of uranium in liquid alloys.

HIGH TEMPERATURE EQUILIBRIA

The failure of solid metal fuels to operate at high fission rates or at high temperatures has led to a large amount of work on alternative fuels. The ideal fuel material has a high melting point, with a structure of high symmetry that undergoes no phase transformations over a wide temperature range. These conditions are satisfied by several compounds of uranium and plutonium — notably the dioxides, the mono-carbides, nitrides, sulphides and phosphides. Other compounds, notably the higher carbides, are used in composite materials.

For economy of fuel assembly, fuel materials are usually used with as large a cross-sectional area as is practicable — i.e. with as high a centre temperature as the design will allow. This is often set by the desire to retain most of the fission gases within the solid, although operation with molten cores in vented fuel elements has been proposed in some designs. The materials are fabricated by a variety of techniques, including cold-pressing and sintering, with or without a sintering aid, hot-pressing and arc-casting, and fuels are in contact with a variety of materials during preparation and in use. As complete a knowledge as possible of equilibria at high temperatures, including vaporization processes, is therefore highly desirable.
The thermodynamic properties of the uranium dioxide phase were assessed at a panel convened by the IAEA in March 1964 [6] and the uranium-carbon and plutonium-carbon systems at another panel meeting in October 1962 [7]. The plutonium-oxygen system is the subject of another paper to this Symposium by Markin and Rand. Only the main features need be reviewed here.

The fluorite structure of UO₂ is remarkable for its ability to accommodate considerable quantities of oxygen in interstitial positions at high temperatures with only minor changes in the positions of the uranium atoms. The oxygen sub-lattice is extremely mobile and the high-temperature structures can be quenched only by taking extreme precautions. The thermodynamics of the UO₂+X region have been investigated by many techniques at temperatures up to 1500°C; there is very good agreement between the different methods except at values of X below 0.02. The phase diagram based on these results, and some crystallographic and electrical conductivity work at high temperatures, is shown in Fig. 2 with some oxygen isobars added. The U₄O₉ structure may be regarded as an ordered form of the UO₂+X structure and is again based on the fluorite structure, with a higher density than UO₂, as are the tetragonal oxides referred to as "γ₁" and "γ₂"; U₃O₈ has an orthorhombic structure of much lower density. Any excess oxygen in UO₂ will then cause phase precipitation on cooling, but no density decrease unless the compo-

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2 MARKIN, T.L., RAND, M.H., these Proceedings 1, SM-66/32, Session 2.
sition exceeds UO$_{2.25}$. Oxidation at low temperatures beyond UO$_{2.25}$ — for example, during the removal of carbonaceous binder added before pressing — should be avoided, since the formation of U$_3$O$_8$ on heating can shatter the compact.

PuO$_2$ does not absorb excess oxygen, except on the surface, but an oxygen deficient PuO$_{2-x}$ phase is stable above 650°C. PuO$_2$ and UO$_2$ can form a complete range of solid solutions, and these are important fuels for fast reactors. These solid solutions can absorb excess oxygen (by oxidation of U(IV)) and be reduced to MO$_{2-x}$ (by reduction of Pu(IV)). An oxygen-potential v. composition plot at one temperature is shown in Fig. 3 [8]. The
very steep rise in $\Delta G(O_2)$ as the stoichiometric composition is approached is mainly due to the big difference in the heat evolved on filling on oxygen lattice vacancy and in placing an extra oxygen on an interstitial site surrounded by a complete lattice. The absolute analysis of the oxygen metal ratio in (UPu)O$_{2x}$ is difficult; by reference to Fig. 3, it is reasonable to define the stoichiometric composition as that for which $\Delta G(O_2) = -103$ kcal at 850°C.

Values of the oxygen activities in a series of solid solutions of varying U/Pu ratio are in reasonable agreement if the composition is expressed as the mean oxidation number of the cation of varying valence - plutonium below MO$_{2,00}$ and uranium above MO$_{2,00}$. Fig. 4 is a plot of $\Delta G(O_2)$ against temperature for a number of compositions; also plotted in Fig. 4 are the oxygen potentials of some mixtures of H$_2$O/H$_2$ and CO/CO$_2$ [9]. Plotted in this way, the data are of immediate practical application. For example: (a) oxides reduced with fairly wet H$_2$ (H$_2$O/H$_2$ = 10$^{-2}$) are nearly stoichiometric at any temperature and can safely be cooled in this gas composition; (b) a 10/1, CO/CO$_2$ mixture becomes only slightly oxidizing towards stoichiometric solid solutions at high temperatures, while a mixture of 1% CO in CO$_2$ is more highly oxidizing above 1000°C but would not oxidize beyond a uranium valency of 4.002 at 500°C. Accurate control of composition is essential, since deviations from stoichiometry affect thermal conductivity, the rate of diffusion of fission gases and the chemical state of fission products - a topic mentioned later.

In practice, a large temperature gradient will exist from the centre to the outside of an operating fuel element. The distribution of oxygen in a dense mass of (U, Pu)O$_2$ in a temperature gradient cannot, of course, be calculated directly from these results; the problem should be attacked by the methods of non-equilibrium thermodynamics which are to be discussed in one section of this Symposium. However, redistribution of oxygen may well occur via the gaseous phase in a practical case, because of the system of cracks and pores formed in a fuel element due to thermal stresses. The atmosphere inside a fuel element usually contains some H$_2$ and CO or CO$_2$, and thus H$_2$O or CO$_2$ could act as oxygen carriers. In this case, the composition will tend to follow a line of constant H$_2$O/H$_2$ or CO/CO$_2$ ratio (Fig. 4) and a stoichiometric oxide will remain of nearly constant composition unless either the centre temperature is high enough to cause appreciable volatility effects or the material of the can acts as an oxygen getter.

The thermochemic data on oxide fuels at temperatures above 1500°C is not yet in a completely satisfactory state. It is certain that UO$_2$ can lose oxygen at these temperatures providing the conditions are sufficiently reducing and that the composition in equilibrium with uranium metal becomes UO$_{2-x}$, with x increasing as the temperature is raised. Results on UO$_{2-x}$ may have considerable application to the design of oxide fuel elements for very highly-rated reactors; running with molten cores has been proposed, with an inevitable increase in fission-product release, which might be accommodated by venting. Much new work on this problem will be reported to this Symposium and it is pointless to review previous work at this stage. Of immediate interest is the prediction of oxygen potentials at which some reduction of UO$_2$ would occur. Measurements at 2400°C give the value of $\Delta G(O_2)$ in
equilibrium with \( \frac{O}{U} = 1.99 \) as \(-100 \pm 5\) kcal [10]. Taking a value for \( \Delta S(O_2) \) from the work on \( \text{PuO}_2\_x \) reported to this Symposium by T.L. Markin, or from the data for \( \text{CeO}_2\_x \) [11], we calculate the \( -\Delta G(O_2) \) at other temperatures as shown in Fig. 5. This crude approximation predicts that no sensible reduction of \( \text{UO}_2 \), except to uranium metal, will occur at temperatures below 1600°C, which is in reasonable agreement with experiment, and that a gas mixture in equilibrium with stainless steel at 700°C will not cause reduction of \( \text{UO}_2 \) except above 2000°C; this consideration is then unlikely to be a limiting one, since gas release by other mechanisms is already rapid at 2000°C. Reduction at temperatures above 1600°C should occur if the oxide is canned in zirconium.
Vaporization processes are important at high temperatures. \( \text{UO}_2-x \) yields \( \text{UO} \) and \( \text{UO}_2 \); \( \text{UO}_{2+x} \) yields \( \text{UO}_2 \) and \( \text{UO}_3 \) and \( \text{O} \) or \( \text{O}_2 \). Values for the heats of formation of these vapour species have been given [6]. A report that \( \text{UO}_4 \) constitutes another stable vapour species under oxidizing conditions indicates that further mass spectrometric surveys of the vapour species should be made [12].

The U-C phase diagram proposed by the carbide panel [7] must be modified in the light of later work. The UC phase can exist with some deficiency of carbon at temperatures above 1300°C [13], the minimum carbon content of \( \text{UC}_{0.96} \) being reached at 1700°C; above 2000°C, there is a wide range of solubility of carbon in UC. The \( \text{UC}_2 \) phase is substoichiometric. The terminal composition of cubic 'UC\(_2\)' above 1800°C has been determined as \( \text{UC}_{1.86}\pm0.02 \).
and that of tetragonal \('UC_2'\) as \(UC_{1.96\pm0.04}\). A composite phase diagram based on the work of these and other authors is sketched in Fig. 6, but many details cannot be regarded as settled. The Pu-C phase diagram is very different, owing to (i) the wider range of stoichiometry of the PuC phase at low temperatures; the phase limits have been given as \(PuC_{0.75}\) to \(PuC_{0.92}\) at 610°C, (ii) the appearance of another phase, \(Pu_3C_2\), at low temperatures in preparations which are cooled slowly. PuC melts peritectically at 1654°C. \(Pu_3C_3\) is the most stable and easily prepared plutonium carbide and melts peritectically at 2050°C; \(Pu_2C_3\) is in equilibrium with carbon up to about 1750°C. The

![Phase Diagram for the U-C system (reproduced, by permission, from the USAEC report LA-2942)](image)

Great difference between the U-C and Pu-C systems is the lower stability of the plutonium carbides; the free energies of formation at 25°C are: UC, \(-22\) kcal; PuC \(\approx\) \(-1\) kcal. Complete ranges of solid solution are possible between UC and PuC, and \(U_2C_3\) and \(Pu_2C_3\) \([14]\); the addition of plutonium carbides to U-C alloys containing 50-60 at.% of carbon lowers their melting points but raises the \(M_2C_3 + MC + MC_2\) transformation temperature to 2000°C or above. Much more work is needed before the data on the Pu-C and U-Pu-C can be regarded as firmly established; in particular, more data on carbon activities are required, particularly in plutonium systems.
From considerations of the binary systems only, one predicts that UC will not be thermodynamically compatible with Ta, Nb, Zr or Ti, but should be compatible with Mo and W. Reaction will, of course, be limited by kinetic considerations: PuC and tantalum have shown no evidence of interaction in 30 min at 1200°C. The importance of the complete investigation of ternary systems in compatibility studies is dealt with in the next section.

Reference to the phase diagrams shows that the preparation of single-phase carbides is a problem of some difficulty. It is also important; a metal-UC mixture has poor irradiation properties while the carbon activity in equilibrium with UC-U_2C_3 mixtures is high enough for them to be carburizing towards most steels. The accurate control of the composition of material prepared by low-temperature sintering methods has been shown to be possible by strict attention to analysis. The preparation of single-phase material by arc melting has also been achieved but is more difficult; plutonium segregation in (U, Pu)C has been observed in some preparations quenched from a melt [14]. It would be convenient to be able to control the stoichiometry of the preparations at a late stage in their manufacture. The most obvious method is removal of excess carbon with hydrogen. The composition of zone-melted rods has been adjusted by heating them under 16 to 25 mm Hg pressure of dry H_2 at 1800°C in the presence of tantalum shields which acted as a carbon sink; it is worth noting that the CH_4 pressure under these conditions would be expected to be 2 X 10^{-4} mm Hg at 1800°C. The removal of carbon at lower temperatures should be easier provided diffusion in the solid is rapid enough. The CH_4/H_2 ratio for the UC_2 + 2H_2 ⇌ UC + CH_4 reaction is (3 to 8) X 10^{-3} for a total pressure of 1 atm at 1100°C. The reduction of powders of UC_2 and of (U, Pu)C_3 has been carried out at 1000°C [16]; the products were of the single-phase, monocarbide-type, but contained oxygen in solid solution, presumably from H_2O in the H_2.

The many studies made of the vaporization processes over UC have not given results which are in good agreement [7] and further experiments are to be reported to this Symposium. The congruent vaporization composition for the temperature range 2100-2300°C has been reported to be UC_{1.065±0.025} [17]. The volatility of an unknown plutonium-containing species from PuC and (U, Pu)C at temperatures above 1500°C is high [18], p ≤ 10^{-6} atm at 1550°C; this is of considerable importance since redistribution of plutonium in fuel elements run with high centre temperatures would be possible; no firm thermochemical data are available yet.

Because of the excellent moderating properties of hydrogen, hydride systems with reasonably low equilibrium pressures of hydrogen have been proposed for use in specialized reactors where weight has to be kept to a minimum. A dispersion of uranium in zirconium hydride has been proposed as a homogeneous fuel [19]; measurements of the equilibrium pressure suggest that this dispersion behaves as a mixture of uranium metal in zirconium hydride at ~700°C, despite the well-known stability of UH_3 at lower temperatures, and the uranium can be seen to precipitate out. The hydride systems are of interest since migration of hydrogen in a temperature gradient has been experimentally demonstrated; one bar of α-ZrH in a temperature gradient of 55°C/in showed a concentration of hydrogen in the cooler regions in 1344 hours.
Enough has been said in this section to indicate the type of data of practical use in systems operating at high temperatures. It is essential to know activities as a function of temperature and of composition, and measurements of equilibria, including vapour-solid equilibria, must be made at high temperatures. The essential values cannot be calculated with sufficient accuracy from standard heats and entropies of formation of the stoichiometric compounds, particularly since wide non-stoichiometric ranges are often stable at temperatures of practical interest.

TERNARY PHASES

It is worth stressing that the nuclear engineer has a special interest in thermochemical work on ternary or multi-component systems. This interest arises from several causes. Firstly, it is often desirable to use mixed fertile-fissile fuel elements to prolong irradiation times - for example UC₂-ThC₂ in the Dragon reactor, or UO₂-PuO₂ and UC-PuC in fast reactors. Then a 3-component phase may possess desirable physical or chemical properties. For example, UO₂ will dissolve in ZrO₂ or ThO₂ to give a solid solution having the fluorite structure which is stable towards oxidation in the sense that no U₃O₈-like phase of lower density can be formed so long as the proportion of UO₂ is below a limiting value. Again, monocarbide fuels which are stable in the presence of graphite, and could therefore be coated with pyrolytic carbon, can be made by dissolving UC in ZrC, NbC and other monocarbides; since the free energy of the reaction UC+C → UC₂ is only about -1 kcal, the reduction of the activity of UC can easily be sufficient to suppress the formation of UC₂, or of U₂C₃. The lowering of the activity also causes a lowering of volatility - (U, Zr)C has successfully been used as a fuel in a thermionic converter operating at 2000°C [20].

The correlation of thermodynamic quantities with the phase diagrams, and the treatment of a ternary system on the basis of the three binary systems, has been undertaken by Rudy [21] with particular reference to mixed carbide and to boride-carbide phases. The width of the (M, UC)-C portion of the phase diagram is correlated with the variation of UC activity by a regular solution approximation and the heats of mixing; the latter are calculated from the positions of the tie-lines in the HfC-UC-MC (M = Nb, Zr, Ta) pseudo-ternary systems as determined by X-ray examination of quenched specimens. However, some care must always be exercised in interpreting phenomena at high temperatures from the results of room temperature observations - for example, recent differential thermal analysis results by Farr and Bowman [22] suggest that cubic UC₂ can dissolve ZrC at high temperatures, which implies that some of the details of Rudy's calculations may have to be revised.

The importance of actual study of the ternary systems always involved in compatibility problems is illustrated by the U-C-Fe, U-C-Ni and U-C-Cr systems. UC reacts with nickel to form UNi₅. UC-Fe and UC-Cr form simple eutectic systems with no interaction; but Fe-Cr alloys containing 8% to 98.5% Cr react with UC to form UFe₂ and Cr₂₃C₆. With stainless steel, Fe-Ni and Fe-Cr eutectic alloys melting at 1000°C can be formed,
although no reaction is observed between stoichiometric UC and austenitic stainless steel below 850°C [22].

There is also a practical and economic incentive to the study of ternary and higher order systems, since it is often difficult and therefore expensive to eliminate impurities during preparation or re-processing. Knowledge or prediction of the effect that relatively minor constituents can have on fuel or structural material enables the engineer to specify realistic standards.

The carbide systems afford again one of the best examples. The free energy differences for the formation of the various uranium carbides from each other are small, and the effect of impurities large enough to alter the phase diagram completely. Thus, \( \text{UC}_2 \) can dissolve 1 wt.% of oxygen, and this is sufficient to lower the heat of formation of this phase by about 5 kcal. The oxygen-saturated tetragonal \( \text{UC}_2 \) phase is then the most stable phase in equilibrium with graphite at all temperatures, whereas \( \text{U}_2\text{C}_3 \) is the highest stable carbide below 1500°C in the pure carbide system. UC and UN form a continuous range of solid solutions, but the percentage of UN necessary to render this phase stable in the presence of graphite has not been established with certainty.

The U-C-N-O and U-Pu-C-N-O systems are important since the cheapest way of preparing carbide fuels is by reaction of the oxides with carbon. Recent information [23] indicates that uranium oxycarbides \( \text{UC}_x\text{O}_y \), with \( x+y=1 \), are stable with \( y = 0.05 \) on the carbon-rich side, in equilibrium with \( \text{U}_2\text{C}_3 \), and with \( y = 0.35 \) on the oxygen-rich side, in equilibrium with \( \text{UO}_2 \).

The thermodynamics have been discussed in terms of ideal solution behaviour. There are some direct measurements: the pressure of CO over the three phases \( \text{U, UO}_2 \) and \( \text{UC}_{0.75}\text{O}_{0.25} \) have been measured at 1700°C [24] and result in a free energy of formation of \(-38 \text{ kcal} \) for the solid solution phase, as compared with \(-22 \text{ kcal} \) for UC.

\( \text{U(C}_x\text{N}_y\text{O}_z \) phases with \( x+y+z=1 \) can also be formed and may be regarded as solid solutions of UN in \( \text{U(C}_x\text{O}_1-x) \), where the UN acts as an inert diluent. The solubility of oxygen in PuC and \( \text{(U, Pu)C} \) is larger than in UC and solid solutions of PuN in UC have been proposed as fast reactor fuels; 15% solid solution of PuN in UC is said to be stable in vacuum at 1800°C. Uranium oxycarbides containing < 5 mol % UO are also stable in vacuum at 1800°C but have been reported to be unstable under irradiation at 1000°C, disproportionating [25] according to

\[
\text{U(C}_{1-x}\text{O}_x) \rightarrow (1 - 2x)\text{UC} + x\text{CO} + 2x\text{U}
\]

Further work on the activities of elements in the MX phases, and on their stability under irradiation, is urgently necessary. Some new work is to be reported to this Symposium by Imoto and Stöcker.\(^3\)

A further example of 'impurity' thermochemistry arises in the dispersed fuels in graphite used in reactors of the Dragon type. The migration processes of fission products such as barium, strontium, caesium and cerium around the circuit depend on their volatility; one is dealing here with a very dilute 'solution' or dispersion of the fission product elements in

\(^3\) IMOTO, S., STÖCKER, H.J., these Proceedings 2, SM-66/14, Session 8.
graphite and the possible 'trapping' effects of the impurities present in graphite must be taken into account. Effusion and transpiration experiments designed to measure the vapour pressure of barium in barium/graphite mixtures [26] are in progress but no definitive results have been published.

A valuable field for which even empirical qualitative rules would be useful is the effect of small quantities of 'impurity' on the activities in a two component system. Wagner [27] has derived relations which are applicable when the interactions between the ions of an alloy can be disregarded; this can be assumed as a first approximation when only positive ions are present. Unfortunately, the underlying assumption in Wagner's treatment is not valid for many of the impurity elements – oxygen, nitrogen, etc. with which we are most concerned.

RADIATION DAMAGE

Some mention has already been made of the effects of radiation damage on phase stability. We must therefore examine how far the concepts and data of thermochemistry can be expected to apply to nuclear materials during the operation of reactors, as distinct from during preparation and processing. There seems to have been no attempt to enlarge the formalism of thermochemistry to include systems in a radiation field, though gravitational and electric fields have been taken into account. Irradiation of gaseous systems leads to the production of atoms, ions or molecules in highly excited states, the concentration of which in a given radiation field tends to a steady-state value in the absence of a reactant which removes them efficiently; the precise nature of the primary species is seldom known. The primary process in the irradiation of solids leads to the production of small volumes, containing $10^5-10^6$ atoms, which have been heated to an effective temperature of thousands of degrees for about $10^{-11}$ s, a period of perhaps $10^5$ atomic vibrations. For longer times, there remain regions in the solid with high local concentrations of interstitials and vacancies; fission fragments produce a high local density of displaced atoms in a cylindrical region about $10^2$ Å in radius and $10^5$ Å long.

Apart from some measurements of the specific heat of metals being irradiated in a reactor, the data on the thermochemical consequences of irradiation damage refer to post-irradiation examinations. The most obvious consequences are order $\leftrightarrow$ disorder and phase transformations. The precipitation of stable phases from solid solutions which are metastable is often accelerated by irradiation, owing to enhancement of diffusion over short distances by the augmented local defect concentrations. These phenomena are of great importance because of consequent changes in the mechanical properties of important structural metals; thus, aluminium nitride is thought to precipitate out of aluminium-killed steels [28] and NbC precipitates have been identified in grain-boundary regions of irradiated 20% Cr:20% Ni:Nb stabilized austenitic steel after tensile testing or heating at temperatures above 700°C [29].

Phase changes induced by irradiation often consist of transformation to a structure similar to that which is stable at higher temperatures; the
production of the γ-phase in irradiated U-Mo alloys is one example already
given. It is tempting to ascribe such transformations to the high tempera-
tures generated in the thermal 'spike', but the mechanism is more compli-
cated than this and depends also on structural considerations and the oppor-
tunities for nucleation of new structures. Transformation to a structure
which is thermally stable at high temperatures does not always occur; one
of the most striking examples of this is the comparative stability of coesite,
the synthetic high-pressure modification of silica, under irradiation con-
ditions that transform all the natural crystalline modifications, trydimites,
crystobalite and quartz, to the vitreous state. The transformation of the
monoclinic form of zirconia to the cubic form, thermally stable above 1900°C,
is effected by fission product damage but only in the presence of certain im-
purities [30]; the cubic form is stable to 800°C on post-irradiation annealing.
Certain materials – quartz, zircon, U₃O₈ – are rather readily transformed
to a disordered, glass-like state (metamict) in which all long range order
has been destroyed.

Some direct evidence of the effect of irradiation on thermochemical
properties has been given by measurements of stored energy. These have
been reported for some metals [31], diamond, SrC [32], graphite [31] and
U₃O₈ [33]. A large amount of work has been carried out on graphite because
of the practical importance of limiting the energy release during annealing
treatments, which may have to be applied from time to time to the graphite
used as a moderator in gas-cooled reactors. The energy release on an-
nealing irradiated graphite has been measured by differential methods and
the total energy stored has been measured by combustion calorimetry.
General features are illustrated by the results in Fig. 7; the energy stored
in the structure is still increasing after a fast flux exposure of 15×10²¹ n/cm²
to amounts greater than 500 cal/g, with 250 cal/g remaining after annealing
at 1000°C. Some recent results suggest that saturation occurs at about
500 cal/g for irradiation at 150°C [34]. In this structure, an appreciable
fraction of the damage remains at high temperatures; the "c" spacing does
not recover completely below 1500°C.

The energy stored in U₃O₈ reaches a maximum of 21.4 kcal/mole (25.5
cal/g) at a total integrated thermal flux of over 10¹⁷ n/cm², with complete
destruction of the lattice [33]. On annealing, the energy is released in a
fairly narrow temperature range, that depends on the irradiation dose re-
ceived; complete restoration of the original crystal structure has occurred
below 720°C. Childs and McGurn point out that the maximum amount of
energy stored is of the same order as the latent heat of fusion of several
oxides.

Radiation damage usually anneals out in a series of steps on raising
the temperature, corresponding to the movement of different types of defects
or defect clusters. Radiation damage in UO₂, as shown by changes in lattice
parameter, is virtually completely annealed out below 1000°C [35]. Fission-
induced damage in UC anneals out in two main stages, at 150°C and 510°C,
and the lattice parameter completely recovers its original value at 650°C [36].
Typical annealing temperatures following fast neutron damage are as follows:

- **Copper** - max. 600°C
- **NaCl** - 250 to 400°C
- **Vitreous silica** - 300 to 1000°C
- **SiC** - 100 to 950°C
- **BeO** - 800 to 1400°C

We can conclude from this brief survey that excess enthalpy effects due to radiation damage are small above 300°C in the case of metals and small above 700°C for most of the high-melting compounds of technical interest, with the exception of graphite and beryllia. It is, however, necessary to remember the effect of irradiation on fluid phases in any calculation of equilibria. There is a little evidence on the behaviour of the UO₂-CO₂-CO system under irradiation in pile; CO₂/CO mixtures, which should be reducing towards UO₂⁺X (see above), are oxidizing in an irradiation field at low temperatures, producing a disordered form of UO₂⁺X which is stable to 600-650°C [37]. The oxidizing tendency becomes less marked as the temperature rises and was negligible above 500°C under irradiation in BEPO; this result may, however, depend on the irradiation flux.
TRANSMUTATION EFFECTS

The chemical changes consequent upon transmutation reactions persist to high temperatures, unless the foreign atoms are rejected from the host lattice. Particular attention has been paid to the mechanical changes consequent upon the production of rare gas atoms which can aggregate and form bubbles — the production of tritium and helium by the $^9$Be$(n, \alpha)^7$He$\rightarrow^6$Li$(n, \alpha)^3$H reactions, and the production of helium from $^{10}$B$(n, \alpha)^7$Li, which leads to important effects at high temperatures in steels containing boron impurity and dominates the behaviour of boron alloys, $\text{B}_4\text{C}$ and metal borides used as control materials. In high thermal neutron fluxes, reactions such as $^{54}\text{Fe}(n, \gamma)^{55}\text{Fe} \rightarrow^{55}\text{Mn}$ may become important and, in the high fast neutron fluxes now proposed for highly-rated breeder reactors, reactions such as $^{54}\text{Fe}(n, p)^{54}\text{Mn}$ and $^{40}\text{K}(n, \alpha)^{38}\text{Ce}$ could lead to chemical interactions which have to be considered. The cross-section of $\text{N}(n, p)\text{C}$ is large enough to lead to appreciable quantities of hydrogen being produced in nitride fuel materials, though deleterious results have not been reported to date.

One particular field which may be amenable to the application of thermochemical arguments is the prediction of the chemical state of fission products. In many designs of highly-rated power reactors, enriched fuel will be expected to run to a burn-up of about 10% of all metal atoms. Very appreciable quantities of the more abundant fission product elements will be produced. The chemical state and distribution of the fission products will affect the mechanical properties of the fuel and its compatibility with the canning material or coolant.

As an example, we consider the case of oxide fuels, where the thermochemical data is reasonably complete. The actual concentration of fission products will depend on the isotope undergoing fission and the rate of burn-up, and the results obtained will depend critically on these parameters. We take the case of the thermal fission of $^{235}\text{U}$, exposed to $10^{13}$n/cm$^2$ for 100 days and cooled for 100 days [38]; the fission data were taken from Blomeke and Todd [39] (Table I).

The values for $\Delta G(O_2)$ in equilibrium with some typical fission product elements are shown in Fig. 8. We shall assume that the fuel element will be operated with a surface temperature of 750°C and therefore that radiation damage effects can be neglected. The oxygen liberated by fission of $^{235}\text{U}$ can be imagined as dissolved in the oxide matrix, in which oxygen is extremely mobile at these temperatures, and redistributing by combining with fission products so that $\Delta G(O_2)$ is a minimum.

The data in Fig. 8 are not all that are required. We need to know also which of the fission product elements form solid solutions in the oxide fuel, and what effect this has on the values of $\Delta G(O_2)$ as a function of oxygen concentration. It is known that $\text{UO}_2$ will form solid solutions with $\text{ZrO}_2$, and it can be inferred from results on $\text{(U, Th)}\text{O}_{2+x}$ that the oxygen potentials will be similar to those for $\text{UO}_{2+x}$. $\text{UO}_2$ also forms solid solutions with $\text{Y}_2\text{O}_3$, and rare-earth and alkaline-earth oxides; these all show a considerable tendency to absorb sufficient excess of oxygen to complete the fluorite lattice of $(\text{U, M})\text{O}_2$ and it is known that the oxygen potential for stoichiometric $(\text{U, Y})\text{O}_2$ fluorite solid solutions is close to that for $\text{UO}_2$. Some X-ray investigations
TABLE I
CHEMICAL FORM OF FISSION PRODUCTS IN OXIDE FUELS
Yields in atoms/100 fissions of $^{235}$U

<table>
<thead>
<tr>
<th>F.P.</th>
<th>Yield</th>
<th>Yield remaining as element</th>
<th>No. of oxygen atoms combined as oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>30.5</td>
<td>-</td>
<td>61.0</td>
</tr>
<tr>
<td>Xe</td>
<td>20.6</td>
<td>20.6</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>19.8</td>
<td>[19.8]</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>18.1</td>
<td>27-36</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>18.1</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>17.5</td>
<td>35.0</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>13.3</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>11.6</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>6.8</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>6.2</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>6.2</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>4.8</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>Pr</td>
<td>4.5</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>3.8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>3.8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Pm</td>
<td>2.8</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>2.7</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>2.5</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>1.6</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>1.3</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

184.6-193.6

of irradiated and annealed UO$_2$ indicate that the barium and strontium are not in solid solution, while the zirconium and most of the rare earths are [38]. As burn-up proceeds, new phases appear at the grain boundaries; the analysis of several of these with an electron-microprobe analyser showed the concentration in them of Mo, Ru, Ce and Ba [9]; cerium differs from the other rare earths in that some isotopes have volatile precursors of appreciable
half-life, and this may explain the concentration of cerium alone in grain boundaries.

We can now draw up an oxygen balance, having regard to the data in Fig. 8, and this is summarized in Table I. We see that 185–194 of the 200 oxygen atoms "liberated" per 100 fissions are accounted for by oxidation of the zirconium, rare earths and alkaline earths, in segregated phases or in solid solution in the UO₂, as appropriate. The noble metals and caesium will certainly not oxidize; the molybdenum may be partially oxidized to MoO₂ to maintain the oxygen balance. We are neglecting the possible formation of compounds such as SrMoO₄.

Such calculations are, of necessity, approximate but are probably accurate enough to indicate that the oxygen potential does not vary much during
the use of a $^{235}\text{U}$ fuel. We may note, in passing, that a rise in the oxygen potential (higher oxygen pressure) would be expected in the case of $^{239}\text{Pu}$ fission. In the case of uranium fuels, it is not likely that much oxidation of a stainless steel can will occur. The $\Delta G(\text{O}_2)$ value plotted in Fig. 8 for the oxide layer on stainless steel was found by direct measurements using the galvanic cell technique [40]. The oxygen potential at 1011°C was initially that of Fe/FeO if the oxide layer was thick, or close to the value for Cr/Cr$_2$O$_3$ if the oxide layer was thin; over several hours, the value drifted to that shown for all thicknesses of oxide. A zirconium-alloy can, however, would certainly be reducing towards the fuel at high burn-up, enough to retain all the uranium as U(IV) at least, and appreciable oxidation of the inside of the can would be expected; such oxidation has been reported during some irradiations in zircalloy [41]. Finally, we may note that there is no chance of uranium or plutonium metal appearing on prolonged irradiation unless the material of the can acts as an efficient oxygen getter. No uranium metal was seen in the series of irradiations referred to above, which were carried out in nickel or steel cans. Reports of uranium metal in the high temperature regions of oxide fuels have always referred, so far as we are aware, to irradiations carried out in Zircalloy. Reference to Fig. 5 shows that portions of the fuel at temperatures above 1600°C might be expected to reduce to UO$_2$-X in a zirconium can, as discussed above.

Similar calculations cannot be carried out with the same degree of certainty in the case of carbide fuels. Radiation damage is again not expected to exert a serious influence above 750°C, but the carbon mobility is low and equilibrium configurations may not be attained. Further, the thermodynamic data are not known accurately enough — in particular, we lack information on the free energies of formation of the lower carbides of the rare earth metals and of the activity of carbon in solid solutions of these metals in UC; however, UC-YC solid solutions have been made. 80 carbon atoms per 100 fissions are accounted for by the formation of zirconium and rare earth monocarbides, which may be presumed to be rather more stable than UC; the remaining carbon could be used in converting CeC to CeC$_2$, which is slightly more stable than UC. It is then unlikely that uranium metal will be formed, or that the system will become carburizing towards stainless steel as burn-up proceeds, but better data are needed. The Mo, Cs, Ru, Sr and Ba will almost certainly remain as metals. We note that the activity of carbon in stainless steels as a function of concentration is not known; such steels have not been studied as fully as pure $\gamma$-iron-carbon solid solutions.

In all such calculations, the formation of ternary compounds, e.g., molybdates in oxides or UMoC$_2$ in carbides, should be considered. One is in reality using the thermochemical approach to plan a sensible series of irradiation experiments — the thermochemical as well as the physical state of fuel materials must be controlled if reproducible results are to be expected — rather than to predict with any certainty the final state of such a complicated system.
FLUID PHASES

We have concentrated so far on problems arising in the thermochemistry of solid materials. The field for the application of thermochemistry to problems involving liquid phases is no less vast — and may, indeed, be even greater, since equilibrium is more readily attained. Various types of nuclear reactor have been proposed or are under construction using liquid fuels or blankets or both, and many schemes for the preparation and processing of fuel materials depend on equilibration with liquids or gases. We do not propose to review here the application of thermodynamic measurements to processing in aqueous solutions, nor shall we discuss the important problem of phase stability in homogenous aqueous reactors. We may also note that the study of the rates of solution and deposition is as important as the study of equilibrium conditions in all liquid systems.

Liquid Metals

A great deal of effort has been applied to the development of a thermal reactor, graphite moderated, with a liquid fuel, in particular a dilute solution of uranium (enriched in \(^{235}\text{U}\)) in bismuth. A fair amount of data has been accumulated both on the solid phases in the U-Bi system and on dilute solutions of uranium in bismuth and more work will be reported at this Symposium; for mole fractions of uranium from \(4 \times 10^{-4}\) to \(10^{-2}\), the activity coefficient was found to be approximately constant and equal to \(6 \times 10^{-4}\) at 700°C by EMF measurements, in approximate agreement with measurements made over a range of temperatures by an optical absorption technique [22]. Measurements were also made of the activity coefficients of Ce, Th and Zr in bismuth. Extensive tests have also been carried out on the compatibility of these liquid alloys with graphite and container materials. As in all liquid systems, any solubility will result in material transport down temperature gradients. Magnesium was added to control oxygen and high zirconium concentrations seemed to protect carbon steel loops from corrosion, presumably due to colorant films or zirconium nitride and carbide [42].

The aim of the LAMPRE experiment at Los Alamos is to develop fast reactors fuelled with molten plutonium alloy contained in cans cooled by a liquid metal. One favoured fuel is the low melting eutectic between plutonium and Fe-90.5 at.% Pu, m.p. 410°C. This is a highly corrosive liquid; tantalum or Ta-alloys show some promise as container material, being protected by a thin zone of Ta\(_2\)Fe\(_7\). The operation of LAMPRE has not given any evidence of difficulty from fission products though unknown precipitates have been seen and the behaviour of fission products remains to be studied.

Liquid metals are used as coolants in heterogeneous as well as homogenous reactors. Variants of these include reactors using past or slurry fuels, "settled bed" reactors in which the cooling metal flows between spheres of fuel and the more conventional fast reactor designs, such as DFR, with liquid sodium or sodium-potassium alloy flowing past canned fuel elements. The prevention of corrosion and material transport are the key problems in all such reactors. \(\text{Na}_2\text{O}\) is, of course, a fairly unstable oxide, but oxygen in liquid sodium can be oxidizing towards metals which form far more stable oxides, and is also the cause of one means of decarburization by forming CO.
The oxygen content can be controlled by cold-trapping — freezing out precipitated oxide — or by hot trapping, in which the oxygen reacts with zirconium or another metal that forms a very stable oxide. The corrosion of austenitic steels at 600-700°C was stopped by lowering the oxygen content of flowing sodium below $5 \times 10^{-3}$ ppm, though nickel is leached from nickel-base alloys. Liquid lithium leaches carbon from stainless steels and destroys carbide, oxide or sulphide precipitates that form at the grain boundaries. Hydrogen is also soluble in Na-K alloys; a study of the embrittlement of niobium by hydrogen in sodium has been analysed [43] to give values for the activity of hydrogen in sodium as a function of composition. There is uncertainty about these values, however, and the general field of the thermochemistry of oxygen, hydrogen and carbon (and possibly nitrogen and sulphur) in liquid metals is one that should be expanded. In particular, it is important to study the influence of one solute upon the activity of another, e.g. of dissolved oxygen on dissolved hydrogen, and the form in which carbon can be transported is not clear.

Molten Salts

A very large effort in thermochemistry has been expended in determining phase relations in mixtures of molten fluorides, and lately in determining activity coefficients as well, in support of the MSRE at Oak Ridge. This work is to be reviewed in another paper to this Symposium, and we need therefore only mention it here. The fuel composition is about $65\%$ LiF, $29\%$ BeF$_2$, $5\%$ ZrF$_4$ and $1\%$ UF$_4$; this flows through a graphite matrix in a container of INOR-8, a specially developed nickel-base alloy of Ni, Mo, Cr and Fe. The formation of UF$_3$ by reaction with the container and with the graphite ($4\text{UF}_4 + \text{C} \rightarrow \text{CF}_4 + 4\text{UF}_3$) has to be considered and measurements of activity coefficients of UF$_4$ and UF$_3$ in these salt mixtures are crucial [42]. Irradiation and transmutation effects have to be considered. Considerable quantities of F$_2$ gas have been found in capsules irradiated and then cooled, but there is good evidence that this is due to radiolysis of the solid fluorides, by fission product decay at temperatures below 100°C. In the molten state, recombination processes are presumably fast enough to maintain a very low-steady state concentration of fluorine, though the measurement of some equilibrium property under irradiation conditions would be very interesting.

The changing concentrations of cations as fission proceeds will also affect thermochemical equilibria. The problem here is precisely the same as for solid fuels (see above), and the principle exactly the same; the fluorine "liberated" by the fission of uranium will combine with fission-product cations, or attack the container material, or oxidize cations in the melt, and the balance achieved will depend on the chemical potential of fluorine dissolved in the melt, which is characteristic of these various reactions. It appears that cations of the alkaline earths, alkali metals, rare earths and zirconium will dissolve in the melt in their normal valency states, and that molybdenum and ruthenium may exist as metals, possibly plating out on the graphite [44].

Recently, some interest has revived in molten salt fast reactors. These would have to be based on chlorides, because of the moderating properties
of fluorine. Substantial solubilities of UCl$_3$ and PuCl$_3$ in NaCl–KCl mixtures has been predicted, with melting points below 500°C. A further possibility is that such a fuel could be cooled by spraying molten lead through the fuel salt [45]. This proposal seems very attractive from the engineering point of view, limiting the area of heat exchanger material in the core, but it raises complex questions of compatibility and much thermochemical work, both on solutions in alkali halides and on dilute solutions in liquid lead, will be necessary to resolve them.

**Processing problems**

The "conventional" method of separating fissile and fertile material from fission products is to dissolve irradiated fuel in aqueous solutions and apply solvent extraction techniques. Many other schemes have been proposed; all depend upon some phase distribution phenomena and therefore upon thermochemical data. The practical application of thermochemical data to the processing of fuels by equilibrating with molten salts at high temperatures is to be discussed in another paper to this Symposium$^4$.

Examples of other processes that have been examined include:

(i) **Melt refining.** Irradiated metal fuels are melted in a lime–zirconia crucible. Volatile fission products are volatilised away and the fission products which form very stable oxides, (Y, Ba, Sr, rare earths) react with the zirconia and solid oxides are deposited. The molybdenum, ruthenium and much of the fission product zirconium remains in the metal. The relatively small amounts of fuel material remaining in the oxide layers are recovered by suspending the oxides in a molten halide mixture and equilibrating with suitable molten metals.

(ii) **Oxidation-reduction.** The removal of the more volatile fission products, but not of the rare earths and zirconium can be effected by successive reactions such as [46]

\[
\begin{align*}
\text{UO}_2 & \quad \text{O}_2 \quad \text{H}_2 \quad \text{UO}_2 \\
\text{UC} & \quad \text{O}_2 \quad \text{U}_3\text{O}_8 \quad \text{C} \quad \text{UO}_2 \\
\text{UC} & \quad \text{N}_2 \quad \text{U}_2\text{N}_3 + \text{C} \quad \rightarrow \quad \text{UC}
\end{align*}
\]

Molybdenum can be removed as MoO$_3$ at temperatures above 1000°C. It might even be possible to remove uranium as UO$_3$, but apparently this has never been tried.

(iii) **Chloride volatility processes** [47, 48]. Aluminium and molybdenum canning materials may be removed from irradiated fuel by treatment with HCl gas. Uranium dioxide can be converted to UCl$_4$ by reaction with CCl$_4$, and separated from elements that form less volatile chlorides, such as barium, cerium and rare earths, by distillation, particularly if inactive CeO$_2$ is added as a hold-back carrier.

(iv) Fluoride volatility processes [47, 48]. These exploit the well-known volatility of UF$_6$ and PuF$_6$ and have been developed further than any other high-temperature processes. The relative volatilities of the main fluorides of uranium and plutonium are as follows:

<table>
<thead>
<tr>
<th>Temperature (°K) for which p = 10^-6</th>
<th>10^-3</th>
<th>1 (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuF$_3$</td>
<td>1350</td>
<td>1700</td>
</tr>
<tr>
<td>UF$_4$</td>
<td>980</td>
<td>1225</td>
</tr>
<tr>
<td>PuF$_4$</td>
<td>930</td>
<td>1100</td>
</tr>
<tr>
<td>UF$_6$</td>
<td></td>
<td>330</td>
</tr>
<tr>
<td>PuF$_6$</td>
<td></td>
<td>335</td>
</tr>
</tbody>
</table>

I, Te, Nb, Ru, Sb and Mo form volatile fluorides and CrF$_5$ and ZrF$_4$ have appreciable volatility. In a typical process, UF$_6$ is made with F$_2$ at 500°C and the process gas scrubbed with NaF; CrF$_5$ and ZrF$_4$, NbF$_5$, and PuF$_6$ are held at 400°C and other volatile fluorides, with UF$_6$, absorbed on NaF at 100°C; MoF$_6$ is removed by raising the bed temperature to 150°C and the UF$_6$ swept off at 400°C. The TcF$_6$ and NpF$_6$, which may not be separated from the UF$_6$ at this stage, are separated by irreversible sorption by MgF$_2$ at 100°C. Exceptionally high decontamination factors have been reported.

One of the attractive features of molten salt reactors is the possibility of processing by means of volatility procedures. A melt containing LiF-BeF$_2$-ZrF$_4$-UF$_4$ plus fission products is vacuum distilled to remove most of the LiF, BeF$_2$, and ZrF$_4$, leaving the UF$_4$ and rare earths behind. This residue can then be treated with F$_2$, yielding UF$_6$. It would be feasible to use such a process to remove the bred uranium from a blanket fluoride containing LiF, BeF$_2$, and ThF$_4$, though such a process cannot be used to separate UF$_6$ and PuF$_6$. Handling PuF$_6$ presents some problems because of the ease of thermal dissociation; it is possible that this property might be exploited to separate PuF$_6$ from UF$_6$.

CONCLUSION

Apart from a specific interest in the thermochemistry of the actinide elements and of elements having a low neutron capture cross-section, the thermochemical topics of major interest to people in the nuclear energy industry may be listed as follows:

(a) Measurements of equilibria and calorimetry at high temperatures, above 500°C, by which thermodynamic constants are determined as a function of composition across ranges of homogeneity;

(b) Measurements of activity coefficients in ternary and in multiple systems, and the development of methods by which these can be estimated;

(c) Further measurements and analysis both of steady-state and of rate processes occurring in temperature gradients;

(d) The influence of irradiation on the position of equilibrium and on rate processes.

The papers presented to this Symposium are evidence of considerable advances in many areas of practical interest.
ACKNOWLEDGEMENT

We are indebted to several of our colleagues, and in particular to Dr. E. J. McIver, Dr. E. Wait, Dr. T. L. Markin and Dr. D. A. Dominey, for permission to mention results prior to full publication.

REFERENCES

DISCUSSION

H. SKINNER (Chairman): The strain energies in irradiated graphite samples appear to be well established. How were the values determined experimentally?

L. E. J. ROBERTS: Most of the results were obtained by comparing the heats of combustion of irradiated and unirradiated graphite. References will be found in the paper presented by J. E. Brocklehurst et al. to the Second Industrial Carbon and Graphite Conference, London (April 1965).

P. NAGELS: In the annealing experiments with irradiated UO$_2$, three annealing stages have been observed. Do you have any idea of their nature, i.e. can you make a correlation between these stages and the movement of point defects in UO$_2$?

L. E. J. ROBERTS: The X-ray results on irradiated UO$_2$ indicate the formation of clusters of defects as irradiated proceeds. An analysis of the profiles of the diffraction lines during annealing indicates the formation and disappearance of such clusters. The annealing stages at the lower temperatures may refer to the movement of point defects or of small clusters to form larger ones; the high-temperature stages probably refer to the movement of the larger clusters to grain or sub-grain boundaries, where their influence on the matrix UO$_2$ is minimized.
Session 1

CALORIMETRY AT HIGH TEMPERATURES
Introductory comment

For many reasons the need for thermodynamic data applying at increasingly high temperatures, up to 2000°C and even beyond, is becoming increasingly apparent. Nevertheless it remains true that good measurements above 500°C and even above 200°C are still very hard to make in a laboratory. The challenge to calorimetrists has been met in various ways including adaptation of the traditional types of calorimeter by the use of adiabatic shields and automatic control so that one can deal with the problem at higher temperatures. New types of calorimeters are also beginning to make their appearance. Certainly I think that the problems now facing calorimetrists in this high-temperature range are less formidable than they were 10 or 20 years ago and there is every reason to expect that good data can be obtained within the next decade. Certainly there is no reason at all why an experimentalist should shun the possibility of making an investigation merely because it looks as though he is going to have to work at 1000°C. New materials and new techniques are now available and indeed some applications of high-temperature calorimetry will be described in Session 1.
CALORIMETRY AT HIGH TEMPERATURES

F. GRØNVOLD
UNIVERSITY OF OLSO, BLINDERN, NORWAY

Abstract — Résumé — Аннотация — Resumen

CALORIMETRY AT HIGH TEMPERATURES. Reliable data for the thermal behaviour of substances, and for the reactions between them, are required at increasingly higher temperatures both for fundamental and practical purposes. Calorimetry affords the most direct, and in several cases the only way of procuring such data with sufficient accuracy. The recent developments in calorimeters for heat-capacity, heat of transition and heat of reaction, solution and mixing studies at high temperatures (≥ 250°C) are reviewed. Some consideration is given to the choice of constructional materials for calorimeters, to measurement of temperature and energy, and to the control of the temperature of the closest surroundings, that is shields and thermostat. For heat-capacity studies a considerable number of calorimeters have been described during the last ten years. The majority of them operate below 500°C, with accuracies varying from ± 5 to ± 0.1%. Calorimeters for use above 1000°C are rare, and the temperature limit seems at present to be 1700°C. The thermal characteristics of higher-order transitions are preferably studied in calorimeters with adiabatic shield. First-order transitions, fusion and precipitation are studied also in more or less elaborate calorimeters with an isothermal shield. High-temperature reaction calorimeters have been developed considerably in the same period, and the accuracies improved from about ± 5% to ± 0.5% in the 500°C region. One main line of application has been in the determination of heats of mixing for liquid alloys, and in solution calorimetry within liquid metals. For such uses the operating range has been extended to 1100°C. Heats of reaction between solids and corrosive gases have been determined at 775°C, and heats of reaction between solid components determined up to 1400°C with reasonable accuracy.

CALORIMETRIE A HAUTE TEMPERATURE. Les études fondamentales et les applications pratiques exigent des données précises sur le comportement des diverses substances et les réactions entre ces substances, à des températures de plus en plus élevées. La calorimétrie offre le moyen le plus direct et, dans certains cas, le seul moyen d'obtenir ces données avec la précision voulue. L'auteur passe en revue les perfectionnements récents dont ont bénéficié les calorimètres destinés à l'étude, à haute température (≥ 250°C), des questions suivantes: capacité thermique, chaleur de transition et chaleur de réaction, de solution et de mélanges. Il examine les questions ci-après: choix des matériaux pour la fabrication des calorimètres; mesure de la température et de l'énergie; contrôle de la température du milieu ambiant immédiat, c'est-à-dire écrans et thermostat. Au cours de ces dix dernières années, on a décrit un nombre considérable de calorimètres destinés à l'étude de la capacité thermique. La plupart fonctionnent à une température inférieure à 500°C, avec une précision d'environ ± 5 à ± 0,1%. Les calorimètres pouvant être employés à plus de 1000°C sont peu nombreux; il semble qu'aujourd'hui, aucun ne soit utilisable au-delà de 1700°C. Pour étudier les caractéristiques thermiques des transitions d'ordre supérieur, il est préférable d'utiliser des calorimètres à écran adiabatique. Les transitions du premier ordre, la fusion et la précipitation peuvent aussi être étudiées à l'aide de calorimètres plus ou moins perfectionnés munis d'un écran isotherme. Pendant la même période, on a mis au point un grand nombre de calorimètres pour réactions à haute température et leur précision a été portée d'environ ± 5 à ± 0,5% autour de 500°C. On les a utilisés essentiellement pour la détermination des chaleurs de mélange des alliages liquides et pour la calorimétrie des solutions dans les métaux liquides. Pour ces applications, la température de fonctionnement a été portée à 1100°C. On a déterminé avec une précision satisfaisante les chaleurs de réaction entre solides et gaz corrosifs à 775°C et les chaleurs de réaction entre solides à des températures allant jusqu'à 1400°C.

КАЛОРИМЕТРИЯ ПРИ ВЫСОКИХ ТЕМПЕРАТУРАХ. Для исследовательских и практических целей требуется надежные данные о тепловом поведении веществ и о реакциях между ними при все большем увеличении температуры. Калориметрия является самым непосредственным и в некоторых случаях единственным способом получения таких данных с достаточной степенью точности. Рассматриваются последние достижения в области калориметров для теплоемкости, тепла перехода и тепла реакции, раствора и исследования смещения при высоких температурах (≥ 250°C). В определенной степени учитываются выбор материалов для калориметров, измерение температуры и энергии и контроль температуры непосредственного...
Calorimetry is a time-honoured scientific procedure for extracting information on the amount of energy associated with a chemical reaction or a physical process. A century ago, impelled by the endeavour to utilize heats of reaction as a measure of chemical affinity, work in calorimetry was focused strongly on reactions at room temperature; then, fifty years ago, calorimetry began its advance towards investigations around the absolute zero of temperatures and today it is challenging the thermal chaos. High-temperature calorimetry is continuously extending its temperature range and improving in accuracy; it affords the possibility of studying reactions and species alien to the ambient conditions and it allows establishment of phase diagrams and the study of reactions which do not take place with sufficient velocity at room temperature. Thus, a heat of formation might be determined directly at high temperature, but only indirectly by means of combustion or solution calorimetry at room temperature. Accuracies within 0.01% in the latter experiments can result in 1% inaccuracy in the final value, which is inferior to the capabilities of modern high temperature calorimeters.
Delineation of heat capacities by differentiating enthalpy increments obtained by drop calorimetric methods might be possible when the enthalpy of the substance in the reference state is independent of the rate of cooling. This is presumably the case for transitions of electronic nature, like ferro- to paramagnetic transitions and ionic charge redistribution, but certainly not for the majority of phase transitions, for structural order-disorder transitions, defect formations and melting processes. In practice, delineation of even a reversible transition requires considerable care, and the accuracy is limited by uncertainties in determining the temperature of the hot sample. As an example of this, high-temperature heat-capacity values for nickel oxide obtained in this laboratory (see Fig. 1) are compared with differential enthalpy values by Tomlinson et al. [1] and King and Christensen [2]. The low temperature data by Seltz et al. [3] and King [4] are also shown in the figure.

![Figure 1](image.png)

**FIG. 1.** Heat capacities of nickel oxide; — data by Tomlinson et al. [1]; —— data by King and Christensen [2]; □ data by Seltz et al. [3]; ○ represents present data; △ data by King [4].

The main purpose of improving the accuracy in calorimetry is to permit of more penetrating analyses and further knowledge of chemical bonding, electronic energy states, order-disorder phenomena, the liquid state, etc. However, the more exacting demands of the modern chemical industry and high temperature technology also motivate the need for new and improved thermochemical data. It is a common saying that entropies can be estimated with adequate accuracy without resource to further experimental data, but this statement ought to be questioned in connection with high temperature chemistry. An error in $\Delta S$ of 10 cal mole$^{-1}$ degC$^{-1}$ acquires considerable importance at high temperatures. An error smaller than 15 kcal/mole may...
generally be expected, according to Wilcox and Bromley [5], in estimating enthalpies of formation of simple inorganic compounds by using their estimation procedure with parameters evaluated from experimental data on three or more compounds involving the ions. The uncertainty in Gibbs energy at 1500°C for a metal boride or carbide is thus more likely to be occasioned by lack of entropy values than by poor enthalpy data.

Calorimetric measurements are supplemented by determinations of electromotive forces and of equilibrium concentrations, from which Gibbs energy data might be derived. The enthalpy and entropy data obtained from the temperature dependence of the reactions are, however, often subject to considerable errors. The comparison of highly accurate calorimetric and equilibrium data is of interest, and will no doubt cast more light on the presence of residual disorder in many substances.

The present survey intends to cover some of the developments that have been made in the construction and application of high temperature calorimeters during the last ten years. To restrict the topic somewhat, I shall here only consider calorimeters where the temperature of the calorimeter vessel can be raised to at least 250°C, and the problems connected with measuring energies at higher temperatures become apparent. Thus the extensive literature on "drop" calorimeters will not be considered, although data have been obtained for temperatures exceeding those achieved by a real high temperature calorimeter. The differential thermal analysis (DTA) method has not been included in view of the qualitative nature of its results, but it ought to be remarked that the border line between good DTA and poor calorimetry shows considerable overlap. In preparing this survey the author has found the review papers by Kubaschewski and Dench [6], Wittig [7, 8] and Kubaschewski and Hultgren [9] very useful.

2. CALORIMETRIC EQUIPMENT

2.1. General

In order to measure quantitatively the energy involved in a reaction or process, comparisons or calibrations of the calorimeter - i.e. the reaction vessel or sample container with its content, associated equipment and casing - have to be carried out. The inherent difficulties in defining the boundary of the calorimeter are circumvented by calibrating the system under conditions resembling those for the reaction or process as closely as possible. Known quantities of energy might be provided thermally from a suitable reaction or process of which the thermal energy is already determined, or directly by dissipation of electrical energy. In high temperature calorimeters the temperature rise is commonly measured with a thermocouple or a resistance thermometer. For accurate evaluation of the temperature rise the closest surroundings of the calorimeter, i.e. its jacket or shield, are usually held at a constant temperature (an "isothermal" calorimeter) or made to follow the temperature of the calorimeter surface as closely as possible (an "adiabatic" calorimeter).
2.2. Constructional materials

The choice of constructional materials for high temperature calorimeters will often constitute a compromise with regard to mechanical properties, thermal conductivity, emissivity and cost. Special care has to be taken to avoid materials undergoing transitions or reactions at the temperature of interest. The possible adverse effect of ferromagnetism should also be considered. Polished copper is used \[10, 11, 12\] up to about 400°C, aluminium up to 500°C for both the jacket \[13, 14\] and the calorimeter \[14\]. A uranium-glass sphere, silver coated on the outside, serves \[15\] as container up to 500°C. A calorimeter of nickel has been operated \[16\] in a vacuum at 700°C. For temperatures below 800°C silver is frequently used \[17, 18, 19, 20\] and platinum \[21, 22\] occasionally. Monel is suitable \[23\] in a vacuum up to 1000°C, and oxidation-resistant steel \[24\] in air up to 1100°C. For temperatures of up to 1600°C a molybdenum crucible, surrounded by radiation shields of molybdenum, is used \[25\]. The container problem may become very significant as the temperature is increased; graphite is extensively used with liquid metals, and fused quartz finds many applications, as does tantalum \[26\]. Mackenzie \[27\] has prepared a table as a guide in the choice of container materials for liquid oxides, salts and metals.

In connection with the use of corrosion-resistant alloys, it should be noted that Douglas et al. \[28, 29\] have observed anomalies in the heat capacities of 80%Ni-20%Cr, 73%Fe-26%Cr and 76%Ni-15%Cr-8%Fe alloys in the range 500 to 700°C. A thermal anomaly in a titanium stabilized 18%Cr-9%Ni steel calorimeter has also been observed \[30\]. De-vitrification of silica glass occurs to some extent in my heat capacity calorimeter around 750°C. Errors might then arise from the heat of crystallization of β-quartz, the lower heat capacity of crystalline quartz as compared to glass in this region, and from the heat of transition between α- and β-quartz at 575°C.

2.3. Heat exchange

The heat exchange between calorimeter and surroundings can be considered in terms of the size of the heat transfer (rate) coefficient and the temperature differential. The value of the former can be calculated approximately as a function of temperature from appropriate physical data and heat flow equations \[31\]. As an illustration, the results for my 50 cm³ heat capacity calorimeter are shown in Fig. 2. Even though the solid conduction is caused by 36 alumina-insulated 0.5-mm diam. Pt (and PtRh) wires, it is only a fraction of the air conduction. It would of course have been possible to build a vacuum calorimeter, but the air conduction is a useful aid in heat transfer between the calorimeter and heater and for obtaining good response from the thermocouples. The heat transfer coefficient for conduction between calorimeter and shield, both of silver, is larger than that for radiation even at 1000 K. For copper, molybdenum and platinum the radiative heat transfer coefficient would have been about three times as high.

For solution calorimeters, solid conduction is evidently of great importance, and its influence has been compensated by using twin calorimeters \[32, 33, 34\]. There are limits, however, as to how identical they can be made and positioned in the jacket.
The basic problems of heat exchange in adiabatic calorimeters have been considered recently by West [35]. His analysis shows that the heat exchange due to transients at the beginning and end of a heating period can be made to cancel. The remaining heat exchange is the same for intermittent and continuous heating methods, and its magnitude cannot be determined by varying the heating rate.

2.4. Measurement of energy

Three methods are commonly in use for the controlled introduction of energy in a calorimetric system for calibrating purposes: (1) transforming a measured quantity of electrical energy into heat; (2) introducing a substance of already-determined heat capacity and at a known temperature into the calorimeter; and (3) letting a reaction — for which the energy has been determined previously — take place in the calorimeter. Method (1) is most directly related to the unit of energy and is capable of better than 0.01% accuracy when proper precautions are taken. The heater-lead problem has recently been discussed by Ginnings and West [36]. At high temperatures, shielding of the lead wires to avoid AC pick-up and stray electromotive forces become rather important; also, the power loss due to breakdown of the lead-wire insulation, i.e. resulting in an effective shunt resistance across the heater, must be considered.

Electrical calibration is a standard procedure in high temperature heat-capacity calorimetry. The "inverse drop method" consisting in dropping a piece of cold metal with known heat capacity, via a hole, into the hot sample and measuring the decrease in temperature is, however, in use for metals up to 1440°C [37, 38, 39]. For high-temperature reaction-calorimeters, electrical calibration is now common [13, 32, 40, 41]. It has been used successfully [24] up to 1100°C. Calorimeters for heat of solution studies at
high temperature are usually calibrated using either an inert solid substance like tungsten [42, 43], or a cold solvent, i.e. tin, in the case of a tin solution calorimeter [44, 48], or copper [49, 50]. For calibrations in salt mixtures gold and tungsten are used [33, 51].

Method (3) is used mostly for comparison purposes.

For reaction and solution calorimeters, the heat effects can be compensated, to diminish corrections for heat exchange with the surroundings, either electrically [52], or by pre-heating or cooling the components [53] or the solute [46], or by adding auxiliary substances [45, 46].

2.5. Measurement and control of temperature

Encapsulated platinum resistance thermometers of high accuracy and stability for use up to about 500°C are commercially available. In extending the range to higher temperatures, one line of approach has been to embed the wire in a ceramic, another to use heavier wire. In the first case the temperature coefficients acquire values considerably different from those of pure, strain-free platinum, making numerous and frequent calibrations necessary. In the second case, with an ice-point resistance of 0.25 Ω [54], a temperature increment of about 0.01°C corresponds to a change of 10 μΩ and requires a sensitive Mueller bridge/galvanometer system or an isolating potential-comparator circuit [55] for its detection. The present author found a spiral of 0.2 mm 90%Pt-10%Rh wire to be self-supporting and stable up to 800°C when wound on a mica frame, and such a (40 Ω) resistor has been used successfully for several years. Calibration was somewhat tedious since the thermometer showed deviations from the quadratic equation, \( R_T = a + bT + cT^2 \), valid for pure platinum on the International Practical Temperature Scale. After considerable experimentation a 25 Ω platinum resistor was developed which showed the necessary stability under regular use up to 800°C.

Decreasing or variable insulation properties of the resistor support and of the lead wire tubes at higher temperatures make accurate temperature measurements increasingly difficult, even with a stable resistor. Thus, in my heat capacity calorimeters, the insulation between resistance thermometer and calorimeter is, typically, greater than \( 10^{10} \, \Omega \) at room temperature, equal to about \( 10^8 \, \Omega \) at 500°C and about \( 10^6 \, \Omega \) at 750°C.

While the use of resistance thermometers is of special value for accurate measurements of temperature and drift of a calorimeter, thermocouples are in more general use and are unexcelled when it comes to determining and controlling temperature differences. Among the most used thermocouple materials are chromel-alumel, Pt/90%Pt-10%Rh and Pt/87%Pt-13%Rh. Although the \( \frac{dE}{dT} \) values for chromel-alumel thermocouples are about four times higher, the Pt/PtRh are correspondingly more stable and do not become brittle. When sheathed thermocouples (Thermocoax) can be used, brittleness is no longer of importance, and the stability of a chromel-alumel thermocouple for example is considerably improved. Instability and electrochemical effects [56] impair the accuracy of thermocouple measurements at high temperatures, and recent advances in automatic optical pyrometry make the latter method increasingly attractive.
One problem in connection with thermocouple measurements is that spurious EMF's are developed to a varying extent when the wires are subject to a temperature gradient. Platinum can be difficult in this respect; 90%Pt-10%Rh is better, both from this point of view and with regard to mechanical properties at high temperatures, and so seems to be the best lead wire for differential measurements.

In contrast to the easy visual observation of a mirror-galvanometer deflection in a thermocouple circuit, the electrical amplification of the signal for use in a control circuit might pose severe difficulties when the temperature is higher than 350 - 500°C. Proper earthing and the use of rather low heater voltages, which are also at a low potential with respect to ground, are essential. I use 1 mm silver wires for earthing the shields, a maximum of 20 V DC on the heaters, and pass the thermocouple wires through earthed stainless steel tubes.

The temperature control systems for shields (jacket) and thermostat show wide variety. For ordinary control action, two-position controllers, actuated by a deflection galvanometer of some sort, are rather common. Continuous control can be obtained using resistance thermometers in Wheatstone bridge circuits, together with a detector amplifier and power regulator [41, 45, 46]. To improve control, it is essential that the thermal contacts between heater, heater assembly and thermometer are as good as reconcilable with the requirements of electrical insulation. Sheathed thermocouples and heater wires with short response time are available and are highly recommended. Electrical contact between two thermocouples is, of course, of no consequence for control action if an isolating potential comparator circuit is used [55, 57].

When a very exacting temperature control is needed, controllers capable of integral and derivative action, in addition to the usual proportional action, are desirable. A control system in use for high temperature heat capacity measurements has been described [58]. I use a modified version for thermostat and shield control purposes. A schematic circuit diagram is shown in Fig. 3. The sensing elements consist of two Pt/90%Pt-10%Rh thermocouples, one located in the calorimeter and the other close to the heater windings of the thermostat. An external, adjustable potential is provided for off-setting

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**FIG. 3. Schematic diagram of temperature control system.**
the balance point, or for set-point control of the thermostat, depending upon
the switch position. The signal goes to a microvolt amplifier whose output
feeds a current adjusting controller. The output has to be further amplified
in order to govern a 2.5 kVA saturable inductor.

3. CALORIMETERS AND THEIR APPLICATIONS

3.1. Classification

As noted by Wittig [7] there has been no rational system of notation for
calorimeters, and some designations, like isothermal, combustion and ice
calorimeter do not refer to comparable, or even to the most essential
characteristics. In accordance with his analysis calorimeters might be
classified by considering three variables: the calorimeter temperature $T_c$,
the temperature of its surroundings $T_s$, and the amount of heat produced in
the calorimeter per unit time, $L$.

A really isothermal calorimeter is one for which $T_c = T_s$ = constant and
only the heat input $L$ varies, as for example in the ice, carbon dioxide or
diphenyl ether calorimeters, where the heat evolution results in a phase
transition and is measurable in form of a volume change due to the transition.
Very often, however, the word isothermal has been used for calorimeters with
only $T_s$ constant, i.e. for isothermal shield calorimeters. Kubaschewski and
Hultgren [9] have suggested the name isoperibol for such calorimeters, since
the temperature of the surroundings is kept as constant as possible for
optimum evaluation of the heat transfer. The majority of high temperature
calorimeters for heat of reaction measurements are operated on this principle,
as are likewise many drop calorimeters. Usually, in the latter type of
calorimeters, a heated body is introduced into the calorimeter at room
temperature, or at a moderately high temperature. Less frequently, a cold
body is dropped into a hot calorimeter. In the isothermal shield or isoperibol
category come also many static- and rotating-bomb and aqueous-solution
calorimeters. Vacuum type calorimeters have, since the days of Nernst and
Eucken, most frequently been operated with isothermal shields. The heat
inputs have been both intermittent and continuous.

Keeping $T_c$ and $L$ constant results in a constant temperature difference
between calorimeter and surroundings, a principle utilized in heat flow
calorimeters.

The condition $T_c = T_s$ applies to another main group of calorimeters,
namely those of the adiabatic (or better adiabatic-shield) type, where the
attempt is made to make the heat exchange between calorimeter and sur-
roundings as small as possible. Calorimeters of this type have been success-
fully used for low-temperature heat-capacity determinations and, when
reliable, precise automatic temperature regulating equipment is available,
are increasingly used in high temperature work. For heat of reaction
measurements adiabatic calorimeters are, in spite of their potentialities,
rather uncommon.

The three groups of calorimeters will be considered under two different
headings, depending on whether the calorimeter in question has primarily
been used for studying physical processes (non-reacting systems) or chemical reactions (reacting systems).

3.2. Physical process studies

Heat capacity calorimeters have been operated with quasi-isothermal shielding by Holetzko [37], Krauss and Warncke [38] and Krauss [39] for measurements on iron, nickel and chromium up to 1440, 1160 and 1327°C, respectively. For iron the results at 800°C are about 20% lower than those recently reported by Dench and Kubaschewski [59], at about 900 and 1300°C they agree, and at 1420°C Holetzko's results are 20% higher. The data for nickel agree to within 1% with the data by Pawel and Stansbury [60] in the range 400 to 600°C.

Adiabatic shield operation is much more common for heat capacity calorimeters, but relatively few investigators use intermittent energy inputs with temperature equilibration between inputs. The first good work was reported from Pittsburgh by Wallace et al. [10] and Johnston et al. [61,62] on magnesium-cadmium alloys, having a precision better than 0.2% up to 550°K. The work has been continued by Sterrett and Wallace [63] on tantalum, and by Saba et al. [63] on ditantalum hydride. Even better precision was obtained by West and Ginnings [14] on measurements on aluminium oxide, and by West [64] on sulphur in a calorimeter of unique construction. A calorimeter for use up to 600°K has been described by Trowbridge and Westrum [20] and used for measurements on penta-erythrityl chloride, bromide and iodide [65] and on tetra-uranium enneaoxide, U$_4$O$_9$ [66].

In one of my calorimeters for measurements on very corrosive substances (see Fig. 4), the sample container is of vitreous silica. The sealed container is enclosed in a silver calorimeter, surrounded by shields and a heavy guard body, also of silver. To test the performance of the calorimeter, measurements on aluminium oxide, kindly furnished by the National Bureau of Standards, Washington, have been carried out. In the upper part of Fig. 5 the deviations of the individual measurements from a smooth curve are shown. The curve shows a maximum deviation of about +0.2% from the data by Furukawa et al. [67] at 500°K. In the lower part of the figure, deviations of data by West and Ginnings [14], Shmidt and Sokolov [21] and Trowbridge and Westrum [68] from the given smooth curve are shown. The agreement must be considered as satisfactory, since for the present measurements a container with low thermal conductivity has been used. Measurements have been carried out on several compounds, among them iron selenides, nickel selenides, chromium mono-antimonide and uranium oxides [69].

Measurements with continuous energy inputs comprise many different aspects, and a few of these will be mentioned. The thermal counterpart of structural and magnetic transitions is the subject of several studies. Jost et al. [18] have measured the heat capacity of silver(I) and copper(I) iodide and determined the enthalpy and entropy of the silver-ion disorder in β-AgI. An automatic registering calorimeter is described by Maeda [70] and is used for rough heat capacity determinations on iron sulphides up to about 400°C. The heat capacity of uranium has been determined up to 800°C by North [71] and more recently, Kay and Loasby [19] reported data on plutonium. Values
of the heat of transition for five solid state changes and for the heat of fusion at 638°C are given. In analysing the heat capacity data, large electronic contributions were found. Heat capacity measurements on U₃O₈ by Popov et al. [72] in the calorimeter constructed by Popov and Galchenko [73] show anomalous behaviour, probably due to a transition around 650°K.

Heat capacities and transitions connected with changes in the layer structures of FeCl₂ [74], FeBr₂ [75], FeI₂ [76] and CoBr₂ [77] have been reported by Gregory and coworkers. Measurements are carried out to 500°C, and a standard deviation of 2% on aluminum oxide values from the values by Furukawa et al. [67] is obtained.

In the calorimeter by Stansbury et al. [23] data on high purity copper, nickel and several nickel-rich alloys have been determined with an absolute error less than 0.5% at temperatures between room temperature and 600°C by Pawel and Stansbury [60]. The necessity of obtaining data for different heating rates to arrive at true heat capacities is stressed, and is illustrated for the case of copper. At about 600°C the apparent heat capacity using a heating rate of approximately 1.5 degC/min is 4% higher than the corrected value. As a result of trying to separate the magnetic heat capacity contribution in nickel, Pawel and Stansbury [77] find that the non-integral number of unpaired spins in nickel corresponds to 30% 3d⁸ and 70% 3d¹⁰ states rather than 60% 3d⁹ and 40% 3d¹⁰ states.

The upper temperature limit of adiabatic vacuum calorimeters was considerably advanced by Backhurst [25]. Automatically controlled, the instrument gives a continuous record of heat capacity from 600 to 1600°C for solid and liquid metals. Measurements on titanium were carried out to
1080°C, and those on a low-alloy steel extended into the molten state. A sample of about 250 cm$^3$ is needed, which somewhat limits its applications. More recently Dench [79] has described a calorimeter for measuring heat capacities, small heats of reaction and fusion. Dench and Kubaschewski [59] used it for determining heat capacities and heats of transition of pure iron in the range 800 to 1420°C. The Gibbs energy of transition from body centred to face centred structure of iron was calculated as a function of temperature and found to display a maximum of less than 80 J/g-atom at 1140°C. The heat capacity and heat of transition of cobalt have been studied by Braun and Kohlhaas [80] in a new calorimeter [81] in the range 50 to 1400°C with a reported accuracy of 2% at high temperatures.

Quenching, irradiation, and cold working of metals, give rise to storage of energy by accumulation of structural defects. The release of such defects has been studied by White and Koyama [82] in a differential calorimeter by simultaneous heating of a test specimen and a fully annealed reference specimen. Results for high-purity copper are reported with a precision of about 8% for stored energies of the order 20 J/g-atom. Changes in order,
due to structural defects, can be observed by rapidly increasing the temperature of an annealed sample, placing it in a thermostat and measuring the isothermal absorption of energy. Such experiments have been carried out on silver by Åström [83] in an exceptionally well regulated thermostat [84].

Heat capacity measurements on order-disorder transitions in alloys have been performed by Hirabayashi et al. [85] and by LoSacco [86] on the intermetallic compound Cu$_3$Au, by Wollenberger [87] on a 93%Ag-7%Mn alloy, by Scheil and Normann [88] on a 77%Cu-23%Mn alloy, and by Brooks and Stansbury [89] on 83%Cu-17%Al and 83%Cu-17%Ga alloys up to 700°C. For the latter alloys, neutron irradiation at 100°C after slow cooling was found to increase the amount of short range order and to introduce additional vacancies.

In a differential method by Arell [90] for determining transition energies in ammonium chloride and ammonium bromide, one of two identical samples is kept just below the temperature of transition and the other heated to between 15 and 20°C above the transition temperature for completion of the transition in the twin calorimeter. By slowly cooling into the transition region it is possible to have different polymorphic modifications in the sample containers at the same temperature. On further cooling of the two samples the transition energy can be measured by an electrical compensation method.

For heat capacity studies on high polymers up to 300°C, calorimeters have been constructed by Worthington et al. [91] and by Karasz [92].

3.3. Chemical reaction studies

High temperature reaction calorimeters have been the subject of interesting developments during the last ten years. Continuing the developments by Kubaschewski and Walter [93], Ticknor and Bever [42] and McKisson and Bromley [44], apparatuses were constructed by Kleppa [13], and Wittig and Huber [40] that allowed of a considerable increase in the precision of the measurements. The isothermal shield calorimeter by Kleppa was particularly suited for the study of endothermal heats of solution and mixing in alloy systems. The cooling of the calorimeter when the components were mixed by means of the combined charging and stirring device could then be compensated for electrically. The calorimeter was first used for re-determining the heats of mixing liquid lead and tin, both present in the calorimeter at the temperature in question. Further results appeared soon afterwards and were reviewed by Kleppa [94].

A calorimeter of similar type for measuring heats of solution of germanium, aluminium, and silver in tin in vacuum at 700°C is described by Mathieu [16].

The calorimeter of Wittig and Huber [40] differed from that of Kleppa; for one thing the jacket was temperature controlled instead of the thermostat, which made the initial adjustments less time-consuming. The first measurements by Wittig and Huber were made on liquid bismuth-lead and bismuth-tin alloys. The data for the former corresponded well with those of Kleppa [95]. Data on other binary liquid systems of the metals Zn, Cd, In, Tl, Sn, Pb were published and discussed further by Wittig [96]. In a new type of calorimeter Wittig and Gehring [24] extended the temperature range to 975°C for
heat of mixing studies on silver and tin. A simple calorimeter for use up to 1110°C, and capable of an accuracy of ±10%, was described by Oriani and Murphy [49]. In extending the method to 1200°C by high-frequency induction heating, Benz and Elliott [50] used copper as solvent for determining the heats of solution for tin and nickel in copper.

In contrast to the calorimeters by Kleppa and by Wittig, both of which can accommodate solid and liquid components, the calorimeter by Ticknor and Bever [42] was designed for adding solids only, usually with a temperature of 0°C, into the liquid tin. The calorimeter was used to study cold working (Bever and Ticknor [97]) and annealing (Greenfield and Bever [98]). Recently Misra et al. [48] determined the heats of formation of intermetallic compounds in the gold-tin system, with a liquid tin or a liquid tin-bismuth alloy as solvent. Measurements of heat capacity and the enthalpy of fusion for the compound AuSn were carried out in a constant-temperature-gradient calorimeter. Another calorimeter, for addition of solid samples, was constructed by Orr et al. [45]; in this the samples were charged from an electrically heated thermostat. It was used [99] for determining the heats of formation of silver-cadmium alloys at 35°C, and by Orr and Rovel [100] for investigating the thermodynamics of the structural modifications of AgZn.

Differential calorimetry was applied by Oriani and Murphy [32] for measuring the enthalpy of formation of solid silver-gold, gold-copper, and silver-copper alloys. Differences in the heats of solution of the prepared alloy and its pure components (simultaneously added to each of the twin cells containing liquid tin) were measured by electrical compensation. The method was applied to studies of ordering in precious metal alloys [101]. A sensitive twin calorimeter was constructed by Kleppa [33] and used in a series of investigations on fused salt systems, metallic systems and oxides. It represents an adaptation of the microcalorimeters developed by Calvet and his school [52]. A modified version of the calorimeter is now in operation [102]. A study of the heats of mixing in binary fused salts has recently been carried out by Murgulescu and Marchidan [22].

I have constructed a quasi-isothermal reaction calorimeter, see Fig. 6, and used it for determining the heats of formation of iron selenides and nickel selenides. Selenium is sealed into a Pyrex tube, which is placed into a quartz tube, open at the top. These tubes are next put into a larger quartz tube, containing iron and nickel, which is then evacuated, sealed and placed in the calorimeter. When the calorimeter temperature approaches 775°C, adjustments are made so that the temperature increase becomes less than 0.02 degC/min. After an hour or two the selenium container bursts and the reaction can then take place. The results of a reaction experiment are shown in Fig. 7. The system is calibrated electrically, and data for the heats of formation within the homogeneity ranges of the solid selenides are obtained with a precision of better than 1%.

An isothermal calorimeter for reactions involving gases at 250°C is reported by Lacher et al. [26] and results are obtained on the hydrogenation of alkyl halides. In a calorimeter for use up to 700°C, the heat of decomposition of ammonia was determined by Wittig and Schmatz [103]. More recently a constant heat flow calorimeter has been developed by Wittig and
FIG. 6. Schematic drawing of high temperature reaction calorimeter.

FIG. 7. Temperature-time relationship in a heat of formation experiment for NiSe$_{1.18}$. 
Schilling [104] and tested by determining the heat of decomposition of nitrous oxide.

Adiabatic high-temperature reaction calorimeters have been developed further by Kubaschewski and coworkers for studying slow reactions. In a calorimeter for use up to 1000°C cylindrical compacts of metal powders were made, and rapidly heated to a temperature at which the reaction went to completion within two hours. Further development by Dench [79] resulted in a device having many interesting features and suitable for use up to 1400°C. Heats of formation of iron-chromium, nickel-chromium, and iron-nickel alloys were determined.

REFERENCES

[40] WITTIG, F. E. and HUBER, F., Z. Elektrochem. 60 (1956) 1131.
[55] DAUPHINEE, T. M., Canad. J. Phys. 31 (1953) 577: see also ref. [54], page 269.
[58] WEST, E. D., GINNINGS, D. C., Rev. sci. Instrum. 28 (1957) 1070.
[69] GRÖNVOLD, F., unpublished data.
GRØNVOLD

A HIGH TEMPERATURE ISOTHERMAL CALORIMETER

J.R. LACHER, H. GOTTLIEB, P. FOWELL AND J. D. PARK
UNIVERSITY OF COLORADO, BOULDER, COLO., UNITED STATES OF AMERICA.

Abstract — Résumé — Аннотация — Resumen

A HIGH TEMPERATURE ISOTHERMAL CALORIMETER. A calorimeter is described which operates isothermally. Since there are no temperature differences between the calorimeter and its surroundings, no corrections due to heat losses by radiation and conduction need to be applied. The heat supplied to the calorimeter by the chemical reacting is substituted directly by electrical heating. The calorimeter has been used to measure heats of reactions involving gases. The catalyst chamber consists of a cylinder about 7.5 in. long and 1.5 in. in diameter. It is constructed of annealed tantalum which is found to be completely resistant to corrosion at 250°C. The chamber is closed with a Teflon plug and surrounded by a tantalum heat exchanger for removing exit gases. The reacting gases are led to the catalyst chamber in tantalum tubes. The chamber is suspended from a circular plate into a quart Dewar filled with a volatile liquid. For operation at 250°C, (CH₃ - CH₂H₄) - C₂H₄ - O₃Si (b.p. 320°C/630 mm) is suitable. As a chemical reaction takes place, the heat is transferred to this liquid. Also contained in the Dewar is a sintered brass frit, through which pure hydrogen may be passed to cool the volatile liquid by evaporation. An electrical heater is also located in this liquid. In making a run, cooling hydrogen is passed through the frit at a constant rate for several days. During this period electrical heating is supplied at a constant rate just sufficient to balance the cooling (5-10 cal/min). The balance is read on a differential platinum thermometer extending both into the calorimeter and the surrounding air space. The gaseous reactants are then led to the catalyst chamber at controlled rates. The electrical heat input is reduced so that the total heat again balances the cooling and the calorimeter is again at the same temperature as its surroundings. The reduction of the rate of electrical heating thus corresponds to the rate of evolution of heat by the reaction. The rate of formation of products is measured. The results obtained on the hydrogenation of alkyl halides are summarized.

CALORIMETRE ISOTHERMIQUE A HAUTE TEMPERATURE. Les auteurs décrivent un calorimètre qui fonctionne dans des conditions isothermiques. Comme il n’existe aucune différence de température entre le calorimètre et le milieu, il n’y a pas lieu d’apporter des corrections pour tenir compte des pertes de chaleur par rayonnement et conduction. La chaleur fournie au calorimètre par la réaction chimique est compensée directement par un chauffage électrique. Le calorimètre a été employé pour mesurer la chaleur de réactions dans lesquelles des gaz interviennent. La chambre de catalyse se compose d’un cylindre d’environ 19 cm de longueur et 3,8 cm de diamètre. Elle est construite en tantale recuit qui présente une résistance absolue à la corrosion à 250°C. La chambre est fermée par un bouchon en Teflon et entourée d’un échangeur de chaleur en tantale permettant d’évacuer les gaz dégagés. Les gaz qui interviennent dans la réaction sont amenés dans la chambre de catalyse par des tubes en tantale. La chambre est suspendue à une plaque circulaire et plongée dans un vase Dewar en quartz rempli d’un liquide volatile. Pour le fonctionnement à 250°C, on peut utiliser du (CH₄ - CH₂H₄) - C₂H₄ - O₃Si (point d’ébullition 320°C sous 630 mm de pression). Lorsque la réaction chimique se produit, la chaleur est transmise au liquide. Le vase Dewar contient en outre un appareil en laiton frité dans lequel on peut faire passer de l’hydrogène pur en vue de refroidir le liquide volatile par évaporation. Un dispositif de chauffage électrique se trouve également placé dans le liquide.

Pour chaque opération, on fait passer de l’hydrogène par l’appareil de refroidissement à un débit constant durant plusieurs jours. Pendant ce temps, l’appareil de chauffage électrique fournit, à un taux constant, juste assez de chaleur pour compenser le refroidissement (5-10 cal/min). L’équilibre est indiqué par un thermomètre différentiel en platine disposé de manière à plonger à la fois dans le calorimètre et l’air environnant. Puis, les gaz qui interviennent dans la réaction sont envoyés dans la chambre de catalyse à des débits contrôlés. La chaleur fournie par le dispositif de chauffage électrique est diminuée de telle sorte que la chaleur totale compense de nouveau le refroidissement et que le calorimètre revienne à la même température que le milieu. La réduction du taux de chauffage électrique correspond ainsi au taux de dégagement de chaleur par la réaction. On mesure le taux de formation des produits. Les auteurs donnent un aperçu des résultats qu’ils ont obtenus pour l’hydégénation d’halogénures d’alkyle.
INTRODUCTION

During the past several years, in the Chemistry Department of the University of Colorado, isothermal vapour phase calorimeters have been constructed with an operating temperature of up to 250°C [1]. The first
of these used an oil bath as a thermostat [2] and had a maximum operating
temperature of only 130°C. Later a calorimeter was constructed utilizing
a condensing vapour as a source of constant temperature and this was able
to operate at 250°C [3]. The use of a condensing vapour, however, proved
experimentally inconvenient due to the difficulty of maintaining the system
leak-free. Therefore an electrically operated calorimeter was designed [4, 5].
This calorimeter was operated at 100°C and gave good results for several
reactions.

Since many reactions of interest require a higher temperature to go to
completion, an attempt was made to operate this calorimeter at 250°C. At
this temperature, however, many modifications were found to be necessary.
Corrosion problems forced us to reconstruct parts of the calorimeter with
tantalum. The new modified calorimeter is described in this paper. In
addition, details are given of the various difficulties encountered with the
old calorimeter, and the modifications required. Some data on the hydro-
genation of alkyl halides are summarized.

THE CALORIMETER

The inner part of the calorimeter is shown in Fig. 1. The complete
calorimeter is shown in Fig. 2. The calorimeter reaction chamber consists
of a tantalum cylinder 7.5 in long, 1.5 in in diameter, and 0.02 in thick. It
is suspended from a circular iron plate. Catalyst is placed in the chamber
through the opening in the bottom. This is closed with a tight fitting Teflon
plug, held in position with a brass plate, which in turn is held by three rods
connected to another brass plate at the top of the reaction chamber. The
rods pass through the bottom brass plate and are threaded at the ends, the
nuts being tightened to form a good seal between the Teflon plug and the
tantalum.

The reactant gases enter the chamber through metal tubes attached to
the top of the chamber. The product gases leave from the bottom and pass
through a heat exchanger, looped up and down the walls of the reaction
chamber. This entire unit is enclosed by a quart Dewar vessel filled with
a suitable volatile liquid. The heat of reaction is transferred to this liquid.
The Dewar is supported on springs in an iron cylinder, 14.5 in long and
3.5 in i.d. the top of which is, when assembled, bolted to the iron plate
holding the reaction chamber. The surface of the Dewar is ground flat so that
a good seal may be formed between it and the iron plate, using a Teflon
O-ring which fits into a groove in the plate. A further Teflon O-ring is used
to form a seal between the plate and the iron cylinder. Hydrogen gas is
bubbled through the volatile liquid by means of a sintered brass frit located
just below the reaction chamber. This serves to remove heat from the
liquid. The hydrogen then passes out through a reflux condenser which
condenses the vaporized cooling liquid.

The calorimeter heater, H6, is constructed of 4 ft of nichrome wire
and has a resistance of about 40 ohms. It is located just above the frit.
Teflon-coated wire leads pass to two spark plugs, fixed in the iron plate,
which serve to insulate the leads from the plate. The leads continue as
heavy copper wire, thickly coated with asbestos, to insulate them from
FIG. 1. Isothermal calorimeter. The catalyst chamber and heat exchanger are made of tantalum with a Teflon plug to seal the bottom.
FIG. 2. Cross-section of calorimeter and thermostat showing the schematic arrangement of the platinum thermometers T1, T2, T3, T4, T5, the massive aluminium cylinders A, B, and the copper cup C. See text for details.
other parts of the calorimeter. Outside the calorimeter, two sets of leads are connected to these heater leads, one set for measuring the voltage drop across the heater, the other for carrying the heater current. Two platinum resistance thermometers wired differentially (T4 and T5) are used to detect any difference in temperature inside the Dewar and in the surrounding constant reference temperature area. These thermometers are also wired so that they may be read separately.

The catalyst chamber is surrounded by two large concentric aluminium cylinders, A and B. This arrangement has been used by Kelen [4]. The walls of the large outer cylinder are 2 in thick and 3 ft deep, and the inner cylinder 3 in thick and 27 in deep. Their external diameters are 17 in and 12 in respectively. Air space separates the two cylinders. On top of these sit aluminium lids 1 and 2, both of which are 2 in thick. Lid 2 may be lifted off the smaller aluminium cylinder, together with copper cup C, the gas entry and exit tubes, and the reaction chamber.

Five heaters are used to maintain the inner calorimeter and air space at a fixed arbitrary temperature in the range 249.5 to 250.5°C and constant to ±0.001°C. Heaters H1 and H2 (5 and 12 ohm, respectively) are wound around cylinder A. H1 provides a constant source of heat, and H2 an intermittent source. Together these heaters maintain the cylinder at the required temperature. Heaters H4 and H3 (both 20 ohm), wrapped alternatively round copper cup C, provide a constant and intermittent source of heat for the cup to hold it at the required temperature. This cup, located above lid 2 and extending to the top of the calorimeter, consists of a thin walled copper cylinder 5 in in diameter and 17 in long, filled to three-quarters depth with 15 lb of copper shot. Above the shot is a metal plate, and the rest of the cup is filled with vermiculite. To ensure adequate temperature control for the cup, the heaters must be as close as possible to the copper wall so as to have as little heat lag as possible. The purpose of the cup is to prevent heat loss on top of the instrument, through the 6 in diameter hole in lid 1, and to control the temperature of the entering reaction gases and the condensing cooling liquid. On top of lid 1 is a further heater H5 (20 ohm), maintained at around 250°C, but not fitted with a thermostat.

The reactant gas entry and exit tubes are made of 0.25 in o.d. annealed tantalum tubing of 0.02 in wall thickness. They are heliarc welded, under an inert gas, to the catalyst chamber and are continuous with no joints right to the top of the calorimeter. They are connected to the tubes from the flowmeter systems, when assembled, by means of Teflon tubing.

The whole calorimeter is surrounded by a vermiculite filled hull, D, and a vermiculite filled lid E which rests on top of lid 1. This provides adequate insulation for the satisfactory thermostat operation.

Platinum resistance thermometers are inserted into cylinder B (T1) for temperature reading of this inner cylinder, into A (T2) to operate intermittent heater H2, and into C (T3) to operate intermittent heater H3 in addition to the differential thermometer already described, (T4 and T5). Thermally and electrically shielded leads from thermometer T1 are connected with a Mueller bridge, where suitable current amplification allows the resistance to be read to $10^{-4}$ ohm (corresponding approximately to $10^{-3}°C$). The differential thermometer is connected in a similar manner. Thermono-
meters T2 and T3 are connected in Wheatstone circuits, with balance arms consisting of variable resistance boxes, set equal to the resistance of the respective thermometers at the fixed operating temperature. Galvanometers in these two Wheatstone circuits operate on/off electronic devices, one for each of the intermittent heaters. These auxiliary heaters are switched on automatically when the temperature of the cup or cylinder drops below, and off when the temperature rises above the chosen temperature. All thermometers are wired so as to cancel out or compensate for the lead resistances.

It is necessary to have three separate flow systems for the calorimeter: one for each of the reactant gases, and one for the hydrogen which bubbles through the volatile liquid. The flow systems are basically the same and consist of a variable level bubbler, a capillary flowmeter, and a back pressure manometer. The gases pass through calcium sulphate drying tubes before entering the calorimeter. The flowmeters are calibrated for the particular gas being used since the flow rate for a given head on the flowmeter depends on the density of the gas. All hydrogen used was oxygen-free (National Bureau of Standards).

OPERATION OF THE CALORIMETER

The assembled calorimeter is allowed to reach the set temperature over a period of four days. The cooling hydrogen is then turned on at a carefully controlled flow rate and the calorimeter heater H6 also switched on. The current through the heater is adjusted so that the cooling exactly balances the heat input, as indicated by the differential thermometer. This procedure may take up to 6 h for an exact balance point to be obtained. Readings of current and voltage are taken and the heat input per minute calculated. The reactant gases are then turned on at a carefully controlled flow rate, one of the reactants in about two-fold excess. The current through the heater is now reduced so that the reaction heat and electrical heat just balance the cooling, readings of current and voltage again being taken. The heat generated per minute by the reaction may then be calculated. An analysis of the rate of production of one of the reaction products can then be used to calculate the heat of reaction. Thus, if one of the reaction products is an acid gas, the exit gases are passed through a series of water bottles, for a given time, and the absorbed acid estimated with alkali.

It is essential during a run that the temperature of the inner cylinder, (as measured by thermometer T1), and of the calorimeter and surroundings, (T4 and T5) should remain at their normal equilibrium value since otherwise the returning condensed liquid at cup temperature will have a different effect depending on the temperature of the calorimeter fluid. In practice it has been found that no balance point can be obtained if the thermometers do not all remain at their equilibrium value. The temperature of the surroundings and of the inner cylinder are interdependent.

Since the whole procedure of obtaining two balance points is very time consuming, it is preferable to operate the calorimeter so that exactly the same cooling rate is produced each time. The reaction may then be started immediately without having to obtain a balance point for the cooling hydrogen.
For this purpose the flowmeters must be finely controllable and kept at constant temperature (temperature controlled room) so that the liquid density remains constant.

It is necessary to ensure that the reactant gases separately produce no heating effect. It was found that on passing one gas there was an initial heat effect but that after a period of about three hours all thermometers returned to their normal equilibrium temperature by themselves. Also runs on the heat of formation of hydrogen chloride from hydrogen and chlorine gave the correct answer.

DISCUSSION OF MODIFICATIONS INCORPORATED INTO THE NEW CALORIMETER

Many modifications had been made to the old calorimeter before, because of corrosion problems, it was necessary to reconstruct many parts of the calorimeter using tantalum. These were all incorporated into the new calorimeter and are discussed below.

The reactions first considered were the hydrogenations of several alkyl halides using palladium on charcoal as catalyst. The heats of formation of many alkyl halides are known to within only about 2 kcal/mole and it is hoped that, using this calorimeter, it will be possible to reduce the error by a factor of ten. In these reactions a hydrogen halide is one of the reaction products. Previous experience had shown that when an acid gas was produced the exit tubing, which was made of monel metal, became corroded after a while. While this effect was small at 100°C and did not interfere with operation of the calorimeter, at 250°C the corrosion was so bad that the exit tube became blocked and the calorimeter was rendered unusable. Test experiments showed that up to 10% of the acid gas was lost during its passage through the calorimeter. An analysis of the yellow incrustation produced showed it to be largely nickel halide, together with some copper halide, presumably produced by the acid gas attacking the monel reaction chamber and exit tubing. (Monel is a mixture of iron, copper, and nickel.) Nickel bromide sublimes and could easily be carried up with the exit gases, solidifying in the cooler part of the exit tube.

It was decided, therefore, to see if a more suitable material could be found which would be less prone to corrosion with acid gases. Glass had previously been tried but could not be used because of the difficulty of maintaining the necessary ground glass joints leak-free at the operating temperature, quite apart from its fragility. A series of corrosion tests were carried out outside the calorimeter, using various materials. The test conditions were approximately those in the calorimeter where the corrosion occurred, namely a mixture of hydrogen halide and hydrogen at the same flow rates, and maintained at 250°C. The materials tried were pure nickel, two grades of monel, copper, silver, silver solder (which had been used in joining the monel), gold-plated silver, Teflon-coated metal, and annealed tantalum. The tests showed that the monel was, as expected, responsible for the blockage. Also all materials except the Teflon-coated metal and tantalum were found to be attacked sufficiently for them to be unsuitable
for use in construction of the calorimeter. Silver and silver solder rapidly formed a coating of halide which, however, did not prevent further attack. Neither was gold plating, even of reasonable thickness, adequate to prevent the silver underneath from being attacked. Teflon-coated metal was found to be suitable, no change in weight of coated silver being observed, the Teflon coating remaining intact. When, however, an attempt was made to coat the exposed surfaces of the calorimeter, using Teflon emulsion, it was difficult to get an even coating and the Teflon peeled and cracked where there was any unevenness. Tantalum was found to be completely suitable and it was decided to reconstruct the whole of the inner calorimeter with annealed tantalum, using heliarc welds to join the metal.

Orsil BF 1, tetra (2-ethyl hexyl) silicate, had previously been used for operation at 250°C, though with a different frit arrangement and under different controlled temperature conditions, and had provided an adequate cooling rate. However, Orsil was found to give a very small cooling rate in our calorimeter, quite inadequate for accurate results. In addition, Orsil removed from the calorimeter after use was found to have a higher boiling point from the Orsil distilled before use. It thus gave varying cooling rates. It was decided to change the cooling liquid. The choice of a suitable cooling liquid is not easily made since it must be stable at 250°C over a long period of time, be non-corrosive, and have a constant boiling point, 50 to 70°C above 250°C, such that it has adequate vapour pressure to give a cooling rate of around 10 cal/min under the calorimeter conditions. Tetra (2-ethyl butyl) silicate, b.p. 320°C at 630 mm Hg, was chosen. This compares well with that of Orsil, which has a b.p. 360°C at the normal laboratory pressure of 630 mm Hg.

The main difficulty encountered in attempting to operate the old calorimeter was as follows: on turning on the hydrogen cooling stream, the reading on the differential thermometer - after an initial drop due to the expected cooling of the liquid in the Dewar - increased suddenly, corresponding to a wide departure from equilibrium (isothermal) conditions. In addition, after about 20 min the temperature of the cup started to drop from 250°C and could not easily be re-regulated. The increase in the differential reading could have been due either to an increase of temperature at the lower thermometer in the Dewar vessel or, more probably, to a fall in temperature at the upper reference thermometer. The differential thermometer circuit was therefore altered so that the thermometers could be read separately, again taking the lead resistances so that these cancelled or coupled differentially. It was found that the upper thermometer did not remain at constant temperature and that this did in fact drop suddenly. The explanation of this seemed to be that either the incoming hydrogen or the returning condensing cooling liquid was not brought completely up to temperature by the cup heater and, in the process, the cup and the area below the cup, where the upper thermometer was situated, cooled down. In earlier operation much of the evaporating liquid had been allowed to escape so that this effect was largely avoided. However, it was felt that the resulting loss in cooling liquid would affect the back pressure on the frit hydrogen and hence make it less easily controllable; it is, of course, essential that the flow rate of frit hydrogen remains absolutely constant. In addition, it had in the past been continually
necessary to replace the cooling liquid as it was lost. An attempt was made to operate the calorimeter non-isothermally by raising the temperature of the cup to 260°C, keeping the rest of the calorimeter at 250°C. However this system, though overcoming the difficulties described above, proved to be extremely difficult to operate and no accurate balance points could be obtained: operation under these conditions was abandoned.

Preheating the incoming hydrogen stream produced no improvement so it was decided that the whole condenser system and cup should be completely rebuilt. This was done in several stages, each being an improvement on the earlier, until in the final arrangement the difficulty was completely overcome. First, the condenser at the top of the calorimeter was changed from a water cooled one to a copper spiral in air so that the condensing liquid would not undergo such a large drop in temperature. Second, the tube between the cup and the Dewar (the bottom part of the condenser system) was heavily insulated with asbestos so that the fluctuations in the temperature of the returning liquid would not immediately be apparent in the temperature of the calorimeter surroundings. Third, the walls of the upper thermometer were insulated from the cup with several layers of glass tape. Fourth, after an attempt to heat the top of the condenser tube to approximately 250°C it was decided to extend the cup to the top of the calorimeter, it previously reaching only 4 in above lid 2. The heater wires were wound around the cup with as little insulation as possible so that fluctuations in cup temperature could be immediately compensated for by the heat from the on/off heater. At the base of the cup, around the heaters, a further area was filled with aluminium shot to maintain a high heat-capacity sink in this region. Last of all, the part of the condenser in the area between the top of the Dewar, through the cup and to the top of the calorimeter was filled with copper shot to slow down the liquid flow of the returning condensing cooling liquid and to prevent the vapour from condensing too far up the spiral. With these five modifications no further trouble was experienced with the temperature control of the cup or in keeping the constant reference temperature.

The frit and heater were altered to increase the cooling rate and to make them more serviceable. Previously the frit material had been silver soldered in its housing and had a central hydrogen inlet passing through it. The temperature required to silver solder tended to block the frit, and the inlet at the base of the frit housing, so that any knocks on the inlet tube did not effect the frit, and the frit material was sealed into its housing at room temperature with a lead gasket. This arrangement provided a large area of evenly-distributed fine bubbles.

The previous heater consisted of a spoked Teflon disc, with resistance wire wound round it, and was situated just above the frit. In the new arrangement a Teflon block, in the form of a truncated cone with surface grooves parallel to the axis, has resistance wire wound around it. This avoids an earlier trouble of hydrogen collecting in one large bubble just under the heater. Small bubbles were now able to pass right to the top of the cooling liquid, being deflected round the reaction chamber by the cone. The Teflon cone was attached to the brass plate at the base of the catalyst chamber.

Several other minor modifications were carried out. The gas flow systems were improved to allow of a finer control of the flow rates, par-
particularly those of the cooling hydrogen and limiting reactants. The calorimeter heater leads were at first insulated with ceramic material, where these passed through lid 2 and cup C, but the ceramic tended to crack, and so heavy copper wire with a thick asbestos coating was used instead and found serviceable. In earlier experiments, too, tapered metal-to-metal joints had been used to connect the gas inlet tubes in the calorimeter to the tubes from the flow systems. These joints proved a constant source of trouble due to leakage and stripped threads, and Teflon washers, though preventing leaks, were not serviceable. The joints were eliminated by connecting the tubes directly with Teflon tubing. This gives leak-free joints, and the Teflon tubing has the advantage of being easy to remove or change if necessary.

### Table I

**Heat of Formation of Hydrogen Chloride at 250°C**

<table>
<thead>
<tr>
<th>H₂ flow (10⁴ moles/min)</th>
<th>HCl formation (10⁴ moles/min)</th>
<th>Energy rate (cal/min)</th>
<th>ΔHₜ(HCl) (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>3.913</td>
<td>8.737</td>
<td>22 330</td>
</tr>
<tr>
<td>19</td>
<td>3.864</td>
<td>8.512</td>
<td>22 030</td>
</tr>
<tr>
<td>19</td>
<td>2.470</td>
<td>5.707</td>
<td>22 910</td>
</tr>
<tr>
<td>19</td>
<td>3.620</td>
<td>8.360</td>
<td>23 090</td>
</tr>
<tr>
<td>19</td>
<td>3.600</td>
<td>7.788</td>
<td>21 040</td>
</tr>
<tr>
<td>21</td>
<td>3.585</td>
<td>7.795</td>
<td>21 740</td>
</tr>
<tr>
<td>21</td>
<td>3.728</td>
<td>7.875</td>
<td>21 120</td>
</tr>
<tr>
<td>21</td>
<td>3.680</td>
<td>8.530</td>
<td>23 190</td>
</tr>
<tr>
<td>19</td>
<td>3.544</td>
<td>8.333</td>
<td>23 510</td>
</tr>
<tr>
<td>19</td>
<td>3.390</td>
<td>7.956</td>
<td>23 470</td>
</tr>
<tr>
<td>19</td>
<td>3.339</td>
<td>7.806</td>
<td>23 380</td>
</tr>
</tbody>
</table>

Mean 22 530 cal/mole HCl

### Additional Notes on the Operation of the Calorimeter

For a series of several runs, the following procedure has been found to be the quickest and most convenient. The frit cooling hydrogen is turned on at a constant, controlled rate and left on continuously for a period of six days or so, during which time several runs may be made. Before the first run a frit balance is obtained by adjusting the heat input so that the differential thermometer gives the correct reading for isothermal conditions, i.e. 0.0220 ohms. The reactants are then turned on and a further
TABLE II

HEATS OF HYDROGENATION OF ALKYL HALIDES AT 25°C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$-\Delta H$ (cal/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_2\text{Cl}+\text{H}_2$ $\rightarrow$ $\text{CH}_4+\text{HCl}$</td>
<td>19 318</td>
<td>[3]</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{Cl}+\text{H}_2$ $\rightarrow$ $\text{C}_2\text{H}_4+\text{HCl}$</td>
<td>16 559</td>
<td>[3]</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_7\text{Cl}+2\text{H}_2$ $\rightarrow$ $\text{C}_3\text{H}_6+2\text{HCl}$</td>
<td>51 188</td>
<td>[3]</td>
</tr>
<tr>
<td>$\text{n-C}_3\text{H}_7\text{Cl}+\text{H}_2$ $\rightarrow$ $\text{C}_3\text{H}_6+\text{HCl}$</td>
<td>15 700</td>
<td>[6]</td>
</tr>
<tr>
<td>$\text{iso-C}_3\text{H}_7\text{Cl}+\text{H}_2$ $\rightarrow$ $\text{C}_3\text{H}_6+\text{HCl}$</td>
<td>13 950</td>
<td>[6]</td>
</tr>
<tr>
<td>$\text{CH}_3\text{Br}+\text{H}_2$ $\rightarrow$ $\text{CH}_4+\text{HBr}$</td>
<td>17 580</td>
<td>[7]</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{Br}+\text{H}_2$ $\rightarrow$ $\text{C}_2\text{H}_4+\text{HBr}$</td>
<td>14 110</td>
<td>[7]</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_7\text{Br}+2\text{H}_2$ $\rightarrow$ $\text{C}_3\text{H}_6+2\text{HBr}$</td>
<td>47 610</td>
<td>[8]</td>
</tr>
<tr>
<td>$\text{n-C}_3\text{H}_7\text{Br}+\text{H}_2$ $\rightarrow$ $\text{C}_3\text{H}_6+\text{HBr}$</td>
<td>13 570</td>
<td>[6]</td>
</tr>
<tr>
<td>$\text{iso-C}_3\text{H}_7\text{Br}+\text{H}_2$ $\rightarrow$ $\text{C}_3\text{H}_6+\text{HBr}$</td>
<td>10 770</td>
<td>[6]</td>
</tr>
<tr>
<td>$\text{n-C}_3\text{H}_7\text{F}+\text{H}_2$ $\rightarrow$ $\text{C}_3\text{H}_6+\text{HF}$</td>
<td>22 885*</td>
<td>[9]</td>
</tr>
<tr>
<td>$\text{iso-C}_3\text{H}_7\text{F}+\text{H}_2$ $\rightarrow$ $\text{C}_3\text{H}_6+\text{HF}$</td>
<td>21 106*</td>
<td>[9]</td>
</tr>
</tbody>
</table>

*Reaction Temperature 248°C.

balance is obtained. When the run is completed, the heat input rate is turned up again to the original frit balance point rate. The apparatus is then left overnight to settle down and is ready for starting another run straight away on the following day, and so on. During all the time that the hydrogen is left on, any variation of the frit balance point is immediately apparent. If the differential reading is only slightly different from 0.0220 (± 0.0015) ohms from day to day, the temperature reading on the differential thermometers may be taken as the equilibrium value; if the differential reading is greater than this, the heat input can be adjusted so that the difference falls again to within the given range. In practice, all this only takes a short time. The procedure avoids the difficulty of varying frit values or the necessity for making a time-consuming frit determination before each run.

The calorimeter has been tested to determine if it operates properly by carrying out the reaction of hydrogen with chlorine. Hydrogen was used in excess and the results are summarized in Table I. They give a mean value of -22,530 cal/mole for the heat of formation of hydrogen chloride. Using the older calorimeter [3], a mean value of -22 200 cal/mole was obtained at 248°C. Rossini's value [10] for the heat of formation of hydrogen...
chloride corrected to the above temperature is \(-22.225\) cal/mole. We have also re-measured the heat of hydrogenation of methyl chloride and obtained a value of \(-19.870\) cal/mole.

This compares favourably with an earlier value of \(-19.665\) cal/mole at 248°C [3]. The present calorimeter essentially substitutes chemical energy for electrical energy under conditions where there are no heat exchanges between the calorimeter and its surroundings. It is still necessary to know that the catalyst is at a steady state and that no secondary reactions take place on it. Some typical reactions which we have studied are given in Table II where the data, except for the fluorides, have been corrected to 25°C. This gives us sufficient information to calculate the heat of formation of the alkyl halides.

ACKNOWLEDGEMENTS

This research is being supported by a National Science Foundation grant, GP-2933, in chemistry.

REFERENCES

HEATS OF MIXING IN BINARY SYSTEMS OF MOLTEN SALTS. The heat of mixing is an important thermodynamic property in binary mixtures. As a result of the recent development of high-temperature calorimetry we have been able to determine directly the heat of mixing in binary systems of molten salts. In this work we present the results of thermochemical measurements carried out in our laboratories for the systems (Rb-K)Cl; (Rb-Na)Cl; (Ag-Na)Cl; (Na-K)Br and (Br-Cl)Na for different concentrations and temperatures. In our view, the most significant components of the heat of mixing are the ionic contribution and the polarization energy of the ions. Consequently, use could be made of a relation of the form:

$$\Delta H^M = Q_i - Q_p.$$ 

The heat of mixing can then have either positive or negative values depending on the sign and the preponderance of the $Q_i$ and $Q_p$ energies.
Таким образом, энергия смешения может иметь как положительные, так и отрицательные значения в зависимости от знака и относительного количества энергий $Q_i$ и $Q_p$.

CALORES DE MEZCLA EN SISTEMAS BINARIOS DE SALES FUNDIDAS. El calor de mezcla ocupa un lugar importante entre las propiedades termodinámicas de las mezclas binarias. Como consecuencia de los últimos adelantos en calorimetría a temperaturas elevadas, los autores se propusieron determinar directamente el calor de mezcla en sistemas binarios de sales fundidas. En la memoria, presentan los resultados de mediciones termoquímicas efectuadas en los siguientes sistemas:

(Rb-K)Cl; (Rb-Na)Cl; (Ag-Na)Cl; (Na-K)Br y (Br-Cl)Na

a diversas concentraciones y temperaturas. Los autores consideran que las componentes más importantes del calor de mezcla son la contribución iónica y la energía de polarización de los iones. En consecuencia, se podrá aplicar una relación de la forma:

$$\Delta H^M = Q_i - Q_p.$$

De esta manera, la energía de mezcla puede tener valores tanto positivos como negativos, según el signo y la preponderancia de las energías $Q_i$ y $Q_p$.

L'étude des sels fondues pris individuellement et le développement des théories concernant plus particulièrement les mélanges binaires sont assez limités, par suite du manque de données expérimentales. Les facteurs tels que la charge de l'ion, la dimension, la polarisabilité, la possibilité de former des complexes, bien qu'assez nombreux, ne constituent qu'une partie des facteurs susceptibles de provoquer des déviations, aussi bien négatives que positives, par rapport aux données idéales.

L'une des voies les plus importantes permettant de caractériser un système consiste à déterminer ses propriétés thermodynamiques. Au cours de ces dernières années, l'étude des mélanges binaires de sels fondues s'est considérablement développée dans ce sens. Parmi les propriétés thermodynamiques, les chaleurs de mélange occupent une place importante.

La détermination des chaleurs de mélange à l'aide de la calorimétrie à des températures élevées (500-900°C) constitue une des méthodes récentes permettant de donner une explication partielle du comportement des mélanges binaires de sels fondues.

Les premiers essais de ce genre, effectués par Kleppa [1] à l'aide du calorimètre Calvet, ont eu pour objet la détermination de la chaleur de mélange des nitrates alcalins fondu.

Dans le présent mémoire, nous décrivons un calorimètre pour des températures élevées, que nous avons construit; nous décrivons également le procédé de détermination de la chaleur de mélange de systèmes binaires de sels fondu à l'aide de ce calorimètre.

PARTIE EXPERIMENTALE

Afin d'étudier les systèmes binaires d'halogénures alcalins, nous avons construit un calorimètre de platine (fig.1). Le calorimètre aussi bien que les récipients contenant les sels (A et B) et la paroi thermostatique sont en platine de 0,3 mm d'épaisseur.
Pour la mesure des effets thermiques se produisant à l'intérieur du calorimètre, nous avons construit, en laboratoire, un thermocouple différentiel Pt-PtRh à 50 soudures chaudes et 50 soudures froides. Le fil des thermocouples, de 0,3 mm de diamètre, avait été vieilli au préalable. Les thermocouples étaient isolés au moyen de petits tubes de quartz. Les soudures chaudes étaient directement montées sur le calorimètre, tandis que les soudures froides étaient montées sur l'écran. Les conducteurs de liaison sur potentiomètre étaient blindés, afin d'éliminer l'éventualité des courants de fuite et des courants induits. Pour son étalonnage électrique, on a monté sur le calorimètre un élément de chauffage bifilaire (E) en platine de 0,2 mm de diamètre ayant une résistance de 13 Ω à 20°C. Le courant électrique d'étalonnage était fourni par une batterie d'accumulateurs de grande capacité.

L'instrument de mesure des effets thermiques était un potentiomètre Dieselhorst à faible résistance intérieure, avec un galvanomètre «multiflex» dont la résistance d'entrée était de 25 Ω. Pendant les mesures, on a déterminé un zéro expérimental représentant la différence de température entre le calorimètre et l'écran thermostatique. Les déterminations ont été faites en enregistrant la déviation du spot du galvanomètre en fonction du temps. Aucune déviation du galvanomètre attribuable à l'établissement ou à l'interruption des circuits de chauffage n'a été observée durant les mesures.
L'étalonnage du calorimètre a été fait aussi bien en le chauffant qu'en le refroidissant. Dans le premier cas, on a utilisé l'élément de chauffage électrique bifilaire en platine. Afin d'égaliser l'effet de la batterie d'accumulateurs, le courant d'étalonnage a d'abord été introduit durant cinq minutes dans une résistance ballast ayant la même valeur. La quantité de chaleur dégagée dans le calorimètre a été calculée au moyen de la formule

\[ Q_{el} = 0,239 \text{ E.I.t.} \]  

où les symboles gardent leur signification habituelle (E = force électromotrice, I = intensité, t = temps). En outre, l'étalonnage électrique par chauffage a été utilisé ultérieurement pour les déterminations mêmes.

L'étalonnage du calorimètre par refroidissement a été effectué en utilisant comme agent réfrigérant l'argent métallique fin (titre 1000/1000). L'argent, sous forme de segments de fil de 2 mm de diamètre, maintenu à la température ambiante dans un bloc de laiton nickelé, a été introduit dans le calorimètre par l'orifice central. La variation, avec la température, de la capacité calorique de l'argent étant donnée par la relation

\[ C_p = 5,60 + 1,50 \cdot 10^{-3} T \]  

avec une précision de 1% dans le domaine de températures compris entre 273 et 1234°K, on en déduit la relation de travail

\[ \Delta H_T - \Delta H_{298} = 5,60 T + 0,75 \cdot 10^{-3} T^2 - 1735 \text{ cal/mole} \]  

qui est valable pour une mole d'argent (107,88 g). Nous avons utilisé des quantités d'argent variant entre 2 et 5 g.

La température durant les expériences était mesurée au moyen d'un thermocouple de Pt-PtRh introduit dans le calorimètre.

Avant de les introduire dans le calorimètre, les sels utilisés, d'une pureté p.a., étaient séchés, fondus et maintenus sur du pentoxyde de phosphore anhydre sous vide.

**RESULTATS**

Au moyen de ce calorimètre, nous avons déterminé les chaleurs de mélange des systèmes (Br-Cl)Na, (Na-K)Br, (Ag-Na)Cl, (Rb-K)Cl et (Rb-Na)Cl à diverses concentrations, à la température de 860°C.


Le système bromure de sodium-bromure de potassium qui, de même que le système précédent, forme en se refroidissant des cristaux mixtes avec un minimum très marqué, possède des chaleurs de mélange négatives.
TABLEAU I

CHALEUR DE MELANGE DU SYSTEME
(\text{Br-Cl})_{\text{Na}} A 860°C

<table>
<thead>
<tr>
<th>NaBr(x)</th>
<th>0.2</th>
<th>0.3</th>
<th>0.5</th>
<th>0.7</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^M$ (cal/mole)</td>
<td>30</td>
<td>38</td>
<td>50</td>
<td>45</td>
<td>37</td>
</tr>
</tbody>
</table>

* $\Delta H^M$ = chaleur de mélange (heat of mixing).

TABLEAU II

CHALEUR DE MELANGE DU SYSTEME
(Na-K)Br A 860°C

<table>
<thead>
<tr>
<th>KBr(x₁)</th>
<th>0,2</th>
<th>0,3</th>
<th>0,5</th>
<th>0,7</th>
<th>0,8</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔHM (cal/mole)</td>
<td>-73</td>
<td>-118</td>
<td>-140</td>
<td>-125</td>
<td>-84</td>
</tr>
</tbody>
</table>

Le système chlorure d'argent - chlorure de sodium forme, en se refroidissant, une solution solide continue entre le point de fusion de NaCl et celui de AgCl. Pour la chaleur de mélange, on a obtenu des valeurs positives qui, dans le cas du mélange équimoléculaire et à la température de 860°C, n'ont pas dépassé la valeur de 35 cal/mole. Ces valeurs sont données au tableau III et à la figure 2.

Le système chlorure de rubidium - chlorure de potassium forme également, en se refroidissant, des cristaux mixtes ayant un point minimum sur le diagramme de fusion. Pour la chaleur de mélange, on a obtenu de faibles valeurs positives, que l'on trouve au tableau IV et à la figure 2.

TABLEAU III

CHALEUR DE MELANGE DU SYSTEME
(Ag-Na)Cl A 860°C

<table>
<thead>
<tr>
<th>NaCl(x₁)</th>
<th>0,2</th>
<th>0,5</th>
<th>0,8</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔHM (cal/mole)</td>
<td>16</td>
<td>35</td>
<td>19</td>
</tr>
</tbody>
</table>

TABLEAU IV

CHALEUR DE MELANGE DU SYSTEME
(Rb-K)Cl A 860°C

<table>
<thead>
<tr>
<th>RbCl(x₁)</th>
<th>0,3</th>
<th>0,5</th>
<th>0,7</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔHM (cal/mole)</td>
<td>15</td>
<td>21</td>
<td>13</td>
</tr>
</tbody>
</table>

Le système chlorure de rubidium - chlorure de sodium, à l'encontre des systèmes précédents, forme en se refroidissant un eutectique à 541°C. Lors du mélange des deux sels, on a obtenu des valeurs négatives assez élevées pour la chaleur de mélange. Ces valeurs sont données au tableau V et à la figure 2.
TABLEAU V

CHALEUR DE MELANGE DU SYSTEME
(Rb-Na)Cl A 860°C

<table>
<thead>
<tr>
<th>RbCl(χ₁)</th>
<th>0,25</th>
<th>0,50</th>
<th>0,75</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH^M (cal/mole)</td>
<td>-76</td>
<td>-238</td>
<td>-103</td>
</tr>
</tbody>
</table>

CONCLUSION

La conclusion générale que l'on peut tirer des données énumérées dans ce mémoire ainsi que dans [3] est que les interactions entre les ions des sels fondus complètement dissociés diffèrent beaucoup entre elles et dépendent des facteurs mentionnés dans la première partie du mémoire.

Nous sommes d'avis que les composantes les plus importantes de la chaleur de mélange sont la contribution ionique et l'énergie de polarisation des ions. Dans ce cas, c'est une relation de la forme

ΔH^M = Q_1 - Q_p

qui devrait être valable.

De cette façon, l'énergie de mélange pourrait acquérir des valeurs aussi bien négatives que positives selon les valeurs des énergies Q_1 et Q_p et, bien entendu, suivant que c'est l'une ou l'autre de ces deux énergies qui prédomine.

REFERENCES

EMPLOI D'UN CALORIMÈTRE SOUS VIDE POUR LA MESURE DES CHALEURS DE DISSOLUTION DE Ge, Al ET Ag DANS Sn A 700°C; MESURES DES ENTHALPIES DE Sn, ZrB₂, TiB₂, BN ET B₄C.

J.-C. MATHIEU, F. DURAND ET E. BONNIER
ECOLE NATIONALE SUPERIEURE D'ÉLECTROCHIMIE ET D'ÉLECTROMETALLURGIE, GRENOBLE, FRANCE

Abstract — Résumé — Аннотация — Resumen

USE OF A VACUUM CALORIMETER TO MEASURE THE HEATS OF DISSOLUTION OF Ge, Al AND Ag IN Sn AT 700°C; ENTHALPY MEASUREMENTS ON Sn, ZrB₂, TiB₂, BN AND B₄C. The calorimeter employed was similar in principle to that used by Kleppa and was designed to operate at temperatures of 700°C or above. It was made of nickel and consisted of an oven and a system of damping screens at high vacuum. The thermogram is registered directly in numerical form; then, taking the heat loss to obey Newton's Law, the temperature-time results are evaluated on a computer to give the heat released in the particular experiment. The apparatus is calibrated using synthetic sapphires from the National Bureau of Standards.

The apparatus, designed for the measurement of heats of dissolution, also permits of enthalpy determination: the authors have measured that of tin at 700°C, a value which has so far always been extrapolated, as well as those of ZrB₂, TiB₂, BN and B₄C between 300 and 750°C. Then, with regard to alloy formation, measurements have been made on the heat of dissolution of silver, germanium and aluminium in Sn at 700°C. In the last-mentioned system, the measurements supplement, for low aluminium concentrations, the EMF measurements by Massart.
мнения в олове при 700°С. По этой последней системе настоящие измерения уточняют проведенные Массаром измерения электродвижущей силы в области поведения алюминия в состояниях очень высокого разбавления.

EMPLEO DE UN CALORIMETRO AL VACIO PARA DETERMINAR LOS CALORES DE DISOLUCION DEL Ge, Al y Ag EN Sn A 700°C; MEDICION DE LAS ENTHALPIAS DEL Sn, ZrB₂, TiB₂, BN Y B₄C. El calorímetro utilizado, análogo en principio al de Kleppa, ha sido concebido para funcionar a una temperatura superior o igual a 700°C. Construido de níquel puro, está formado por un horno y un sistema de pantallas amortiguadoras en un vacío elevado. Para evaluar la cantidad de calor desprendida, los termogramas se registran directamente en forma numérica y el período de pérdida de calor, representado por la ley exponencial de Newton, se trata mediante una calculadora. La calibración del aparato se realiza con ayuda de zafiros sintéticos del National Bureau of Standards.

Ideado para medir calores de disolución, el aparato ha sido empleado también para determinar entalpas, entre ellas, la del Sn a 700°C, dato que hasta ahora se obtenía por extrapolación, y las del ZrB₂, TiB₂, BN y B₄C entre 300 y 750°C. En lo que respecta a la formación de aleaciones, las mediciones realizadas se refieren a los calores de disolución del Ag, Ge y Al en el Sn a 700°C. En este último sistema, las mediciones realizadas confirman, para el Al muy diluido, las mediciones de fuerza electromotriz efectuadas por Massart.

1. INTRODUCTION

Le Laboratoire de métallurgie de l'Ecole nationale supérieure d'électrochimie et d'électrométallurgie de Grenoble s'est orienté depuis quelques années vers des mesures physico-chimiques dans les alliages métalliques liquides. Parmi toutes les grandeurs mesurables, l'enthalpie de mélange présente un intérêt primordial. La méthode permettant d'atteindre cette grandeur de la façon la plus directe est la calorimétrie. Dans ce mémoire les auteurs relatent la réalisation et les premiers essais du calorimètre à dissolution qu'ils ont réalisé.

2. CONCEPTION

La partie essentielle d'un calorimètre est son thermostat. Dans notre appareil il est constitué d'un bloc de nickel «Mond» (fig. 1) possédant une grande capacité calorifique par rapport à celle de la cellule de mesure placée en son centre. Sa température est maintenue constante à l'aide d'un système d'écrans amortisseurs suivant le principe de Tian [1]. Une régulation tout ou rien rend périodique et d'amplitude E la température T du corps chauffant:

\[ T = T_0 + \frac{E}{2} \sin 2\pi \nu t \]

Après le \( n \)ième écran l'amplitude \( E_n \) est d'autant plus faible que
- la fréquence \( \nu \) de la régulation est plus grande; elle est ajustée grâce au dispositif d'alimentation,
- la capacité calorifique des écrans est plus grande,
- la constante de transfert d'un écran à l'autre est plus petite.

Tian a appliqué ce raisonnement en 1923 sur une enceinte maintenue à la température ambiante; en 1954 Kleppa a construit sur ce principe un calorimètre pouvant fonctionner jusqu'à 500°C.
En ce qui concerne l'appareil présenté ici, nous avons étudié tous les éléments pour travailler jusqu'à 1200°C. Cette température ainsi que les conditions de Tian ont fait choisir le nickel «Mond» comme matériau de construction des amortisseurs. En outre cet élément pur, bon conducteur de la chaleur, rend homogène la température de chaque écran. Une fois ce matériau choisi, nous nous sommes fixés un rapport $E_n/E = 1/10000$ et le calcul fournit alors le nombre d'écrans et leurs dimensions.
3. REALISATION

Le Laboratoire a confié la réalisation de ce projet à la société ARAM de Lyon, qui a su, malgré les difficultés que cela présentait, maintenir intégralement les impératifs de base de la conception.

Le premier impératif est de réaliser une enceinte étanche. En effet, il est indispensable de travailler en atmosphère contrôlée ou sous vide pour empêcher toute réaction parasite sur les métaux liquides. Le thermostat se trouve dans un enceinte de 80 l. Une pompe à palettes de 25 m$^3$/h et une pompe à diffusion de 600 l/s assurent un vide de 10$^{-6}$ torr. Comme une partie de cette enceinte se trouve chauffée à la température du résistor, le calorifuge qui l'entoure est placé dans une deuxième enceinte étanche, où une pompe de 10 m$^3$/h assure un vide de 10$^{-2}$ torr. Ce détail de construction réduit la diffusion des gaz à travers la paroi chaude et supprime les risques de déformation mécanique.

Le corps chauffant qui entoure complètement les écrans est constitué de deux viroles et de deux flasques en nickel sur lesquelles sont enroulés quatre résistors «Thermocoax». Sous vide ce type de chauffage présente de nombreux avantages, mais sa forme actuelle ne nous permet pas de dépasser sans risques 800°C, et limite les performances de l'appareil.

Chaque élément du corps chauffant est asservi indépendamment par un régulateur «Pyrelectron». La tension d'alimentation est stabilisée à 1%. Un autotransformateur «Variac» principal contrôle la puissance totale admise dans les résistors. Chaque résistor est également alimenté par l'intermédiaire d'un autotransformateur, ce qui permet d'ajuster la fréquence de régulation. Cette fréquence constitue le premier paramètre intervenant dans l'amortissement. Les autres paramètres sont la capacité calorifique qui doit être grande, ce qui impose que les amortisseurs soient épais, et la constante de transfert qui doit être petite, ce qui impose un poli spéculaire de ceux-ci. Le bloc isotherme pèse 16 kilos, il est de ce fait insensible aux faibles dégagements de chaleur produits dans la cellule de mesure. La température de ce bloc est mesurée à l'aide d'un couple «Chromel-Alumel» et enregistrée en continu. La cellule actuelle de mesure est constituée d'un creuset en graphite nucléaire contenant le métal solvant, et de huit couples «Chromel-Alumel» montés en différentiel entre la paroi du creuset et le bloc isotherme. La pile ainsi constituée fournit une f. é. m. de 160 μV/°C qui est amplifiée et enregistrée.

Pour diminuer le transfert thermique entre la cellule et le thermostat, un écran d'acier inoxydable poli entoure le creuset.

4. MISE EN ŒUVRE

Les mesures rapportées ici ont été effectuées avec de l'étain comme solvant. Chaque série de mesures comporte plusieurs étalonnages et plusieurs dissolutions; elle dure environ quinze jours.

Une centaine de grammes d'étain «Prolabo R.P.» préalablement fondu sous vide est introduite dans la cellule. Le calorimètre est mis sous vide, puis en chauffe, pendant une période de trois à onze jours (suivant la tempéra-
ture désirée), jusqu'à ce que s'établisse l'équilibre entre la cellule et le bloc isotherme. L'équilibre atteint, un échantillon d'étain venant d'un sas thermostaté à 20°C tombe dans le bain liquide en vue d'un étalonnage. La quantité de chaleur ainsi introduite est la variation d'enthalpie de l'étain de 20°C à la température de travail. Elle donne naissance à une température différentielle $\Delta T$ qui est l'écart entre la température de la cellule et celle du thermostat, la variation de température différentielle atteint au maximum un demi degré, c'est-à-dire 80 $\mu$V. La courbe enregistrée présente un fond parasite sinusoidal de ± 0,15 $\mu$V et une dérive linéaire qui est corrigée. Cette courbe (fig. 2) présente deux périodes; la première correspond à l'absorption de chaleur dans la cellule, la seconde correspond au retour à l'équilibre initial.

\[ \Delta T = C \frac{dQ}{d\tau} + k \cdot \Delta T \cdot d\tau \]

Au cours de la deuxième période, il n'y a plus d'absorption de chaleur, c'est le retour à l'équilibre selon la loi de Newton:

\[ \ln \Delta T = \frac{k}{C} \tau + C^c \]
La figure 3 montre que cette loi est effectivement vérifiée et permet de calculer la constante $k/C$; celle-ci intervient dans l'évaluation du quotient $Q/C$:

$$\frac{Q}{C} = \Delta T + \frac{k}{C} \int_0^\tau \Delta T \, d\tau = \Delta T^*.$$

Calculé pour les points de la deuxième période, $\Delta T^*$ est théoriquement indépendant de $\tau$. La figure 2 montre un palier défini à $4/1000^e$ près sur 19 min, qui commence dès la fin de la première période, c'est-à-dire, suivant la température et la cinétique de dissolution, de 4 à 10 min après le maximum. Lors de l'étalonnage le palier fournit la capacité calorifique $C$ du calorimètre. Immédiatement après une série d'échantillons de métal à étudier est dissoute dans l'étain. Elle donne des courbes de températures différentielles analogues à celle décrite qui, traitées de façon identique, fournissent la chaleur de dissolution de l'élément considéré dans l'étain liquide.

Après une série d'additions dont le poids total est toujours très faible, l'appareil est réétalonné à l'Al$_2$O$_3\alpha$ fournie par le National Bureau of Standards. Comme la variation de $C$ demeure en permanence inférieure à 0,5%, nous n'avons jamais eu jusqu'ici à faire de correction d'étalonnage.
L'ensemble des calculs nécessaires à l'obtention de $\Delta T^*$ est effectué sur l'ordinateur IBM 7044 du Laboratoire de calcul numérique de Grenoble. Il faut néanmoins intégrer graphiquement la courbe dans sa première période et relever point par point les ordonnées de la deuxième période ce qui est un travail long et fastidieux. Nous l'avons simplifié en couplant l'enregistreur graphique avec un enregistreur numérique. Construit à partir d'un Digipot K (Benson-France), il provoque toutes les trente secondes l'impression de la valeur numérique de l'ordonnée et sa perforation sur bande 8 canaux en code IBM. La bande perforée entre directement comme données pour le programme de calcul numérique. Comme la totalité de l'échelle est représentée par 1000 valeurs numériques, cet enregistrement est au moins aussi précis que le relevé graphique tout en apportant une rapidité d'exécution indispensable à l'obtention de nombreux résultats.

5. RESULTATS

5.1 Enthalpie de Sn à 1016°K et 964°K

Un premier type de mesures a porté sur l'enthalpie de Sn. En effet cet élément est tout indiqué comme étalon lors de la détermination d'enthalpies partielles de divers métaux dans l'étain liquide. Or les données de la littérature (Kelley [2] et Hultgren [3]) présentent une divergence considérable dans le domaine de température où nous travaillons. Nous avons donc mesuré l'enthalpie de l'étain en utilisant de l'alumine α NBS comme étalon. Les résultats de ces mesures effectuées à deux températures sont portés dans le tableau I.

| TABLEAU I |
| ENTHALPIE DE L'ETAIN |

<table>
<thead>
<tr>
<th>$H_{T_0} - H_{T_0}$ cal/at.g</th>
<th>Ce travail</th>
<th>R.HULTGREN</th>
<th>K.K.KELLEY</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{1016}^°K - H_{293,25}^°K$</td>
<td>6 623,3</td>
<td>6 640,8</td>
<td>6 916,8</td>
</tr>
<tr>
<td>$H_{964}^°K - H_{293,15}^°K$</td>
<td>6 299,6</td>
<td>6 284,1</td>
<td>6 537,2</td>
</tr>
</tbody>
</table>

La valeur obtenue à 964°K est la moyenne de 21 mesures, l'écart relatif maximal par rapport à cette moyenne est de 0,5%. Ce nombre important d'essais a été effectué en vue de tester la fidélité du calorimètre. Le résultat obtenu à 1016°K est la moyenne de six mesures.

Nos résultats sont trop peu nombreux pour fournir une valeur de la chaleur spécifique de l'étain liquide. Le parfait accord entre nos mesures et
les valeurs tabulées par Hultgren à partir de ses propres mesures effectuées entre 505°K et 821°K, nous conduit à adopter les données de cet auteur.

5.2 Enthalpies de TiB₂, ZrB₂, BN et B₄C

Pour tous les corps inertes vis-à-vis de l'étain liquide notre calorimètre fonctionne comme un enthalpimètre; le bain métallique liquide est un excellent support thermique pour le transfert aux couples. Dans ce cadre d'applications secondaires, nous avons déterminé l'enthalpie de composés réfractaires nouveaux susceptibles de par leurs propriétés physiques et chimiques de remplacer avantageusement le graphite comme matériau de construction de nos cellules de mesures. Ces composés difficiles à obtenir purs et stoéchio-métriques nous ont été fournis par MM. Meyer et Pastor des Laboratoires de la Société d'électrochimie et d'électrométallurgie et les Aciéries électriques d'Ugine avec les analyses suivantes:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ti (mol%)</th>
<th>B (mol%)</th>
<th>C (mol%)</th>
<th>Fe (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB₂</td>
<td>67,75</td>
<td>29,75</td>
<td>1,04</td>
<td>0,62</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>78,95</td>
<td>17,90</td>
<td>0,9</td>
<td>0,41</td>
</tr>
<tr>
<td>B₄C</td>
<td>77,10</td>
<td>21,7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN</td>
<td></td>
<td></td>
<td>95,9%</td>
<td></td>
</tr>
</tbody>
</table>

L'inertie chimique de ces composés vis-à-vis de l'étain a été contrôlée par analyse spectrographique d'émission du lingot d'étain; cette analyse conclut à l'absence de Zr et de Ti et à de faibles traces de B dans l'étain. Le tableau II rapporte les résultats obtenus. La plupart des mesures ont été doublées et sont en bon accord entre elles. Dans le tableau II figurent également les résultats des travaux les plus récents (Krestovnikov [4], King [5], Stull [6], Margrave [7]) obtenus à partir des formules de lissages données par leurs auteurs. Il faut noter que les mesures calorimétriques d'enthalpie de ces composés sont actuellement peu abondantes. La divergence entre nos mesures et celles de la littérature est, à notre avis, principalement due à la différence de pureté des composés utilisés.

5.3 L'enthalpie partielle de mélange d'alliages riches en Sn

En fait notre appareil a été conçu pour la mesure des chaleurs de dissolution d'éléments ou d'alliages à haute température. Dans la série des mesures présentées ici, nous avons étudié la dissolution du Ge, de l'Ag et de l'Al dans l'étain suivant la réaction:

\[(\text{Sn})^T + \langle \text{Me} \rangle^{293^\circ K} \rightarrow (\text{Sn, Me})^T.\]

Lors de cette addition la fraction molaire x nulle ou petite varie de dx faible (dx ≠ 0,002 at. g). L'enthalpie du métal soluté de 293°K à T est prise dans la littérature, Kelley [2] pour le Ge et Hultgren [3] pour l'Al et l'Ag. Si Me est liquide à la température T, comme c'est le cas pour l'Al, l'effet thermique mesuré, rapporté à un atome-gramme de soluté, conduit, compte tenu de l'enthalpie du métal étudié, à l'enthalpie partielle \(\bar{\Delta}H_{\text{Me}}\) pour la
<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$T_0^\circ K$</th>
<th>$H_T$-$H_{T_0}$</th>
<th>$H_{T}$-$H_{T_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1014.6</td>
<td>293.45</td>
<td>10 960</td>
<td>10 616</td>
</tr>
<tr>
<td>1013.6</td>
<td>293.85</td>
<td>10 829</td>
<td>10 594</td>
</tr>
<tr>
<td>960.6</td>
<td>295.05</td>
<td>10 080</td>
<td>9 598</td>
</tr>
<tr>
<td>960.0</td>
<td>295.35</td>
<td>9 930</td>
<td>9 583</td>
</tr>
<tr>
<td>858.6</td>
<td>299.05</td>
<td>8 371</td>
<td>7 755</td>
</tr>
<tr>
<td>858.6</td>
<td>299.10</td>
<td>8 400</td>
<td>7 755</td>
</tr>
<tr>
<td>759.6</td>
<td>299.10</td>
<td>6 507</td>
<td>6 120</td>
</tr>
<tr>
<td>660.9</td>
<td>292.95</td>
<td>5 076</td>
<td>4 668</td>
</tr>
<tr>
<td>660.8</td>
<td>293.25</td>
<td>5 116</td>
<td>4 665</td>
</tr>
</tbody>
</table>

**Enthalpie de $\text{TlB}_2$ en cal.mole$^{-1}$**

a) A. N. KRESTOVNIKOV

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$T_0^\circ K$</th>
<th>$H_T$-$H_{T_0}$</th>
<th>$H_{T}$-$H_{T_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1014.5</td>
<td>293.70</td>
<td>5 977</td>
<td>6 073</td>
</tr>
<tr>
<td>1015.6</td>
<td>293.50</td>
<td>6 064</td>
<td>6 086</td>
</tr>
<tr>
<td>960.6</td>
<td>295.30</td>
<td>5 451</td>
<td>5 498</td>
</tr>
<tr>
<td>960.4</td>
<td>295.25</td>
<td>5 389</td>
<td>5 496</td>
</tr>
<tr>
<td>859.4</td>
<td>297.70</td>
<td>4 524</td>
<td>4 453</td>
</tr>
<tr>
<td>859.1</td>
<td>298.00</td>
<td>4 555</td>
<td>4 450</td>
</tr>
<tr>
<td>759.6</td>
<td>298.90</td>
<td>3 499</td>
<td>3 573</td>
</tr>
<tr>
<td>660.6</td>
<td>293.30</td>
<td>2 582</td>
<td>2 599</td>
</tr>
</tbody>
</table>

b) E. G. KING

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$T_0^\circ K$</th>
<th>$H_T$-$H_{T_0}$</th>
<th>$H_{T}$-$H_{T_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1014.6</td>
<td>293.65</td>
<td>11 396</td>
<td>11 068</td>
</tr>
<tr>
<td>1014.1</td>
<td>293.85</td>
<td>11 415</td>
<td>11 056</td>
</tr>
<tr>
<td>961.1</td>
<td>295.35</td>
<td>10 438</td>
<td>10 137</td>
</tr>
<tr>
<td>959.6</td>
<td>295.65</td>
<td>10 362</td>
<td>10 108</td>
</tr>
<tr>
<td>858.9</td>
<td>298.80</td>
<td>8 704</td>
<td>8 378</td>
</tr>
<tr>
<td>858.9</td>
<td>298.90</td>
<td>8 715</td>
<td>8 377</td>
</tr>
<tr>
<td>759.4</td>
<td>299.05</td>
<td>6 835</td>
<td>6 750</td>
</tr>
<tr>
<td>660.8</td>
<td>293.25</td>
<td>5 326</td>
<td>5 267</td>
</tr>
<tr>
<td>660.9</td>
<td>293.05</td>
<td>5 342</td>
<td>5 270</td>
</tr>
</tbody>
</table>

c) D. R. STULL

d) J. L. MARGRAVE

fraction atomique $x + (dx/2)$ et pour la température $T$. Pour le Ge et l'Ag la grandeur obtenue est la chaleur de dissolution: $H^{(T)}_{Me} - H^{(T)}_{Me} = \Delta H_{Me};$ on peut déduire de cette dernière l'enthalpie partielle en prenant comme référence le métal Me liquide sous refroidi à la température $T$. 
Tous les métaux employés dans ces manipulations ont une pureté supérieure à 99,95%. Les résultats obtenus sont portés dans le tableau III et représentés sur la figure 4.

### TABLEAU III

<table>
<thead>
<tr>
<th>Système Ge–Sn</th>
<th>Système Ag–Sn</th>
<th>Système Al–Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 963,5°K</td>
<td>T = 964°K</td>
<td>T = 960°K</td>
</tr>
<tr>
<td>X_{Ge at.g} %</td>
<td>ΔH_{Ge}</td>
<td>X_{Ag at.g} %</td>
</tr>
<tr>
<td>0,430</td>
<td>9,610</td>
<td>0,282</td>
</tr>
<tr>
<td>0,802</td>
<td>9,620</td>
<td>0,672</td>
</tr>
<tr>
<td>1,024</td>
<td>9,582</td>
<td>0,953</td>
</tr>
<tr>
<td>1,158</td>
<td>9,590</td>
<td>1,483</td>
</tr>
<tr>
<td>1,313</td>
<td>9,485</td>
<td>2,060</td>
</tr>
<tr>
<td>1,475</td>
<td>9,597</td>
<td>2,407</td>
</tr>
<tr>
<td>1,732</td>
<td>9,700</td>
<td>2,718</td>
</tr>
<tr>
<td>1,976</td>
<td>9,570</td>
<td>3,116</td>
</tr>
<tr>
<td>2,154</td>
<td>9,690</td>
<td>3,657</td>
</tr>
<tr>
<td>2,405</td>
<td>9,590</td>
<td>4,275</td>
</tr>
<tr>
<td>2,598</td>
<td>9,530</td>
<td>4,650</td>
</tr>
<tr>
<td>2,717</td>
<td>9,650</td>
<td>4,916</td>
</tr>
<tr>
<td>2,874</td>
<td>9,560</td>
<td>5,220</td>
</tr>
</tbody>
</table>

L’étude de la dissolution du Ge a été effectuée à 963,5°K dans une gamme de concentration de 0 à 0,03 at. g. A cette température la dissolution du Ge est spontanée et ne présente aucune difficulté (signalons par contre que des essais de dissolution effectués à 1013°K avec du Si ont échoué). Le lissage par les moindres carrés des résultats conduit à l’expression

$$
\Delta H_{Ge} = 9597 + 43,3 \times x_{Ge}
$$

où $x_{Ge}$ représente la concentration en Ge exprimée en atome-gramme.
FIG. 4. Chaleurs de dissolution des systèmes Ag-Sn, Ge-Sn, Al-Sn.

La variation de $\overline{\Delta H}_{\text{Ge}}$ avec la concentration est négligeable devant la dispersion des résultats qui atteint 1%.

L'enthalpie partielle limite $\overline{\Delta H}^\infty$ du Ge dans l'étain est de 2040 cal. À notre connaissance aucune mesure de cette grandeur n'a été effectuée. Seule la valeur estimée à 1600 cal par Bonnier, Desré, Durand [8] peut être comparée à ce résultat.

Les solutions diluées d'Ag dans Sn ont déjà été étudiées par de nombreux auteurs à des températures inférieures à la nôtre qui est de 964 K. Nos résultats sont représentés analytiquement par l'équation:

$$\overline{\Delta H}_{\text{Ag}} = 3685 - 6200 x_{\text{Ag}}$$

où $x_{\text{Ag}}$, concentration en Ag exprimée en atome-gramme, varie de 0 à 0,05.
Autour de cette droite la dispersion maximale est de 2%. Notre valeur limite est encadrée par celle obtenue par Kleppa [9] à 723 K: 3590 cal et celle déterminée par Oriani et Murphy [10] à 915 K: 3797 cal; ces derniers auteurs proposent dans l'intervalle de variation 0 – 0,012:

$$\Delta H_{Ag} = 3797 - 8510 \times Ag$$

L'écart entre ces résultats et les nôtres est inférieur à 3%. L'accord peut être considéré comme satisfaisant si l'on suppose que $$\Delta H_{Ag}$$ ne varie pas avec la température. L'enthalpie partielle de l'Ag déduite de nos résultats est de 842 cal; elle est en bon accord avec la valeur, 870 cal, sélectionnée par Hultgren [3] et déduite des mesures effectuées par Oriani à 723 K.

Notre étude sur le système Al–Sn a été effectuée à 960 K. A cette température l'Al liquide se dissout très facilement dans le Sn. Nous obtenons directement l'enthalpie partielle $$\Delta H(Al)$$ de cet élément. Dans l'intervalle de concentration 0 – 0,031, nos résultats sont représentés par l'équation:

$$\overline{\Delta H(Al)} = 3466 - 4065 \times A1$$

L'enthalpie partielle limite 3466 cal est en très bon accord avec le résultat déduit des mesures effectuées à 537 K par Cohen et Bever [11] qui est 3440 cal. Compte tenu de la dispersion maximale (3%), la valeur de Pool et Lundin [12] (3550 cal) déduite de mesures à 750 K est également en bon accord avec notre résultat. Par contre les valeurs des coefficients de $$x_{Al} -10 \times 750$$ et -12 160 respectivement sont très différentes de notre valeur. Nos résultats sont comparés sur la figure 5 à ceux obtenus dans notre laboratoire par Massart, Durand et Bonnier [13] par la méthode des forces électromotrices. Ils précisent le domaine des faibles concentrations en aluminium, l'accord est remarquable compte tenu de ce que les deux méthodes sont de principes très différents.

6. CONCLUSION

Les mesures reportées ici sont les premières effectuées avec notre calorimètre à haute température. Elles montrent ses possibilités pour des mesures éventuelles d'enthalpie d'échauffement et surtout d'enthalpies partielles limites qui sont des caractéristiques fondamentales des systèmes métalliques binaires et peuvent servir de paramètre dans les modèles d'interaction et en particulier dans celui que nous publierons prochainement. Les développements envisagés actuellement concernent d'autres métaux solvants à point de fusion plus élevé.
FIG. 5. Comparaison des résultats relatifs au système Al-Sn avec les mesures par f. é. m. de Massart.
REFERENCES

L. E. J. ROBERTS: I should like to ask Dr. Grønvold two questions concerning the heat capacity of U₄O₉. Is the transition at about 350°K connected with the minimum in the thermal expansion curve, and have you estimated the enthalpy or entropy of the transition involved?

F. GRØNVOLD: In answer to your first question, yes, I believe so. A minimum value of lattice constants was found at a temperature about 10°C above the heat capacity maximum, but both effects seem related to an order-disorder process presumably involving the oxygen ions in the compound. Values for the enthalpy and entropy of transition in U₄O₉ have been estimated, and will be reported in the paper by Dr. Westrum.

R. E. GRACE: I am very interested in the reaction calorimeter which you described for measuring heats of formation of iron selenides. I did not understand how the selenium vapour contacts the metal powder in order for the reaction to begin. Would you please describe this? Does the selenium pressure matter in your results?

F. GRØNVOLD: In the reaction calorimeter the selenium is enclosed in a Pyrex tube. At the operating temperature of 775°C the glass creeps and finally bursts due to the selenium pressure of about 2 atm. The gas then attacks the metal in the outer tube. With iron and nickel the reaction goes to completion within a few minutes. The experiments with cobalt were unsatisfactory since the reaction was not complete after half an hour.

The heat of reaction values obtained have to be corrected for the selenium vapour present before and after the reaction in order to obtain the standard enthalpy of formation of the selenides according to the equation

\[ xMe(s) + Se(g) = Me_xSe(s) \]

H. SKINNER (Chairman): According to your figures, the radiation loss at 1000°C was 0.2 joules per 1°C. Presumably if the temperature is increased further, this loss becomes the main loss from the calorimeter. Assuming it is possible to measure this loss, would it therefore not be possible to devise a calorimeter based on the fact that this loss occurs?

F. GRØNVOLD: I think this is a question of isothermal shield calorimetry versus adiabatic calorimetry. In both cases you return to the same problem, that of accurate temperature measurement and control.

---

H. SKINNER (Chairman): My point really is that it might in fact be easier to operate a calorimeter at 2000°C than at 1000°C.

Paper SM-66/90 (J. R. Lacher et al.)

H. SKINNER (Chairman): The cooling of the calorimeter by streaming hydrogen gas through the calorimetric fluid requires control of the flow-rate of the gas. How carefully was the flow-rate controlled?

J. R. LACHER: For a period of 8 to 12 h, the flow-rate of the hydrogen can be controlled to a variation of less than 1%. This gives sufficient time to obtain a balance of the reactants in the catalyst chamber.

Paper SM-66/20 (I. G. Murgulescu and D. I. Marchidan)

J. R. LACHER: We have examined some of your data; the results are shown in the following Table A. The first column gives the liquid pair investigated and the second and third columns $D_1$ and $D_2$ give the sum of

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$\Delta D$</th>
<th>$\Delta H^M$ at $X=\frac{1}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl - NaBr</td>
<td>2.76</td>
<td>2.90</td>
<td>0.14</td>
<td>50</td>
</tr>
<tr>
<td>KCl - KBr</td>
<td>3.14</td>
<td>3.28</td>
<td>0.14</td>
<td>56</td>
</tr>
<tr>
<td>KCl - RbCl</td>
<td>3.14</td>
<td>3.29</td>
<td>0.15</td>
<td>21</td>
</tr>
<tr>
<td>NaCl - AgCl</td>
<td>2.76</td>
<td>3.07</td>
<td>0.31</td>
<td>35</td>
</tr>
<tr>
<td>NaCl - KCl</td>
<td>2.76</td>
<td>3.14</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>NaBr - KCl</td>
<td>3.28</td>
<td>2.90</td>
<td>0.38</td>
<td>-140</td>
</tr>
<tr>
<td>NaI - KI</td>
<td>3.11</td>
<td>3.49</td>
<td>0.38</td>
<td>-133(^a)</td>
</tr>
<tr>
<td>NaNO(_3) - KNO(_3)(^b)</td>
<td>3.14</td>
<td>3.52</td>
<td>0.38</td>
<td>-111(^a)</td>
</tr>
<tr>
<td>NaCl - RbCl</td>
<td>2.76</td>
<td>3.29</td>
<td>0.53</td>
<td>-238</td>
</tr>
</tbody>
</table>

\(^a\) From Kleppa and co-workers. \(^b\) Estimated diameter of NO\(_3\)\(^-\) by Kleppa.

the crystal radii for the two salts involved. These are in ångströms and are taken from Pauling, "The Nature of the Chemical Bond." The fourth column gives the difference between columns two and three. The last column gives the heat of mixing at a mole fraction $1/2$. When $\Delta D$ is small, the heat of mixing is small and positive. Under these conditions one might expect an increase in volume on mixing and perhaps an increase in excess entropy. But except in the case of NaCl-AgCl, when $\Delta D$ becomes large
the heat of mixing becomes large and negative. The volume change on mixing and the excess entropy change would probably be negative.

D. I. MARCHIDAN: The relationship you have noted between interionic distances and heats of mixing in binary systems cannot be generally applied. All the theories formulated up to the present are based on the lattice parameters of individual salts, and generally derived from the Wasastjerna relationship; such are, for example, the relationships of Murgulescu and Steinberg, Kleppa and Hersh, Lumsden, etc.

In order to obtain a relationship which is valid for all binary mixtures, the terms to be borne in mind are the ion contribution, the residual covalent energy, the ion polarization energy, the repulsion energy, and the vibration energy.

O. J. KLEPPA: Our work on the binary alkali nitrates, chlorides, bromides and iodides leads us to conclude that there are two principal contributions to the enthalpy of mixing: a negative Coulombic enthalpy term which depends quadratically on interionic distance, and a positive term which arises in the main from the van der Waals interaction between second-nearest-neighbour cations.

A. BÜCHLER: The value of $\Delta H^M$ given by Dr. Marchidan for LiCl-RbCl seems quite large, of the order of values found for some alkali-halide-GroupII halide mixtures. May I ask if Professor Kleppa expects his theory to fit this case?

O. J. KLEPPA: The value is of the same order of magnitude as our own (see J. chem. Phys. 42 (1965) 1309).

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E. F. WESTRUM, Jr. (Discussion Leader): I should like to ask why the figure for the thermal leakiness modulus designated by $K$ in the bottom part of Fig. 3 of your paper is so high in comparison with Dr. Grønvold's data.

J. - C. MATHIEU: My diagram is for 750°C. We do have some curves similar to those of Dr. Grønvold, but for 400°C. I would therefore suggest that the difference in temperature is an important factor.

F. GRØNVOLD: Our calorimeter also operated at 750°C. It would seem to me that the higher $K$-values for the calorimeter you described are partly related to the fact that the radiative heat transfer coefficient between nickel surfaces is higher than that between silver surfaces.

General Discussion

O. KUBASCHEWSKI: I should like to stress a point made by Dr. Grønvold, and also by Dr. Roberts in his introductory lecture. Metallic and semi-metallic phases tend to be non-stoichiometric, the homogeneity ranges widening in general with increasing temperature. The thermodynamic properties of these phases are important for practical and theoretical application. Very often, the compositions involved cannot be retained by
quenching. Reliable thermochemical methods at high temperatures have therefore to be further developed. This applies to calorimetric as well as free-energy methods. High temperatures are also necessary for the study of sluggish reactions.

At present, high-temperature reaction calorimeters of reasonable accuracy are operated up to a temperature of 1400°C or so. Some progress may still be achieved by switching from the adiabatic method to the thermopile, but it is unlikely that the temperature for the operation of calorimeters for condensed reactions with acceptable accuracy can substantially exceed 1500°C. Heat-capacity measurements are in principle more convenient, and the temperature of operation can be pushed higher.

In order to derive the greatest benefit from reaction calorimeters, small changes in composition should be studied. Some progress in this direction has already been made.

L. E. J. ROBERTS: I should like to add one comment to what Dr. Kubaschewski has said. It is often possible to measure equilibria at high temperatures and estimate partial molar free energies in non-stoichiometric systems, but it is seldom possible to measure temperature coefficients accurately. Therefore direct calorimetric measurements of enthalpies at temperatures up to 1500°C are of the utmost importance in giving direct values of partial molar enthalpies and entropies.

O. J. KLEPPA: I should like to make a general comment on the direction of future developments in high-temperature calorimetry. As Dr. Grønvold has shown, the contribution of radiation to the process of heat transfer becomes very large at very high temperatures. This sets practical temperature limits for adiabatic calorimetry. Therefore it must be anticipated that effective calorimetry at very high temperatures must be based on designs which allow of dependable integration of Newton's law. The obvious solution is a calorimeter of the Calvet type. In such a calorimeter precision may be high, even at quite elevated temperatures.

O. KUBASCHEWSKI: We have come to exactly the same conclusions, and are now undertaking the construction of a Calvet calorimeter.

H. SKINNER (Chairman): Professor Calvet has also reached the same conclusions, and in fact my earlier remark that it may be easier to operate at 2000°C than at 1000°C stems from him.

F. E. WITTIG: The precision of the usual isoperibolic method depends on the value of the time constant $T_c = E/K$ (where $E$ is the energy equivalent and $K$ the heat exchange constant). At higher temperatures, $K$ will increase and $T_c$ decrease. Our work has shown that in our calorimeter at 1000°C, a 1% precision of electric calibration ($E$) can be obtained even with time constants $T_c$ as low as 300 s. At higher temperatures the precision decreases as a result of the decrease in $T_c$. Vacuum calorimeters may give lower values of $K$ and higher values of $T_c$. In this way the isoperibolic method may perhaps be extended to about 1400°C. The use of smaller calorimeters with lower values of $E$, giving lower time constants, may however result in loss of precision even at temperatures below 1000°C. Therefore precision depends not only on temperature, affecting $K$, but also on the dimensions of the calorimeter, which affect $E$. A major source of error is the second time constant of the reaction crucible.
Quasi-isothermal (Calvet) and isothermal (Wittig) heat flow calorimeters eliminate the influence of the time constants, and therefore seem to be more promising at higher temperatures. When such methods are used, electric calibration only concerns the value of K. The value of E does not affect the results, and should probably be kept as small as possible. Our method works with a constant heat flow, accurately determined from the electric power. The reaction heats are found from the changes in electric energy. In this way, calibration and determination of the heat of reaction are done in the same run.

The use and the precision of calorimeters at higher temperatures seem therefore to be limited only by experimental difficulties of exact temperature measurement and control, and of providing an accurately determined amount of electric heat to the equipment.

O. J. KLEPPA: I foresee serious difficulties with the problem of precise calibration at 2000°C.

E. F. WESTRUM, Jr. (Discussion Leader): In view of the remark by Dr. Roberts and the general agreement of the succeeding speakers that the Tian-Calvet calorimeter is the answer for the future, I wonder if it would not be possible, for example, to measure the enthalpies of decomposition reactions and of an oxide decomposing to another oxide with a high-temperature Tian-Calvet type of calorimeter, and thereby obtain accurate evaluations of these quantities which at present are assessed by non-calorimetric means.

H. SKINNER (Chairman): I agree. We hope at some stage to attempt this.
Session 2

EMF METHODS, INCLUDING SOLID ELECTROLYTES
Chairman: H. NOWOTNY

INTERNATIONAL UNION OF PURE AND APPLIED PHYSICS
THE EMF METHOD IN STUDYING THERMODYNAMIC
AND KINETIC PROPERTIES OF COMPOUNDS
AT ELEVATED TEMPERATURES

H. SCHMALZRIED
MAX-PLANCK-INSTITUT FÜR PHYSikalische CHEMIE,
GÖTTINGEN, FEDERAL REPUBLIC OF GERMANY

Abstract — Résumé — Аннотация — Resumen

THE EMF METHOD IN STUDYING THERMODYNAMIC AND KINETIC PROPERTIES OF COMPOUNDS AT ELEVATED TEMPERATURES. After a brief historical outline on the use of solid electrolytes in high temperature electrochemistry, expressions for the EMF of mixed ionic plus electronic electrolytes are given. A number of electrolytes and their limits of applicability are discussed. Examples of the use of solid electrolytes in the field of thermodynamics are presented, namely investigations on (1) the free energy of formation of binary and ternary compounds, and (2) the thermodynamics of binary alloys and binary ionic crystals with a broad homogeneity range. Examples in the field of kinetics are the studies of (1) the phase boundary reaction during oxidation of metals, (2) diffusion of oxygen in metals, (3) nucleation of metals during reduction of oxides of sulphides and (4) polarization studies.

METHODE DE LA FORCE ELECTROMOTRICE DANS L’ETUDE DES PROPRIETES CINETIQUES ET THERMODYNAMIQUES DE COMPOSES A HAUTE TEMPERATURE. Apres un bref exposé historique sur l’emploi d’électrolytes solides dans les études électrochimiques à haute température, l’auteur indique des expressions pour la force électromotrice de mélanges d’électrolytes ioniques et électroniques. Pour plusieurs électrolytes, il examine dans quelles limites il est possible de les utiliser. En ce qui concerne l’emploi d’électrolytes solides en thermodynamique, l’auteur cite, à titre d’exemple, a) les études sur l’énergie libre de formation de composés binaires et ternaires, et b) les études sur la thermodynamique d’alliages binaires et sur celle de cristaux ioniques à gamme d’homogénéité étendue. Dans le domaine de la cinétique, il mentionne l’étude des questions suivantes: a) réactions aux limites de phases pendant l’oxydation de métaux; b) diffusion de l’oxygène dans les métaux; c) formation de centres de métal dans la réduction d’oxides ou de sulfure; d) polarisation.

МЕТОД ЭДС ПРИ ИЗУЧЕНИИ ТЕРМОДИНАМИЧЕСКИХ И КИНЕТИЧЕСКИХ СВОЙСТВ СОЕДИНЕНИЙ ПРИ ПОВЫШЕННЫХ ТЕМПЕРАТУРАХ. После короткого исторического очерка об использовании твердых электролитов в высокотемпературной электрохимии даются выражения для эдс смешанных ионных и электронных электролитов. Анализируется ряд электролитов и пределы их применимости. Приводятся примеры использования твердых электролитов в области термодинамики, а именно: исследования 1) свободной энергии об разования соединений, состоящих из двух и трех элементов, 2) термодинамики бинарных сплавов и 3) бинарных ионных кристаллов с широкой областью гомогенности. Примеры в области кинетики являются: изучение 1) фазовой пограничной реакции в ходе окисления металлов, 2) диффузии кислорода в металлах, 3) образования зародышей металлов в ходе восстановления окислов сернистых соединений, изучение поляризации.

EL METODO DE LA FUERZA ELECTROMOTRIZ PARA ESTUDIAR LAS PROPIEDADES THERMODINAMICAS Y CINETICAS DE COMUESTOS A TEMPERATURAS ELEVADAS. Después de exponer sucintamente los aspectos históricos del empleo de electrolitos sólidos en la electroquímica a temperaturas elevadas, el autor presenta en la memoria expresiones correspondientes a la fuerza electromotriz de electrolitos mixtos iónicos y electrónicos. Analiza luego una serie de electrolitos y los límites de su aplicabilidad y presenta ejemplos del uso de electrolitos sólidos en el campo de la termodinámica, especialmente investigaciones sobre a) la energía libre de formación de compuestos binarios y ternarios y b) sobre la termodinámica de aleaciones binarias y de cristales iónicos binarios con un amplio intervalo de homogeneidad. Entre los ejemplos en el campo de la cínética cabe citar los estudios de a) la reacción en la interfase durante la oxidación de metales, b) la difusión del oxígeno en metales, c) la nucleación de metales durante la reducción de óxidos o sulfuros y d) los estudios de polarización.
INTRODUCTION

Although liquid electrolytes are not completely excluded, this survey deals essentially with solid electrolytes. This restriction may perhaps be justified in the attempt to assess the large amount of new work done with solid electrolytes in the past few years.

A brief glance through the literature shows that EMF methods at high temperatures have become more and more popular among physical chemists over the last ten years. The reason why might be found in the increasing interest in high temperature materials, in the increasing work on fuel cells, and in a few stimulating papers [1, 2] published about ten years ago. Nevertheless one has to remember that the so-called Nernst glower, operating at very high temperatures and fabricated of 85 wt.% ZrO₂, 15 wt.% Y₂O₃, and having a lifetime of hundreds of hours on direct current, was already used as early as 1900. Furthermore, an electrolyte consisting of 90% ZrO₂, 10% MgO which was investigated in 1902 by Reynolds [3], a student of Nernst, was chosen in 1937 by Baur and Preis [4] when setting up fuel cells. And already in 1943 Wagner [5] gave the correct explanation for the transport mechanism in doped zirconia. In view of this it is rather surprising that, even in 1965, meetings on EMF methods for studying properties of compounds at high temperatures neglected the work published in a small number of papers between 1904 and 1950 in which solid electrolytes were used for thermodynamic studies [6-10]. Among these early solid electrolytes were glass, porcelain and, especially, the halides.

In investigating thermodynamic and kinetic properties of compounds, solid electrolytes can be used in two, basically different, ways: (1) With proper combinations of electrodes, electrolytes and compounds, and applying a known electric potential to the galvanic cell, one may study partial conductivities of compounds; (2) Under open circuit conditions, the EMF gives information about the change in the Gibbs free energy for the virtual cell reaction occurring on passing one faraday, keeping all intensive parameters constant.

From the first kind of experiment, information on disorder (point defects) of the compound can be obtained; with the second kind of experiment one can study thermodynamics of compounds, especially if no liquid or solid junction occurs. Furthermore, under certain conditions, one may also use electrolytes as potential probes in order to study kinetic processes, as will be mentioned later. However, the second type of experiment will be the one discussed in some detail.

SOLID ELECTROLYTES AND THE DETERMINATION OF ACTIVITIES OR PARTIAL PRESSURES

In this brief survey it is not intended to present a solution of the general problem, that is the calculation of the electromotive force of solid galvanic cells involving phases of locally variable composition. Instead a case of practical importance will be discussed and the reader will be referred to the literature for more general information [11].
Considering the situation depicted in Fig. 1 (Cell I), which in some form or other is basic to all the investigations reported in this session, one can formulate flux equations for all mobile species in the electrolyte. The fluxes,

\[ \mathbf{j}_i = - \frac{\sigma_i}{F^2} \nabla \tilde{\mu}_i \]  \hspace{1cm} (1)

in equivalents/cm²s and referred to the crystal lattice as reference frame¹, are given under isothermal conditions by

if we assume that the movement of ions (and electronic defects) of species i occurs independent of the movement of all other species (besides coupling by a diffusion potential). \( \tilde{\mu}_i = (\bar{\mu}_i + \Theta) \) is the electrochemical potential per equivalent i. Taking into account that under open circuit conditions

\[ \sum_i \mathbf{j}_i = 0 \]

\[ \bar{\mu}(X_2) = \tilde{\mu}(X^{n^-}) - \mu_\Theta, \text{ with } \frac{1}{2} X_2 + n_\Theta = X^{n^-} \]

\[ d\mu_\Theta = -d\mu_\Psi, \text{ where }^2 \Theta + \Theta = 0 \]

and at the phase boundaries \( \tilde{\mu}_\Theta \) (electrode) = \( \tilde{\mu}_\Psi \) (electrolyte), one obtains after integration the EMF of Cell I [12] :

\[ E = \frac{1}{F} \int_{\mu'} \frac{1}{\mu''} d\tilde{\mu}(X_2) \]  \hspace{1cm} (2)

¹ Since \( \text{div } \mathbf{j}_i = 0 \) inside the electrolyte, transport numbers \( t_i \), defined with reference to this system, correspond to the conductivity ratio \( \sigma_i/\sigma_{\text{total}} \), as measured by electrical transport measurements using blocking electrodes and inert markers.

² \( \Theta, \Psi \) = excess electron, defect electron (electron hole).
It is obvious from Eq. (2), that for practical applications of solid electrolytes to measure chemical potential differences, \( t_{\text{ion}} \) should not be too small. Principally one has to know \( t_{\text{ion}} \) as a function of \( \mu(X_2) \) in order to determine \( \mu''(X_2) \) from a measurement of \( E \), if \( \mu'(X_2) \) is given.

It is interesting to note that the electrical potential changes essentially over the phase boundaries electrode/electrolyte (see Fig. 1), and is almost constant throughout the electrolyte if \( t_{\text{ion}} = 1 \). However, if \( t_{\text{ion}} \neq 1 \), the difference of the potential drops in the phase boundaries is reduced by a diffusion potential inside the electrolyte.

Since mobilities of ionic defects are usually much smaller than those of electronic defects, we can assume that in solid electrolytes, for which \( t_{\text{ion}} \) is of the order of unity, the number of electronic defects is quite small compared with the number of ionic defects. In other words, useful solid electrolytes have an ionic type of disorder, meaning that \( \sigma_{\text{ion}} \) is independent of \( \mu(X_2) \) in the potential range of interest. Under this condition we may assume ideal behaviour of electrons and holes, which then yields for the ionic transference number

\[
t_{\text{ion}} = \frac{\sigma_{\text{ion}}}{\sigma_{\text{total}}} \left[ 1 + \left( \frac{\sigma_{\text{ion}} \mu(X_2)}{\sigma_{\text{ion}}} \right)^{-1} \right]^{-1}
\]

(3)

\[
t_{\text{ion}} = \left[ 1 + \left( \frac{p(X_2)}{p_\Theta} \right)^{1/n} + \left( \frac{p(X_2)}{p_\Theta} \right)^{-1/n} \right]^{-1}
\]

(4)

Here \( p(X_2) \) is the partial pressure of \( X_2 \), defined by

\[
\mu(X_2) = \mu^0(X_2) + RT \ln p(X_2)
\]

where \( \mu(X_2) \) is the chemical potential of \( X_2 \) per mole. Now \( p_\Theta \) and \( p_\Theta \) are constants for a given temperature if the mobility of electrons and holes is independent of their concentrations. They are essentially the partial pressures of \( X_2 \) for which \( t_{\text{ion}} = 0.5 \), and depends on the electrical charge of the ions and the type of disorder. Inserting Eq. (4) in Eq. (2) and integrating, one obtains (\( p_\Theta \gg p_\Theta \), see also [13]):

\[
E = \frac{RT}{F} \ln \left[ \frac{\left( \frac{\mu'(X_2)}{\mu''(X_2)} \right)^{1/n} \ln \left( \frac{\mu'(X_2)}{\mu''(X_2)} \right)}{\left( \frac{\mu'(X_2)}{\mu''(X_2)} \right)^{1/n} + \ln \left( \frac{\mu'(X_2)}{\mu''(X_2)} \right)} \right]
\]

(5)

This function is plotted in Fig. 2, keeping \( \mu''(X_2) \) constant. If \( p_\Theta \gg p'(X_2) \), \( p'(X_2) \approx p_\Theta \), Eq. (5) yields the well known formula for isothermal and reversible transport of one mole of gas \( X_2 \) from the compartment with \( p'(X_2) \) to the compartment with \( p''(X_2) \)

\[
E = \frac{RT}{F} \ln \left[ \frac{p''(X_2)}{p'(X_2)} \right]
\]

(6)
A theoretical calculation of $p_{\Theta}$ and $p_{\Theta}$ is generally not possible, since a number of parameters, such as mobilities and defect concentrations, are usually unknown [13]. Experimental determination is possible either from EMF measurements (as indicated for Sm$_2$O$_3$ [14] in Fig. 3) or by determining the partial conductivities as a function of $\mu (X_2)$. Examples for MgO [13, 15] and AgBr [16] can be found in the literature. A survey on polarization methods using galvanic cells to determine partial conductivities has been given by Wagner [17].

Several difficulties may arise when using solid electrolytes to determine activities, especially at high temperatures. Four of the effects are discussed in the following paragraphs.

(1) A number of electrolytes are made by sintering materials with high melting points. Thus molecular transport from one side to the other side of the electrolyte becomes possible via pores or grain boundaries. The influence on the EMF depends upon the transport properties of electrolyte and electrodes, and is difficult to estimate quantitatively [13]. A check for gas tightness is recommended.

(2) Mixed potentials [18, 19] arise, if there is more than one possible electrode reaction. For example, if metal and metal oxide mixtures are used to establish certain oxygen partial pressures on both sides of an oxygen electrolyte pellet in an inert atmosphere, one has to realize that there are principally no inert atmospheres with respect to Me, MeO. Thus a mixed potential arises, given by the rate of oxygen transfer between electrodes (Me,MeO) and the so-called inert atmosphere, and by the geometry of the galvanic cell.

---

From Eq. (2), it follows that

$$\left[ -\frac{dF}{d\mu^{\Theta} (X_2)} \right]_{F(X_2) = \text{const.}} = \frac{t_{\text{ion}}}{F}$$

---
(3) At high temperatures, reactions between electrolyte and adjacent solid phases are possible. The reaction rate depends on the transport properties of the reaction product, which may be a solid solution or an intermediate phase, and the driving forces are given by the change of free energy for the solid state reaction [20]. The following example (Fig.4, Cell II) may be considered:

Assuming that \( t_{O^{--}} = 1 \) in zirconiaw, \( t_{A^{+}} + t_{Zr^{4+}} + t_{O^{--}} = 1 \) in the zirconate, and that the transference numbers in these phases are independent of the activities of the components, one can proceed according to Eq.(1), having \( \Sigma j_j = 0 \) for each phase under open circuit conditions. After some calculation, this yields for the EMF of Cell II, taking into account the equilibrium conditions for the phase boundaries:

\[
E = \frac{1}{F} \left[ \tilde{\mu}_{O^{2-}}(II) - \tilde{\mu}_{O^{2-}}(I) + (t_{Zr^{4+}} + t_{A^{+}}) \Delta G_{AZrO_3}^0 \right]
\]  

where  
\[ \Delta G_{AZrO_3}^0 = \tilde{\mu}_{AZrO_3}^0 - \tilde{\mu}_{AO}^0 - \tilde{\mu}_{ZrO_2}^0. \]

From this example it becomes obvious that reactions in the solid state between electrolyte and adjacent phases do influence the EMF as long as \( t_{O^{--}} \) in the reaction product is not unity. In a similar way one may obtain expressions for the EMF of Cell II if electrons and/or holes contribute to the electrical conductivity of AZrO_3. In general, transport properties of the reaction products are not known, and consequently a correction for reactions forming solid solutions or intermediate phases is virtually im-

---

4 Eq. (7) can be easily confirmed by regarding the overall reaction if 1 faraday of positive current is transported from the right side to the left side of the Cell II, assuming local equilibrium at the phase boundary ZrO_2|AZrO_3 and AZrO_3|A, AO.
possible. As a rule, however, solubilities in solid electrolytes are lower than in liquid electrolytes, whereas interference of electronic conduction may become more serious in solid electrolytes.

(4) A final point must be mentioned. In formulating the virtual cell reaction of galvanic cells, the valencies of ions transported across the electrolyte must be known. In other words, the effective charge of point defects responsible for the ionic transport must be known. Kroger [21] has pointed out that even at temperatures necessary for solid electrolyte operation, there may be some doubt about the effective charges of defects. He discusses EMF measurements using Al₂O₃ as a solid electrolyte in this sense. One has to remember, however, that variability of valences always results in electronic conduction in solids.

**ELECTRICAL PROPERTIES AND APPLICATIONS OF SOME SOLID ELECTROLYTES**

In this section a number of examples from the literature are given to illustrate specific points, with special reference to the electrical properties of the electrolytes. The most important types of galvanic cells, in which the following electrolytes have been used, are:

- **A|AX|Me₂,X₂** (Formation-type)  
  III
- **A|AX|BX|B** (Daniell-type)  
  IV
- **A₂,A₁X|BX|A₂,AgX** (Displacement-type)  
  V

For Cell V, BX is used as an auxiliary electrolyte, and can also be glass [22,23] or porcelain [9,24].

Solid electrolytes may be characterized at a given temperature in a rational way by pₑ and pₒ, the partial pressures of the electro-negative component for which electron hole or excess electron conduction becomes predominant. For partial pressures pₑ > p(X₂) > pₒ electrolytes are useful in order to determine chemical potentials, provided that reactions with adjacent phases and/or electrodes do not interfere. However, it is necessary to point out that electron and hole conduction may be decisively influenced by small amounts of impurities acting as donors or acceptors. Therefore pₑ and pₒ may differ appreciably for electrolytes with different impurity levels. Kroger [25], in a recent paper, has discussed this question in some
detail for ZrO₂(+CaO), to which different amounts of donors and acceptors
have been added [26]. The effects could only be explained by assuming that
most of the ionic imperfections in ZrO₂(+CaO) were neutral associates.

In Table I pΘ and pΘ are given for several electrolytes used in high
temperature electrochemistry. Other solid electrolytes are BeO, CaO,
SrO [45], PbCl₂ [27-30], BaCl₂ [31], and the corresponding fluorides PbF₂,
SrF₂, MgF₂ [32-34] which, because of the lower polarizability of the anion, should
generally show less electronic conductivity than the corresponding chlorides.
Calcium fluoride especially has been extensively used as a solid electrolyte
at high temperatures [34-36]. In further applications of these solid halides,
especially the fluoride, one has to be aware of the fact that pΘ and pΘ are not
yet known and thus, under highly reducing conditions, these electrolytes may
eventually become excess electron conducting.

Finally work in the field of high temperature electrochemistry should be
mentioned, in which CuBr [30, 38, 39], AgBr [40], and AgI [37, 41, 42] have
been used as solid electrolytes.

TABLE I

<table>
<thead>
<tr>
<th>pΘ AND pΘ FOR A NUMBER OF OXIDES</th>
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<tbody>
<tr>
<td>T (°C)</td>
</tr>
<tr>
<td>ZrO₂ (+CaO)</td>
</tr>
<tr>
<td>ThO₂ (+CaO)</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>Sm₂O₃</td>
</tr>
<tr>
<td>SiO₂ (quartz glass)</td>
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</tbody>
</table>

DISCUSSION OF SOME SPECIAL APPLICATIONS OF GALVANIC CELLS
INVOLVING SOLID ELECTROLYTES

Whereas cells of the type Pt, O₂|ZrO₂(+CaO)|A, AO|Pt, Cell V, have
been extensively used to determine the free energy of formation of binary
oxides AO from the elements [2, 51-53] (very recent work is concerned with
MoO₂ and Cr₂O₃), some authors have successfully applied EMF methods to
study the thermodynamics of ternary compounds. While the activities of all
components are fixed in binary systems by the co-existence of two phases
(A, AO or AO, O₂(g)), in ternary systems three co-existing phases are
needed. If the phase diagram of the ternary system A-B-O shows, for example, that the phases A, B₂O₃ and AB₂O₄ coexist, the cell

\[
Pt \left| A, B₂O₃, AB₂O₄ \right| ZrO₂(+CaO) \left| A, AO \right| Pt \tag{VI} \]

measures the free energy of formation of AB₂O₄ from AO and B₂O₃ directly, as can be seen from the virtual cell reaction upon passing 2 faradays of oxygen ions from right to left. Instead of using zirconia as a solid electrolyte, one may use an electrolyte which has a cation in common with the oxide mixture, working in an atmosphere of given oxygen potential. As an example, we may regard the cell

\[
Pt, O₂ \left| AO \right| AF₂ \left| ABO₃, BO₂ \right| O₂, Pt \tag{VII} \]

where A can be calcium or lead and B can be silicon or titanium.

Using these rules, the free energy of formation of a number of aluminates, chromites, ferrites, titanates and silicates have been measured [34, 35, 54-56].

To study the thermodynamics of solid solutions (A, B), galvanic cells of type

\[
A \left| \text{electrolyte} \right| \text{AX} + A \tag{VIII} \]

have been extensively used [57]. Displacement reactions such as

\[
AX + B = BX + A \tag{IX},
\]

(A, B = metal in solid solution) tend to decrease the theoretical EMF of Cell VIII,

\[
E = - \frac{RT}{z_A} \cdot \ln a_A
\]

if B is not much more noble than A (\(\Delta G^o\) strongly positive)[58]. Use of solid electrolytes can improve this situation, as Rapp and Maak [59] have shown for Ni-Cu-alloys. They used a galvanic cell of the general type

\[
A \left| AO \right| ZrO₂(+CaO) \left| (A, B) \right| AO \tag{IX} \]

which is applicable if \(|\Delta G^o(AO)| > |\Delta G^o(BO)|\), such that essentially pure AO is coexisting with alloy (A, B). One obtains for the activity \(a_A = \exp (-2F \Phi / RT)\).

This method is immediately applicable to a number of systems [60, 61]. In a similar way one may study solid solutions of oxides in the galvanic cell as

\[
B \left| (A, B)O \right| ZrO₂(+CaO) \left| B, BO \right| \tag{X} \]
where \( a_{BO} \) (in \((A, B)O\)) is also given by \( \exp (-2EF/RT) \), see Ref. [62]. Ionic compounds exhibit a finite range of homogeneity. Two extreme examples are with AgI and Br, \( \delta(a_{Ag} = 1; T = 277^\circ C) = -10^{-12} \) and \( \delta(a_{Ag} = 10^{-8}; T = 277^\circ C) = +10^{-8} \); with Fe\(_2\)O\(_3\), \( \delta(a_{Fe} = 1; T = 1000^\circ C) = 0.05 \) and \( \delta(a_{Fe} = 0.1; T = 1000^\circ C) = 0.125 \). It is well known [63, 64] that \( \delta \) as a function of the component activity yields valuable information on the behaviour of atomic imperfections in crystals. If the homogeneity range is broad enough, and chemical methods are appropriate to measure or predetermine the deviation from the stoichiometric composition \( \delta \), galvanic cells can be used to measure the component activities as a function of \( \delta \) (e.g., WO\(_x\) and U\(_{1-x}\)O\(_2\), ZrO\(_2\)(+CaO) as solid electrolyte [65-68]). However, if the homogeneity range is too small, and \( \delta \) cannot be determined with chemical methods, EMF measurements in connection with coulometric titration may yield in a very elegant way the information required. This has been shown for silver-sulphide [69] (using AgI as a solid electrolyte) and for copper-sulphide, copper-selenide, and copper-telluride [38-39] (using CuBr as a solid electrolyte). The cells were of the type

\[
\text{Pt} \mid \text{Me} \mid \text{MeX} \mid \text{Me}_y \text{S} \mid \text{Pt}
\]

XI

Recently [70] zirconia was successfully used in the same way to study oxygen potentials in ferrites as a function of the oxygen to metal ratio (see also Ref. [71]).

Some final examples may demonstrate applications of galvanic cells in kinetic investigations. The basic idea is simply to use solid electrolytes as probes for time dependent chemical potentials in a way similar to that in which metal leads are used to measure time-dependent electrical potentials.

![Fig. 5. Set-up for measurements of kinetic parameters of phase ii. i = zirconia electrolyte, iii = quartz tube. EMF versus time curve for the oxidation of Fe(II) to wüstite.](image)

Tare [72] has determined the phase boundary reaction rate constant for the oxidation of iron foils in CO\(_2\)/CO-mixtures. To this end a thin Fe-foil was sintered on a polished ZrO\(_2\)(+CaO) surface (see Fig. 5). While the other side of the electrolyte was kept at a constant reference potential, at the beginning the oxygen potential of the CO\(_2\)/CO-mixture was such that Fe-metal co-existed. After the sudden increase of the oxygen potential in the gas
atmosphere due to increasing the CO₂/CO-ratio, an EMF versus time curve, as plotted in Fig. 5, was measured. Since the thickness of the Fe-foil was chosen so that all diffusion processes in the foil were fast in comparison to the phase boundary reaction (i.e., there is essentially no activity gradient for oxygen in the foil), the EMF reflects the phase boundary reaction rate. The reaction rate constant for the reaction:

\[ \text{CO}_2(g) = \text{O} \text{(in wüstite)} + \text{CO} \text{(g)} \]

can be calculated from the thickness of the foil and the time \( \Delta t \) needed to convert all Fe into "FeO". Values agree to within a factor of 2 with results obtained using other methods [73, 74].

It is interesting to note that in this way one can measure the supersaturation necessary to nucleate the first oxide nuclei on the Fe-foil. Actual values are scattered, the average is between 5 and 8%.

Investigations on the reduction kinetics of silver-sulphide with AgI and CuBr as solid electrolytes respectively have been made by Kobayashi and Wagner [75]. Removal of sulphur by the reaction:

\[ \text{S} \text{(in sulphide)} + \text{H}_2(g) = \text{H}_2\text{S}(g) \]

was measured as a function of the applied potential to a galvanic cell of type XI.

The galvanic cell Pt | Ag| AgI | Ag₂S | Pt was used to measure the supersaturation during nucleation of metallic silver upon reducing Ag₂S with hydrogen [76]. At 400°C the diffusion coefficient of silver in Ag₂S is high enough to establish essentially uniform silver activity in the Ag₂S-tablet during reduction. First a well-defined Ag/S ratio in Ag₂S was established by applying a certain potential to the cell in an argon atmosphere. Then the argon was replaced by slowly flushing with H₂, and the open circuit potential was read as a function of time. Figure 6 shows a typical curve, from which the supersaturation and the driving force for the transfer of silver ions and electrons from Ag₂S

![Figure 6](image_url)
to the metal can be easily read. Following theoretical considerations it is found that the supersaturation is rather low, i.e. about 2 - 3%.

Finally, it may be stressed again that polarization and EMF methods are not yet fully used in studying kinetic properties of compounds at high temperatures [77]. Further, by investigating new materials, or by combining known high temperature electrolytes with other metalloids, it should be possible to extend EMF methods to the fields of the thermodynamics and kinetics of sulphides, nitrides, etc. And last but not least, non-isothermal cells and double cells in which different activities are established by applying different electrical potentials should be mentioned. These can give valuable information, as was shown recently [78].

REFERENCES

[34] TAYLOR, R.W., SCHMALZRIED, H., I. phys. Chem. 68 (1964) 2444.
[53] MATSUSHITA, Y., GOTO, K., J. Faculty Engng, University of Tokyo 27 (1964) 217.
[72] TARE, V.B., SCHMALZRIED, H., Rate constants of gas-solid reactions involving oxygen, measured with the help of ZrO2 (+CaO) as a solid electrolyte, to be published.
THE APPLICATION OF OXYGEN CONCENTRATION CELLS WITH THE SOLID ELECTROLYTE ZrO$_2$·CaO TO THERMODYNAMIC RESEARCH

Y. MATSUSHITA AND K. GOTO
UNIVERSITY OF TOKYO, JAPAN

Abstract — Résumé — Аннотация — Resumen

THE APPLICATION OF OXYGEN CONCENTRATION CELLS WITH THE SOLID ELECTROLYTE ZrO$_2$·CaO TO THERMODYNAMIC RESEARCH. Six experimental studies are discussed, involving the application of oxygen concentration cells using the solid electrolyte ZrO$_2$·CaO (providing pure anion conduction as migration of oxygen defects) to basic research in process metallurgy:

1. The standard free energies of formation of FeO, Fe$_3$O$_4$, SnO, PbO, Cu$_2$O, CuO and Ta$_2$O$_5$ have been measured and expressed as functions of temperature in the range 500 to 1300°C.

2. The oxygen pressure in liquid PbO-SiO$_2$ solution has been measured at 800 to 1100°C; the chemical activities of PbO and SiO$_2$ and thermodynamic properties of PbO-SiO$_2$ solution have been calculated.

3. One of the authors has measured the chemical activity of tin in liquid Pb-Sn binary solution at 700 to 900°C, and the thermodynamic properties of Pb-Sn alloys have been calculated.

4. This author has also developed an oxygen gauge to measure the partial pressure of oxygen in high-temperature gases in the range of $P(O_2) = 10^{-1}$ to $10^{-20}$ atm and 500-1300°C. Self-consistent and reproducible EMF values with various gas mixtures have been obtained.

5. The rates of oxidation or reduction of pure iron and iron oxides by a CO-CO$_2$ gas mixture were calculated from the EMF results obtained with the oxygen gauge at 900-1000°C.

6. The oxygen pressure in liquid iron, containing various amounts of carbon up to the saturation value, or saturated with oxygen, has been measured with the reference electrodes of graphite or (Ni + NiO) powder. It appears that this method could be used to determine the oxygen content in liquid iron at 1500-1600°C. In addition, possibilities for applying oxygen concentration cells to the basic study of process metallurgy have been suggested and industrial applications have also been discussed.

EMPLOI DES CELLULES À CONCENTRATION D'OXYGÈNE AVEC ELECTROLYTE SOLIDE DE ZrO$_2$·CaO, DANS LES RECHERCHES EN THERMODYNAMIQUE. Le mémoire a trait à six travaux de recherche fondamentale sur les processus métallurgiques, faits au moyen des cellules à concentration d'oxygène avec électrolyte de ZrO$_2$·CaO, lequel assure une conduction anionique pure grâce à la migration de défauts d'oxygène. Ces travaux sont les suivants:

1. Les énergies libres types de formation de FeO, Fe$_3$O$_4$, SnO, PbO, Cu$_2$O, CuO et Ta$_2$O$_5$ ont été mesurées pour des températures de 500 à 1300°C et exprimées en fonction de la température, les valeurs obtenues étant comparées aux données publiées.

2. La pression d'oxygène dans la solution liquide PbO-SiO$_2$ a été mesurée pour des températures de 800 à 1100°C, l'équilibre étant réalisé à l'aide de plomb à l'état liquide. Les activités chimiques de PbO et SiO$_2$, ainsi que les propriétés thermodynamiques de la solution ont été déterminées.

3. L'un des auteurs a mesuré l'activité chimique de l'étain dans une solution liquide binaire de Pb-Sn pour des températures de 700 à 900°C. Il a déterminé par des calculs les propriétés thermodynamiques d'alliages Pb-Sn.

4. En outre, il a mis au point un manomètre à oxygène pour mesurer la pression partielle de l'oxygène dans les gaz à haute température (500 à 1300°C) dans l'intervalle $10^{-1}$ à $10^{-20}$ atm. Il a obtenu des valeurs autoconsistantes et reproductibles pour la force électromotrice avec des mélanges gazeux différents.

5. Les vitesses d'oxydation ou de réduction du fer pur et des oxydes de fer par un mélange gazeux CO-CO$_2$ ont été mesurées au moyen du manomètre entre 900 et 1000°C.

6. Au moyen des électrodes de référence en graphite ou en poudre de (Ni + NiO), on a mesuré la pression d'oxygène dans du fer à l'état liquide, à différents teneurs en carbone, saturé d'oxygène. Il semble que cette méthode pourrait servir à déterminer la teneur en oxygène du fer à l'état liquide entre 1500 à 1600°C. Enfin, les auteurs indiquent d'autres possibilités pour l'emploi de cellules à concentration d'oxygène dans les études fondamentales sur les processus métallurgiques, et ils discutent aussi leur application industrielle.
MATSUSHITA and GOTO

APPLICATION OF OXYGEN CONCENTRATION CELLS WITH SOLID ELECTROLYTE ZrO2 - CaO FOR THERMODYNAMIC INVESTIGATIONS. Six experimental investigations, concerned with the application of oxygen concentration cells with the ZrO2 - CaO electrolyte (which provides pure anion conductivity due to oxygen ion migration) for basic studies in metal processes:

1) Standard free energies of formation FeO, Fe3O4, SnO, PbO, Cu2O, CuO and Ta2O5 were measured and expressed as functions of temperature in the range 500 - 1300°C.

2) The oxygen pressure in liquid PbO-SiO2 solution, in equilibrium with liquid lead, was measured at 1100°C. Chemical activities of PbO and SiO2 and thermodynamic properties of the PbO-SiO2 solution were also calculated.

3) One of the present authors measured the chemical activity of tin in the Pb-Sn binary liquid solution at temperatures from 700 to 900°C. Thermodynamic properties of the Pb-Sn alloys were also calculated.

4) This author also designed an oxygen manometer for measuring partial oxygen pressures in high-temperature gases in the range 500 - 1300°C. Self-consistent and reproducible e.m.f. data were obtained for various gaseous mixtures.

5) Using a reference electrode of graphite or Ni + NiO, the oxygen pressure in liquid iron containing various carbon contents was measured. This method can be used for determining the oxygen content in liquid iron at 1500 - 1600°C. Furthermore, possible applications of oxygen concentration cells for basic studies in metal processes, and their possible industrial uses are also discussed.

INTRODUCTION AND EXPERIMENTAL PRINCIPLE

An oxygen concentration cell consists of two electrodes separated by an electrolyte through which the transference of electrical charge is accomplished predominantly by the migration of oxygen ions.

Although the phase diagram of ZrO2 - CaO system is not yet well established throughout the whole concentration range, it was known [1-5] that the
solid solution of ZrO$_2$ and CaO (mole fraction of CaO is less than 0.15) provides pure oxygen anion conduction at the temperature range of 500-2300°C.

The present authors have extensively studied the application of this rather new EMF method to thermodynamic research. The construction of the cell can schematically be shown as follows:

<table>
<thead>
<tr>
<th>Electrode I</th>
<th>Solid Electrolyte</th>
<th>Electrode II</th>
</tr>
</thead>
<tbody>
<tr>
<td>with $P^I(O_2)$</td>
<td>ZrO$_2$·CaO</td>
<td>with $P^{II}(O_2)$</td>
</tr>
</tbody>
</table>

 EMF

If both thermal and chemical equilibria are attained at both electrodes with oxygen pressures of $P^I(O_2)$ and $P^{II}(O_2)$, respectively, the reversible electromotive force, $E$ is simply given by the following equation.

$$E = \frac{RT}{n_F} \ln \left[ \frac{P^I(O_2)}{P^{II}(O_2)} \right]$$

where $R$ is the gas constant, $T$ is absolute temperature in °K, $F$ is Faraday's constant, and $n$ is the valence of oxygen ion in the solid electrolyte, ZrO$_2$·CaO. Therefore, $n$ is 2 for all the following experiments without any exception as long as ZrO$_2$·CaO is used as the electrolyte. The experimental principles of the six researches which will be introduced are given as follows:

(1) Standard free energies of formation $[6]$ of FeO, Fe$_3$O$_4$, SnO, PbO, Cu$_2$O, CuO and Ta$_2$O$_5$ have been determined by the measurement of the equilibrium oxygen pressure within the electrode, which consisted of metal powder and its oxide powder, and given that the equilibrium oxygen pressure in the reference electrode is known with an accuracy better than that of the standard free energies of formation of other metal oxides. The mixture of nickel and NiO powder was used as the reference electrode. The standard free energies of the metal oxides, $\Delta F^0_\Phi$ were calculated from Eq. (2) and expressed as functions of temperature in the range 500-1300°C.

$$\Delta F^0_\Phi = +RT \ln P^I(O_2)$$

(2) The oxygen pressure $[7]$ in liquid PbO-SiO$_2$ solution in equilibrium with liquid lead has been measured with the reference electrode of (Ni + NiO) combination at 800, 900, 1000 and 1100°C. Once the equilibrium oxygen pressure is determined, one can calculate the chemical activity of PbO in the PbO-SiO$_2$ binary system, using the Eq. (3):

$$\Delta F^0_\Phi = -RT \ln \left( \frac{a(PbO)}{P^I(O_2) a(Pb)} \right)$$

where $a(PbO)$ and $a(Pb)$ are the chemical activities of PbO and Pb, $\Delta F^0_\Phi$ is the standard free energy of formation of PbO determined in experiment (1). Also, one can calculate the activity of silica and other thermodynamic properties of the PbO-SiO$_2$ system.
(3) The chemical activity [8] of tin in liquid tin-lead solution equilibrated with tin oxide has been determined using a similar procedure to that in experiment (2), at 700, 800 and 900°C.

(4) The partial pressure [9] of oxygen in high temperature gases in the range of $P(O_2) = 10^{-1}$ to $10^{-20}$ atm. has been measured in the region 500-1300°C using several kinds of reference electrode in which the equilibrium oxygen pressure is simply given at each constant temperature. The experimental principle is the same as in the above mentioned experiments but one electrode is designed to be suitable as a gas electrode.

(5) The rates [10] of oxidation or reduction of pure iron or iron oxides by a CO-CO$_2$ gas mixture at 900 to 1000°C have been determined by following the change of EMF with time that was caused by the change of the CO-CO$_2$ ratio of the exit gas due to the reaction. The rates of reactions can be calculated from the flow rate of the in-flowing gas mixture of CO-CO$_2$ and the change of the composition noted in the out-flowing gas mixture, the change being determined by the measurement of the EMF.

(6) The oxygen pressure [11] in liquid iron, containing various quantities of carbon up to the saturation value, or saturated with oxygen, has been measured with reference electrodes of graphite or (Ni+NiO) powder. Once the oxygen pressure in liquid iron is known, this EMF method might be used as a quick oxygen analyser. Using this principle, the present authors measured the de-oxidation rate of liquid iron by silicon, aluminium and manganese at 1550°C.

In addition to the above six experimental tasks, other possibilities of applying the oxygen concentration cells to the thermodynamic and kinetic studies of process metallurgy will be suggested and industrial applications will also be discussed in the following sections.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental apparatus for the study of the oxygen concentration cells is generally composed of: (1) gas cleaning and flow-rate control systems for CO, CO$_2$, Ar, and O$_2$ gases; (2) the reaction chambers, platinum ribbon, nichrome wires, silicon carbide, or Globar heating elements; (3) various types of oxygen concentration cells; and (4) a potentiometer with an external galvanometer. The oxygen concentration cells used for the measurement of the standard free energies of formation of metal oxides were as follows:

(1) $\text{Pt} \cdot \text{Ni} \cdot \text{NiO} | \text{ZrO}_2 \cdot \text{CaO} | \text{Pb} \cdot \text{PbO} \cdot \text{Pt}$

(2) $\text{Pt} \cdot \text{Ni} \cdot \text{NiO} | \text{ZrO}_2 \cdot \text{CaO} | \text{Sn} \cdot \text{SnO} \cdot \text{Pt}$

(3) $\text{Pt} \cdot \text{Ni} \cdot \text{NiO} | \text{ZrO}_2 \cdot \text{CaO} | \text{Fe} \cdot \text{FeO} \cdot \text{Pt}$

(4) $\text{Pt} \cdot \text{Ni} \cdot \text{NiO} | \text{ZrO}_2 \cdot \text{CaO} | \text{FeO} \cdot \text{Fe}_3 \text{O}_4 \cdot \text{Pt}$

(5) $\text{Pt} \cdot \text{Ni} \cdot \text{NiO} | \text{ZrO}_2 \cdot \text{CaO} | \text{Cu} \cdot \text{Cu}_2 \text{O} \cdot \text{Pt}$
(6) Pt·Ni·NiO|ZrO₂·CaO|Cu₂O·CuO·Pt

(7) Pt·Ni·NiO|ZrO₂·CaO|Ta·Ta₂O₅·Pt

(8) Pt·Ni·NiO|ZrO₂·CaO|Mo(O)·Pt(II)|ZrO₂·Mn·Pt(III)·MnO|ZrO₂·Fe·Pt(IV)·Fe₃O₄
(This cell has four electrodes)

(9) Ni·Pt(I)·NiO|ZrO₂·CaO|Mn·Pt(II)·MnO|ZrO₂·Fe·Pt(III)·FeO|ZrO₂·Cu·Pt(IV)·Cu₂O
(This cell also has four electrodes)

The oxygen concentration cell used for the measurement of the oxygen pressure in liquid PbO-SiO₂ solution was as follows:

(10) Ni·NiO·Pt|ZrO₂·CaO|Pb(I)·(PbO+SiO₂)slag

The oxygen concentration cell used for measurement of the chemical activity of tin was as follows:

(11) Sn·SnO₂|ZrO₂·CaO|(Pb+Sn)alloy·SnO₂

The cells used to measure the oxygen pressure in high temperature gases were as follows:

(12) CO·CO₂:FeO (Solvent of O₂)·Pt|ZrO₂·CaO|Fe·FeO·Pt

(13) CO·CO₂:Pt|ZrO₂·CaO|Ni·NiO·Pt

(14) CO·CO₂:FeO (Solvent of O₂)·Pt|ZrO₂·CaO|Cu·Cu₂O·Pt

(15) Air or Ar+O₂:Pt|ZrO₂·CaO|Ni·NiO·Pt

The "Oxygen Gauge" used for the measurement of the rate of the reduction or oxidation of pure iron oxides or pure iron was of the same type as cell (13) above. The oxygen concentration cells used for the measurement of the oxygen pressure in liquid iron were as follows:

(16) Pt·Ni·NiO|ZrO₂·CaO|Fe·FeO·Pt (Saturated by O₂)

(17) Pt·Ni·NiO|ZrO₂·CaO|Fe·C·Pt (Saturated by C)

(18) Graphite|ZrO₂·CaO|Fe-O-C (Intermediate carbon range)

All the metals and the oxides used in the above cells were of powder form, of grain size less than 100 mesh, and of chemical-reagent-grade purity, except in the cases of FeO and Ta₂O₅. The zirconia, stabilized with lime to suppress the phase transformations during heating and cooling, usually contains about 0.15-0.08 moles of CaO, traces of Fe₂O₃ and TiO₂. There
was no observable difference in the performance of the electrolyte as a pure anion conductor due to the migration of oxygen vacancies when the stabilized zirconia, irrespective of whether it was manufactured in the United States of America, Western Germany, Japan or the laboratory had been used as the solid electrolyte, $\text{ZrO}_2\cdot\text{CaO}$, in the above cells. In particular, some of the experimental runs of Pb-Sn system were carried out with the electrolyte of crucible shape made by one of the present authors from zirconyl nitrate and calcium carbonate to compare the performance of the commercial stabilized zirconia crucible with the home-made pure $\text{ZrO}_2\cdot\text{CaO}$ solid solution as an oxygen anion conductor. The chemical analyses of lead-tin alloys in the study of the activity measurement of tin and the chemical analyses of PbO-SiO$_2$ slags have been carried out, respectively, as required by the American Standards of Testing Materials and by Japan Industrial Standards after the experimental runs. In the study of oxygen pressure in liquid iron, the oxygen content has been determined by the vacuum fusion analysis with a micro-Orsat for the iron samples, taken by pipetting samples with silica tubes of diameter of around 5-8 mm during the experimental runs. Also X-ray analysis was applied to check the mutual solubility of the $\text{ZrO}_2\cdot\text{CaO}$ solid electrolyte and PbO-SiO$_2$ liquid slags. Many different shapes of oxygen concentration cell have been explored in this survey, starting with the layered tablet shape, and proceeding to the U-shape, H-shape, double crucible structure and long-tube shape with the one end closed. The cell design might prove very important, particularly in the study of fuel cells in which the combustion energy of gaseous fuels is taken out directly as electrical energy through a solid electrolyte such as $\text{ZrO}_2\cdot\text{CaO}$. To give two examples, Fig. 1 shows schematically the construction of the cell with four electrodes and the cell used to measure the oxygen pressure in liquid PbO-SiO$_2$ slags. For further details of the experimental apparatus and procedure, the reader is referred to the two papers [12] [13] by the present authors.

**EXPERIMENTAL RESULTS AND DISCUSSION**

The standard free energies of formation of the metal oxides have been obtained and are as follows (see also Fig. 2):

**Ferrous oxide (500°C to transition point of $\alpha \rightarrow \gamma$ iron)**

$$\text{Fe}(s) + \frac{1}{2}\text{O}_2(g) = \text{FeO}(s); \ \Delta F_f^0(\text{cal}) = -57,610 + 14.13T(\degree\text{C}) \pm 300$$

**Triferric tetroxide (500°C to transition point of $\alpha \rightarrow \gamma$ iron)**

$$3\text{Fe}(s) + 2\text{O}_2(g) = \text{Fe}_3\text{O}_4(s); \ \Delta F_f^0(\text{cal}) = -236,600 + 63.33T(\degree\text{C}) \pm 1000$$

**Plumbous oxide (a. 500°C to m. p. of PbO)**

For further details of the experimental apparatus and procedure, the reader is referred to the two papers [12] [13] by the present authors.

**Plumbous oxide (b. m. p. of PbO to 1150°C)**

$$\text{Pb}(l) + \frac{1}{2}\text{O}_2(g) = \text{PbO}(l); \ \Delta F_f^0(\text{cal}) = -40,840 + 17.82T(\degree\text{C}) \pm 100$$
Stannous oxide (500°C to 1100°C)
\[ \text{Sn}(s) + \frac{1}{2} \text{O}_2(g) = \text{SnO}(s); \quad \Delta F_f^0(\text{cal}) = -61000 + 23.72T(°C) ± 50 \]

Cupric oxide (500°C to 900°C)
\[ \text{Cu}(s) + \frac{1}{2} \text{O}_2(g) = \text{CuO}(s); \quad \Delta F_f^0(\text{cal}) = -33640 + 23.66T(°C) ± 300 \]

Cuprous oxide (500°C to m.p. of copper)
\[ 2\text{Cu}(s) + \frac{1}{2} \text{O}_2(g) = \text{Cu}_2\text{O}(s); \quad \Delta F_f^0(\text{cal}) = -35360 + 16.68T(°C) ± 100 \]

Tantalum oxide (800°C to 1200°C)
\[ 2\text{Ta}(s) + \frac{5}{2} \text{O}_2(g) = \text{Ta}_2\text{O}_5(s); \quad \Delta F_f^0(\text{cal}) = -413800 + 70.66T(°C) ± 300 \]

Recently, Elliott and Gleiser [14] have published an excellent compilation of thermodynamic data including the thermodynamical properties of many metals and metal oxides. The data in this compilation seem most up-to-date and reliable, so that \( F_f^0 \) from this compilation are given by broken lines in Fig. 2 for comparison with our results. Except for the data on \( \text{Ta}_2\text{O}_5 \), the present results, in general, agree quite well with the data in the compilation.

The reproducibility of the EMF was very good and the range of scattering was \( < ±1000 \text{ cal} \). Particularly, the \( \Delta F_f^0 \) of FeO was completely coincident with the data in the compilation, in which the FeO figures had been measured much more accurately than the \( \Delta F_f^0 \) of the other oxides, and by many investigators, for example Humphrey, King and Kellog [15], Darken and Gurry [16], Schenck, Dingmann, Kirscht and Wasselkock [17], Gokcen [18], Coughlin, King and Bonnickson [19]. The complete coincidence of the present \( \Delta F_f^0 \) of FeO with the previous data suggests two significant interpretations: (1) it is allowable to use the Ni + NiO combination as the reference electrode and (2) regardless of whether the structures of the cells have two or four electrodes, the commercial stabilized zirconia performs well as the pure anion conductor. Also, it was known that the oxide-oxide combinations such
as FeO + Fe$_3$O$_4$, or Cu$_2$O + CuO could provide the stable equilibrium oxygen pressure.

The measured oxygen pressure in liquid PbO-SiO$_2$ solution is shown in Fig. 3 as functions of the mole fraction of SiO$_2$. From the figure, it is clear that the oxygen pressure of PbO-SiO$_2$ solutions equilibrated with pure lead increases at higher temperature and decreases with the increase of the silica content. Fig. 4 gives the chemical activities of PbO and SiO$_2$ at 900,
FIG. 3. Partial pressure of oxygen in PbO-SiO\textsubscript{2} melts.

1000 and 1100°C. Richardson and Webb [20] and Sawamura et al. [21] measured the chemical activity of PbO and SiO\textsubscript{2} by other methods, the results of which seemed to nearly coincide with the present results. The free energy of mixing, the enthalpy and the entropy of mixing of the liquid PbO-SiO\textsubscript{2} solution were calculated by the conventional methods and shown in Fig. 5.

The results of the activity measurement on Pb-Sn system are presented in Fig. 6 for 700, 800 and 900°C. The activity of lead was calculated by Gibbs-Duhem equation as for the case of the PbO-SiO\textsubscript{2} system. However, the valence, n, was 2 for the calculation of the activity of tin, possibly because the virtual electrode reaction was Sn + ½O\textsubscript{2} → SnO, although the tin oxide used was SnO\textsubscript{2}. This fact implies that the stable oxide with metallic tin is SnO at the experimental temperature. This deduction may be also supported by the fact that the standard free energy of formation of SnO by the cell, Sn·SnO\textsubscript{2}·ZrO\textsubscript{2}·CaO·Ni·NiO agreed quite well with that in the compilation by
Elliott and Gleiser [14]. Niwa et al. [22] measured the activity of tin at 800°C in liquid Sn-Pb solution. The results were coincident with the activity of tin at 800°C, by Goto and St. Pierre [8].

Figures 7 and 8 show the measured EMF against the volume percentages of CO\(_2\) in the CO-CO\(_2\) gas phase at 1000°C and of O\(_2\) in the Ar-O\(_2\) gas phase at 900°C, respectively. The Ni+NiO combination was used as the reference.
FIG. 5. Free energy, enthalpy and entropy of mixing in the system PbO-SiO$_2$.

electrode for Fig. 7 and Fig. 8, but the other combinations such as Cu + Cu$_2$O or Fe + FeO were also successfully used. The sensitivity of the cells was so good that the EMF changed spontaneously if the composition of the incoming gas was changed. The lifetime of the oxygen gauge may become a problem of interest to industry and it is now known that the lifetime was longer than 80 h at 800-1000°C. The measurable range of the oxygen pressure is $10^{-1} - 10^{30}$ atm.

The rates of the oxidation or reduction of pure iron oxides have been determined by measuring the change of the composition of the waste gas.
FIG. 6. Activities of Sn and Pb in the system Sn-Pb.

as shown in Fig. 9 and Fig. 10. Figure 9 shows the change of the EMF and course of the reaction expressed in terms of the volume of CO gas produced per unit area of the reaction surface (cm$^3$/mm$^2$) after the two minutes which are necessary to get constant composition of the entry gas by the present gas input system. The reaction taking place is Fe + CO$\rightarrow$ FeO + CO.

Figure 10 shows the course of the reduction for the reaction Fe$_3$O$_4$ + CO $\rightarrow$ 3 FeO + CO$_2$. Also, similar data have been obtained for the reactions of 3 FeO + CO$_2$ $\rightarrow$ Fe$_3$O$_4$ + CO and FeO + CO $\rightarrow$ Fe + CO$_2$. From the change of the gas composition due to the reaction, we can calculate the rate of the reaction from:

$$v_1 = \frac{a - x}{100} \times V \times \frac{1}{6000}$$

where a is the volume percentage of CO$_2$ of the flow-in gas, x is that of CO$_2$.
of the waste gas, \( V \) is the flow rate of the flow-in CO\(_2\) gas (cm\(^3\)/min in standard state) and 6000 mm\(^2\) is the area of the reaction surface of an iron plate. In the above equation, the reaction rate, \( v_1 \) is expressed by the amount of CO produced by the oxidation (or of CO\(_2\) in case of the reduction) per minute per square millimeter of surface, so that the units of \( v_1 \) are given by cm\(^3\)/min-mm\(^2\). If one wants to express the rate by the weight decrease, one can calculate the reaction rate in mg/min-mm\(^2\) by a simple equation.

The oxygen pressure of Fe + FeO had been measured up to 1550°C and proves completely coincident with the calculated values based upon the data in the compilation by Elliott and Gleiser[14]. This result implies that the solid electrolyte, ZrO\(_2\)·CaO is a pure anion conductor at least up to 1550°C. However, the P(O\(_2\)) values in liquid iron saturated with graphite were higher than those calculated, possibly due to the lack of equilibrium within both the reference electrode and the liquid iron. Figure 11 shows the relation between the measured EMF and the oxygen contents in liquid iron of intermediate carbon range which have been determined by the vacuum fusion analysis. The scattering of the data is mostly caused by the difficulty of sampling liquid iron for the gas analysis. Nevertheless, Fig. 11 demonstrates the possibility of the application of this EMF method to the quick and continuous oxygen analysis in liquid steel. Figure 12 shows an example of the de-
oxidation curves resulting from silicon addition, expressed in terms of the measured EMF change. Similar deoxidation curves have been measured for manganese and aluminium additions to liquid steel. From the EMF change after silicon addition, one can obtain the usual deoxidation curves (the change of oxygen content with time) using the relation presented by Fig. 11. The readers may find the greatest significance of the EMF method lies in that the present result only determines the dissolved oxygen content in liquid iron. Conventional oxygen analysis, such as the vacuum fusion method and argon carrier gas method can determine only the total oxygen content, including

FIG. 8. EMF versus \% CO$_2$ in CO-CO$_2$ gas mixture.
FIG. 9. Change of EMF and the amount of gas reacted. $\text{Fe} + \text{CO}_2 = \text{FeO} + \text{CO}$.

the non-metallic oxide inclusions, such as $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{MnO}$, and $\text{FeO}$. Another EMF method of oxygen analysis has been successfully developed by Ohtani and Sambongi [23] with the solid electrolyte $\text{MgO}$. However, the conduction mechanism of $\text{MgO}$ is not clearly known. In addition to the
present work, Matsushita et al. [24] have been working on the industrial application of the oxygen gauge to measure the oxygen pressure in the waste gas of an open hearth furnace continuously, using the steam ejector to take out the waste gas from the furnace. Extensive reliability and lifetime tests have been carried out and several charts have been recorded showing the EMF change during the operation of the furnace.

FIG. 10. Change of EMF and the amount of gas reacted. $\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$. 

<table>
<thead>
<tr>
<th>Gasflowrate</th>
<th>CO₂%</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.8 c/min.</td>
<td>58.5%</td>
<td>850°C</td>
</tr>
<tr>
<td>97.8</td>
<td>55.2</td>
<td>900</td>
</tr>
<tr>
<td>99.9</td>
<td>59.3</td>
<td>900</td>
</tr>
<tr>
<td>84.7</td>
<td>64.8</td>
<td>900</td>
</tr>
<tr>
<td>101.1</td>
<td>62.4</td>
<td>950</td>
</tr>
</tbody>
</table>
FIG. 11. Relation between EMF and oxygen content in liquid iron at 1550°C.

FIG. 12. Change of EMF after addition of silicon at 1550°C.
CONCLUSIONS

The above six kinds of experiment have been carried out using the oxygen concentration cell technique in conjunction with the solid electrolyte, ZrO₂·CaO. The following conclusions can be drawn.

(1) The solid solution of ZrO₂ and CaO containing 0.03-0.15 moles of CaO performs as pure oxygen anion conductor at the temperature range of 500-1600°C.

(2) The oxygen concentration cells can, in general, be used to determine the chemical activities of components in liquid or solid alloys and in oxide slags.

(3) The oxygen concentration cells can, in general, be used to determine the reaction rates or the mass transfer rates which are related to the change of the oxygen pressure at the reaction sites.

(4) The above cell technique can be applied for industrial purposes, for example as an oxygen gauge in high temperature furnaces or with high temperature materials in solid or liquid states.

ACKNOWLEDGEMENTS

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REFERENCES

[13] MATSUSHITA, Y., GOTO, K., J. Faculty of Engng Univ. of Tokyo (B) 27 1 (1964) 217 (Distributed to main libraries of the universities all over the world).
MEASUREMENTS OF THE THERMODYNAMIC STABILITIES OF THE NIOBIUM AND TANTALUM OXIDES USING A HIGH-TEMPERATURE GALVANIC CELL

W. L. WORRELL
UNIVERSITY OF CALIFORNIA, LAWRENCE RADIATION LABORATORY, BERKELEY, CALIF., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

MEASUREMENTS OF THE THERMODYNAMIC STABILITIES OF THE NIOBIUM AND TANTALUM OXIDES USING A HIGH-TEMPERATURE GALVANIC CELL. Thermodynamic data for Nb$_2$O$_{4.8}$, NbO and Ta$_2$O$_5$ have been obtained from six different galvanic cells operating between 1030 and 1300°K. The electrolyte used is a solid-solution of either ThO$_2$ (94 wt. %)-Y$_2$O$_3$ or ThO$_2$ (98.6 wt. %)-CaO which remains an ionic conductor at lower oxygen activities and higher temperatures than the more commonly used zirconia-based electrolytes. The YFeO$_3$ phase was detected on the surface of the ThO$_2$-Y$_2$O$_3$ electrolyte where it had been in contact with the Fe, Fe$_{0.95}$O electrode. More stable readings were obtained using the ThO$_2$-CaO electrolyte with the Fe, Fe$_{0.95}$O electrode.

A comparison between the temperature variation of the Gibbs energy of formation of Nb$_2$O$_{4.8}$ obtained in this study and that of Nb$_2$O$_5$ from calorimetric data indicates that the homogeneity range of the pentoxide increases with increasing temperature. Two independent Gibbs-energy-of-formation equations were determined for NbO. Values from the two equations differ by 600 calories, but the data from one of the NbO cells are suspected of containing a systematic error. There is considerable disagreement between the enthalpy and entropy values for NbO obtained in this study and those calculated from thermal data. It is suggested that this difference may indicate a homogeneity range for NbO.

The thermodynamic stability of Ta$_2$O$_5$ obtained in this study is in excellent agreement with the thermal data. The effect of the solubility of oxygen in niobium and tantalum on the results for NbO and Ta$_2$O$_5$ is discussed.
MEDICION DE LA ESTABILIDAD TERMODINAMICA DE LOS OXIDOS DE NIÓBIO Y TANTALO, CON UNA CELDA GALVANICA DE ALTA TEMPERATURA. Con seis celdas galvánicas diferentes, funcionando a una temperatura comprendida entre 1030 y 1300°K, se obtuvieron datos termodinámicos para el Nb2O4 y Ta2O5. Se utilizó un electrolito consistente en una solución sólida de ThO2 (94% en peso) - Y2O3 o ThO2 (98,6% en peso) - CaO, que conserva sus características de conductor iónico a menores actividades de oxígeno y temperaturas más elevadas que el electrolito más comúnmente usado, a base de óxido de circonio. La fase YFeO3 se detectó en la superficie del electrolito ThO2 - Y2O3, donde había estado en contacto con el electrodo Fe, Fe92O. Se obtuvieron valores más estables utilizando el electrolito ThO2 - CaO con el electrodo Fe, Fe92O.

La comparación de la variación de la energía de formación de Gibbs en función de la temperatura para el Nb2O4, obtenida en este estudio, y la correspondiente al Nb2O4, calculada a partir de datos calorimétricos, demuestra que el intervalo de homogeneidad del pentóxido aumenta al crecer la temperatura. Para el NbO se determinaron dos ecuaciones independientes para la energía de formación de Gibbs. Los valores obtenidos con ambas ecuaciones difieren en 600 calorías; sin embargo, es posible que los datos procedentes de una de las celdas de NbO estén afectados por un error sistemático. Hay una discrepancia considerable entre los valores de entalpia y de entropía para el NbO calculados en este estudio y los obtenidos a partir de datos térmicos. Es posible que esta diferencia indique la existencia de un intervalo de homogeneidades para el NbO.

La estabilidad termodinámica del Ta2O5 obtenida en este estudio concuerda muy bien con la deducida de los datos térmicos. En la memoria se examina la influencia ejercida por la solubilidad del oxígeno en el nióbio y en el tántalo sobre los resultados correspondientes al NbO y al Ta2O5.

1. INTRODUCTION

In 1957 Kiukkola and Wagner [1] clearly demonstrated the potential use of galvanic cells with solid-oxide electrolytes to obtain reliable thermodynamic data at elevated temperatures. Most investigations since 1957 have used a zirconia-based electrolyte because of the availability of zirconia-calcia tubes which, if of sufficient purity, function quite satisfactorily as electrolytes. However, Schmalzried [2] and Steele and Alcock [7] have shown that n-type electronic conduction becomes significant in the commercially available zirconia-based tubes at oxygen activities below 10−15 at 1000°C, and these tubes cannot be used to investigate systems with extremely low oxygen activities. Recently several studies [3-8] have been reported in which a
thoria-based electrolyte was used. Because this electrolyte remains a purely ionic conductor in the low oxygen activity region [7], it was used in this galvanic study of the thermodynamic stabilities of the niobium and tantalum oxides.

Niobium forms three stable oxides, \( \text{Nb}_2\text{O}_5 \), \( \text{NbO}_2 \) and \( \text{NbO} \) [9]. The pentoxide possesses a homogeneity range which varies from \( \text{Nb}_2\text{O}_{4.8} \) to \( \text{Nb}_2\text{O}_5 \), but no significant homogeneity range has been detected for either \( \text{NbO}_2 \) or \( \text{NbO} \) [9]. Because the \( \text{Nb}_2\text{O}_5 \) phase was in equilibrium with \( \text{NbO}_2 \), the thermodynamic properties obtained in this study apply to the \( \text{Nb}_2\text{O}_{4.8} \) composition.

Although several tantalum oxides have been reported in the literature [10] there is evidence [11,12] that only tantalum pentoxide is stable. From a study of the defect structure of \( \text{Ta}_2\text{O}_5 \), Kofstad [13] concludes that \( \text{Ta}_2\text{O}_5 \) is essentially a line compound with a very limited range of homogeneity.

2. EXPERIMENTAL STUDY

2.1. Materials

Niobium, iron, tantalum, \( \text{Fe}_2\text{O}_3 \), \( \text{Nb}_2\text{O}_5 \) and \( \text{Ta}_2\text{O}_5 \) powders (-325 mesh) of 99.9+% purity were purchased from commercial sources. The \( \text{NbO}_2 \), \( \text{NbO} \), and \( \text{FeO} \) were obtained by hydrogen reduction of \( \text{Nb}_2\text{O}_5 \) and \( \text{Fe}_2\text{O}_3 \). Electrode pellets (0.5 in diam. and 0.25 in thick) were prepared by pressing the appropriate metal-oxide mixture at 20 tons/in\(^2\) and oxide-oxide mixture at 10 tons/in\(^2\).

The thoria-based electrolytes were prepared from -325 mesh powders of high purity (99.9+%) \( \text{ThO}_2 \) and either \( \text{Y}_2\text{O}_3 \) or \( \text{CaO} \). Mixtures of either 98.6 wt.\% \( \text{ThO}_2 \) and 1.4 wt.\% \( \text{CaO} \) or of 94 wt.\% \( \text{ThO}_2 \) and 6 wt.\% \( \text{Y}_2\text{O}_3 \) were pressed (10 tons/in\(^2\)) into pellets of 0.5 in diam. and 0.25 in thick. These compositions correspond to a thoria solid-solution containing 3.25% oxygen ion vacancies, which is the region of maximum ionic conductivity [7]. The pressed pellets were heated inductively to 1900-1950°C and held for 3-4 h under a vacuum of 1 \( \times \) 10\(^{-5}\) mm of Hg. During this time the thoria dissolved either the \( \text{Y}_2\text{O}_3 \) or the \( \text{CaO} \) to form a one phase solid-solution.

2.2. Apparatus

The experimental design was similar to that of Kiukkola and Wagner [1]. The reaction and positioning tubes were of high-purity alumina. The reaction tube was encased in platinum foil which was connected to the earthed furnace shell to avoid induced potentials from the resistance windings of the furnace. The reaction tube was positioned vertically in the furnace and sealed at each end with O-rings in brass fittings.

High-purity argon entered the reaction tube after passing through a gas-purification furnace containing Zr-Ti alloy (87.5 at.\% \( \text{Zr} \)) chips at 375°C. This newly available alloy proved to be an excellent oxygen-getter.

The temperature was measured using a Pt/Pt-10\%Rh thermocouple.

The cell EMF was measured using a high input resistance (10 k\( \Omega \)) electronic galvonometer combined with a Leeds and Northrup K-2 potentiometer.
Two springs positioned at the top and bottom of the reaction tube were used to sandwich the electrolyte pellet between the two electrodes. Platinum lead wires were spot-welded to the platinum discs pressed against each electrode. The Pt-10% Rh wire was also spot-welded to the top platinum disc; thus the upper platinum lead served as both an electrode and a thermocouple lead.

After assembling the cell, the reaction tube was evacuated to 5 μm Hg pressure and checked for leaks. The argon flow was then started, and the cell was heated to the desired temperature. After obtaining a stable EMF, the temperature was randomly varied to obtain additional measurements. Occasionally an EMF either higher or lower than the equilibrium value was imposed on the cell. After these polarizations, the EMF always returned to the equilibrium value. The argon flow rate was also increased and decreased to see if the EMF varied with flow rate.

After each run an X-ray diffraction analysis was made of each electrode to confirm that only the initial phases were present.

Using the above procedure, the following galvanic cells were investigated:

\[
\begin{align*}
\text{NbO}_2, \text{Nb}_2\text{O}_{4.8} & \mid \text{ThO}_2(\text{Y}_2\text{O}_3) \mid \text{Fe, Fe}_{0.95} \text{O} \\
\text{NbO}_2, \text{Nb}_2\text{O}_{4.8} & \mid \text{ThO}_2(\text{CaO}) \mid \text{Fe, Fe}_{0.95} \text{O} \\
\text{NbO}, \text{NbO}_2 & \mid \text{ThO}_2(\text{CaO}) \mid \text{Fe, Fe}_{0.95} \text{O} \\
\text{NbO}_2, \text{Nb}_2\text{O}_{4.8} & \mid \text{ThO}_2(\text{Y}_2\text{O}_3) \mid \text{NbO}, \text{NbO}_2 \\
\text{Nb}, \text{NbO} & \mid \text{ThO}_2(\text{Y}_2\text{O}_3) \mid \text{NbO}, \text{NbO}_2 \\
\text{Nb}, \text{NbO} & \mid \text{ThO}_2(\text{Y}_2\text{O}_3) \mid \text{Ta}, \text{Ta}_2\text{O}_5
\end{align*}
\]

A minimum of three experimental runs were made with each of these cells.

3. RESULTS

3.1. NbO$_2$, Nb$_2$O$_{4.8}$ versus Fe, Fe$_{0.95}$O

Galvanic Cell A was the first cell investigated. Although the EMF appeared very stable, slightly lower values for the EMF were obtained after the first 36 h. The ThO$_2$(Y$_2$O$_3$) electrolyte was badly stained where it had been in contact with the Fe, Fe$_{0.95}$O electrode. With re-use, the ThO$_2$(Y$_2$O$_3$) electrolyte gave even lower but steady values for the EMF. After several runs, X-ray diffraction analysis revealed the presence of the YFeO$_3$ phase on the electrolyte surface. Thus a very slow reaction was occurring between the Fe, Fe$_{0.95}$O electrode and the Y$_2$O$_3$ dissolved in the thorium. From a qualitative analysis of the phase relationships in the Y-Fe-O ternary system, it was concluded that the formation of YFeO$_3$ would tend to lower the oxygen...
activity at the Fe, Fe$_{0.95}$O electrode, thus bringing it slightly closer to that of the NbO$_2$, Nb$_2$O$_{4.8}$ electrode and decreasing the EMF slightly.

Measurements were then made using the ThO$_2$(CaO) electrolyte (Cell A') to confirm the initial EMF readings using the ThO$_2$(Y$_2$O$_3$) electrolyte. These values were very stable over extended periods of time. The ThO$_2$(CaO) electrolyte was also slightly stained where it had been in contact with the Fe, Fe$_{0.95}$O electrode. However, the staining was very mild compared to that observed with ThO$_2$(Y$_2$O$_3$), and its X-ray diffraction pattern did not show any extraneous lines.

![Graph showing temperature dependence of the EMF for the galvanic cells investigated.](image)

**FIG. 1.** Temperature dependence of the EMF for the galvanic cells investigated.

The results from Cells A and A' are shown in Fig. 1. Although the initial readings using the ThO$_2$(Y$_2$O$_3$) lie on the accepted line, the later values are 1 to 3 mV too low.
The EMF obtained at 1000°C by Steele and Alcock [7] using similar cells is also shown. It is interesting to note that Steele and Alcock [7] experienced considerable difficulty stabilizing the EMF in the cell Fe, Fe$_{0.95}$O | ThO$_2$(Y$_2$O$_3$) | Nb, NbO. They attributed these difficulties to a very slight electronic conductivity in the electrolyte, possibly caused by the low oxygen activity at the Nb, NbO electrodes. However, the formation of the YFeO$_3$ phase could have been responsible for at least part of the decrease.

Steele and Alcock [7] observed that when the Y$_2$O$_3$ in the ThO$_2$(Y$_2$O$_3$) electrolyte was decreased, the drift in the EMF was lessened, and they attributed this to the higher resistivity of the thoria-based electrolytes containing less Y$_2$O$_3$. However, the less Y$_2$O$_3$ the thoria contains, the less the tendency to form YFeO$_3$. It may be significant that the present author experienced no drifting in Cells D and E where the oxygen activity is very low but the Fe, Fe$_{0.95}$O electrode is absent. Thus it appears wise to dissolve as little Y$_2$O$_3$ or CaO as possible in the thoria if one is using an Fe, Fe$_{0.95}$O electrode.

Ignoring the values from the later ThO$_2$(Y$_2$O$_3$) runs, a straight line was fitted to the data from Cells A and A'. The equation for this line shown in Fig. 2 is:

$$E(\text{mV}) = 239.5 - 0.075 \, T$$  \hspace{1cm} (1)

Using the expression:

$$\Delta G = -nF \varepsilon$$ \hspace{1cm} (2)

and Eq.(1), one obtains

$$\Delta G(\text{cal}) = -11,000 + 3.45T$$ \hspace{1cm} (3)

for the reaction

$$\text{Fe}_{0.95}\text{O} + 2.5 \text{NbO} = 0.95\text{Fe} + 1.25\text{Nb}_2\text{O}_{4.8}$$ \hspace{1cm} (4)

where $\Delta G$ is the Gibbs energy of reaction, $n$ is 2 for O$^-$, $F$ the Faraday equivalent (23.061 cal/mV), and $\varepsilon$ the electromotive force.

3.2. NbO, NbO$_2$ versus Fe, Fe$_{0.95}$O

Several attempts were made to measure the EMF of Cell B. Only one run was successful; in the others the EMF varied appreciably with the argon flow rate.

This variation of the EMF with the argon flow rate most probably indicates a relatively porous electrode-electrolyte interface in which the gaseous atmosphere influences the EMF. It was also observed that the metal-oxide electrodes deformed slightly during a run, and that these ductile electrodes seemed to form a more impervious electrode-electrolyte interface than the more brittle oxide-oxide electrodes. One would thus expect to find the maximum flow rate variation of the EMF in Cell C and the least in Cell E. The
variation of the EMF with argon flow rate was 0.1 mV in Cell E, 0.5 mV in Cells A, A' and D, and 3 to 5 mV in Cells B and C. The uncertainties shown in Fig. 1 indicate the extent of the flow rate variation of the EMF.

Alcock and Steele [6] obtained a mirror finish on the surfaces of their electrolytes by polishing with 0.25 μm diamond paste. In this study the surfaces were not polished, which is probably the cause of the difficulty in obtaining non-porous electrode-electrolyte interfaces in cells B and C.

The two EMF values which were obtained using galvanic Cell B were combined with the data from Cells A and A', and are plotted with the data from Cell C. These are shown as the two triangular points by the NbO, NbO₂-NbO₂, Nb₂O₄.₈ line of Fig. 1.

3.3. NbO, NbO₂ versus NbO₂, Nb₂O₄.₈

The EMF of Cell C also varied with the argon flow rate, and relatively large uncertainties (±3 to 5 mV) have been assigned to these measurements. It should be noted that the maximum change in the EMF was only 5 mV in 270 mV.
The slope of the line drawn through the data of Cells C was determined using the third law method. The entropy of NbO₂ is well established [14-16]. The entropy of Nb₂O₄.₈ was calculated using Eq. (12) which represents the data obtained from Cells A and A'. Because only an estimate was available for the entropy of NbO [14], a value was chosen which would be consistent with the data of Cells D and E.

Once the slope was established, a line was drawn through the data giving more weight to the measurements above 1200°K, because these measurements were more precise and reproducible. It should also be noted that several anomalies have been observed in the heat-content curve of NbO₂ between 1090 and 1200°K [17]. The equation for the NbO, NbO₂-NbO₂, Nb₂O₄.₈ line shown in Fig. 1 is:

$$\text{E(mV)} = 242.0 + 0.03 \text{T}$$

(4)

Using Eq. (2) one obtains:

$$\Delta G (\text{cal}) = -11150 - 1.38 \text{T}$$

(5)

for the reaction

$$\text{NbO} + 1.25 \text{Nb}_2\text{O}_4.8 = 3.5 \text{NbO}_2$$

II

3.4. Nb, NbO versus NbO₂, NbO₂

The measured values from Cell D varied only 0.5 mV with the argon flow rate. The values were also quite stable with time; in some cases the temperature was held constant for 36 h and no drift in the EMF was detected.

It should be mentioned that the time to approach equilibrium was considerably larger in cells of the type D and E. Longer times are probably necessary for the niobium and tantalum to equilibrate with NbO and Ta₂O₅ respectively. NbO and tantalum contain 1 to 3 at. % oxygen when in equilibrium with NbO and Ta₂O₅ [18, 19]. The effect of the oxygen dissolved in tantalum and niobium will be discussed in section 4.4.

Although the precision of the data from Cell D is high, the measured values appear to be 7-8 mV too low. The Steele and Alcock value [7] at 1000°C, shown in Fig. 1, is based on several different types of cells. In the subsequent analysis of the data, it also becomes clear that the data from the Cell D yield a value for $\Delta G_1$ of NbO that is 700 calories less negative than that from Cell C. The more negative value is also more consistent with data from Cell E.

The NbO used in the electrode pellets contained a small amount of niobium. It appears that the niobium was not oxidized during the galvanic cell runs because a trace of niobium was still evident in the X-ray diffraction patterns of the NbO₄, NbO₂ electrodes. The oxygen activity may be slightly decreased at the NbO, NbO₂ electrode due to the presence of niobium, and this could account for the lower values observed in this study. Because of these reasons, a dashed line is shown drawn through the data of Cell D.
The slope of this line was determined using a Third Law analysis; the entropy of NbO was chosen to be consistent with the data from Cells C and E. The equation for the Nb, NbO–NbO, NbO₂ line shown in Fig. 1 is:

\[ E(\text{mV}) = 309.6 - 0.09T \]  

(6)

Using Eq. (2), one obtains:

\[ \Delta G(\text{cal}) = -14,250 + 4.15T \]  

(7)

for the reaction:

\[ \text{NbO}_2 + \text{Nb} = 2\text{NbO} \]  

III

3.5. Nb, NbO versus Ta, Ta₂O₅

The variation of the EMF with the argon flow rate for Cell E was negligible (±0.1 mV). The several points shown in Fig. 1 with large uncertainties are from an early run in which no spring assembly was used to press the electrodes against the electrolyte.

The slope of the line drawn through the data of Cell E was determined using a procedure similar to that for Cells C and D. The equation for this line is:

\[ E(\text{mV}) = 87.1 - 0.043T \]  

(8)

Using Eq. (2), one obtains:

\[ \Delta G(\text{cal}) = -4,020 + 1.98T \]  

(9)

for the reaction:

\[ \text{Nb} + l/5\text{Ta}_2\text{O}_5 = 2/5\text{Ta} + \text{NbO} \]  

IV

No extraneous lines were observed in the X-ray diffraction patterns of the Ta-Ta₂O₅ and the Nb-NbO electrodes. This observation and the stability of the EMF values indicate that the reported suboxides of tantalum [10] are not stable over the experimental temperature range.

4. DISCUSSION

4.1. Gibbs energy of formation of Nb₂O₄.₈

The Gibbs energy of formation of NbO, NbO₂ and Nb₂O₄.₈ could be determined from the measured Gibbs energy changes for reactions I, II and III. However the Gibbs energy change of reaction III is suspected of having a systematic error of 400 to 800 calories. Instead of introducing this error
into all three $\Delta G_f^0$ equations for the niobium oxides, two values for $\Delta G_f^0$ of NbO were calculated from Eqs.(5) and (7), and $\Delta G_f^0$ of Nb$_2$O$_{4.8}$ was calculated from Eq.(3) using literature values [14, 20] for $\Delta G_f^0$ of NbO$_2$.

From the critical evaluation of Schick [14], one obtains the following Gibbs energy equation for NbO$_2$ between 1100 and 1300°K:

$$\Delta G_f^0(cal) = -185600 + 39.0 T$$  \hspace{1cm} (10)

As shown in Fig. 2, there is excellent agreement between Eq.(10) and the high-temperature data [8, 20].

The following Gibbs energy equation for the Fe-Fe$_{0.98}$O reaction has been determined by Blumenthal and Whitmore [21] from a critical review of the pertinent data:

$$\Delta G_f^0(cal) = -63100 + 15.51 T$$  \hspace{1cm} (11)

Adding Eqs.(11) and (3) yields:

$$\Delta G_f^0(cal) = -74100 + 18.96 T$$  \hspace{1cm} (12)

for the reaction

$$2.5 \text{ NbO}_2 + \frac{1}{2} \text{O}_2 = 1.25 \text{ Nb}_2\text{O}_{4.8}$$  \hspace{1cm} V

Using Eqs.(10) and (11), one obtains the following expression for $\Delta G_f^0$ of Nb$_2$O$_{4.8}$ between 1050 and 1300°K:

$$\Delta G_f^0(cal) = -430480 + 93.17 T$$  \hspace{1cm} (13)

The thermodynamic stabilities [14] of Nb$_2$O$_5$ and of Nb$_2$O$_{4.8}$ between 1050 and 1300°K are shown in Fig. 2. The difference in $\Delta G_f^0$ reflects the homogeneity range of the Nb$_2$O$_5$ phase and increases slightly with increasing temperature, perhaps indicating that the homogeneity range is increasing. In the phase diagram for the Nb-O system [22], the homogeneity range of Nb$_2$O$_5$ is indicated by dashed lines and is shown increasing with increasing temperature.

4.2. Gibbs energy of formation of NbO

Using Eq.(5), (10) and (13), one obtains the following equation for $\Delta G_f^0$ of NbO between 1050 and 1300°K:

$$\Delta G_f^0(cal) = -100350 + 21.42 T$$  \hspace{1cm} (14)

On the other hand combining Eqs.(10) and (7) yields:

$$\Delta G_f^0(cal) = -99920 + 21.58 T$$  \hspace{1cm} (15)

for NbO in the same temperature region.
The thermodynamic stability of NbO calculated from Eq. (14) is shown in Fig. 2, in which it is compared to both that given in the critical review by Schick [14] and to that obtained by Lavrent'ev et al. [8]. The values for $\Delta G^\circ_f$ calculated from Eq. (15) would be about 600 calories less negative than those from Eq. (14), but Eq. (15) contains the suspected systematic error of Eq. (7).

Lavrent'ev et al. [8] measured the EMF of the galvanic cell $\text{Fe}, \text{FeO}_{0.95} | \text{ThO}_2(\text{La}_2\text{O}_3) | \text{Nb}, \text{NbO}$. Their experimental data are given by the equation:

$$\Delta G_f^\circ (\text{cal}) = -34500 + 3.15T; \text{ (1114 to 1346}^\circ\text{K})$$

for the reaction

$$\text{Nb} + \text{Fe}_{0.95} = 0.95 \text{Fe} + \text{NbO} \quad \text{VI}$$

Adding Eqs. (11) and (16), one obtains $-97600 + 18.66T$ for $\Delta G_f^\circ$ of NbO. The values of $\Delta G_f^\circ$ calculated from this equation are 400 to 700 calories more negative than the values obtained from Eq. (14) of this study. However, the Lavrent'ev et al. measured EMF values [8] are 20-30 mV higher than those obtained by Steele and Alcock [7] from a similar cell.

Using the high-temperature thermal data of Gel'd and Kusenko [23], values of $-101.0(\pm 2.0)$ kcal/mole and 10.2 $\pm 1.0$ e.u. are obtained from Eqs. (14) and (15) for $\Delta H_f^\circ_{298}$ and $S_f^\circ_{298}$ of NbO respectively. An uncertainty considerably higher than the precision of the experiments has been assigned to these values to reflect the possible shifts in equilibrium composition with temperature of the niobium and niobium oxides. Schick [14] selected a value of $-97.7(\pm 2.0)$ kcal/mole for $\Delta H_f^\circ_{298}$ of NbO and estimated $S_f^\circ_{298}$ of NbO to be $12.0 \pm 1.5$ e.u. Schaefer and Liedmeier [25] recently obtained a value of $-97.0(\pm 1.0)$ kcal/mole for $\Delta H_f^\circ_{298}$ of NbO from combustion calorimetry.

It should be noted that the value of $S_f^\circ_{298}$ of NbO obtained in this study was determined by choosing the value which would give the best fit to the data for Cells C, D and E. Using Schick's selected value ($-97.7$ kcal/mole) for $\Delta H_f^\circ_{298}$ of NbO [14], one would calculate enthalpy terms for Eqs. (14) and (15) which are 3.3 to 3.8 kcal less negative than those obtained in this study. With the calculated enthalpy terms, a value of $13.0 (\pm 0.5)$ e.u. for $S_f^\circ_{298}$ of NbO would be required to obtain the Gibbs energy of formation values obtained in this study. However, a value of 13.0 e.u. for $S_f^\circ_{298}$ of NbO would require the slopes of the EMF versus temperature lines of Cells C, D and E to be opposite from that shown in Fig. 1. This discrepancy between the calorimetric and equilibrium data could be caused by composition variations in the equilibrium phases. For example, the composition of NbO in equilibrium with niobium could vary significantly from the stoichiometric one. Although Brauer [9] in 1941 detected no significant homogeneity range in NbO, the VO phase exists between 44.5 and 54.5 at. % oxygen [10]. The effect of the variation in composition of the niobium in equilibrium with NbO is discussed in section 4.4.
4.3. Gibbs energy of formation of $\text{Ta}_2\text{O}_5$

Subtracting Eq.(9) from Eq.(14), one obtains the following expression for $\Delta G^\circ$ of $\text{Ta}_2\text{O}_5$ per g-atom of oxygen between 1050 and 1300°K:

$$\Delta G^\circ (\text{cal}) = -96320 + 19.44T$$

(17)

The agreement between the values calculated from Eq.(17) and those tabulated in the literature [14, 24] is shown in Fig. 2; they are in such excellent agreement that they appear as one line. Because the thermodynamic stability of $\text{Ta}_2\text{O}_5$ was obtained using Eq.(11), the agreement between the thermal and equilibrium data of $\text{Ta}_2\text{O}_5$ supports the Gibbs-energy-of-formation equation for NbO obtained in this study.

If one uses Eq.(15) instead of (14), one obtains values for $\Delta G^\circ$ of $\text{Ta}_2\text{O}_5$ that are about 0.6 kcal per g-atom oxygen less negative than those calculated from Eq.(17). However, the thermal data for $\text{Ta}_2\text{O}_5$ are well established, and their uncertainty is only ±0.1 kcal per g-atom oxygen. One also would expect excellent agreement between the thermal and high-temperature equilibrium data because the homogeneity range of $\text{Ta}_2\text{O}_5$ has been observed to be very limited [13].

4.4. Influence of the solubility of oxygen in niobium and tantalum

Between 1100 and 1300°K, the saturated-oxygen concentration in niobium varies from approximately 1.4 to 2.3 at.% [18]. Over the same temperature range, the oxygen concentration in tantalum in equilibrium with $\text{Ta}_2\text{O}_5$ increases from approximately 2.5 to 3.0 at.% [19]. Assuming that the activity of oxygen in the metal obeys Henry's law, calculations were made to correct the measured data of Cells D and E. The correction changes both the enthalpy and entropy terms in Eqs.(7) and (9) because the saturated-oxygen concentration varies with temperature. However the correction is quite small. For example, the Gibbs energy of reaction III is increased by only 90 calories at 1200°K.

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REFERENCES

THERMODYNAMIC DATA FOR PLUTONIUM OXIDES

T.L. MARKIN AND M.H. RAND
ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, BERKS., ENGLAND

Abstract — Résumé — Аннотация — Resumen

THERMODYNAMIC DATA FOR PLUTONIUM OXIDES. Thermodynamic data have been obtained for plutonium oxides with O/Pu ratios between 1.53 and 2.00 at temperatures between 700 and 1140°C, using a high temperature galvanic cell, containing solid electrolytes reversible to oxygen ions only and employing two reference electrodes (Ni, NiO and Fe, wustite). A large change in $\Delta G$ of $O_2$ occurs between PuO$_2$ and PuO$_{1.98}$ and the thermodynamic data is sufficiently precise to give reliable values of $\Delta N(O_2)$ and $\Delta S(O_2)$ for all compositions between PuO$_{1.24}$ and PuO$_{1.98}$ for 700 $< t <$ 1140°C.

The plutonium-oxygen phase diagram has recently been re-investigated for O/Pu ratios between 1.50 and 2.00 at temperatures between 25 and 800°C, using a high temperature X-ray powder diffraction camera. A new phase diagram is suggested which attempts to summarize the work of the several investigators.

The thermodynamic data, obtained from EMF cell measurements, agrees with the suggested phase diagram, of which it is entirely independent, extremely well, and an extrapolation of the thermodynamic data from 700°C to room temperature has been made that is consistent with the suggested phase diagram. For the reaction $2<PuO_2> + O_2 \rightarrow 4<PuO_3>$, an estimated value of $\Delta C_P$ has been taken from the value for the corresponding cerium oxide reaction. The partial molar heats and entropies have been calculated for the several phase regions and $\Delta S(0_2)$ and $\Delta N(0_2)$ for the entire region from $<PuO_3>$ to $<PuO_2>$, has been integrated and the heats of formation and standard entropies calculated for $<PuO_2>$ and $<PuO_{1.98}>$.

CONSTANTES THERMODYNAMIQUES DES OXYDES DE PLUTONIUM. Les auteurs ont déterminé les valeurs des constantes thermodynamiques relatives aux oxydes de plutonium dont les rapports O/Pu étaient compris entre 1.53 et 2.00 à des températures de 700 à 1140°C, en utilisant une cellule galvanique pour hautes températures qui contient des électrolytes solides réversibles uniquement à l'égard des ions oxygène, et comporte deux électrodes de référence (Ni, NiO et Fe, wustite). Il se produit une variation considérable de $\Delta G(0_2)$ entre PuO$_2$ et PuO$_{1.98}$ et les constantes thermodynamiques sont connues d'une manière suffisamment précise pour que l'on puisse obtenir des valeurs sûres de $\Delta N(0_2)$ et $\Delta S(0_2)$ pour toutes les compositions allant de PuO$_{1.24}$ à PuO$_{1.98}$ dans l'intervalle de température compris entre 700°C et 1140°C.

Les auteurs ont procédé récemment à de nouvelles recherches sur le diagramme d'équilibre plutonium-oxygène pour les rapports O/Pu allant de 1.50 à 2.00 et des températures comprises entre 25 et 900°C, en utilisant une chambre de diffraction de rayons X du type Debye-Scherrer pour haute température. Ils s'efforcent de faire la synthèse des travaux de plusieurs chercheurs en proposant un nouveau diagramme d'équilibre.

Les valeurs obtenues par la méthode f.e.m. sont en très bon accord avec le diagramme d'équilibre proposé, dont elles sont totalement indépendantes; en outre, une extrapolation de ces valeurs de 700°C à la température ambiante a donné des résultats compatibles avec ce diagramme. Pour la réaction $2<PuO_2> + O_2 \rightarrow 4<PuO_3>$, les auteurs ont calculé la valeur de $\Delta C_P$ à partir de la valeur correspondante relative à la réaction de l'oxyde de cérumium. Ils ont également intégré $\Delta S(0_2)$ et $\Delta N(0_2)$ sur toute la région allant de $<PuO_3>$ à $<PuO_2>$ et calculé les chaleurs de formation et les entropies standard pour $<PuO_2>$ et $<PuO_{1.98}>$.

ТЕРМОДИНАМИЧЕСКИЕ ДАННЫЕ ДЛЯ ОКИСЕЙ ПЛУТОНИЯ. Получены термодинамические данные для окисей плутония с соотношениями O/Pu в пределах между 1.53 и 2.00 при температурах в диапазоне 700 — 1140°C при использовании высокотемпературной гальванической камеры, в которой были применены твердые электролиты, реверсивные только в отношении ионов кислорода, и два эталонных электрода (Ni, NiO и Fe, вустит). Большое изменение в $\Delta G(0_2)$ имеет место между PuO$_2$ и PuO$_{1.98}$, термодинамические данные являются достаточно точными для вывода надежных значений $\Delta N(0_2)$ и $\Delta S(0_2)$ для всех составов между PuO$_{1.24}$ и PuO$_{1.98}$ при 700 $< t <$ 1140°C.

Диаграмма фаз плутоний-кислород недавно была изучена заново для соотношений O/Pu между 1.50 и 2.00 при температурах в диапазоне 25 — 900°C с использованием высоко-
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temperaturny kamery dla poluchienia rentgenogramm typa Debya-Sherrer'a. Predlagates
novaya diagramma faz, v korney predprinimaetsya povyshenie obobshchenue uhitnikih
issledovateley. Termodynamicheskiye dannye, poluchennye v rezultate izmiereniy e.d.s.
av kamere, ocheny xoroshie uoglaetsya s predlozhennoy diagrammoy faz, ot kotorых ona pol-
nost' ne zavist'. Proizvedena ekstrapolatsiya termodynamicheskih dannyh ot 700°C do
komnatnoy temperatury, chto sovmmestno s predlozhennoy diagrammoy faz. Dlya reakcii
2 \( \text{Pu}_2O_3 \rightarrow O_2 + 4 \text{Pu}_2O_6 \) primerenoe znachenie \( \Delta C_P \) zavto na osnoveniy velichinm sostoy-
vusha reakcii oksenny cernia. Dlya nekotorikh oblastey faz i \( \Delta S(O_2) \) raschitany parcial-
noe moljarnoye teplo i entropiya, dlya cely oblasti ot \( \text{Pu}_2O_6 \rightarrow \text{Pu}_2O_6 \) проведeno inte-
griranie \( \Delta H(O_2) \), a dlya \( \text{Pu}_2O_6 \rightarrow _{hex} \) i \( \text{Pu}_2O_6 \rightarrow _{s1} \) raschitany teplopa obrazovaniya i stan-
dartnaya entropiya.

DATOS TERMODINAMICOS CORRESPONDIENTES A LOS OXIDOS DE PLUTONIO. Se han obtenido datos
termodynamicos correspondientes a oxidos de plutonio con relaciones O/Pu comprendidas entre 1,53 y 2,00 a
temperaturas de 700-1 140°C, utilizando una celda galvánica de alta temperatura con electrolito sólido reversi-
vble unicamente con respecto a los iones oxígeno y dos electrodos de referencia (Ni, NiO y Fe, wustita). Se
produce una considerable variación de \( \Delta G(O_2) \) entre \( \text{Pu}_2O_6 \) y \( \text{Pu}_2O_6 \) y la precisión con que se conocen los datos
termodynamicos permite asignar valores fidedignos a \( \Delta H(O_2) \) y \( \Delta S(O_2) \) para todas las composiciones entre
\( \text{Pu}_2O_6 \) y \( \text{Pu}_2O_6 \), a 700 < t < 1140°C.

En los ultimos tiempos se ha vuelto a estudiar a temperaturas entre 25 y 900°C el diagrama de fases
plutonio-oxígeno para relaciones Pu/O comprendidas entre 1,50 y 2,00, empleando una cámara de difracción de
rayos X tipo Debye y Scherrer para alta temperatura. Se sugiere un nuevo diagrama de fases que procura resumir
los trabajos de varios investigadores.

Los datos termodynamicos obtenidos por la medición de la fuerza electromotriz de la celda concuerdan
satisfactoriamente con el diagrama de fases sugerido, del cual son totalmente independientes; asimismo, la
extrapolación de esos datos desde 700°C hasta la temperatura ambiente es compatible con el diagrama de fases
propuesto. Para la reacción \( 2 \text{Pu}_2O_3 + O_2 \rightarrow 4 \text{Pu}_2O_6 \), se estimó el valor de \( \Delta C_P \), tomando del dato
correspondiente a la reacción del óxido de cerio. Se calcularon los calores y entropías molares parciales, para
las distintas zonas del diagrama de fases; se integraron \( \Delta S(O_2) \) y \( \Delta H(O_2) \) en toda la zona desde \( <\text{Pu}_2O_3>_{hex} \) hasta
\( \text{Pu}_2O_6 \) y se calcularon los calores de formación y las entropías tipo para \( <\text{Pu}_2O_3>_{hex} \) y \( <\text{Pu}_2O_6>_{s1} \).

1. INTRODUCTION

Considerable quantities of plutonium will be produced by the magnox
reactors in Britain in the 1970's and investigations are in progress on the
use of this fissile material in place of \( ^{235}U \) for enriching thermal reactors.
A considerable effort is being put into the development of ceramic fuels with
mixed (U, Pu) oxides and carbides for the Prototype Fast Reactor at Dounreay.
Thermodynamic measurements are being made to yield information that will
enable the composition of these oxides to be controlled during preparation
and the phase stability of (U, Pu) oxides is being studied under various con-
ditions. Some idea of the phase stability and oxygen potentials of (U, Pu)
oxides could be obtained from the uranium-oxygen and plutonium-oxygen phase
diagrams and related thermodynamic data but, whereas the uranium-oxygen
phase diagram and thermodynamic data for O/U ratios between 2,00 and 2,25
were already well established, there was very little thermodynamic data for plu-
tonium oxides and the plutonium-oxygen phase diagram was established only for
O/Pu ratios > 1,80 [1, 2]. The region below Pu\(_{0.79}\) was hypothetical rather
than based on experiment. The plutonium-oxygen phase diagram has there-
fore been reginvestigated, using a high temperature X-ray camera [3]; in ad-
dition, a high temperature galvanic cell, reversible to oxygen ions only [4]
has been used to obtain thermodynamic data for plutonium oxides with O/Pu
ratios between 1.51 and 2.0. It is the purpose of this paper to report an
assessment of the thermodynamic data obtained from the EMF cell and to show how this data fits the suggested phase diagram, which had been established by entirely independent means.

2. EXPERIMENTAL DETAILS

A high temperature 19 cm Unicam camera was used for the X-ray measurements and the temperature of the silica capillaries was determined by measuring the lattice parameter of platinum which was coated on the outer surface of the capillary.

EMF measurements were made using the cells

\[
\text{PuO}_{2-x}\mid \text{ThO}_2, \, \text{Y}_2\text{O}_3\mid \text{ZrO}_2, \, \text{CaO}\mid \text{ThO}_2, \, \text{Y}_2\text{O}_3\mid \text{Ni, NiO or Fe, FeO}.
\]

The second electrolyte of \(\text{ThO}_2 + 8\) mole \% \(\text{Y}_2\text{O}_3\) was used in conjunction with the tube of stabilized \(\text{ZrO}_2\) because direct contact with substoichiometric \(\text{PuO}_2\) causes reduction of \(\text{ZrO}_2\). The data for the Ni, NiO reaction was assessed recently [5] and the assessment was based partially on the equation

\[
\Delta G(\text{O}_2) \, (\text{cal}) = -126 \, 210 + 31.01 \, T(\degree\text{K})
\]

for the Fe, wustite reaction. The following equation was finally chosen for the Ni, NiO equilibrium,

\[
\Delta G(\text{O}_2) \, (\text{cal}) = -113,300 + 41.5 \, T(\degree\text{K})
\]

Good agreement between the Ni, NiO and Fe, FeO reference electrodes was obtained as long as the Fe, FeO/electrolyte interface was cleaned on the Fe, FeO side between each set of measurements and the next. Discrepancies of up to 4 kcal were found between cells using Ni, NiO and Fe, FeO if this simple precaution was not observed.

EMF measurements have been made on \(\text{CeO}_{2-x}\) and the thermodynamic data obtained have been compared with similar data obtained by Bevan et al. [6] from CO/CO\(_2\) equilibria. \(\Delta G(\text{O}_2)\) values agree to better than 1 kcal.

The O/Pu ratio of pellets, used for the X-ray and EMF cell measurements, was determined to \(\pm 0.003\) by allowing the pellet to react at 800\(^\circ\text{C}\) with a measured excess of pure oxygen necessary to oxidize the oxide to \(\text{PuO}_2\), in a gas handling system. The excess oxygen was measured. Experiments to check the surface adsorption of oxygen by pellets of \(\text{PuO}_2\) showed that the surface adsorption was negligible. Rand and Jackson [7] have shown that \(\text{PuO}_2\) combines with excess oxygen by adsorption on the surface and the excess oxygen adsorbed is proportional to the surface area.

3. RESULTS

Fig. 1 shows a plot of lattice parameter versus temperature for \(\text{PuO}_{2-x}\) where \(0.39 \leqslant x \leqslant 0\). Since publication of the lattice parameter versus temperature plot [3], the thermal expansion of the platinum used as a temperature standard has been reinvestigated; the temperatures previously reported were found to be 30 to 40\(^\circ\text{C}\) too low. These temperatures have been
FIG. 1. Lattice parameter versus temperature plot for PuO$_2$-$x$ where $0.39 \leq x \leq 0$. 
corrected in Fig. 1. The grossly non-stoichiometric phase for \( t < 340^\circ\text{C} \) is body centred cubic (\( O/Pu = 1.52 \)) but no lines attributable solely to a body centred cubic phase (\( h, k, l \) of different parity) were seen for the grossly non-stoichiometric phase at \( t > 340^\circ\text{C} \) (\( O/Pu = 1.61 \)) for either the phase in equilib-rium with \( \text{PuO}_{2-x} \) or the single phase region, and it is probable that \( \langle \text{PuO}_{1.61} \rangle \) at \( t > 340^\circ\text{C} \) is face centred cubic. The lattice parameters of the face centred cubic phases have been doubled in Fig. 1 in order to plot all the parameters on the same figure. To avoid confusion, hexagonal \( \text{PuO}_{1.50} \) will be written \( \langle \text{PuO}_{1.50} \rangle_{\text{hex}} \), body centred cubic \( \text{PuO}_{1.52} \) as \( \langle \text{PuO}_{1.52} \rangle_{\text{cub}} \) and cubic \( \text{PuO}_{1.61} \) as \( \langle \text{PuO}_{1.61} \rangle_{\text{cub}} \). Previous workers have postulated the existence of a eutectoid at \( \text{PuO}_{1.71} \) at \( t \sim 300^\circ\text{C} \) on the evidence from thermal expansion and electrical conductivity measurements [1, 2, 8, 9] but the high temperature X-ray data prove conclusively that a eutectoid at \( \text{PuO}_{1.71} \) does not exist. For \( O/Pu \) ratios between 1.51 and 1.61 at \( t > 450^\circ\text{C} \), \( \langle \text{PuO}_{3} \rangle_{\text{hex}} \) and \( \langle \text{PuO}_{1.61} \rangle_{\text{cub}} \) are in equilibrium but the phases in the region between 340 and 450°C are uncertain owing to slow rates of phase transformation. Fig. 2 shows the suggested phase diagram which summarizes the numerous investigations of the plutonium-oxygen phase diagram.

Fig. 3 shows a plot of the oxygen potential, expressed as \( \Delta G(\text{O}_2) \) \([=RT \ln p(\text{O}_2)]\) at \( t = 750, 900 \) and \( 1050^\circ\text{C} \) versus \( O/Pu \) ratio for a number of plutonium oxides with \( O/Pu \) ratios between 1.52 and 2.0, as obtained from EMF measurements at temperatures between 700 and 1140°C. The experimental points are plotted in Fig. 3; the curves drawn in Fig. 3 were adjusted slightly to be consistent with the phase diagram. The oxygen potential of \( \langle \text{PuO}_{3} \rangle_{\text{hex}} \) was too low to measure by the EMF technique. The EMF corresponding to the two phases \( \langle \text{PuO}_{3} \rangle_{\text{hex}} + \langle \text{PuO}_{1.61} \rangle_{\text{cub}} \) was always obtained. \( \text{ThO}_2, \text{Y}_2\text{O}_3 \) solid electrolytes cannot be used satisfactorily below 700°C and, therefore, it was not possible to measure oxygen potentials in the \( \langle \text{PuO}_{1.61} \rangle_{\text{cub}} + \langle \text{PuO}_{2-y} \rangle_{\text{cub}} \) two phase region at \( 340^\circ\text{C} < t < 680^\circ\text{C} \). However, the thermodynamic data obtained from 700–1140°C is sufficiently precise to give reliable values of \( \Delta H(\text{O}_2) \) and \( \Delta S(\text{O}_2) \) for all compositions between \( \text{PuO}_{1.62} \) and \( \text{PuO}_{1.98} \). Fig. 4 is a partial molar free energy diagram derived from the thermodynamic data and the Pu-O phase diagram; it is convenient to discuss the data with reference to the various phase regions.

3.1. \( \langle \text{PuO}_{1.61} \rangle_{\text{cub}} \) to \( \langle \text{PuO}_2 \rangle \) region

Smoothed data obtained by interpolation of experimentally-determined isothersms are as in Table I.

It can be seen from Fig. 3 that an enormous change in \( \Delta G(\text{O}_2) \) occurs between \( \text{PuO}_2 \) and \( \text{PuO}_{1.90} \) (35 kcal at 900°C); whereas from \( \text{PuO}_{1.90} \) to \( \text{PuO}_{1.61} \), \( \Delta G(\text{O}_2) \) changes only by a further 15 kcal at 900°C. Fig. 4 shows that the values of \( \Delta G(\text{O}_2) \) for \( \text{PuO}_{1.85} \) and \( \text{PuO}_{1.90} \) meet at 670°C, the point at which the two-phase region \( \langle \text{PuO}_{1.61+x} \rangle + \langle \text{PuO}_{2-y} \rangle \) begins, in good agreement, both as to composition limits and temperature, with the other phase diagram data [1-3, 8, 9]. The approximate course of the \( \langle \text{PuO}_{1.61} \rangle_{\text{cub}} + \langle \text{PuO}_{2-y} \rangle_{\text{cub}} \) two-phase curve can be plotted down to 450°C by extrapolating the isoplests for \( \text{PuO}_{1.63} \) to \( \text{PuO}_{1.75} \) to the temperatures for the two-phase boundary indicated by the phase diagram. A more accurate extrapolation can be made to
FIG. 2. Plutonium-oxygen phase diagram
room temperature by considering the integral values of $\Delta H(0_2)$ and $\Delta S(0_2)$ (see 3.5) and this assessment yields the values given in Table II.

3.2. $\langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}}$ to $\langle \text{PuO}_{1.61} \rangle_{\text{cub}}$ two-phase region

Values for $\Delta G(0_2)$ for the two-phase region $\langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}}$ and $\langle \text{PuO}_{1.61} \rangle_{\text{cub}}$ were calculated from the EMF measurements at $t = 700-1100^\circ C$ on pellets with O/Pu ratios of 1.533, 1.551 and 1.588, employing Ni, NiO and Fe, FeO as the reference electrodes. The agreement between the several sets of results was extremely good, as expected, for three compositions in a two-phase region; no point was further from the best straight line than 400 cal. Mean values of $\Delta G(0_2)$ are plotted in Fig. 3; derived values for $\Delta H(0_2)$ and $\Delta S(0_2)$ were used in the following calculations.

3.3. Integrated $\Delta H$ and $\Delta S$

The partial molar heat and entropy values can be integrated for the whole region $\langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}}$ to $\langle \text{PuO}_2 \rangle_{\text{cub}}$ according to the equation

$$\Delta Z = \frac{1}{(x_2 x_1)} \int_{x_1}^{x_2} \Delta Z(0_2) dx$$
FIG. 4. Partial molar free energy diagram derived from thermodynamic data and Pu-O phase diagram
TABLE I
PuO\(_2\) SINGLE-PHASE REGION (1.65 < z < 2.00)

<table>
<thead>
<tr>
<th>z</th>
<th>-(\Delta S(\text{O}_2)) (e.u.)</th>
<th>-(\Delta H(\text{O}_2)) (kcal)</th>
<th>Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.65</td>
<td>20.0</td>
<td>178.0</td>
<td>520 to 1100</td>
</tr>
<tr>
<td>1.70</td>
<td>20.8</td>
<td>176.0</td>
<td>610 to 1100</td>
</tr>
<tr>
<td>1.75</td>
<td>26.8</td>
<td>180.5</td>
<td>630 to 1100</td>
</tr>
<tr>
<td>1.80</td>
<td>40.0</td>
<td>192.5</td>
<td>655 to 1100</td>
</tr>
<tr>
<td>1.85</td>
<td>54.7</td>
<td>205.0</td>
<td>670 to 1100</td>
</tr>
<tr>
<td>1.90</td>
<td>69.3</td>
<td>219.8</td>
<td>670 to 1100</td>
</tr>
<tr>
<td>1.95</td>
<td>85.8</td>
<td>233.5</td>
<td>625 to 1100</td>
</tr>
<tr>
<td>1.98</td>
<td>96.4</td>
<td>241.0</td>
<td>~250 to 1100</td>
</tr>
</tbody>
</table>

TABLE II
\(<\text{PuO}_{1.61+x}\> + <\text{PuO}_{2-y}\> TWO-PHASE REGION

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Phase limits</th>
<th>-(\Delta G(\text{O}_2)) (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>1.61</td>
<td>1.98</td>
</tr>
<tr>
<td>427</td>
<td>1.62</td>
<td>1.98</td>
</tr>
<tr>
<td>527</td>
<td>1.65</td>
<td>1.97</td>
</tr>
<tr>
<td>627</td>
<td>1.75</td>
<td>1.95</td>
</tr>
</tbody>
</table>

where x is the O/Pu ratio, and \(\Delta Z = \Delta H \text{ or } \Delta S\). The results used were calculated from the smoothed curves in Fig. 3. We find for

\[2<\text{PuO}_2>_{\text{hex}} + \text{O}_2 \rightarrow 4<\text{PuO}_2>_{\text{cub}} ; \Delta H_{1150} = -196.9 \text{ kcal} ; \Delta S_{1150} = -43.0 \text{ e.u.}\]

\(<\text{PuO}_2>_{\text{hex}}\) is \(<\text{PuO}_{1.51}>_{\text{hex}}\) because we have no thermodynamic data for the single phase region \(<\text{PuO}_{1.50}>_{\text{hex}}\) to \(<\text{PuO}_{1.51}>_{\text{hex}}\).

Unfortunately, there are no accurate calorimetric data for the heat of formation and standard entropy of \(<\text{PuO}_2>_{\text{hex}}\). \(\Delta C_p\) for the above reaction at 500°C has been estimated to be close to zero from the value for the corresponding cerium oxide reaction. Thus we have

\[\Delta H_{298} = -196.9 \text{ kcal} ; \Delta S_{298} = -43.0 \text{ e.u.}\]
The extrapolation of the partial molar free energy data to temperatures lower than those measured in the EMF cell shows that lines for PuO$_2$ and PuO$_{1.98}$ must bend over considerably between 700°C and room temperature, in order not to intersect with the $\langle$PuO$_2$$_{\text{hex}} + $PuO$_{1.61}$$_{\text{cub}}\rangle$ two-phase line above about 400°C. The lattice parameter measurements [3] and the electrical conductivity measurements of McNeilly [2] show that the phase in equilibrium with $\langle$PuO$_{1.61}$$_{\text{cub}}$ and $\langle$PuO$_{1.52}$$_{\text{cub}}$ is slightly substoichiometric PuO$_{2-x}$ . PuO$_{1.98}$ is probably the lower limit of the single phase region below PuO$_2$ at and near room temperature. The curvature of the $\Delta G$(O$_2$) v. temperature line for PuO$_2$ may be due to the fact that PuO$_2$ can adsorb oxygen on its surface below 600°C; thus some oxygen may occupy low energy sites on crystal faces of oxides close to PuO$_2$ at low temperatures but not at high temperatures.

The curvature may be provisionally taken into account by introducing a high negative value of $\Delta C_p$ for the region near PuO$_2$, although of course this procedure is purely formal. Since we have taken $\Delta C_p$ for $2\langle$PuO$_2$$_{\text{hex}} + \text{O}_2-\rightarrow 4\langle$PuO$_2$$_{\text{cub}}$ to be zero at 500°C, we must incorporate a positive value of $\Delta C_p$ in some other part of the system to compensate for the negative values near PuO$_2$. EMF measurements for the single phase region between $\langle$PuO$_{1.61}$$_{\text{cub}}$ and $\langle$PuO$_{1.98}$$_{\text{cub}}$ have shown that $\Delta C_p$ is very nearly zero.

It is therefore convenient to take the following values of $\Delta C_p$.

<table>
<thead>
<tr>
<th>O/Pu</th>
<th>1.52 to 1.61</th>
<th>1.61 to 1.98</th>
<th>1.98 to 2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta C_p$ (e.u.)</td>
<td>+7</td>
<td>0</td>
<td>-38.5</td>
</tr>
</tbody>
</table>

We can calculate $\Delta \tilde{S}$(O$_2$) and $\Delta \tilde{H}$(O$_2$) for (i) $\langle$PuO$_2$$_{\text{hex}} + $PuO$_{1.61}$$_{\text{cub}}\rangle$ two-phase region, (ii) $\langle$PuO$_{1.61}$$_{\text{cub}}$ to $\langle$PuC$_{1.61+x}$$_{\text{cub}}$ single-phase region, and (iii) $\langle$PuO$_{1.98-y}$$_{\text{cub}}$ to $\langle$PuO$_2$$_{\text{cub}}$ single-phase region, at 627°C and these values can be combined with the integral value of $\Delta S_{900}$ and $\Delta H_{900}$ for $2\langle$PuO$_2$$_{\text{hex}} + \text{O}_2-\rightarrow 4\langle$PuO$_2$$_{\text{cub}}$, which, with $\Delta C_p = 0$, are independent of temperature to give $\Delta \tilde{S}$(O$_2$) and $\Delta \tilde{H}$(O$_2$) at 627°C for the two-phase region $\langle$PuO$_{1.61+x}$$_{\text{cub}} + $PuO$_{1.98-y}$$_{\text{cub}}$. Similar calculations were made for temperatures of 527, 427, 340 and 230°C, the latter giving $\Delta \tilde{S}$(O$_2$) and $\Delta \tilde{H}$(O$_2$) for the $\langle$PuO$_{1.52}$$_{\text{cub}} + $PuO$_{1.98}$$_{\text{cub}}$ two-phase region. O/Pu ratios for $\langle$PuO$_{1.61+x}$$_{\text{cub}}$ and $\langle$PuO$_{1.98-y}$$_{\text{cub}}$ at 627, 527, 427 and 340°C are given at the end of section 3.3. Heat and entropy values can now be calculated for the two-phase regions and the results are shown in Table III. These values allow us to complete the entire partial molar free energy diagram, shown on Fig. 4.

It is very satisfactory to find that the intersections of the isoplests for PuO$_{1.65}$ to PuO$_{1.85}$ with the $\langle$PuO$_{1.61+x}$ + $\langle$PuO$_{2-y}$ region reproduce with considerable accuracy the phase diagram obtained independently by Gardner et al.[3]. There is a small discrepancy for the phase transition temperature for PuO$_{1.618}$; the figure suggested by Gardner et al.[3] (corrected for platinum temperature recalibration – see 3.3) was 480°C; the thermodynamic data indicate a temperature of 425°C. The latter figure has been accepted in drawing the phase diagram (Fig. 2), because the shape of the lattice parameter versus temperature plot between 340 and 500°C does not allow the temperature of the phase transition for PuO$_{1.618}$ to be fixed with any precision.
TABLE III

\[ \text{O}_2 \to 2 \text{[O]}_{\text{PuO}_x} \]

<table>
<thead>
<tr>
<th>Region</th>
<th>( -\Delta S(\text{O}_2) ) (e.u.)</th>
<th>( -\Delta H(\text{O}_2) ) (kcal)</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle \text{Pu}<em>2\text{O}<em>3 \rangle</em>{\text{hex}} + \langle \text{PuO}</em>{1.61} \rangle_{\text{cub}} )</td>
<td>71.0 - 16.1 log T</td>
<td>189.8 - 7T</td>
<td>450-1100</td>
</tr>
<tr>
<td>( \langle \text{PuO}<em>{1.52} \rangle</em>{\text{cub}} + \langle \text{PuO}<em>{1.61} \rangle</em>{\text{cub}} )</td>
<td>34.0</td>
<td>191.2</td>
<td>340-450</td>
</tr>
<tr>
<td>( \langle \text{PuO}<em>{1.52} \rangle</em>{\text{cub}} + \langle \text{PuO}<em>2-x \rangle</em>{\text{cub}} )</td>
<td>43.0</td>
<td>196.9</td>
<td>25-340</td>
</tr>
</tbody>
</table>

4. HEATS OF FORMATION AND STANDARD ENTONIES OF \( \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}}, \langle \text{PuO}_{1.61} \rangle_{\text{cub}} \) AND \( \langle \text{PuO}_2 \rangle_{\text{cub}} \)

The values obtained above can be combined with the data for \( \langle \text{PuO}_2 \rangle \) to give the heats of formation and standard entropies for \( \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}} \) and \( \langle \text{PuO}_{1.61} \rangle_{\text{cub}} \).

There is good agreement in the two measurements by Holley et al. [11] and Popov and Ivanov [12] of the heat of combustion of \( \alpha \)-Pu; the weighted mean of their results is \( \Delta H_f \langle \text{PuO}_2 \rangle = -252.8 \pm 0.8 \) kcal. Measurements by Sandenaw [13] of the low temperature heat capacity of PuO₂ show spurious peaks, perhaps due to self-damage, and the derived standard entropy (16.3 e.u.) implies a very small magnetic contribution for a compound containing an ion with four unpaired electrons. We have preferred the estimate of 19.7 e.u. by Westrum, Hatcher and Osborne [14] based on the relation between the standard entropies of ThO₂, UO₂ and NpO₂ and the number of unpaired electrons on the corresponding M⁴⁺ ion.

The data derived in 3.5 may be written

\[ 2\langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}} + \text{O}_2(g) = 4 \text{PuO}_2(s); \Delta H_{298} = -196.9; \Delta S_{298} = -43.0 \]

and thus lead to values for the heat of formation and standard entropy of

\( \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}}; \Delta H_f = -407.2 \) kcal; \( S_{298} = 36.4 \) e.u.

The free energy data for the \( \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}} + \langle \text{PuO}_{1.61} \rangle \) two-phase region give

\[
\frac{1}{0.11} \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}} + \text{O}_2(g) \rightarrow \frac{2}{0.11} \langle \text{PuO}_{1.61} \rangle;
\]

\( \Delta H_{1150} = -181.7 \) kcal; \( \Delta S_{1150} = -21.7 \) e.u.
With an assumed constant $\Delta C_p$ of +7 e.u., these give $\Delta H_{298} = -187.7$ kcal and $\Delta S_{298} = -31.2$ e.u., and thus for

$$\frac{1}{2} \left< \text{Pu}_2\text{O}_3 \right>_{\text{hex}} + 0.055 \text{O}_2(g) = \left< \text{PuO}_{1.61} \right>_{\text{cub}}; \quad \Delta H_{298} = -10.3 \text{ kcal}; \quad \Delta S_{298} = -1.7 \text{ e.u.}$$

These in turn give for

$$\left< \text{PuO}_{1.61} \right>_{\text{cub}}; \quad \Delta H_f = -213.9 \text{ kcal}; \quad S_{298} = 19.2 \text{ e.u.}$$

REFERENCES

SOLID-STATE EMF TECHNIQUES*
THE FREE ENERGIES OF FORMATION OF NiCl$_2$, CoCl$_2$
AND SEVERAL DOUBLE SALTS OF KCl

J.J. EGAN
BROOKHAVEN NATIONAL LABORATORY,
UPTON, NEW YORK,
UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

SOLID-STATE EMF TECHNIQUES: THE FREE ENERGIES OF FORMATION OF NiCl$_2$, CoCl$_2$ AND SEVERAL DOUBLE SALTS OF KCl. The free energy of formation of each of the following double salts was determined: KMgCl$_3$, KCaCl$_3$, K$_2$SrCl$_4$, KSr$_2$Cl$_4$, and K$_2$BaCl$_4$. The results are of interest in the kinetic theory of solid reactions, the elucidation of phase equilibria and in the study of lattice energies of ionic compounds.

Cells of the following type were employed:

$$\text{Cl}_2(\text{g}) - C \left| \text{KCl}(s) \right| \text{K}^+_{\text{glass}} \left| \text{KCl}(s) \right| \text{C} - \text{Cl}_2(\text{g})$$

where (K$^+$)$_\text{glass}$ refer to the special glass used that was conductive only to K$^+$ ions. Experimental details of the cell construction and operation are presented. The following two cells were also operated, at 400 and 450°C, to measure the free energy of formation of CoCl$_2$ and NiCl$_2$.

$$\text{Co, CoCl}_2(s) \left| \text{BaCl}_2(s) \right| \text{AgCl}(20\text{M}) \left| \text{NaCl}(s) \right| \text{Ag}$$

$$\text{Ni, NiCl}_2(s) \left| \text{BaCl}_2(s) \right| \text{AgCl}(20\text{M}) \left| \text{NaCl}(s) \right| \text{Ag}$$

where BaCl$_2$ was used as an auxiliary solid electrolyte. Since the thermodynamic properties of AgCl-NaCl solid solutions are known, the free energies of formation of CoCl$_2$ and NiCl$_2$ can be calculated. Results are presented and compared with previous values obtained from thermochemical studies.

MESURE DES FORCES ELECTROMOTRICES EN PHASE SOLIDE: ENERGIE LIBRE DE FORMATION DE NiCl$_2$, DE CoCl$_2$ ET DE CERTAINS CHLORURES DOUBLES DE POTASSIUM ET D'UN AUTRE METAL. L'auteur a déterminé l'énergie libre de formation de chacun des six doubles ci-après: KMgCl$_3$, KCaCl$_3$, K$_2$SrCl$_4$, KSr$_2$Cl$_4$, et K$_2$BaCl$_4$. Les résultats présentent un intérêt pour la théorie cinétique des réactions en phase solide, pour la détermination des équilibres de phases et pour l'étude des énergies réticulaires de composés ioniques.

L'auteur a employé des cellules du type suivant:

$$\text{Cl}_2(\text{g}) - C \left| \text{KCl}(s) \right| \text{K}^+_{\text{verre}} \left| \text{KCl}(s) \right| \text{C} - \text{Cl}_2(\text{g})$$

(K$^+$)$_\text{verre}$ se réfère au verre spécial, conducteur d'ions K$^+$ seulement qui a été utilisé. Il présente des détails expérimentaux sur la construction et le fonctionnement de la cellule. Les deux cellules des types ci-après ont été également utilisées à 400 et 450°C pour mesurer l'énergie libre de formation de CoCl$_2$ et NiCl$_2$:

$$\text{Co, CoCl}_2(s) \left| \text{BaCl}_2(s) \right| \text{AgCl}(20\text{M}) \left| \text{NaCl}(s) \right| \text{Ag}$$

* The work was performed under the auspices of the USAEC.
МЕТОДЫ ИСПОЛЬЗОВАНИЯ ЭДС ТВЕРДОГО СОСТОЯНИЯ. СВОБОДНАЯ ЭНЕРГИЯ ОБРАЗОВАНИЯ NiCl₂, CoCl₂ И НЕКОТОРЫХ ДВОЙНЫХ СОЛЕЙ KCl. Определяли свободную энергию образования каждой из следующих двойных солей: K₉Cl₂, K₉CaCl₂, K₉SrCl₂ и K₉BaCl₂. Результаты представляют интерес для кинетической теории твердых реакций, объяснения фазовых равновесий и изучения энергий решетки ионных соединений.

Использовались ячейки следующего типа:

\[ \text{MgCl}_2(тв) || \text{KCl}(тв) || \text{BaCl}_2(тв) \]  

где стекло (K⁺) соотносится со специальным стеклом, проводящим только ионы K⁺. Даются экспериментальные детали конструкции и действия ячейки. Кроме того, при температуре 400° и 450°C использовались следующие две ячейки для измерения свободной энергии образования CoCl₂ и NiCl₂:

\[ \text{Co, CoCl}_2(тв) || \text{BaCl}_2(тв) || \text{AgCl (20 M%) NaCl (тв) || Ag} \]  

(II)

\[ \text{Ni, NiCl}_2(тв) || \text{BaCl}_2(тв) || \text{AgCl (20 M%) NaCl (тв) || Ag} \]  

(III)

donde \text{BaCl}_2 se usado como electrolito sólido auxiliar. Como se conocen las propiedades termodinámicas de las soluciones sólidas AgCl-NaCl, es posible calcular las energías libres de formación del CoCl₂ y del NiCl₂. El autor presenta algunos resultados y los compara con valores anteriores obtenidos en estudios termoquímicos.
INTRODUCTION

Several double salts exist between KCl and the alkaline earth chlorides. In this work the free energies of formation have been measured using a glass electrolyte conductive only to $K^+$ ions. The values are of interest in the study of solid-solid reactions between KCl and the alkaline earth chlorides [1, 2] since the reaction rates depend not only on the transport properties of the ions, but also on the free energies of the double salts formed. The results may also be of use in the study of phase equilibria in these systems [3] as well as in studies of the lattice energies of ionic compounds [4].

The following cells were operated in the temperature range 450° to 550°C:

<table>
<thead>
<tr>
<th>Cell</th>
<th>Reaction</th>
<th>Reaction</th>
<th>Reaction</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\text{Cl}_2 - \text{C}</td>
<td>\text{KCl(s)} (\text{glass})</td>
<td>\text{KMgCl}_3(\text{s})</td>
<td>\text{C-Cl}_2</td>
</tr>
<tr>
<td>II</td>
<td>$\text{Cl}_2 - \text{C}</td>
<td>\text{KCl(s)} (\text{glass})</td>
<td>\text{KCaCl}_3(\text{s})</td>
<td>\text{C-Cl}_2</td>
</tr>
<tr>
<td>III</td>
<td>$\text{Cl}_2 - \text{C}</td>
<td>\text{KCl(s)} (\text{glass})</td>
<td>\text{K}_2\text{SrCl}_4(\text{s})</td>
<td>\text{C-Cl}_2</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{Cl}_2 - \text{C}</td>
<td>\text{KCl(s)} (\text{glass})</td>
<td>\text{K}_2\text{SrCl}_5(\text{s})</td>
<td>\text{C-Cl}_2</td>
</tr>
<tr>
<td>V</td>
<td>$\text{Cl}_2 - \text{C}</td>
<td>\text{KCl(s)} (\text{glass})</td>
<td>\text{K}_2\text{BaCl}_4(\text{s})</td>
<td>\text{C-Cl}_2</td>
</tr>
</tbody>
</table>

The reaction at the left-hand electrode of cell I is

$$\text{KCl} = K^+ + \frac{1}{2}\text{Cl}_2 + 1e$$

and at the right-hand electrode,

$$K^+ + \frac{1}{2}\text{Cl}_2 + 1e + \text{MgCl}_2 = \text{KMgCl}_3$$

with the glass conducting $K^+$ from the left-hand to the right-hand compartment. The over-all reaction on passing one faraday of electricity is then

$$\text{KCl(s)} + \text{MgCl}_2(\text{s}) = \text{KMgCl}_3(\text{s})$$

The reactions occurring in the other four cells are similar. The free energy for the reaction is then given by

$$\Delta G^0 = -FE$$

where $F$ is the Faraday constant and $E$ the EMF of the cell.
The following two cells have been operated to measure the free energy of formation of \( \text{CoCl}_2 \) and \( \text{NiCl}_2 \).

\[
\text{Co, CoCl}_2(s) \mid \text{BaCl}_2(s) \mid \text{AgCl (20 M %)} \mid \text{NaCl} \mid \text{Ag} \quad \text{VI}
\]
\[
\text{Ni, NiCl}_2(s) \mid \text{BaCl}_2(s) \mid \text{AgCl (20 M %)} \mid \text{NaCl} \mid \text{Ag} \quad \text{VII}
\]

where the overall reactions on passing one faraday are

\[
\frac{1}{2}\text{Co} + \text{AgCl(NaCl)} = \frac{1}{2}\text{CoCl}_2 + \text{Ag} \quad (1)
\]

and

\[
\frac{1}{2}\text{Ni} + \text{AgCl(NaCl)} = \frac{1}{2}\text{NiCl}_2 + \text{Ag} \quad (2)
\]

The properties of solid \( \text{AgCl-NaCl} \) mixtures have been previously investigated by Panish et al. [5] by examining the cell

\[
\text{Ag} \mid \text{AgCl-NaCl} \mid \text{C}-\text{Cl}_2 \quad \text{VIII}
\]

where the cell reaction is

\[
\text{Ag} + \frac{1}{2}\text{Cl}_2(g) = \text{AgCl(NaCl)} \quad (3)
\]

and the free energy change is

\[
\Delta G_{\text{VIII}} = -F E_{\text{VIII}}
\]

Combining the above equations one obtains for the free energies of formation of \( \text{CoCl}_2 \) and \( \text{NiCl}_2 \):

\[
\frac{1}{2} \Delta G^0(\text{CoCl}_2) = -F(E_{\text{VI}} + E_{\text{VIII}})
\]
\[
\frac{1}{2} \Delta G^0(\text{NiCl}_2) = -F(E_{\text{VII}} + E_{\text{VIII}})
\]

**EXPERIMENTAL**

The cell design used for the measurements on double salts is shown in Fig. 1. A large outer quartz tube contains the cell and is filled with flowing chlorine gas at one atmosphere pressure, supplied from a cylinder. A wire
wound furnace (not shown), controlled to approximately $\pm 2^\circ$C, maintains the cell at temperature. A special glass, described by Portnoy, Thomas and Gurdjian [6], conductive only to potassium ions, and blown into the form of a tube, holds the KCl. This tube also contains a graphite electrode as shown. The double salt is contained in a larger quartz crucible. To assemble the cell, the KCl and the KCl+alkaline earth mixture were added to the cell in the proper proportions, melted, and then re-frozen for the measurements. The graphite electrodes were thus frozen into the salts.
The temperature of the salt is measured with a thermocouple inside a closed quartz protection tube which is immersed in the double salt. The entire apparatus is vacuum tight to avoid any reaction with the atmosphere.

The cells were all operated for a period of approximately one month, and results were reproducible with temperature cycling.

The cell design used for the measurements on CoCl$_2$ and NiCl$_2$ was the same as that used for other chlorides as previously described [7]. Briefly, intimate mixtures of nickel metal powder and NiCl$_2$ are pressed into pellets, as are the BaCl$_2$ and AgCl-NaCl mixtures. These pellets are assembled between platinum electrodes inside a vacuum-tight quartz container, and the cell then operated at 400 and 450°C under purified argon gas.

RESULTS

The results for the double salt cells are shown in Table I. The order of stability decreases from MgCl$_2$ to BaCl$_2$. From the measurements it can be seen that K$_2$BaCl$_4$ is unstable below 500°C.

The results for NiCl$_2$ and CoCl$_2$ are given in Table II and are compared with results obtained from thermal data and compiled by Wicks and Block [8].

### TABLE I

**THERMODYNAMIC PROPERTIES OF SOLID DOUBLE SALTS**

<table>
<thead>
<tr>
<th>Cell</th>
<th>Reaction</th>
<th>Temperature (°C)</th>
<th>EMF (volts)</th>
<th>ΔG (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>KCl+MgCl$_2$ = KMgCl$_3$</td>
<td>450</td>
<td>0.208</td>
<td>-4795</td>
</tr>
<tr>
<td>II</td>
<td>KCl+CaCl$_2$ = KCaCl$_3$</td>
<td>550</td>
<td>0.207</td>
<td>-4773</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>0.195\textsuperscript{a}</td>
<td>-4495</td>
</tr>
<tr>
<td>III</td>
<td>$\frac{3}{2}$ KCl+KSt$_2$Cl$_5$ = K$_2$SrCl$_4$</td>
<td>550</td>
<td>0.0145</td>
<td>-500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>0.0045\textsuperscript{a}</td>
<td>-155</td>
</tr>
<tr>
<td>IV</td>
<td>KCl+2SrCl$_2$ = KSt$_2$Cl$_5$</td>
<td>550</td>
<td>0.101</td>
<td>-2329</td>
</tr>
<tr>
<td>V</td>
<td>2KCl+BaCl$_2$ = K$_2$BaCl$_4$</td>
<td>550</td>
<td>0.013</td>
<td>-600</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td></td>
<td>(K$_2$BaCl$_4$ unstable)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Extrapolated.
### TABLE II

**THERMODYNAMIC PROPERTIES OF CoCl$_2$ AND NiCl$_2$**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$E_{VI}$</th>
<th>$E_{VIII}$</th>
<th>$\Delta G^\circ$(CoCl$_2$) (kcal)</th>
<th>$\Delta G^\circ$(NiCl$_2$) (kcal)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
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### ACKNOWLEDGEMENTS

The author wishes to acknowledge the help of Mr. J. Bracker who assembled and operated the cells described in this report, and to Dr. R. Wiswall who offered helpful suggestions.

### REFERENCES

THE FREE ENERGIES OF FORMATION OF THORIUM BORIDES FROM MEASUREMENTS ON SOLID EMF CELLS

S. ARONSON AND A. AUSKERN
BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK, UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

THE FREE ENERGIES OF FORMATION OF THORIUM BORIDES FROM MEASUREMENTS ON SOLID EMF CELLS. Two compounds, ThB₄ and ThB₆, have been observed in the thorium-boron system. Little thermodynamic information is available on these compounds. Thermodynamic data have, therefore, been obtained in this study from measurements on solid electrochemical cells at 800-950°C. The EMF cells employed were of the types

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{B} \quad (I)
\]

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{Th}_4 \quad (II)
\]

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{Th}_4 \quad (III)
\]

\(\text{Th}_4\) represents thorium metal containing dissolved boron in equilibrium with ThB₄. The standard molar free energies of formation of ThB₆ and ThB₄ at 850°C were calculated to be -54.5 kcal/at.-g of Th and -52.0 kcal/at.-g of Th, respectively.

MESURE DES ENERGIES LIBRES DE FORMATION DES BORURES DE THORIUM A L'AIDE DE CELLULES A ELECTROLYTE SOLIDE. Dans le système thorium-bor, les auteurs ont constaté la présence de deux composés, à savoir ThB₄ et ThB₆. La thermodynamique de ces composés est mal connue. En vue de combler cette lacune, on a procédé à des mesures de constantes thermodynamiques, au moyen de cellules électrochimiques solides à des températures de 800 à 950°C. Les cellules électrochimiques employées appartiennent aux types suivants:

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{B} \quad (I)
\]

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{Th}_4 \quad (II)
\]

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{Th}_4 \quad (III)
\]

\(\text{Th}_4\) représente du thorium métallique contenant du bore dissous en équilibre avec ThB₄. Les énergies libres molaires types de formation de ThB₆ et ThB₄ à 850°C sont respectivement de -54.5 kcal/at.-g de Th et -52.0 kcal/at.-g de Th.

СВОБОДНАЯ ЭНЕРГИЯ ОБРАЗОВАНИЯ БОРИДОВ ТОРИЯ НА ОСНОВЕ ИЗМЕРЕНИЙ ТВЕРДЫХ ЭДС-ЯЧЕЕК. В системе торий-бор наблюдали два соединения ThB₄ и ThB₆. По этим соединениям имеется довольно мало термодинамической информации. Поэтому в данном исследовании термодинамические данные были получены в результате измерений твердых электрохимических ячеек при температуре 800-950°C. Использовавшиеся ЭДС-ячейки были следующих типов:

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{B} \quad (I)
\]

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{Th}_4 \quad (II)
\]

\[
\text{Th, ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ThB}_4, \text{Th}_4 \quad (III)
\]
Thα представляет собой металлический торий, содержащий растворенный бор, в равновесии с ThB₄. Было рассчитано, что стандартная молярная энергия образования ThB₄ и ThB₆ при 850 °C составляла соответственно -54,5 ккал/г-атом Th и -52,0 ккал/г-атом Th.

LAS ENERGIAS LIBRES DE FORMACION DE LOS BORUROS DE TORIO, MEDIDAS CON CELDAS DE ELECTROLITO SOLIDO. En el sistema torio-boro se ha comprobado la existencia de dos compuestos, a saber, ThB₄ и ThB₆, sobre los cuales se dispone de escasa información termodinámica. En el presente estudio, por lo tanto, se han obtenido datos termodinámicos partiendo de mediciones realizadas con celdas electroquímicas sólidas a 800-950°C. Se emplearon celdas electroquímicas de los tipos siguientes:

\[
\begin{align*}
\text{Th, } \text{ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ ThB}_4, \text{ B} & \quad (I) \\
\text{Th, } \text{ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ ThB}_6, \text{ ThB}_4 & \quad (II) \\
\text{Th, } \text{ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ ThB}_6, \text{ Th}_\alpha & \quad (III)
\end{align*}
\]

Thα representa torio metálico que contiene boro disuelto, en equilibrio con ThB₄. La energías libres molares típicas de formación de ThB₄ y ThB₆ a 850°C, se calculan respectivamente en -54,5 kcal/g-at. Th, y -52,0 kcal/g-at. Th.

INTRODUCTION

Two compounds, ThB₄ and ThB₆, have been observed in the thorium-boron system [1-4]. ThB₆ has a face-centred cubic structure and ThB₄ is tetragonal. The experimental observations of Brewer et al. [1] indicate that the melting point of ThB₄ is above 2500°C. The melting point of ThB₆ has been reported as 2195°C [2]. Little thermodynamic information is available on these compounds [5,6]. Thermodynamic information has, therefore, been obtained from measurements on solid electrochemical cells. The technique employed is similar to that used in previous studies in the thorium-carbon system [7, 8].

EXPERIMENTAL

The EMF cells employed were of the types

\[
\begin{align*}
\text{Th, } \text{ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ ThB}_6, \text{ B} & \quad (I) \\
\text{Th, } \text{ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ ThB}_6, \text{ ThB}_4 & \quad (II) \\
\text{Th, } \text{ThF}_4 | \text{CaF}_2 | \text{ThF}_4, \text{ ThB}_6, \text{ Th}_\alpha & \quad (III)
\end{align*}
\]

Thα represents thorium metal containing dissolved boron in equilibrium with ThB₄.

In each case, the reaction at the left-hand electrode is Th-4e=Th⁴⁺. At the right-hand electrode, the reactions are

\[
\text{ThF}_4 + 6\text{B} + 4\text{e} = \text{ThB}_6 + 4\text{F}^- \quad (1a)
\]
The value of \( y \) depends on the solubility of boron in thorium and has not been determined.

The overall cell reactions are

\[
\begin{align*}
\text{ThF}_4 + 2\text{ThB}_6 + 4e &= 3\text{ThB}_4 + 4\text{F}^- \quad (2a) \\
\text{ThF}_4 + y \text{ThB}_4 + 4e &= (1 + y)\text{Th}_\alpha + 4\text{F}^- \quad (3a)
\end{align*}
\]

Fluoride ions are transported from the right-hand electrode to the left-hand electrode through the solid \( \text{CaF}_2 \) electrolyte. The free energy for each reaction, \( \Delta F \), is obtained from the cell EMF, \( E \), using the standard relationship

\[
\Delta F = -nFE
\]

(4)

\( F \) is Faraday's number and \( n \), the number of equivalents of fluoride ion transferred, has the value 4.

Thorium powder (<0.1% metallic impurities) and boron powder (99.5% pure) were obtained from Electronics Space Products, Inc., Los Angeles.

The thorium borides were prepared by heating mixtures of thorium and boron powders, pressed into the shape of cylinders, in vacuo at either 1400-1450°C for two to three hours or at 1000°C for 300-500 h. Both treatments produced similar material in the two-phase regions containing either \( \text{Th}_\alpha \) and \( \text{ThB}_4 \) or \( \text{ThB}_4 \) and \( \text{ThB}_6 \). The X-ray diffraction patterns and EMF data were similar. The samples containing excess boron, which should have only contained the equilibrium phases \( \text{ThB}_6 \) and \( B \), also contained \( \text{ThB}_4 \) after treatment at 1000°C. \( \text{ThB}_4 \) was not observed in the samples heated to 1400°C. These observations indicate that \( \text{ThB}_4 \) forms more rapidly than \( \text{ThB}_6 \) and then reacts with additional boron to form \( \text{ThB}_6 \). This conclusion appears to be somewhat at variance with the report that \( \text{ThB}_4 \) can be formed from the elements at a lower temperature (800°C) than \( \text{ThB}_4 \) (950°C) [9].

The EMF cell apparatus was identical to that used for measurements on thorium carbides and has been described in connection with that work [8].

RESULTS AND DISCUSSION

EMF measurements were made on the various thorium boride compositions at temperatures of 800-950°C. The cells were first heated overnight at 800°C. EMF measurements were then made over the temperature range each day for two or three days. The EMF values were constant to 5 mV from day to day. Samples which were heat-treated at 1000°C and 1400°C behaved similarly except in the case of boride samples with a B/Th atomic ratio greater than 6. In the latter case, as noted in the previous section, only the
samples prepared at 1400°C were properly equilibrated. The B/Th atomic ratios of the original powder mixtures were 2 and 3 for Cell III, 5 and 5.5 for Cell II and 7.5 and 8 for Cell I. Data obtained on a number of samples are shown in Fig. 1. In the case of Cell I, instability occurred at temperatures above 900°C, resulting in a continuous decrease in EMF. The reason for this instability is not known. EMF data was only obtained up to 800°C for this cell.

The free energies of the reactions occurring in the three cells, calculated at 850°C, are

\[
\begin{align*}
-54.4 \pm 2 \text{kcal/g-atom Th} & \quad \text{I} \\
-47.1 \pm 2 \text{kcal/g-atom Th} & \quad \text{II} \\
-1.4 \pm 1 \text{kcal/g-atom Th} & \quad \text{III}
\end{align*}
\]

The limits of error are based on the reproducibility of the data on each sample, the variation in EMF values between samples in the same group and a qualitative estimate of the reliability of the EMF technique used.

The standard molar free energy of formation of ThB₆ at 850°C is, thus, \(-54.4\) kcal/g-atom Th. The standard molar free energy of formation of ThB₄ at 850°C calculated from the data on Cells I and II is \(-52.0\) kcal/g-atom Th. It is observed in Fig. 1 that the slopes of the EMF versus temperature plots
are somewhat variable and have some curvature. Because of this variability, information could not be obtained on the entropies and enthalpies of the reactions.

The low EMF values on Cell III indicate that the solution of boron in thorium metal to the solubility limit does not result in a large decrease in thorium activity. It is likely, therefore, that boron is soluble to only a limited extent in thorium metal. A comparison of the free energies of formation of ThB₄ and ThB₆, -13 and -9 kcal/g-atom B respectively, indicates that ThB₆ is relatively unstable compared to ThB₄. This is qualitatively in agreement with the observation of Brewer et al. [1] who could not find ThB₆ in thorium-boron samples heated above 1500°C. It is not, however, in accord with the results of Glaser [5] on hot-pressed mixtures of thorium, boron and carbon powders. Glaser concluded that ThB₄ was not stable in the presence of carbon and reacted to form ThB₆. The available thermodynamic data on thorium borides and carbides indicate, however, that ThB₄ should not be converted to ThB₆, at least, at 850°C. For the reaction

\[3\text{ThB}_4 + 2\text{C} = 2\text{ThB}_6 + \text{ThC}_2\] (5)

the free energy change, based on the data in this study, is +19 kcal. The free energy of formation of ThC₂ at 850°C is -28 kcal/g-atom Th [7, 8].

It seems likely that the conversion of ThB₄ to ThB₆ observed by Glaser may have resulted from the presence of oxygen as an impurity in the system. Thus, ThO₂, but not ThC₂, was observed by Glaser in his final products. Matterson and Jones [9] noticed an increase in both ThB₆ and ThO₂ contamination on ThB₄ samples hot-pressed with colloidal graphite. They attributed this to the oxidation of ThB₄.

It is difficult to compare the free energies of formation of the thorium borides with thermodynamic data on borides of other metals since information on the latter was not obtained in the same temperature range. The estimated heats of formation of UB₄ and UB₁₂ at room temperature [10] are -15 and -9 kcal/g-atom B respectively which are in the same range of values as the free energies of formation of ThB₄ and ThB₆. The heats of formation of hexaborides [11] vary over a wide range having estimated values of -4, -8, -14 and -19 kcal/g-atom B for YB₆, SrB₆, CeB₆ and LaB₆ respectively.

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REFERENCES

THERMODYNAMIC PROPERTIES OF ALLOYS OF IRON AND SILICON. The Fe-Si phase diagram is complex. At 1000°C, there are FeSi₂ (β), FeSi phases and solid solutions of silicon in α and α' iron. EMF measurements were made on the electrochemical cells:

\[ \text{Fe|Fe}^{2+}, \text{KI+Nal|Fe-Si at 600-800°C molten} \]

The alloys were prepared from particularly pure components by powder metallurgy and protracted annealing. Studies were made of ten alloys with silicon content between 85 and 4% in all the phase fields in the diagram section at 1000°C. We calculated the integral thermodynamic quantities ΔG, ΔH and ΔS for the formation of the silicides FeSi₂ (β), FeSi and Fe₃Si at the mean temperature for the experimental range (1000°C), and also (using the thermal capacity of the silicides, the iron and the silicon) at 298, 1188 and 1798°C. The heats of formation of the silicides mentioned at 298°C (kcal/mole) are -19.4, -17.6, and -22.4, respectively. The data existing in the literature enable us to calculate the heat of formation of FeSi₁₇₃ (α-leboite) at 298°C and this is found to be -14.4 kcal/mole. The heats calculated by us are 1.5-3 kcal higher than the experimental values of Corber and Olsen. The heats of mixing calculated by us for liquid alloys agree well with data in the literature.

The data obtained can be regarded as due to the change in the character of the bond in silicides from metallic to covalent when the silicon content is increased. From the data for alloy solutions of silicon in α-iron, the iron activities were calculated. It was found that the α ≠ α' transformation observed is a real phase transformation. The two-phase range is wider than shown in the phase diagram (from data in the literature). Conversion of the iron activities in solid solution to liquid solution gives good agreement with the data of Chipman.
ВЕЧЕР, ГЕЙДЕРИХ И ГЕРАСИМОВ

En partant des valeurs relatives aux alliages (solutions de silicium dans du fer alpha) on a calculé les activités du fer. Il a été constaté que la transformation observée antérieurement $\alpha \rightarrow \alpha'$ est une véritable transformation de phase. La région à deux phases est plus large que ne semble l’indiquer le diagramme d’équilibre (établi d’après les valeurs publiées). L’activité du fer en solution liquide calculée à partir de celle du fer en solution solide est en bon accord avec les valeurs trouvées par Chipman.

ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА СПЛАВОВ ЖЕЛЕЗА С КРЕМНИЕМ. Фазовая диаграмма Fe-Si сложна. При 1000°K имеются фазы FeSi$_2$ ($\beta$), FeSi и твердые растворы кремния в железе $\alpha$ и $\alpha'$. Измерялись ЭДС электрохимических ячеек:

$$\text{Fe} | \text{Fe}^{2+} , \text{KJ} + \text{NaJ} | \text{Fe-Si} \text{ расплав} \text{ при } 600 - 800^\circ\text{C}.$$ 

Сплавы готовили из особо чистых компонентов методом порошковой металлургии и длительным отжигом. Изучены десять сплавов с содержанием кремния от 85 до 4%, лежащих во всех фазовых полях разреза диаграммы при 1000°К. Вычислены интегральные термодинамические величины $\Delta_G$, $\Delta_H$ и $\Delta_S$ для образования силицидов FeSi$_2$(S), FeSi и Fe$_3$Si при средней температуре опыта $\Delta_G$irov 1000°K), а также (с использованием теплоемкостей силицидов, железа и кремния) при 298°, 1188° и 1798°К. Теплоты образования указанных силицидов при 298°K (кал/моль) равны $-19,4, -17,6$ и $-22,4$ соответственно. Имеющиеся в литературе данные позволяют вычислить теплоту образования FeSi$_2$ ($\alpha$-лебо́йта) при 298°K, равную $-14,4$ ккал/моль. Вычисленные нами теплоты больше экспериментальных величин Корбера и Ольсена на 1,5 - 2 ккал. Рассчитанные нами теплоты смешения для жидких сплавов хорошо согласуются с литературными данными.

Полученные данные могут быть истолкованы как следствие изменения характера связи в силицидах от металлического к ковалентному при увеличении содержания кремния. Из данных для сплавов — растворов кремния в а-железе были рассчитаны активности железа. Найдено, что отмеченное выше превращение $\alpha + \alpha'$ является настоящим фазовым превращением. Двухфазовая область шире, чем указывается на фазовой диаграмме (по литературным данным). Пересчет активностей железа в твердом растворе к жидким растворам показывает хорошее согласие с данными Чипмена.

PROPIEDADES THERMODYNAMICAS DE LAS ALEACIONES DE HIERRO Y SILICIO. El diagrama de equilibrio Fe-Si es muy complejo. A 1000'K se observa la presencia de las fases siguientes: FeSi$_2$ (B), FeSi y soluciones sólidas de silicio en hierro $\alpha$ y $\alpha'$. Los autores medieron las fuerzas electromotrices de las celdas electroquímicas:

$$\text{Fe} | \text{Fe}^{2+} , \text{KJ} + \text{NaJ} | \text{Fe-Si} \text{ fundidos entre } 600 \text{ y } 800^\circ\text{C}.$$ 

Las aleaciones se prepararon a partir de componentes puros por pulvimetalurgia y se sometieron a un recocido prolongado. Los autores estudiaron diez aleaciones con un contenido de silicio comprendido entre 85% y 4%, situadas en todas las fases del diagrama de equilibrio a 1000°K. Calcularon los valores integrales de $\Delta_G$, $\Delta_H$ y $\Delta_S$ correspondientes a la formación de los siliciuros FeSi$_2$(B), FeSi y Fe$_3$Si a la temperatura media del intervalo experimental (1000°K), así como (utilizando el calor específico de los siliciuros de hierro y del silicio) a 298, 1188 y 1798°K. Los calores de formación de los mencionados siliciuros a 298°K ascienden a $-19,4$, $-17,6$ y $-22,4$ kcal/mol, respectivamente. Los datos publicados permiten calcular el calor de formación del FeSi$_2$ ($\alpha$-leboíta) a 298°K, que es igual a $-14,4$ kcal/mol. Los calores calculados por los autores son superiores a los datos experimentales de Corber y de Olsen en 1,5 - 3 kcal. Por otra parte, los calores de mezcla, calculados para las aleaciones líquidas, concuerdan satisfactoriamente con los datos publicados.

Los datos obtenidos pueden explicarse como un resultado de la modificación que sufre el carácter del enlace en los siliciuros; en efecto, el enlace metálico se transforma en covalente al aumentar el contenido de silicio. A partir de los datos correspondientes a las aleaciones (soluciones de silicio en hierro $\alpha$) se calculó la actividad del hierro. Se halló que la transición $\alpha \rightarrow \alpha'$ observada anteriormente constituye una verdadera transformación de fases. La región bifásica es más ancha que la indicada en el diagrama de equilibrio (basado en los datos publicados). La actividad del hierro en soluciones líquidas, calculada a partir de la actividad del hierro en solución sólida concuerda satisfactoriamente con los datos obtenidos por Chipman.

Фазовая диаграмма системы железо - кремний включает ряд соединений с различными типами связей от ковалентной до металлической. В
высших силицидах железа связи между различными атомами, по-видимому, не равноценны и также имеют различный характер. Особенный интерес вызывает полупроводниковое соединение FeSi₂ (β-лебоит), устойчивый при достаточно высоких температурах.

В ряде исследований [1, 2, 3, 4] высечен характер фазовой диаграммы в области FeSi — Si, хотя имеются и расхождения в деталях. Мы пользовались для этой области диаграммой предлагаемой Сидоренко и Гельдом [2].

Область упорядоченных сплавов вблизи состава Fe₃Si не может считаться достаточно изученной и вызывает разногласия [6, 7, 8, 9]. Здесь мы внесли изменения на основании собственных результатов. В основном мы использовали диаграмму в справочнике Хансена и Андерко [5] (рис. 1).

Нами изучались термодинамические параметры образования из простых веществ соединения и твердых сплавов железа с кремнием методом электро-движущих сил (эдс) с жидким электролитом. Измерялась (при 600 — 800°) эдс электрохимической ячейки: Fe(t) | Fe⁺² → в расплаве KJ + NaJ | Fe — Si (т) Потенциалобразующим процессом в элементе является реакция

$$\text{Fe} + \text{Fe}_x \text{Si}_y = \text{Fe}_{x+1} \text{Si}_y,$$

где x, y ≫ 1.

Известно, что для равновесного процесса в элементе:

$$\Delta G = -zFE; \quad \Delta S = zF\left(\frac{\partial E}{\partial T}\right)_p; \quad \Delta H = -zFE + zF\left(\frac{\partial E}{\partial T}\right)_p;$$

где z — заряд иона, переносящего ток (в данном случае Fe⁺²), F — число Фарадея и E — эдс.

В изучаемой системе эти величины равны парциальным величинам для железа (металл I).

$$\Delta G = \mu_1 - \mu_1^0; \quad \Delta S = S_1 - S_1^0; \quad \Delta H = H_1 - H_1^0;$$

Электролитом в ячейке (1) служил расплав йодидов калия и натрия (42% KJ, температура плавления 585°С). При использовании расплава KCl + LiCl мы не смогли получить воспроизводимых результатов, возможно, вследствие реакции на электроде:

$$2\text{FeCl}_2 + \text{SiCl}_4 \uparrow + 2\text{Fe},$$

вызывающей концентрационную поляризацию в расплаве, а также обеднение кремнием поверхностного слоя электрода.

Попытки измерения эдс в ячейках с твердым электролитом с кислородной проводимостью (а именно ThO₂ + La₂O₃) не привели к положительным результатам, возможно, вследствие появления у твердого электролита электронной проводимости в системах с очень низким парциальным давлением кислорода. Для Si + SiO₂ при 1000°С P₂O₅ ~ 10⁻³⁷ атм. Пользуясь методом Шмальцрида [11] и следуя его допущениям, мы экспериментально оценили долю ионной проводимости для 0,85 ThO₂ + 0,15 La₂O₃ равной 0,38 (в системе Fe, FeO — Si, SiO₂ при 1000°С).
Смесь сухих иодидов дополнительно обезвоживали путем плавления в приборе в токе сухого водорода.

Ионы железа вносили в электролит путем добавления ~ 0,5 г FeCl₂ на 200 г смеси ионидов. FeCl₂ готовили по обычной методике [10]. Сплавы железа с кремнием готовили из карбонильного железа особой чистоты и кремния чистоты 99,99% методом спекания спрессованных таблеток с эвакуированных кварцевых ампулах при 1180 °C (120 часов) и последующего гомогенизирующего отжига при 800 – 850 °C (200 – 500 часов). Фазовый состав сплавов до опыта и, выборочно, после опыта контролировали рентгенографическим анализом. Для однофазных сплавов проводили также химический анализ. Измерения проводили в атмосфере очищенного аргона в
Рис.2. Прибор для изучения ЭДС при высоких температурах: 1 — кварцевый сосуд; 2 — пришлифованная крышка; 3 — сосуды — электрохимические ячейки; 4 — центральный стержень; 5 — спая вольфрамовых токоотводов с платиной.

Кварцевом приборе (рис.2), предварительно эвакуированном до $10^{-4}$ мм рт. ст при 100° и промытом аргоном. Температуру печи регулировали до ±2°, температуру измеряли термопарой с точностью до ±1°, эдс измеряли потенциометрически с точностью не меньше 0,1 милливольт. Равновесные значения эдс (не изменяющиеся в пределах 1 мил в течение 4-5 часов и воспроизводившиеся при возвращении к исходной температуре устанавливали через 50 часов после начала опыта. Затем в течение 100-150 часов проводили измерения при различных температурах, как при повышении ее, так и при понижении. Измеряли эдс для гетерогенных сплавов, содержащих 91,8; 82,3; 71,7; 62,0; 59,1; 57,1; 55,1; 40,0; 36,0 и 33,4%Si (ат), а также для десяти гомогенных сплавов — растворов кремния в железе, содержащих от 24,5 до 5,5%Si (ат).

Зависимость эдс данного сплава от температуры оказалась линейной в пределах ошибок опыта, данные для каждой двухфазной области диаграммы обрабатывали совместно методом наименьших квадратов. Полученные уравнения использованы для получения по уравнениям (2) величин $\Delta G$ (при 1000°К), $\Delta H$ и $\Delta S$ (средних для изученного интервала темпе-
ратур, т.е. относящихся приближенно к средней температуре интервала, близкой к 1000°К.

Линейные уравнения для $\Delta G$ каждой из гетерогенных областей фазовой диаграммы используются для расчета интегральных величин $\Delta G$, $\Delta S$, и $\Delta H$ образования силицидов из Fe(α) и Si. В соответствии с (2), (2а) и (3) из опытных данных вычисляются парциальные величины $\mu_{\text{Fe}} - \mu^0_{\text{Fe}}$ и т.д. Интегральные величины образования грамм-атома сплава из простых веществ вычислены по уравнению Гиббоа-Дюгема для 1000°К:

$$
\Delta G = x_{\text{Si}} \int_0^{x_{\text{Fe}}} (\mu_{\text{Fe}} - \mu^0_{\text{Fe}}) dx_{\text{Si}}. 
$$

Здесь $x_{\text{Fe}}$ и $x_{\text{Si}}$ — атомные доли Si и Fe в сплаве. Для участков диаграммы Si-FeSi₂ и FeSi₂-Fe₀,₄92 Si₀,₅ο8 (левая граница поля фазы $\varepsilon$) интегрирование (4) сводится к умножению постоянных величин $\mu_{\text{Fe}} - \mu^0_{\text{Fe}}$ на разность величин $x_{\text{Fe}}/x_{\text{Si}}$ участника диаграммы и на $x_{\text{Si}}$ в конечной точке. В узкой области фазы интегрирование ведется вдоль прямой, соединяющей уровни $\mu_{\text{Fe}} - \mu^0_{\text{Fe}}$ по обе стороны гомогенной области $\varepsilon$. Затем расчет идет от Fe₀,₅ο3 Si₀,₄₉7 (правая граница области $\varepsilon$) до границы области твердых растворов $\alpha^1$, отвечающей соединению Fe₃Si. В пределах фазы $\varepsilon$ можно интерполировать величины для фазы стехиометрического состава FeSi.

В табл. 1 приводятся парциальные величины для железа при 1000°K и интегральные величины, вычисленные указанным путем. Максимальные ошибки рассчитаны как величины доверительного интервала вероятности 0,95 по известным формулам (3) дисперсионного анализа (см. напр., [28]).

Используя литературные данные для теплоемкостей чистых железа [12] и кремния [13] и их соединений [14-17] и для теплот плавления и превращения Fe(α), Si и силицидов [15, 18], пересчитали результаты (табл. 1) к 298°K (стандартные величины, приведенные в табл.2), к 1188°K — температура эвтектического превращения

$$
\text{FeSi}_{2,33} = \text{FeSi}_{2,33} \text{Fe} + 0,33 \text{Si} = \text{FeSi}_{2,33}
$$

и к 1798°K.

Ошибка, вносимая пересчетом к другой температуре, значительно меньше экспериментальной ошибки исходных данных, поэтому первой ошибкой мы пренебрегали. Величины для фазы FeSi₂,₃₃ (фаза $\xi_\alpha$ диаграммы, или $\alpha$-лебоит), которая не была нами экспериментально исследована, находились следующим путем. Наши данные для $\beta$-лебоита пересчитывали к 1188°K, затем учитывали, что $\Delta G$ для реакции (5) при этой температуре равно нулю, использовали величину $S - S_0$ для FeSi₂,₃₃ по [14]. Таким путем вычисляли $\Delta H_{1188}$ образования FeSi₂,₃₃ при 1188°K, пересчитанную затем к 298°K. Расчет проведен с точностью до $S_0$ (FeSi₂,₃₃), которая больше нуля из-за частичной неупорядоченности переохлажденного $\alpha$-лебоита и неизвестна.
Сравним наши результаты с данными других авторов (табл. 2). Величины энтропий образования согласуются с данными Кренциса и Гельда [14-17] только для β-лебита (FeSi₂). Для остальных соединений наши данные ниже величин Кренциса и Гельда на ≈ 2 ккал/град·моль. Причины этого неясны. Наша энталпия образования FeSi₂ выше значения Корберра и Эльзена [19] на 2,5 ккал/моль. Возможно, что величина [19] занижена, так как при смещении жидкостей и быстрой кристаллизации сплав в калориметре вероятно образование неравновесных смесей в сплавах с составами FeSi₂ и Fe₃Si. Данные для FeSi, где превращений в твердых фазах нет, согласуются лучше.

Рассчитанные нами величины ΔH для образования жидких сплавов при 1798°K согласуются с результатами Корберра и Эльзена [19, 20, 21] в пределах 0,2 ккал/г-ат. отличие от данных Гертмана и Гельда [22] около 1 ккал/г-ат. Наш пересчет к столь высокой температуре может быть связан с накоплением ошибок.

Результаты, полученные для твердых растворов кремния в железе, послужили основой для расчета активности железа в твердом растворе по уравнению:

\[ \ln a_{Fe} = \frac{-2FE}{RT} \]

Стандартное состояние — чистое Fe (α)

На рис. 3 активности железа изображены как функции мольной доли. Необходимо учесть, что погрешность результатов (изображенную вертикальными линиями) отчетливо виден горизонтальный участок кривой, соответствующий гетерогенной области α → α' равновесию между неупорядоченными растворами α и упорядоченными растворами α' (см. рис. 1). Наши результаты согласуются с мнением Осавы и Мурата [6] и других авторов о наличии гетерогенного равновесия α → α', основанным на дилатометрических исследованиях. Авторы других работ [7, 8, 9], опираясь на рентгенографические данные, отрицают наличие гетерогенной области. Следует отметить, что по нашим данным гетерогенная область довольно широка — 12—19% Si (at), тогда как в [6] ее ширина оценивается в 0,5% (at).

Была сделана попытка расчета энтропии образования твердых растворов кремния в железе (вплоть до Fe₃Si) на основе следующих предположений; что неупорядоченный раствор α считается регулярным и конфигурационная энтропия смещения его равной идеальной.

В упорядоченном растворе состава Fe₃Si конфигурационная энтропия оценивается путем графического нахождения степени дальнего порядка S с помощью уравнения для конфигурационной энтропии смещения и принятыми определенными значениями для температуры разупорядочения. Вибрационная энтропия оценивается по методу Маклеллана [23], учитываяшему различие в атомных радиусах компонентов с помощью общей теории упругости, принятая величину Z₀, зависящей от состава и равной в Fe₃Si 1,205 Å. Электронный вклад в энтропию оценен аналогично тому как это сделано Ориани и Мэффи [22] и Радклиффом, Авербахом и Козном [23] с использованием низкотемпературных теплоемкостей из [24, 25]. Магнитная составляющая оценивалась из средних магнитных моментов атома железа в Fe₃Si и в Fe по [26, 27]. Получено при 298 и 1000°K для Fe₃Si.
### Таблица 1

<table>
<thead>
<tr>
<th>Формула</th>
<th>$\Delta \mu_{Fe}$, ккал</th>
<th>$\Delta H_{Fe}$, ккал</th>
<th>$\Delta S_{Fe}$, кал/град</th>
<th>$\Delta G$, ккал</th>
<th>$\Delta H$, ккал</th>
<th>$\Delta S$, кал/град</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSi$_2$</td>
<td>$-15,20 \pm 0,28$</td>
<td>$-21,3 \pm 1,8$</td>
<td>$-6,1 \pm 1,8$</td>
<td>$-5,07 \pm 0,09$</td>
<td>$-7,1 \pm 0,6$</td>
<td>$-2,0 \pm 0,6$</td>
</tr>
<tr>
<td>Fe$<em>{0,492}$Si$</em>{0,508}$</td>
<td>$-14,40 \pm 0,13$</td>
<td>$-15,8 \pm 0,5$</td>
<td>$-1,4 \pm 0,5$</td>
<td>$-7,29 \pm 0,08$</td>
<td>$-9,18 \pm 0,45$</td>
<td>$-1,9 \pm 0,5$</td>
</tr>
<tr>
<td>FeSi</td>
<td>$-3,58 \pm 0,10$</td>
<td>$-3,28 \pm 0,20$</td>
<td>$0,3 \pm 0,2$</td>
<td>$-7,32 \pm 0,08$</td>
<td>$-9,18 \pm 0,45$</td>
<td>$-1,9 \pm 0,5$</td>
</tr>
<tr>
<td>Fe$<em>{0,503}$Si$</em>{0,497}$</td>
<td>$-3,58 \pm 0,10$</td>
<td>$-3,28 \pm 0,20$</td>
<td>$0,3 \pm 0,2$</td>
<td>$-5,40 \pm 0,05$</td>
<td>$-6,1 \pm 0,15$</td>
<td>$-0,7 \pm 0,15$</td>
</tr>
</tbody>
</table>

О результатах, полученных для области твердых растворов ($\alpha$ и $\alpha'$), см. ниже.

### Таблица 2

<table>
<thead>
<tr>
<th>Соединение</th>
<th>$\Delta H_{298}$, ккал/моль</th>
<th>$\Delta S_{298}$, кал/град · моль</th>
<th>$\Delta H_{ж}$ ккал/г-ат</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSi$_2$ ($\xi_6$)</td>
<td>$-19,4 \pm 1,8$</td>
<td>$-3,3 \pm 1,8$</td>
<td>$-2,2$</td>
</tr>
<tr>
<td>$\beta$ - лебоит</td>
<td>$-14,4 \pm 2,4$</td>
<td>$-0,44$</td>
<td>$-6,63$</td>
</tr>
<tr>
<td>FeSi$_{2,33}$ ($\xi_3$)</td>
<td>$-17,6 \pm 0,9$</td>
<td>$-2,6 \pm 1,0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\alpha$ - лебоит</td>
<td>$-22,4 \pm 0,6$</td>
<td>$-1,2 \pm 0,6$</td>
<td>$-0,7$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Соединение</th>
<th>$\Delta H_{298}$, ккал/моль</th>
<th>$\Delta S_{298}$, кал/град · моль</th>
<th>$\Delta H_{ж}$ ккал/г-ат</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pубликуемая работа</td>
<td>$-16,9 \pm 2$</td>
<td>$-19,2 \pm 2$</td>
<td>$-8,6$</td>
</tr>
<tr>
<td>Корбер и Эльзен [19]</td>
<td>$-16,9 \pm 2$</td>
<td>$-19,2 \pm 2$</td>
<td>$-8,6$</td>
</tr>
</tbody>
</table>
Таблица 3

РАСЧЕТ ЭНТРОПИИ Fe₃Si.

<table>
<thead>
<tr>
<th>T/К</th>
<th>( \Delta S_{конф} )</th>
<th>( \Delta S_{абар} )</th>
<th>( \Delta S_{вул} )</th>
<th>( \Delta S_{магн.} )</th>
<th>( \Delta S )</th>
<th>( \Delta S_{эксп} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0</td>
<td>-0,33</td>
<td>+0,06</td>
<td>0</td>
<td>-0,28</td>
<td>-0,3</td>
</tr>
<tr>
<td>1000</td>
<td>0,36</td>
<td>-0,38</td>
<td>+0,2</td>
<td>+0,6</td>
<td>+0,78</td>
<td>-0,7</td>
</tr>
</tbody>
</table>

Рис.3. Активность железа в растворах кремния в а-железе.

Рассчитанная при 298°К величина \( \Delta S(Fe₃Si) \) хорошо согласуется с экспериментальной. При 1000°К согласование хуже. При столь высокой температуре учет только упругих искажений является недостаточным для характеристики колебательной составляющей энтропии образования.

Л И Т Е Р А Т У Р А

Discussion to Session 2

EMF METHODS, INCLUDING SOLID ELECTROLYTES

Discussion Leader: C. WAGNER

FEDERAL REPUBLIC OF GERMANY

Paper SM-66/98 (H. Schmalzried)

O. KUBASCHEWSKI: Can you suggest any nitrides which may be used as electrolytes for the study of transition metal-nitrogen systems at low nitrogen pressures? One can imagine suitable cells for the determination of the metal activities, but these are unlikely to give accurate results at relatively low concentrations of nitrogen. Information on suitable electrolytes for the study of carbon and boron activities in their systems with transition metals would also be very useful.

H. SCHMALZRIED: I do not know of any ionic crystal which conducts only by N, B, or C ions. An example of the possibility referred to in my oral presentation, that of measuring metal activities using auxiliary electrolytes, is the cell

\[ \text{Ag} \mid \text{AgI} \mid \text{Ag}_2\text{S} \mid \text{S}_2\text{Pt} \]

which can be used to measure sulphur.

O. KUBASCHEWSKI: Is Ni, NiO suitable as a standard electrode when thoria-yttria is used as the electrolyte?

H. SCHMALZRIED: Yes.

O. KUBASCHEWSKI: We found that the cell

\[ \text{Cr, Cr}_2\text{O}_3 \mid \text{ThO}_2, \text{Y}_2\text{O}_3 \mid \text{ZrO}_2, \text{CaO} \mid \text{Cr, Cr}_2\text{O}_3 \]

produces an EMF of zero ± 0.5 mV. Is it possible that the combination of the two different electrolytes develops faults due to interactions when one electrode is replaced by Ni, NiO?

T. L. MARKIN: I have some information on this point. We have measured the EMF of the cells

\[ \text{Ni, NiO} \mid \text{ThO}_2, \text{Y}_2\text{O}_3 \mid \text{ZrO}_2, \text{CaO} \mid \text{ThO}_2, \text{Y}_2\text{O}_3 \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}} + \langle \text{PuO}_{1.61} \rangle_{\text{cub}} \]

and

\[ \text{Fe, FeO} \mid \text{ThO}_2, \text{Y}_2\text{O}_3 \mid \text{ZrO}_2, \text{CaO} \mid \text{ThO}_2, \text{Y}_2\text{O}_3 \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}} + \langle \text{PuO}_{1.61} \rangle_{\text{cub}} . \]
No point was further from the mean line than 4 mV on the plot of $\Delta G(O_2)$ versus temperature. We have also measured the EMF of

$$\text{Ni, NiO} | \text{ThO}_2, \text{Y}_2\text{O}_3, \text{ZrO}_2, \text{CaO} | \text{ThO}_2, \text{Y}_2\text{O}_3 | \text{Fe, FeO}$$

and it agrees with the published data. These experiments show that no reaction occurs between Ni, NiO and ThO$_2$, Y$_2$O$_3$ electrolytes.

C. BECKETT: I think the light metal nitrides of aluminium and beryllium might be useful as solid electrolyte materials, since they do not conduct by the electron mechanism as most metallic nitrides do. The calorimetric data on these two nitrides are quite good, and they are quite stable.

W. L. WORRELL: Dr. Schmalzried, you mentioned measuring the EMF using MgO, which exhibits both ionic and electronic conductivity. Did you use gaseous or solid electrodes? I would be somewhat concerned with the use of solid electrodes in this case because of the possible formation of an oxide layer at the electrode-electrolyte interface, which would change the EMF.

You also mentioned that quartz is an ionic conductor at oxygen pressures between 1 and $10^{-16}$ atm. Is the ionic conduction in SiO$_2$ purely anionic?

H. SCHMALZRIED: We used both gaseous and solid electrodes, and found that at the beginning of the experiments the EMF was the same. I agree, however, that after some diffusion of the Ni, NiO and Fe, FeO electrodes into the MgO electrolyte, there were changes in the EMF depending on the different transference numbers.

The ionic transport in quartz is certainly due to impurities, especially sodium, but unless polarization occurs this does not affect the EMF.

Paper SM-66/15 (Y. Matsushita and K. Goto)

There was no discussion of this paper.

Paper SM-66/66 (W. L. Worrell)

There was no discussion of this paper.

Paper SM-66/32 (T. L. Markin and M. H. Rand)

H. A. EICK: In a high-temperature X-ray study of the PuO$_x$ system, using samples prepared by firing a mixture of PuH$_2$ and PuO$_2$, and analysed for oxygen content by weight uptake upon oxidation, Dr. Mulford and I obtained results substantially in agreement with those reported by Dr. Markin. However, some minor differences resulted. These were as follows:

1. The powder diffraction lines of PuO$_2$ were present in the X-ray photographs at 850°C;
2. These lines increased in intensity as the sample was cooled, and decreased in intensity as it was heated, thereby indicating equilibrium;
3. The lattice parameter of the PuO$_{1.61}$ phase was the same in specimens of overall composition PuO$_{1.85}$ and PuO$_{1.75}$.

4. In contrast to the data reported by Markin, we observed the body-centred cubic lines of the PuO$_{1.61}$ phase above 300°C. Care was taken to ensure that the samples were properly sealed. They were heated overnight, then cooled and examined under a microscope to check for any leaks in the capillary. In addition, some of the samples were cycled, and the same results were obtained each time.

T. L. MARKIN: Below 330°C, lines attributable to the body-centred cubic phase were clearly seen on the X-ray diffraction pattern for 1.52 < x < 1.98 in PuO$_2$-x. The body-centred cubic lines were not observed above 330°C for the PuO$_{1.61}$ in equilibrium with PuO$_{1.98-y}$. Neither did we see any of the MnO$_{2n-2}$-type ordering that has been observed in the CeO$_{2-x}$ phase diagram.

The differences between Dr. Eick's results and our results at temperatures greater than 850°C may have been due either to capillary attack, which we have observed usually begins at about 900°C, or to a hair crack in his capillary.

S. ARONSON: Are you, at present, making an effort to interpret the temperature dependence of your free-energy data in the single-phase region of plutonium oxide in terms of a statistical theory of entropy?

T. L. MARKIN: Yes, we are applying a statistical theory to the enthalpy and entropy values. The very large changes in $\Delta H(0^o)$ and $\Delta S(0^o)$ in the transition from PuO$_2$ to PuO$_{1.75}$ indicate that the removal of oxygen from the oxide cannot result in a random distribution of vacancies. Some ordering must be taking place.

Paper SM-66/62 (J. J. Egan)

There was no discussion of this paper.

Paper SM-66/61 (S. Aronson and A. Auskern)

L. E. J. ROBERTS: What precautions had to be taken to ensure equilibrium of the mixed fluoride-boride electrodes, and do you think the slight irreproducibility of these cells is due to the behaviour of the mixed electrode?

S. ARONSON: The thorium boride-thorium fluoride samples were prepared by ball-milling a mixture of the powders and pressing it into a pellet. The cell was heated at 850°C until steady EMF values were obtained. We do not know what is responsible for the slight irreproducibility.

H. NOWOTNY (Chairman): With reference to the reaction

$$3\text{ThB}_4 + 2\text{C} = 2\text{ThB}_6 + \text{ThC}_2$$

(Eq. (5) of your paper, used to evaluate stability) I feel that the problem involved appears to be more complicated. A study of the thorium-boron-carbon system by L. E. Toth, F. Benesovsky, H. Nowotny and E. Rudy
(Mh. Chemie 92 (1961) 956) has revealed the existence of at least four ternary phases (thorium borocarbides).

S. ARONSON: I was not aware of your results on the formation of borocarbides. We have heated mixtures of thorium, boron and carbon to about 1500°C, and noted that the resulting X-ray patterns are complex.

W. L. WORRELL: It is possible that the considerable scatter in your EMF data may be due to the dissolution of ThF$_4$ into CaF$_2$. For example, if the electrode surface is depleted of ThF$_4$, it could affect the EMF measured. Did you check either the electrolyte or the electrode surfaces for this possibility?

S. ARONSON: I do not think the reaction between ThF$_4$ and CaF$_2$ at the electrolyte-electrode interface affected the cell equilibrium. Little reaction was normally observed. We have also tried to form a solid solution of ThF$_4$ in CaF$_2$ by heating a mixture of the two powders for several hundred hours at 1000°C; the two original phases were observed by X-ray diffraction after the treatment.

H. NOWOTNY (Chairman): In any case, I feel that such disturbance would be very minor because of the low mobility of tetravalent ions; the EMF is determined principally by ions of high mobility.


O. KUBASCHEWSKI: Since there are certain differences between the calorimetric heats of formation and those obtained from the temperature coefficients of the EMF results, I wonder whether a complete evaluation of the Fe-Si system has been attempted. The heats and entropies of the liquid solutions are known with reasonable accuracy across the whole range of concentrations and so are the equilibrium diagram and the heats of fusion.

Ya. I. GERAŞIMOVA: The calorimetric data on heats of formation are of course generally more reliable than those calculated from the EMF. However, our calculations for ΔH of formation of those silicides of iron which do not undergo transformation on cooling are in reasonable agreement with the data of Körber and Oelsen, differing appreciably only in the values for FeSi$_2$. There is also satisfactory agreement between our calculated values for liquid iron-silicon alloys and the calorimetric data of Körber and Oelsen, and Gertmann and Geld, mentioned in our paper.

W. L. WORRELL: At our laboratory we have considered measuring the oxygen activity at a Si, SiO$_2$ electrode using a thoria electrolyte. However, we were very worried about the possible reactions between thoria and silicon to form thorium silicides and SiO (g). I would like to ask Professor Gerasimov if there was any indication that a reaction had occurred between the Si, SiO$_2$ electrode and his thoria electrolyte?

Ya. I. GERAŞIMOVA: I can give no definite answer to this question. We have tried to measure the EMF in the system

\[ \text{Fe, FeO} | \text{ThO}_2 - \text{La}_2\text{O}_3 | \text{Si, SiO}_2 \]

for which the result may be predicted, and obtained definite but wrong results at 1000°C. On this empirical basis we excluded this solid electrolyte for
our purposes. The idea that ionic conductivity does not occur in this electrolyte at this temperature (its transference number being less than 1) is quite a tentative one, and we are not defending it.

General Discussion

C. WAGNER (Discussion Leader): I feel that in the general discussion it may be especially important to consider tasks for future research. Firstly, it is obvious that we need further investigations on conduction in solid electrolytes such as doped zirconia, thoria and calcium fluoride. In particular, the oxygen partial pressure range involving prevailing ionic conduction in doped thoria should be determined, and analogous investigations on calcium fluoride seem desirable. Secondly, we may discuss new types of galvanic cells for the determination of thermodynamic quantities. Thirdly, we may discuss which particular substances and which particular binary or ternary systems may most appropriately be investigated by EMF methods.

O. KUBASCHEWSKI: I should like to draw attention to a point that has not yet been sufficiently stressed; the need for adequate gettering. We observed this while working on the system Co-Cu, a eutetic system with relatively small solid solubilities, where it was necessary to attain accuracies much better than ± 1 mV. Stabilized zirconia was used as the electrolyte. It has not yet been possible to exclude water vapour entirely from any ceramic container, and reproducible EMF's of ± 0.1 mV could only be obtained when the electrodes were closely surrounded by a large mass consisting of the electrode mixtures. The necessity of thorough gettering has been confirmed in later work, and it appears that poor gettering affects the contact between the electrodes and the electrolyte, thus producing small but significant "contact potentials".

H. SCHMALZRIED: I think it should once again be stressed that it is impossible to achieve an inert atmosphere in oxide galvanic cells using pellets as electrolytes (instead of tubes, for example); drifting of the EMF or mixed potential may therefore be expected.

W. L. WORRELL: It has been our experience that the major source of gaseous impurities seems to be from the degassing of the alumina positioning and reaction tubes. Thus we prefer to use, instead of a static atmosphere, a flowing, pre-purified argon atmosphere to help sweep out these gaseous impurities. Use of a flowing atmosphere also enables one to check that the EMF does not vary with the argon flow rate, which is an indication that the gaseous atmosphere is not influencing the EMF.

J. DROWART: In connection with the discussion of new applications of galvanic cells suggested by Professor Wagner, I would like to mention that Dr. Rickert and I recently studied by mass spectrometry the composition of the sulphur vapour effusing from the electrochemical Knudsen cell developed by him. The galvanic cell used was the Pt, Ag | AgI, Ag₂S, Pt cell. It was possible, by changing both the EMF applied and the temperature, to study selectively each of the gaseous molecules S₂, S₃, S₄, S₅, S₆, S₇ and S₈ and to determine their thermodynamic properties.
Such combined mass spectrometric-galvanic cell studies can certainly be extended to many other problems in which it is of interest to determine the nature of the gaseous species formed under equilibrium or free surface conditions in galvanic cells, or to obtain thermodynamic or kinetic data simultaneously from EMF and vapour pressure measurements.

C.B. ALCOCK: I would like to suggest that there are definite advantages in the use of vacuum conditions for the operation of high-temperature Knudsen cells. The first of these is that a getter may be used more effectively to combat the deleterious action of vapours emitted by the refractory container. Is there any reason other than tradition for retaining the use of argon in high-temperature cells?

Also, do we know where the limits of thoria-yttria are? Where does the electron transport number become important in these thoria electrolytes?

C. WAGNER (Discussion Leader): I think this is important both in this case and for calcium fluoride, which may be a very important electrolyte in the future.

T. L. MARKIN: I believe the use of a flushing gas is more satisfactory than a vacuum because the oxygen potential of argon can be reduced to very much lower than that of a vacuum.

I should also like to mention that we have measured the electric conductivity of thoria doped up with 8% of yttria as a function of temperature in the region of 1400°C, in argon and in air. We used thorium electrodes on either side of the thoria-yttria electrolyte and in each case we got very nearly the same resistance, which means that the conductivity is virtually ionic over a much wider range of oxygen potentials than has been claimed. This may be either because we had impurities in our thoria trap, or because those who claim pressures of only $10^{-4}$ atm had different impurities. There is no doubt that the presence of impurities makes a tremendous difference to the activation energies of these electrolytes.

C.B. ALCOCK: With regard to vacuum systems, I think one should bear in mind that the quotation of an oxygen partial pressure is not a complete statement. In order to change the composition of the condensed phase one needs to have a high gas capacity. In a vacuum system one can surround the electrodes with a metallic getter. Then if the pressure is kept down to say $10^{-5}$ mmHg, which is a relatively poor vacuum, the water vapour being emitted from the refracting walls of the apparatus must then travel in a collision-free path. The first collision they have will probably be with the getter outside the electrode where they will be absorbed and cause no further trouble. In a gaseous system, on the other hand, the molecules can flow in a gas in which they undergo many collisions and therefore have a better chance of reaching the electrode.

My second point is, how long did Dr. Markin wait when he contacted thoria-yttria with thorium and found no difference in the conductivity? In this connection, as far as I know it has not been stated that thorium electrolytes become electronic below $10^{-5}$ atm at 1000°C; this is simply as far as our experience goes. The limit may in fact be a good deal lower.

T. L. MARKIN: When we changed over the atmospheres we left the system for twenty minutes. In view of later work on zirconium-calcium
oxide, where this long-range ordering occurs after many hours, I agree that we should perhaps have left our thorium-yttria system very much longer.

C. WAGNER (Discussion Leader): I feel that the use of purified argon at atmospheric pressure seems especially appropriate for the investigation of systems involving volatile compounds or components, in order to minimize changes in composition due to vaporization.

J. J. EGAN: To return to an earlier comment by Professor Wagner, it appears from recent work (R. J. Hens and J. J. Egan, Abstracts of the Chemical Society Meeting of May 1965, San Francisco) that CaF$_2$ remains a pure ionic conductor down to partial pressures of F$_2$ equivalent to those found over Mg, MgF$_2$ mixtures. We believe that below these pressures CaF$_2$ will show small amounts of electronic conductivity.

W. L. WORRELL: We have recently studied a cell

$$\text{Nb, NbO} | \text{ThO}_2(Y_2O_3) | \text{Zr, ZrO}_2$$

at 1012°C in which the oxygen potential at the Zr, ZrO$_2$ electrode is in the range of 10$^{-36}$ atm. A small but steady drift in the EMF was observed, which might be an indication that electronic conductivity does occur in the ThO$_2$(94 wt. %)-Y$_2$O$_3$ electrolyte at this low oxygen potential. An X-ray diffraction analysis of the electrode and electrolyte surfaces indicated that no electrode-electrolyte reaction had occurred.

L. E. J. ROBERTS: If one accepts Dr. Markin's data, the indication is that his ThO$_2$(Y$_2$O$_3$) electrolytes were ionic conductors at 10$^{-37}$ atm O$_2$ at 1000°K.

T. L. MARKIN: In our EMF measurements of

$$\text{Ni, NiO} | \text{electrolyte} | \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}} + \langle \text{PuO}_{1.61} \rangle_{\text{cub}}$$

and

$$\text{Fe, FeO} | \text{electrolyte} | \langle \text{Pu}_2\text{O}_3 \rangle_{\text{hex}} + \langle \text{PuO}_{1.61} \rangle_{\text{cub}}$$

the thickness of the electrolyte for the Ni, NiO standard electrode was twice the thickness of the electrolyte for the Fe, FeO standard electrode. Both cells agreed extremely well. If any appreciable electronic conduction occurred, the EMF of the cell employing Ni, NiO as the standard electrode would have been lower than that employing Fe, FeO.

J. G. ASTON: In the summarizing paper of Dr. Schmalzried and in the subsequent papers, it is implied that the systems have come to thermodynamic equilibrium. It also appears that sufficient is known about the transport properties to calculate the time of return to equilibrium after disturbing the system by producing small known amounts of products by electrolysis using currents in both directions.

To what extent are such tests for equilibrium made?

H. SCHMALZRIED: The relaxation time after local equilibrium disturbance at the electrolyte | Me, MeO interface depends on the transport properties of all three phases. There can therefore be no general answer.
One may, however, estimate that in the cell $\text{Ag} | \text{AgI} | \text{Ag}_2\text{S} | \text{S}_2 \text{Pb}$ the relaxation times are quite short, about 0.1 of a second at 350°C, whereas $\text{Pb}_2 \text{O}_3 | \text{ZrO}_2 (\text{+CaO}) | \text{Ni}, \text{NiO} | \text{Pb}$ may take minutes or hours to regain equilibrium, depending on the degree of disturbance.

J. DROWART: Data pertinent to Dr. Aston's question were obtained in the mass spectrometric study of the sulphur vapour produced by polarizing the Pt, $\text{Ag} | \text{AgI} | \text{Ag}_2\text{S}, \text{Pt}$ galvanic cell that I referred to earlier. On the suggestion of Dr. Rickert, two such cells were in fact used, one being polarized externally and the other being allowed to equilibrate with the gas phase. It was observed that this equilibrium established itself rapidly and that the current density-EMF curves obtained are in good agreement with those for single electrochemical Knudsen cells. Further, especially for the molecules $\text{S}_2$ and $\text{S}_2$, for which there are independent thermodynamic data, good agreement was observed between the measured and calculated pressures in the Knudsen cell. This indicates that the latter can indeed be correctly derived from the current through the galvanic cell as was already concluded earlier by Dr. Rickert.
Session 3

VAPORIZATION
Chairman: P. NAGELS

BELGIUM
THERMODYNAMICS OF VAPORIZATION OF NUCLEAR MATERIALS AT HIGH TEMPERATURES

P.W. GILLES
UNIVERSITY OF KANSAS, LAWRENCE, KANS., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

THERMODYNAMICS OF VAPORIZATION OF NUCLEAR MATERIALS AT HIGH TEMPERATURES. Vapori-
zation studies are one of the best, most convenient, and most important ways of obtaining the thermodynamic
properties and phase relationships of refractory nuclear materials. Measurements are made on equilibrium
systems involving at least two phases. The properties of these phases are established by the proportions of the
components, the properties of the pure components and their interaction parameters. Free energy-composition
curves for the gas phase and the several possible condensed phases in a system are discussed in relationship to one
another. The overwhelming effect of pressure on the free energy of the gas phase and the minute effect on
condensed phases are pointed out. The relationship between the free energy-composition curves and the vapor-
zation behaviour of the system is described. The several factors which are important in establishing free energy-
composition curves and, hence, the mode of equilibrium vaporization are discussed. They include the
stability of the gaseous molecules, the absolute and relative stabilities of the various condensed phases, the
composition of the gaseous molecules, the composition of the condensed phases, and the free energies of
sublimation of the elements. A few of the principles associated with congruent vaporization processes and
mass spectrometric measurements are discussed.

THERMODYNAMIQUE DE LA VAPORISATION DES MATIERES NUCLEAIRES A HAUTE TEMPERATURE.
Les études sur la vaporisation constituent un des moyens les meilleurs, les plus pratiques et les plus importants
qui permettent de déterminer les propriétés thermodynamiques et les relations entre phases des matières nucléo-
aires réfractaires. Les mesures portent sur les systèmes en équilibre où interviennent au moins deux phases dont
les propriétés dépendent des proportions et des propriétés des composants purs et de leurs paramètres d'interaction.
L'auteur compare entre elles les courbes de l'énergie libre en fonction de la concentration pour la phase gazeuse
et pour les diverses phases condensées possibles d'un système. Il fait ressortir l'effet prépondérant de la pression
sur l'énergie libre de la phase gazeuse et son effet secondaire sur les phases condensées. Il décrit la relation
entre les courbes de l'énergie libre en fonction de la composition et le comportement du système à la vaporisation.
L'auteur discute les différents facteurs qui présentent une importance pour l'établissement des courbes de
l'énergie libre en fonction de la composition et, par conséquent, le mode de vaporisation équilibrée. Ces
facteurs sont la stabilité des molécules gazeuses, les stabilités absolue et relative des diverses phases con-
densées, la composition des molécules gazeuses, la composition des phases condensées, et les énergies libres de
sublimation des éléments. L'auteur discute quelques-uns des principes associés aux processus de vaporisation
congruents et les mesures obtenues par spectrométrie de masse.

ТЕРМОДИНАМИКА ИСПАРЕНИЯ ЯДЕРНЫХ МАТЕРИАЛОВ ПРИ ВЫСОКИХ ТЕМПЕРА-ТУРАХ. Изучение испарения является одним из лучших, наиболее удобных и наиболее важ-
ных способов получения данных о термодинамических свойствах и соотношениях фаз жаро-
прочных ядерных материалов. Измеряли равновесные системы, которые связаны по крайней
мере с двумя фазами. Свойства этих фаз устанавливали по пропорциям компонентов, свойст-
вам чистых компонентов и параметрам их взаимодействия. Обсуждается взаимосвязь кри-
тических зависимостей свободной энергии от состава для газовой фазы и нескольких возможных
квазиравновесных фаз в системе. Говорится о преобладающем влиянии давления на свободную
энергию газовой фазы и незначительном влиянии на конденсированные фазы. Описывается
связь между критическими зависиимостями свободной энергии от состава и поведением системы при
испарении. Обсуждаются несколько факторов, которые являются важными для установления
критических зависимости свободной энергии от состава и, следовательно, вида равновесного ис-
парения. Они включают устойчивость газообразных молекул, абсолютную и относительную
устойчивость различных конденсированных фаз, состав газообразных молекул, состав конден-
sированных фаз, и свободную энергию сублимации элементов. Описываются несколько prin-
TERMODINAMICA DE LA VAPORIZACION DE MATERIALES NUCLEARES A TEMPERATURAS ELEVADAS.

Los estudios de vaporización constituyen uno de los métodos más satisfactorios, convenientes e importantes para determinar las propiedades termodinámicas y relaciones de fase de los materiales nucleares refractarios. Las mediciones se realizan en sistemas en equilibrio donde intervienen por lo menos dos fases, cuyas propiedades dependen de las proporciones y las propiedades de los componentes puros y sus parámetros de interacción. La memoria analiza las relaciones entre las curvas de energía libre-composición correspondientes a la fase gaseosa y a las varias fases condensadas posibles en un sistema. El autor señala el efecto abrumador de la presión sobre la energía libre de la fase gaseosa y el efecto insignificante de la misma sobre las fases condensadas. Describe asimismo la relación existente entre las curvas en energía libre-composición, y el comportamiento del sistema durante la vaporización. La memoria analiza los distintos factores de importancia para determinar las curvas energía libre-composición y, por consiguiente, el modo de vaporización equilibrada. Dichos factores incluyen la estabilidad de las moléculas gaseosas, las estabilidades absoluta y relativa de las diversas fases condensadas, la composición de las moléculas gaseosas, la composición de las fases condensadas, y las energías libres de la sublimación de los elementos. El autor describe algunos principios vinculados a los procesos de vaporización congruente y de espectrometría de masas.

1. INTRODUCTION

In the previous Symposium on Thermodynamics of Nuclear Materials held in May, 1962, some general principles of vaporization processes were discussed [1]. The steps in a vaporization study, pressure-composition diagrams, and the writing of net reactions were also described. Some of these topics have been considered more recently in greater detail [2]. Kubaschewski [3] has emphasized the importance of thermodynamic properties in determining phase diagrams. He has pointed out the close relationship between the free-energy diagram and the phase diagram, and has illustrated their mutual interconversion.

Thermodynamic properties of substances determine equilibrium vaporization properties just as they determine fusion phenomena. It is customary in the present decade to proceed in the opposite direction, that is, to deduce from vaporization studies thermodynamic properties of gaseous substances and occasionally of condensed substances. In fact, the importance of vaporization studies arises in part from the fact that they are one of the best and most convenient ways of obtaining thermodynamic properties and phase relationships of refractory nuclear materials.

One purpose of the present report is to show the connection between the free energy-composition diagram and the pressure-composition diagram and to discuss their relationships to the vaporization behaviour of binary chemical systems. The principal difference between this discussion and that of Kubaschewski lies in the extent to which the pressure influences the free energy of a phase. In the fusion case, the free energies of the phases are relatively uninfluenced by the pressure, but in the vaporization case the free energy of the gas phase is determined to an overwhelming extent by the pressure. Remarks will also be made relating to the factors that influence equilibrium vaporization phenomena, congruent vaporization, the writing of chemical equations, and mass spectrometry.
2. FREE ENERGY-COMPOSITION DIAGRAMS AND PRESSURE-COMPOSITION DIAGRAMS

A free energy-composition diagram for a two-component system A-B is a constant-temperature, constant-pressure graph in which the free energy of formation of each phase per total gram atom is plotted as a function of the composition of that phase. Such diagrams have been exploited effectively by Darken and Gurrey [4], as well as by Kubaschewski [3], and are now being collected by Hultgren, Orr, Anderson and Kelley [5]. A pressure-composition diagram, like the free energy-composition diagram, is drawn for a constant temperature and is a plot of the total pressure as a function of the composition. It is a phase diagram. It has the appearance of an inverted temperature-composition diagram. This diagram is the most convenient way of summarizing information about vaporization reactions.

Several such diagrams relating to nuclear materials have been published. Diagrams for the uranium-oxygen system have been presented [1, 6, 7], and a partial one appears in the paper by Ackermann and Thorn [8] in this symposium. Alcock, Eick, Rauh and Thorn [9] have presented one for the uranium-carbon system. Resulting from the work of Cater [10-12] is one for the uranium-sulphur system.

Figure 1 shows a schematic free energy-composition diagram for an ideal solution at a temperature of 2000° K. The composition variable is the atom fraction of component B. The upper curve is the entropy of formation

![Free energy-composition diagram and entropy-composition diagram for ideal solution.](image)

for one total gram atom of an ideal solid, liquid, or gaseous solution from its constituent elements in the same state of aggregation. The lower curve shows the free energy of formation per total gram atom of the same solution from the elements. Figure 2 shows $\Delta S$, $\Delta H$, and $\Delta G$ for the formation of
endothermic regular solutions, and Fig. 3 shows the same quantities for exothermic solutions. The dashed curve gives the free energy of the ideal solution.

**FIG. 2.** Free energy-composition, enthalpy-composition, and entropy-composition diagram for endothermic regular solutions.

**FIG. 3.** Free energy-composition, enthalpy-composition, and entropy-composition diagram for exothermic solutions.

Figure 4 shows the free energy of formation of an ideal solid solution from the solid elements and the free energy of formation of one gram atom of an ideal gaseous solution containing no intermediate compound. The gaseous solution has a total pressure of one atmosphere. The reference state for the elements both for the solid solution and for the gaseous solution are the same, namely pure solid elements. The free energy of the gas phase is higher than the free energy of the condensed phase because the temperature is below the normal boiling point for the elements.
FIG. 4. Free energy-composition diagram for ideal solid solutions and ideal gaseous solutions at a total pressure of one atmosphere. The reference states are pure solid elements for the gaseous solutions as well as for the solid solutions.

As the pressure is lowered, relatively little happens to the free energy of formation of the solid or liquid phase, but the free energy of formation of the gas phase diminishes rapidly. In Fig. 5 we show the free energies of formation of the solid phase and the gas phase at the same temperature at a pressure $P_2$, between the sublimation pressures of the components. As the pressure is lowered even more to $P_1$ the gas phase free energy falls as shown in Fig. 6.

The criterion for equilibrium between phases in such a constant temperature, constant pressure system is that the partial molal free energy of each component be the same in all phases. A property of this kind of diagram is that a tangent to a curve intersects each vertical axis at the partial molal free energy of that component in the solution. Hence, a line tangent to two curves connects the partial molal free energies of the components with the compositions of the two phases in equilibrium with each other. The dashed lines in Figs. 5 and 6 are such tangents. They show that at the lower pressure in Fig. 6 both phases are richer in component B. The corresponding pressure-composition diagram for the ideal solution situation illustrated in Figs. 4-6 is shown in Fig. 7 in which the same shift in the composition of both phases with lowering pressure is revealed. The pressures for the three preceding figures are indicated in Fig. 7. If the free energies are given, the pressure-composition diagram can be calculated and, more to the point of this symposium, vice versa.

If a system forms condensed intermediate phases instead of forming continuous solutions, its behaviour may be similar to that indicated in Fig. 8.
FIG. 5. Free energy-composition diagram for ideal solid solutions and ideal gaseous solutions at a total pressure between the sublimation pressures of the elements.

The free energy range covered in this diagram is much larger than in the previous diagrams; accordingly, the gaseous free energy curve is nearly a straight line. I have exaggerated the curvature to illustrate the principles.
FIG. 7. Pressure-composition diagram for ideal solid solutions and ideal gaseous solutions.

FIG. 8. Schematic free energy-composition diagram for intermediate solid phase formation and ideal gaseous solutions at a total pressure between the sublimation pressures for the elements.
The curves at both sides represent the terminal solid solutions and the curve near the bottom represents the free energy of an intermediate phase which is designated AB. If the pressure is sufficiently higher than that for which Fig. 8 is drawn, only condensed phases can exist in the system. The pressure shown in Fig. 8 is less than the sublimation pressure of the component A, but above that for component B. If the system contains pure A, minimum free energy is achieved if only gas is present. On the other hand, in a system containing pure B, the pressure is too high to allow any vapour to be present. A common tangent to indicate a two-phase region has been drawn between the vapour curve and the curve for AB. The vapour is nearly pure A, and AB is slightly A-rich. The other side shows equilibrium between the condensed, nearly pure B phase and the slightly B-rich intermediate phase AB. In the minuscule portion at the left of the diagram, only vapour is present. At the far right side of the diagram, only solid B solution is present.

Figure 9 shows the same system at lower pressure. Now the two-phase regions on both sides of AB involve the gas phase. Figure 10 shows the free energy curves for the lowest pressures at which solids can exist. The two-phase regions on both sides of the phase AB are reduced to a single common point occurring at the composition for which the intermediate phase vaporizes congruently. The pressure-composition diagram corresponding to the free energy-composition diagrams given in Figs. 8-10 is shown in Fig. 11.

FIG. 9. Schematic free energy-composition diagram for intermediate solid phase formation and ideal gaseous solutions at a total pressure less than that of the sublimation pressures of the elements.
In Figs. 12-14 we show free energy curves for the condensed and gaseous phases in a system containing the same condensed phases for the preceding drawings, but from components of greatly different volatilities. As the
pressure is lowered the free energy curve for the gas phase becomes lower than that for the intermediate AB phase in such a way that the compound AB does not vaporize congruently, but rather as shown in Fig. 15. In Fig. 13 the dashed line with the smaller slope connects the gas phase and AB; the other, AB and B. At a unique pressure between that corresponding for Figs. 13 and 14, there is a common tangent to the curves for the gas, the intermediate phase AB, and the B terminal solution, and the three phases are at equilibrium with one another.

The previous diagrams applied to a system in which there is no gaseous compound and in which the elements have volatilities differing by a factor of about $2.5 \times 10^4$ for the first set and about $10^{13}$ for the second set. In many systems, intermediate gaseous compounds are important in the vapour phase. Free energy-composition diagrams of the gas phase are markedly altered, showing a very deep minimum as indicated in Fig. 16. The upper dashed curve represents the behaviour of the gas phase if no gaseous compound is present; and the solid curve, if AB (g) exists. At a slightly lower pressure a single common tangent for the gas phase and the intermediate phase is shown in Fig. 17, indicating that AB vaporizes congruently. Not shown but also following from the curves is the fact that each terminal solution tends to produce a vapour richer in the other component. The pressure-composition diagram corresponding to the free energy curves in Figs. 16 and 17 is shown in Fig. 18.
FIG. 13. Schematic free energy-composition diagram at lower pressure than for Fig. 12.

Systems in which two gaseous species are present would show more complicated curves as would those systems with more than a single condensed phase. Other types of free energy-composition diagrams are possible and could be drawn for more complicated systems which, for example, might contain several compounds.

3. FACTORS INFLUENCING EQUILIBRIUM VAPORIZATION PHENOMENA

The words mode of vaporization refer to the congruence of the processes and the variance of the system which is vaporizing. Reference to the preceding diagrams will indicate that the following factors are of greatest importance in establishing the mode of vaporization of the phases in a two-component system. These factors are arranged in approximately a decreasing order of importance: (1) thermodynamic stabilities of the gaseous molecules, (2) thermodynamic stabilities of the condensed phases, (3) compositions of the gaseous compounds, (4) compositions of the condensed phases, (5) free energies of sublimation of the elements, and (6) curvature
The stabilities of gaseous molecules are of almost overwhelming importance. If a gaseous molecule of great stability exists, the condensed phase of that same composition will tend to vaporize congruently and with a high pressure. Moreover, a condensed phase of a different composition will tend to vaporize incongruently to give a gas of nearly the composition of that gaseous molecule.
FIG. 16. Schematic free energy-composition diagram for solid intermediate phase formation and for ideal gaseous solutions of an intermediate gaseous compound and the elements at a total pressure between the sublimation pressures of the elements.

FIG. 17. Schematic free energy-composition diagram showing the congruent vaporization of a solid intermediate phase producing primarily a single gaseous substance.
FIG. 18. Pressure-composition diagram for a two-component system showing the congruent vaporization of a solid intermediate phase producing primarily a single gaseous substance.

The next most important factor in influencing equilibrium vaporization phenomena is that of the thermodynamic stabilities of the condensed phases. We may consider the hypothetical case of a solid intermediate phase whose stability can be altered. As the stability of that solid compound is increased without a change in the stability of the gas phase, the vapor pressure falls and the tendency for congruent vaporization to occur increases. Inasmuch as equilibrium among the gaseous constituents must also exist, the tendency to vaporize by decomposition into the elements also increases. That the compositions of the gaseous compounds and condensed phases influence their mode of vaporization has already been suggested. The differences in the volatilities of the elements themselves in the absence of gaseous molecules will, as we have seen, influence the mode of vaporization. Finally, the curvature in the free energy-composition curve for the condensed phase may add a slight effect.

4. CONGRUENT VAPORIZATION

A single-phase sample is said to be congruently vaporizing when the composition of the vapour and the composition of the solid are the same, so that prolonged vaporization causes no change in the composition of the sample. Such behaviour has been well established for several binary systems involving nuclear materials, such as the uranium-oxygen system, the uranium-sulphur system and the uranium-carbon system. The composition at which a sample vaporizes congruently may depend on the temperature and may also depend on the experiment.
In a system at high pressure, that is, in the viscous flow region, the transport of matter is governed by the pressure, and the composition of the vapour phase must be exactly that of the condensed phase for congruent vaporization to occur. If the vapour contains only a single species of the same composition as the solid, then the case is simple. If in addition to this species the gas contains decomposition or disproportionation products, the atomic ratio in the vapour must be the same as that in the condensed phase.

On the other hand, at low pressure for the Knudsen experiment, the transport of materials is not given by the pressure alone, but rather by the molecular weight as well. If the only vapour species has the same composition as that of the condensed phase, the case is again simple. But if other species are present, then the molecular weight factor, except in the coincidental case of equal molecular weights, causes the solid composition to be slightly enriched in the heavier constituent. The extent to which the composition in the crucible will be different from the composition in a high-pressure system will depend on the ease with which the composition of the condensed phase can be changed.

The Langmuir vaporization experiment provides an interesting discussion. If the vaporization coefficients for several possible species are all the same, the transport of matter is given by the same equation as for the effusion method, and the composition of the condensed phase must be the same as in the Knudsen experiment.

Thus far in the discussion, stoichiometry has not been mentioned. The composition at which congruent vaporization occurs has just been shown to depend on the particular experiment. In neither the high-pressure case nor the low-pressure case must the congruently vaporizing composition be a stoichiometric one. Notable systems in which non-stoichiometric congruent vaporization occurs are Zr-B\[13\] and U-C \[14, 15\].

It can easily be shown that in a two-component system at constant temperature and constant pressure, if two phases have the same composition, the pressure is either the maximum or the minimum. For the case of congruently vaporizing refractory nuclear materials, it is the minimum pressure case which is of importance. This minimum pressure produces an invariant system, and once a system has reached the congruently vaporizing composition it must remain at that composition as long as the temperature is held constant and no reacting species are introduced into the system. Variation of the composition from that at the minimum causes an increase in the pressure, owing to species containing relatively more of that component in which the condensed phase is rich. Hence the system tends to return to the congruently vaporizing composition.

A sample giving rise to a single vapour of the same composition will always vaporize congruently. Such a case, however, is unusual, for decomposition or disproportionation products are usually present. The partial molal free energies of vaporization of these various substances will, in general, differ from one another. The congruently vaporizing composition at one temperature will not be the congruently vaporizing composition at another. Such a behaviour is suspected in a titanium-sulphur system \[16\] and probably in numerous other systems.
As has been emphasized previously, the chemical equations representing chemical reactions must be balanced; they must reveal the phases that are present; they must realistically present the compositions of those phases; they must show the gaseous species; they must be written consistent with the phase law; and they must indicate whether the process is congruent or not. Let me anticipate the work in some of the subsequent papers by writing chemical equations for the vaporization processes.

In the paper by Ackermann and Thorn [8], the pressures given in Fig. 2 indicate that stoichiometric uranium dioxide vaporizes congruently and that the most important reaction is

\[ \text{UO}_2(s) = \text{UO}_2(g) \]  

(1)

Contributing to an extent of only about three parts per hundred is the reaction

\[ 2\text{UO}_2(s) = \text{UO}(g) + \text{UO}_3(g) \]  

(2)

which produces equal pressures of \( \text{UO}(g) \) and \( \text{UO}_3(g) \); and, finally, contributing to about two parts in ten thousand is the reaction

\[ \text{UO}_2(s) = \text{U}(g) + 2\text{O}(g) \]  

(3)

which produces equal pressures of \( \text{U}(g) \) and \( \text{O}(g) \). These equations all represent congruent vaporization processes.

When the uranium oxide is reduced to \( \text{UO}_{1.95} \), the pressure of \( \text{UO} \) becomes higher than that for any other species. The most important reaction is

\[ \text{UO}(\text{in } \text{UO}_{2-x}) = \text{UO}(g) \]  

(4)

giving a pressure of about 1.5 times that of the \( \text{UO}_2(g) \) pressure in equilibrium with stoichiometric \( \text{UO}_2(s) \), while the \( \text{UO}_2(g) \) pressure has fallen to about 0.6 of its value over stoichiometric \( \text{UO}_2(s) \). The appropriate chemical reaction for this species under these circumstances is

\[ \text{UO}_2(\text{in } \text{UO}_{2-x}) = \text{UO}_2(g) \]  

(5)

The pressure of the \( \text{UO} \) (g) and the \( \text{UO}_2(g) \) will remain fixed so long as the composition of the condensed phase is fixed. Apparently in the laboratory the hypostoichiometric sample is reached only by the pressure of a reducing agent, such as uranium metal, another active metal, or gases in the system. If the pressures given by Ackermann and Thorn [8] are correct, a hypostoichiometric sample cannot be produced from \( \text{UO}_2 \) alone, for it vaporizes congruently at the stoichiometric composition at 2000° K. A partial molal heat of vaporization sufficiently large to cause the sample to become substoichiometric at the highest temperatures should be considered.

Anticipating the report by Storms [15] on the uranium-carbon system, we note that the several species of importance are \( \text{U}(g) \), \( \text{UC}_2(g) \) and carbon.
species. For the vaporization of uranium and UC₂(g) from samples in this system we can write the equations:

In the metal region,

\[ \begin{align*}
U \text{ (in UC}_2 \text{ metal phase)} &= U(g) \\
\text{UC}_2 \text{ (in UC}_2 \text{ metal phase)} &= \text{UC}_2(g)
\end{align*} \]  

In the metal-monocarbide region,

\[ \begin{align*}
&\left( \frac{1-d}{1-d-c} \right) \text{UC}_c \text{(metal phase)} = \left( \frac{-c}{1-d-c} \right) \text{UC}_{1-d} \text{(monocarbide) + U(g)} \\
&\left( \frac{2-c}{1-d-c} \right) \text{UC}_{1-d} \text{(monocarbide) = } \left( \frac{1+d}{1-d-c} \right) \text{UC}_c \text{(metal phase) + UC}_2(g)
\end{align*} \] 

In the monocarbide region,

\[ \begin{align*}
U \text{ (in UC}_1 \delta \text{ monocarbide)} &= U(g) \\
\text{UC}_2 \text{ (in UC}_1 \delta \text{ monocarbide) = UC}_2(g)
\end{align*} \] 

In the monocarbide-dicarbide region,

\[ \begin{align*}
&\left( \frac{2-f}{1-e-f} \right) \text{UC}_1 \text{+e (monocarbide) = } \left( \frac{1+e}{1-e-f} \right) \text{UC}_2 \text{-f (dicarbide) + U(g)} \\
&\left( \frac{1-e}{1-e-f} \right) \text{UC}_2 \text{-f (dicarbide) = } \left( \frac{f}{1-e-f} \right) \text{UC}_1 \text{+e (monocarbide) + UC}_2(g)
\end{align*} \] 

In the dicarbide region,

\[ \begin{align*}
U \text{ (in UC}_2 \gamma \text{ dicarbide)} &= U(g), \\
\text{UC}_2 \text{ (in UC}_2 \gamma \text{ dicarbide) = UC}_2(g)
\end{align*} \] 

And in the dicarbide-graphite region, depending on whether the carbon-saturated dicarbide phase is hypo- or hyperstoichiometric, as either:

\[ \begin{align*}
\text{UC}_2 \text{-g (dicarbide) = (2-g) C (s) + U(g)} \\
\text{gC (s) + UC}_2 \text{-g (dicarbide) = UC}_2(g)
\end{align*} \]  

or

\[ \begin{align*}
\text{UC}_2 \text{+h (dicarbide) = (2+h) C (s) + U(g)} \\
\text{UC}_2 \text{+h (dicarbide) = UC}_2(g) + hC (s)
\end{align*} \] 

In these equations a letter subscript at the beginning of the alphabet gives the departure from stoichiometry at a phase boundary, and one at the end of
the alphabet indicates variability in composition in a single phase region. Similar equations can easily be written for the vaporization of any of the carbon species from any of these regions.

Alternatively, and perhaps to some people more pleasing, would be the set of reactions for the vaporization of uranium and $\text{UC}_2(g)$ from the various two-phase regions,

$$\begin{align*}
\text{U (in metal-monocarbide region)} &= \text{U (g)} \\
\text{UC}_2 \text{ (in metal - monocarbide region)} &= \text{UC}_2(g) \\
\text{U (in monocarbide-dicarbide region)} &= \text{U (g)} \\
\text{UC}_2 \text{ (in monocarbide-dicarbide region)} &= \text{UC}_2(g) \\
\text{U (in dicarbide-graphite region)} &= \text{U (g)} \\
\text{UC}_2 \text{ (in dicarbide-graphite region)} &= \text{UC}_2(g)
\end{align*}$$

The last way of writing these equations is more suggestive of the continuity of the partial molal free energies of vaporization over the entire system. They also do not require a knowledge of the compositions of the condensed phases in equilibrium with each other and they imply, though do not state specifically, the invariance of the system at constant temperature.

6. MASS SPECTROMETRY

At the hands of many people, the mass spectrometric technique has been used for numerous vaporization studies. Originally, it was used for identification of vapour species and for obtaining temperature coefficients of intensity times temperature products so that heats of vaporization could be obtained. It has been extended to give absolute pressure measurements through the use of silver calibration, or through a self-calibration with a combined effusion and mass spectrometric experiment. More recently, particularly in Brussels, it has been used to monitor the course of a preparative reaction and to monitor the approach to a congruently vaporizing composition by revealing the changes in the pressures of the various gaseous constituents. I hope that some additional mass spectrometric results on the uranium-oxygen and uranium-carbon systems not appearing on the printed programme will be presented in the discussion by the Brussels workers [17].

One important feature of the mass spectrometric technique is that partial molal free energies of individual species can be obtained from appropriate mass spectrometric studies.

7 CONCLUSION

We have discussed free energy-composition diagrams and have suggested that they are as useful for vaporization studies as they have been for condensed phase diagrams. The quantitative calculations would follow in a similar fashion. The relationship among free energy-composition diagrams, pressure-composition diagrams, and vaporization behaviours of binary systems have been described, and the thermodynamic properties of substances
influencing vaporization behaviour have been listed. So that the chemistry of vaporization processes will not be forgotten, chemical equations for vaporization reactions to be discussed in this session have been written. Some facts about congruent processes have been stated and the importance of mass spectrometry has been emphasized.

Vaporization studies can be useful for obtaining vapour pressures, heats of sublimation, partial molal heats of sublimation, heats of formation of condensed phases, dissociation energies of gaseous molecules, activity coefficients, phase diagrams, and new substances. Many of these uses will be illustrated in the following papers.

All give vapour pressures and heats of sublimation. Partial molal heats of vaporization are reported by Storms [15]. Heats of formation for condensed phases are given by Alcock, Cornish and Grieveson [18], Ackermann and Thorn [8] and Gebelt and Eick [19]. Dissociation energies are given by Ackermann and Thorn [8] and by Murgulescu and Marta [20]. Activities have been measured by Büchler and Stauffer [21] and by Storms [15]. Phase diagrams are given by Alcock, Cornish and Grieveson [18] and Storms [15]. Finally, new species are reported by Alcock, Cornish and Grieveson [18], Büchler and Stauffer [21], Storms [15], and Murgulescu and Marta [20].

ACKNOWLEDGEMENT

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REFERENCES

[15] STORMS, E. K., "A mass spectrometric study of the vapour pressure of U(g) and UC(g) over various compositions in the uranium-carbon system", these Proceedings 1 (1965).
KNUDSEN EFFUSION STUDIES
OF COMPOUNDS OF URANIUM AND THORIUM
WITH ELEMENTS OF GROUPS IIIb AND IVb

C.B. ALCOCK, J.B. CORNISH AND P. GRIEVESON
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, ENGLAND

Abstract — Résumé — Аннотация — Resumen

KNUDSEN EFFUSION STUDIES OF COMPOUNDS OF URANIUM AND THORIUM WITH ELEMENTS OF GROUPS IIIb AND IVb. Studies have been made of the vaporization of compounds of uranium and thorium with silicon and germanium, and of several other compounds of uranium with lead, tin, indium and gallium under equilibrium conditions. Apart from providing fundamental materials data these studies are of value in a test of the applicability of theories of the stabilities of intermetallic compounds such as those of Kubaschewski and of Mott. It is found as a result of the present measurements that Kubaschewski's theory is semi-quantitatively correct, but there arise a number of difficulties in the simple form of this theory which are given further consideration.

The new phases for which data are reported here are UIn₃, UGa, UGa₂ and UGa₃ together with ThSi₂, Th₃Si₅, Th₃Si, Th₃Si₄ and ThGe₂, ThGe, Th₃Ge, Th₃Ge₂ and Th₃Ge. The relative stabilities of the uranium and thorium compounds are also explicable in terms of Kubaschewski's theory. New measurements have been made of the vapour pressures of gallium and indium metals and the results are different in detail from the literature data. No evidence of volatile oxides could be found which would vitiate the results. In making these measurements, the values obtained by the Knudsen technique were combined with those from transportation measurements.

ETUDE DE COMPOSÉS DE L'URANIUM ET DU THORIUM AVEC DES ELEMENTS DES GROUPES IIIb ET IVb, PAR LA MÉTHODE D'EFFUSION DE KNUDSEN. On a étudié la vaporisation de composés de l'uranium et du thorium avec le silicium et le germanium, et de divers autres composés de l'uranium avec du plomb, de l'étain, de l'indium et du gallium dans des conditions d'équilibre. Indépendamment des données fondamentales sur les matériaux qu'elles permettent d'obtenir, ces études ont aussi de l'intérêt comme preuve de l'applicabilité des théories de la stabilité des composés intermétalliques, telles que celle de Koubachewski et celle de Mott. On peut conclure des mesures faites par les auteurs que la théorie de Koubachewski est correcte du point de vue semi-quantitatif; toutefois, la forme simple de cette théorie donne lieu à des difficultés, que le mémoire étudie plus à fond.

Les nouvelles phases pour lesquelles le mémoire apporte des renseignements sont les suivantes: UIn₃, UGa, UGa₂ et UGa₃; ThSi₂, Th₃Si₅, Th₃Si, Th₃Si₄; ThGe₂, ThGe, Th₃Ge, Th₃Ge₂ et Th₃Ge. Les stabilités relatives des composés de l'uranium et du thorium peuvent également s'expliquer en fonction de la théorie de Koubachewski. Il a été procédé à de nouvelles mesures des tensions de vapeur du gallium et de l'indium métalliques; dans les détails, les résultats diffèrent des données déjà publiées. Il n'a pas été possible de prouver la présence d'oxydes volatiles qui pourraient vicier les résultats. En effectuant les mesures, les auteurs ont combiné les valeurs obtenues par la méthode de Knudsen avec celles provenant des mesures de transport.

ИССЛЕДОВАНИЯ СОЕДИНЕНИЙ УРАНА И ТОРИЯ С ЭЛЕМЕНТАМИ ГРУПП IIIb И IVb МЕТОДОМ ЭФФУЗИИ КНУДСЕНА. Проведены исследования явления выпаривания соединений урана и тория с кремнием и германием и некоторых других соединений урана со свинцом, оловом, индием и галлием в условиях равновесия. Кроме получения данных относительно основных материалов, эти исследования имеют значение при проверке применимости теорий устойчивости межметаллических соединений, например теорий Кубашевского и Мотта. В результате этих измерений установлено, что теория Кубашевского в полуколичественном отношении является правильной, но это порождает ряд трудностей при простой форме этой теории, которые изучаются.

Новыми фазами, данные о которых приводятся здесь, являются UIn, UGa, UGa₂ и UGa₃ вместе с ThSi₂, Th₃Si₅, Th₃Si, Th₃Si₄ и ThGe₂, ThGe, Th₃Ge, Th₃Ge₂ и Th₃Ge. Относитель-
1. INTRODUCTION

1.1. General

Uranium and thorium form a number of intermetallic compounds with the elements of Groups IIIb and IVb. Amongst these compounds are the isostructural compounds of the general formula UX₃. It would seem interesting to compare the stabilities of these compounds with one another and use them to test some theoretical models and predictions. The unique aspect of the UX₃ compounds, which have the Cu₃Au, Pm3m structure, is that they are formed between uranium and the elements of both Groups IIIb and IVb. Thus a constancy of electron/atom ratio cannot be important to their formation.

The silicides of uranium and thorium which have the same stoichiometry also have the same crystal structures [1] and thus a comparison of their stabilities would indicate the effect of the nuclear metal on the stability of the compounds. It is interesting to discover, as will be shown later, that there is a general pattern of a higher stability of the thorium compounds than the comparable uranium ones.

1.2. The use of the Knudsen effusion technique

In a previous study [2] the free energies of formation of the compounds of uranium with Group IVb elements were obtained by the measurement of the vapour pressures of the constituents. The experimental techniques used in the present study were similar to those used in the previous work and, in the case of the uranium-indium and uranium-gallium systems a simple measurement of total weight loss in a Knudsen experiment was found to suffice for determining the free energies of formation of the compounds.
This is because these elements have much higher vapour pressures than uranium metal.

The thorium-germanium system was also one in which simple weight loss measurements could be used because it was possible to equate the weight loss to the pressure of germanium, even over the mixture of solid thorium and the lowest germanide Th₃Ge. The thorium-silicon system has a lower vapour pressure at the thorium-rich end and here it was necessary to work at higher temperatures, above the eutectic, and determine both the silicon and thorium activities in the binary thorium-rich liquid in equilibrium with Th₃Si₂. The condenser and chemical analysis technique was used for this as in the previous uranium-silicon study, Ref. [2].

The only additional technique which was used was a modification of a transportation apparatus [3] for the establishment of the mono-atomicity of gallium and indium vapours. The modification was necessary to allow withdrawal of samples from the hot zone of the furnace to cool in an inert atmosphere before washing in air. The apparatus is shown in Fig. 1.

![Fig. 1. Modified transportation apparatus.](image)

A long glass tube was connected to the furnace tube by means of ground glass joints. The socket of a smaller ground glass joint was let into the glass tube. The cone of the smaller ground glass joint was attached to the cool end of the reaction tube. Thus when the smaller glass joint was closed, the carrier gas was separated from the flushing gas and directed through the reaction tube by gas ports let into the reaction tube behind the cone.

Behind the gas ports, a steel rod was attached to the reaction tube. Two O-ring seals were used at the end of the glass tube. One was used to join the end of the glass tube to the other seal which allowed the steel rod to be moved in and out. Thus samples could be drawn out of the hot zone
to rest between the cooling coils, but still in an inert atmosphere. The sample could then be allowed to cool in this position and an hour was usually allowed for this procedure.

Measurements were made and the results were interpreted in the manner described by Alcock and Hooper [3].

Materials

Calcium-reduced uranium powder and electrolytic thorium were supplied by the Metallurgy Division, AERE, Harwell. Johnson and Matthey, London, provided spectrographically pure gallium, indium, silicon and germanium, which were the other materials used in this study.

1.3. Theoretical

Attempts to predict the stabilities in intermetallic ordered compounds are largely linked with the bond mechanism which is assumed to prevail in the compounds. Kubaschewski [4] takes the view that the bonds are essentially covalent, and that the heat of formation of an intermetallic compound results entirely from the increase in co-ordination which occurs when the elements combine to form the compound. For bond energies he uses the energy of vaporization divided by the number of bonds for like atoms and the arithmetic mean approximation for the bond energy between unlike atoms.

Mott [5], on the other hand, suggests that in the ordered state there is a Madelung contribution to the cohesion resulting from electron transfer between the unlike atoms. This contribution disappears in the disordered state and thus the order-disorder transformation energy can be calculated if one knows the extent of electron transfer. This, in chemical terms, is related to the degree of ionicity of the bonds in the compounds, and Johnson and Feder [6] showed that, using the electronegativity concept of Pauling, their results for uranium compounds could be correlated.

2. RESULTS FOR THE URANIUM SYSTEMS

2.1. General

In order to facilitate the lay-out of results and the discussion, the results for the uranium systems alone will be given first and then these will be discussed. The results for the thorium systems will be given after this together with the relevant comparative discussion with uranium silicides and germanides.

2.2. Uranium-indium and uranium-gallium

In the absence of satisfactory literature data, the vapour pressures of these Group IIIb elements were first determined.
Indium

Knudsen effusion and gas transportation measurements of liquid indium gave results which showed good agreement and these are shown in Table I. The equation for the vapour pressure deduced from these measurements is:

\[ \log_{10} p \text{(atm.)} = 6.08 - \frac{13120}{T} \]

**TABLE I(a)**

RESULTS FOR THE VAPOUR PRESSURE OF PURE INDIUM OBTAINED USING THE KNUDSEN EFFUSION METHOD

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Orifice area (cm²)</th>
<th>Weight loss (mg)</th>
<th>Time (sec)</th>
<th>Vapour pressure (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>907</td>
<td></td>
<td>6.15</td>
<td>19500</td>
<td>9.47 \times 10^{-6}</td>
</tr>
<tr>
<td>930</td>
<td></td>
<td>1.57</td>
<td>3300</td>
<td>1.44 \times 10^{-5}</td>
</tr>
<tr>
<td>947</td>
<td></td>
<td>2.88</td>
<td>4200</td>
<td>2.10 \times 10^{-5}</td>
</tr>
<tr>
<td>965</td>
<td>2.39 \times 10^{-3}</td>
<td>3.43</td>
<td>3480</td>
<td>3.06 \times 10^{-5}</td>
</tr>
<tr>
<td>987</td>
<td></td>
<td>5.39</td>
<td>3600</td>
<td>4.68 \times 10^{-5}</td>
</tr>
<tr>
<td>1009</td>
<td></td>
<td>2.34</td>
<td>1140</td>
<td>6.48 \times 10^{-5}</td>
</tr>
<tr>
<td>1028</td>
<td></td>
<td>3.52</td>
<td>1200</td>
<td>9.32 \times 10^{-5}</td>
</tr>
</tbody>
</table>

Gallium

Knudsen effusion and gas transportation measurements of liquid gallium showed very good agreement with the results of Speiser and Johnston [7] and are shown in Table II.

\[ \log_{10} p \text{(atm.)} = 5.45 - \frac{14040}{T} \]

In all these measurements it was found that the metals gallium and indium did not wet the beryllia crucible and no trace of reaction was apparent.

2.3. Uranium-indium

This was the simpler of the two systems and will be dealt with first. One stoichiometric compound only, UIn₃ occurs in this system, [8, 9]. The solubility of uranium in liquid indium in the temperature range of this investigation, 820-1041°C, was negligibly small [10].
### RESULTS FOR THE VAPOUR PRESSURE OF PURE INDIUM OBTAINED USING THE TRANSPORTATION METHOD

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Flow rate (cm³/min)</th>
<th>Vapour pressure (atm.)</th>
<th>Flow rate (cm³/min)</th>
<th>Vapour pressure (atm.)</th>
<th>Flow rate (cm³/min)</th>
<th>Vapour pressure (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>955°C</td>
<td>10.3</td>
<td>4.70x10⁻⁵</td>
<td>5.4</td>
<td>1.89x10⁻⁴</td>
<td>9.6</td>
<td>2.26x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>12.6</td>
<td>2.16x10⁻⁵</td>
<td>6.9</td>
<td>9.2x10⁻⁵</td>
<td>9.6</td>
<td>2.02x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>13.9</td>
<td>2.18x10⁻⁵</td>
<td>9.4</td>
<td>7.83x10⁻⁵</td>
<td>12.5</td>
<td>2.01x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>14.5</td>
<td>2.21x10⁻⁵</td>
<td>11.2</td>
<td>5.99x10⁻⁵</td>
<td>13.2</td>
<td>2.01x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>15.9</td>
<td>2.22x10⁻⁵</td>
<td>11.9</td>
<td>6.31x10⁻⁵</td>
<td>15.7</td>
<td>2.01x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>17.4</td>
<td>2.30x10⁻⁵</td>
<td>12.1</td>
<td>6.44x10⁻⁵</td>
<td>15.9</td>
<td>2.02x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>19.5</td>
<td>2.22x10⁻⁵</td>
<td>12.4</td>
<td>6.45x10⁻⁵</td>
<td>16.0</td>
<td>2.01x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>20.4</td>
<td>2.05x10⁻⁵</td>
<td>14.0</td>
<td>5.97x10⁻⁵</td>
<td>17.0</td>
<td>2.04x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>14.8</td>
<td>6.06x10⁻⁵</td>
<td>17.2</td>
<td>2.01x10⁻⁴</td>
<td>15.7</td>
<td>2.13x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>16.8</td>
<td>5.90x10⁻⁵</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.3</td>
<td>6.44x10⁻⁵</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.4</td>
<td>6.26x10⁻⁵</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.5</td>
<td>6.08x10⁻⁵</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.3</td>
<td>2.81x10⁻⁵</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results for the indium pressures of the mixture U-UN₃ are shown in Fig. 2. Three complete experiments, with different proportions of the solid phases present were carried out with the orifice area of the cell being changed after each set of measurements. Since the results were not dependent on the orifice area, no problems arising from a vaporization coefficient less than unity were encountered.

From the results, the following free energy equation was calculated

\[
\frac{1}{3} \text{UN}_3(s) \rightarrow \frac{1}{3} \text{U}(\gamma) + \text{In}(g); \quad \Delta G^0 = 68300 - 32.2T \text{ cal.}
\]
TABLE II(a)

RESULTS FOR THE VAPOUR PRESSURE OF PURE GALLIUM
OBTAINED USING THE KNUDSEN EFFUSION METHOD

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Orifice area (cm²)</th>
<th>Weight loss (mg)</th>
<th>Time (sec)</th>
<th>Vapour pressure (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1008</td>
<td>0.782</td>
<td>8580</td>
<td>7.00 x 10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>1038</td>
<td>0.840</td>
<td>5460</td>
<td>1.19 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>1057</td>
<td>1.360</td>
<td>5940</td>
<td>1.79 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>1082</td>
<td>1.368</td>
<td>4140</td>
<td>2.60 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>1095</td>
<td>1.26 x 10⁻³</td>
<td>0.742</td>
<td>2100</td>
<td>2.82 x 10⁻⁵</td>
</tr>
<tr>
<td>1100</td>
<td>0.700</td>
<td>1560</td>
<td>3.59 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>1117</td>
<td>1.214</td>
<td>2235</td>
<td>4.36 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>1140</td>
<td>1.145</td>
<td>1246</td>
<td>7.45 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>1164</td>
<td>2.249</td>
<td>1833</td>
<td>1.00 x 10⁻⁴</td>
<td></td>
</tr>
</tbody>
</table>

Introducing the equation

\[ U(\gamma) \rightarrow U(\alpha); \quad \Delta G^0 = -1850 + 1.85T \text{ cal.} \]

and the equation given for the vaporization of indium, one obtains

\[ U(\alpha) + 3 \ln(\ell) \rightarrow U\ln_3(s); \quad \Delta G^0 = -23050 + 11.32T \text{ cal.} \]

2.4. Uranium-gallium

Evidence for two compounds has been reported, UGa₃ by Iandelli and Ferro [8], and Frost and Maskrey [9], and UGa₂ by Dempster [11]. In the present investigation, three compounds were found to exist: UGa₃, UGa₂ and UGa. The results obtained for the mixtures U-UGa, UGa-UGa₂ and UGa₂-UGa₃ in this system, are shown, together with the compositions, in Fig. 3. As before, variations in the orifice area showed that the vaporization coefficient was unity for the mixtures measured. Combining the results with the data for gallium vaporization and the free energy of the \( \alpha - \gamma \) transformation in solid uranium the following free energy equations were obtained.

\[ U(\alpha) + Ga(\ell) \rightarrow UGa(s); \quad \Delta G^0 = -9800 + 2.05T \text{ cal} \]
\[ U(\alpha) + 2Ga(\ell) \rightarrow UGa_2(s); \quad \Delta G^0 = -20050 + 7.45T \text{ cal} \]
\[ U(\alpha) + 3Ga(\ell) \rightarrow UGa_3(s); \quad \Delta G^0 = -27400 + 12.15T \text{ cal} \]
In no case was there any sign of reaction between the beryllia cells and their contents. After a series of measurements the alloy could always be knocked out of the crucible, and the crucible looked quite clean and white. There were slight signs of some reaction between the gaseous phase in the crucible and the tantalum lids which lost their metallic lustre. However, the orifice areas were found to remain constant within experimental error during use and this reaction was not considered to have any effect on the equilibria between the condensed phases and gaseous phases in the cells.

3. DISCUSSION OF THE URANIUM SYSTEMS

The only results for these systems with which the present work may be compared are those of Johnson and Feder [6] who used an electromotive force method to obtain uranium activities in mixtures of the $\text{UX}_3$ compounds with the appropriate Group IIIb or IVb elements. Although these workers reported their results for the free energy of formation of the compounds in
a four-term equation we prefer the simpler two-term equations suggested by Rand and Kubaschewski [12]. The equations obtained are then

\[ U(\alpha) + 3\text{In}(l) \rightarrow \text{UIn}_3(s); \quad \Delta G^0 = -26700 + 13.7T \text{ cal}; \quad (353^\circ \text{C} \leq T \leq 676^\circ \text{C}) \]

and

\[ U(\alpha) + 3\text{Ga}(l) \rightarrow \text{UGa}_3(s); \quad \Delta G^0 = -41400 + 14.5T \text{ cal}; \quad (370^\circ \text{C} \leq T \leq 740^\circ \text{C}) \]

It can be seen that the equation for the indium compound is in satisfactory agreement with the present work, but that for the gallium compound differs significantly, indicating a considerably higher stability for \( \text{UGa}_3 \)
FIG. 3. Gallium pressures in the U-Ga system.

than has been found here. Unfortunately the temperature intervals over which Johnson and Feder made their studies do not overlap with those used in the present study, and it should be pointed out that the stabilities of the UX₃ compounds obtained here are the result of Gibbs-Duhem integrations over a wide composition range, from equilibrium with pure uranium up to the UX₃ composition. The electro-chemical method should provide a more direct method for obtaining the thermodynamics of the UX₃ compound, and it is only in the gallium-uranium system where disagreement has occurred. In the corresponding studies of uranium-lead, tin and indium the agreement between results for the free energies of formation of the compounds is satisfactory. One source of error in the vapour pressure measurements
which must be considered is that the vapour species over the uranium-gallium alloys may not have been pure monatomic gallium, but a mixture of this species with volatile oxide(s) of gallium. Thus Cochran and Foster [13] consider the results of Speiser and Johnson (loc. cit) for pure gallium to be too high due to such an interaction between the metal and the quartz container used by these workers. It will be seen that the present results agree with those of Speiser and Johnson and that a beryllia container has been used. Even granting that this source of error was present, it must be remembered that the activities of gallium were obtained from the ratios of the calculated gallium pressures over the alloys to that of pure gallium, and the suboxide contribution would decrease rapidly with decreasing gallium activity if the specie were Ga_2O as suggested by Cochran and Foster. Thus the calculated gallium activities would be lower (if the presence of a volatile oxide Ga_2O was ignored when, in fact, this was important) than those calculated as the result of subtracting the oxide contribution. Thus the calculated results presented here represent a low value and cannot be brought lower, indicating greater stability for the UGa_3 compound, by considering volatile gallium oxides. Similarly a UO(g) contribution can be discarded, but this time because of the unmeasurably small value which the pressure of this specie would have at the temperatures used in this study. Clearly some further work is needed to resolve this discrepancy, but for the present we shall accept the vapour pressure results and the smaller stability of UGa_3 which they indicate.

3.1. Theory based on covalent bonding

Now to attempt a theoretical understanding of the measured stabilities of the UX_3 compounds, one fruitful starting point is the theory of Kubaschewski. It is suggested that the stability of intermetallic compounds is the result of an increase in the co-ordination of atoms on formation of the compounds from the constituent elements. There are a number of difficulties in applying this theory in the present context. Fortunately there are no problems arising from the uranium contribution since the change in co-ordination of this element must be constant in forming the series of isostructural UX_3 compounds. The co-ordination numbers of the elements in Groups IIIb and IVb are difficult to define in Kubaschewski's treatment by virtue of the complex crystal structures of the solid elements. It seems reasonable, however, to assume that the co-ordination numbers in the liquid elements will be approximately the same and it is proposed to consider formation of the compounds from solid uranium and the liquid Group IIIb and IVb elements as a basis for comparison. Following Kubaschewski's use of the heat of sublimation as a measure of bond strength times the co-ordination number in the elements, it can be seen that a correlation should now be expected between the heat of vaporization of the elements, and the heats of formation of the UX_3 compounds from α-uranium and the liquid Group IIIb or IVb element.

---

1 The agreement between the Knudsen and transportation measurements for the vapour pressure of gallium lend further confidence in the absence of volatile oxides in any major proportions.
These values, calculated from the experimental results presented in this paper and previous work [2] are shown in Table III.

Two further values may be obtained, for the UAl₃ compound and UTl₃. Using Ivanov, Tumbakov and Podolskaya's calorimetric results for the heat of formation of UAl₃ [14] and vaporization data collected by Honig [15] we obtain $\Delta H^\circ(\text{UAl}_3) = -8.2$ kcal/g-atom and a heat of evaporation of the liquid element of 71 kcal. Johnson and Feder [6] obtain $-3.4$ kcal/g-atom for $\Delta H^\circ(\text{UTl}_3)$ with a heat of evaporation of liquid thallium of 44 kcal [16].

The correlation obtained in this procedure thus seems quite satisfactory, at least semi-quantitatively. Unfortunately, similar data for other systems which could be used for comparison are too sparse.

### Table III

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\Delta H^\circ(\alpha U + 3X(3)) \rightarrow \text{UX}_3(s)$</th>
<th>$\Delta H^\circ$ evap. X(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USi₃</td>
<td>17.2</td>
<td>96</td>
</tr>
<tr>
<td>UGe₃</td>
<td>12.1</td>
<td>85</td>
</tr>
<tr>
<td>USn₃</td>
<td>7.0</td>
<td>72</td>
</tr>
<tr>
<td>UPb₃</td>
<td>4.6</td>
<td>44</td>
</tr>
<tr>
<td>UGa₃</td>
<td>6.8</td>
<td>64</td>
</tr>
<tr>
<td>UIn₃</td>
<td>5.7</td>
<td>60</td>
</tr>
</tbody>
</table>

#### 3.2. Theory based on "ionic" bonding

Mott [5] suggested that the order-disorder transformation energy in solid systems may be described in the following way. In the ordered system AB there will be some electron transfer from the A atoms to the B atoms resulting in small, but probably not integral, charges appearing on the two species which are opposite in sign. There will thus be a Madelung contribution to the cohesion of the ordered compound, the size of which will depend on the amount of charge transfer and the crystal structure of the ordered system. Now on disordering, this component of the cohesion will disappear as the A and B atoms are now randomly mixed. The change in cohesion resulting from this randomizing of these small charges will be the energy of the order-disorder transformation.

Now in the present systems order-disorder transformations do not occur, apparently, in the solid state, but the congruent melting points can be used to give an approximation to the solid state transformation. This is because, energetically, a random solid solution is seldom grossly different from the
corresponding liquid alloy of the same composition, apart from the heats of fusion. It also seems quite likely that the liquids which are formed on melting these compounds will be random mixtures of the two species.

At the melting point of the ordered compound AB(s)

\[ \Delta G_{AB}(s) = \Delta G_{AB}(f) + X_A \Delta G^f_A + X_B \Delta G^f_B \]

where \( \Delta G^f \) is the free energy of fusion of A and \( X_A \) is the mole fraction of A in the AB compound, see Fig. 4. The standard state for the solid compound is the pure solid elements and that for the liquid is the pure liquids. Hence

\[ \Delta H_{AB}(s) - T \Delta S_{AB}(s) = \Delta H_{AB}(f) - T \Delta S_{AB}(f) + X_A \Delta G^f_A + X_B \Delta G^f_B \]

FIG. 4. Free energy of mixing diagram for the A+B system showing three solid compounds. The diagram is for the melting point temperature of the AB compound. The standard states are the solid elements.

If the liquid phase is a regular solution

\[ \Delta S_{AB}(f) = -R(X_A \ln X_A + X_B \ln X_B) \]

Also if \( \Delta H_{AB} \) (disorder) is the heat of formation of the disordered AB solid phase with respect to pure solids as standard state

\[ \Delta H_{AB} \) (disorder) = \Delta H_{AB}(f) \]
Hence

\[ \Delta H_{AB}(s) - \Delta H_{AB}(\text{disorder}) = RT(X_A \ln X_A + X_B \ln X_B) + T \Delta S_{AB}(s) + (X_A \Delta G_A^f + X_B \Delta G_B^f) \]

If the order-disorder transformation has zero energy, i.e. the system has no charge transfer, the right hand side of this last equation should be zero.

The extent to which the right hand side is negative is a measure of the Madelung contribution to the cohesion of the solid compound. A positive value has no physical significance to this model of the order-disorder transformation.

Unfortunately at present the melting points of the compounds and in fact the thermodynamic properties of the liquid systems, are not very well known and a valuable test of this scheme can only be made when further data are available.

3.3. Summary

From the above considerations, the impression is gained that Kubaschewski's covalent bond model is more successful than the ionic model at the present stage of development. Neither approach can be made sufficiently quantitative for precise calculation but it would seem more profitable to attempt to develop the first model rather than the second.

4. RESULTS FOR THE THORIUM SYSTEM

4.1. Thorium-silicon

Jacobson, Freeman, Tharp and Searcy [17] prepared and identified four compounds in this system. The compounds were given the following formulae, \( \text{Th}_3\text{Si}_2 \), \( \text{ThSi} \), \( \text{Th}_2\text{Si}_3 \) and \( \text{ThSi}_2 \). The results of the more recent work by Brown and Norreys [18] indicate the compounds \( \text{Th}_3\text{Si}_5 \) and \( \text{Th}_8\text{Si}_{11} \) in place of \( \text{Th}_2\text{Si}_3 \). Insufficient composition were studied in the present work to resolve this discrepancy, and the simpler, earlier notation of Jacobson et al. will be used.

For the lowest silicon content alloy a two-phase mixture, in the experimental temperature range 1500-1560°C, was used containing 37.5 at. % silicon. Partial pressures of both components were obtained by the condenser method. It was necessary to measure the vapour pressure of pure thorium to obtain the thorium activities and the results were in close agreement with those of Darnell, McCollum and Milne [19]. The vapour pressure of pure silicon has already been published [20].

From the results the following two term free energy equation was calculated.

\[ 3\text{Th}(s) + 2\text{Si}(s) \rightarrow \text{Th}_3\text{Si}_2(s); \quad \Delta G^0 = -64700 + 3.90T \text{ cal.} \]
For the univariant systems Th\(_3\)Si\(_2\) - ThSi, ThSi - Th\(_3\)Si\(_5\) and Th\(_3\)Si\(_5\) - ThSi\(_2\) only silicon vapour pressures were obtained, and the results lead to the following free energy equations.

\[
\begin{align*}
\text{Th}(s) + \text{Si}(s) & \rightarrow \text{ThSi(s)}; \quad \Delta G^0 = -29200 + 1.21T \text{ cal.} \\
3\text{Th}(s) + 5\text{Si}(s) & \rightarrow \text{Th}_3\text{Si}_5(s); \quad \Delta G^0 = -110700 + 2.88T \text{ cal.} \\
\text{Th}(s) + 2\text{Si}(s) & \rightarrow \text{ThSi}_2(s); \quad \Delta G^0 = -39500 + 0.58T \text{ cal.}
\end{align*}
\]

To complete the free energy of formation curve the activities of silicon in the two phase ThSi\(_2\) + liquid Si were obtained from an alloy of 73 at.\% Si at 1500, 1523 and 1560°C.

The silicon pressures over the solid univariant systems are shown in Fig. 5 and the activities in the liquid-solid systems are shown in Table IV.

![Silicon pressures in the Th-Si system.](image)

**Silicon content**

- ▼ 66 at.\%
- ○ 61 at.\%
- ■ 49 at.\%
- □ 64 at.\%
- △ 56 at.\%
- ▽ 46 at.\%
- ○ 42 at.\%

4.2. Thorium-germanium

The existence of six thorium germanides was reported by Tharp, Searcy and Nowotny [21]. The compounds were identified as having the formulae Th\(_3\)Ge, Th\(_3\)Ge\(_2\), ThGe, Th\(_2\)Ge\(_3\), ThGe\(_2\) and ThGe\(_3\). Brown and Norreys concluded from their study of the system [22] that the phases were Th\(_3\)Ge, Th\(_3\)Ge\(_2\), ThGe, Th\(_3\)Ge\(_2\), ThGe\(_1\).\(_6\) and Th\(_0\).\(_6\)Ge\(_2\). Again, the present thermodynamic measurements were not exhaustive enough to decide between the results of
TABLE IV
THORIUM AND SILICON ACTIVITIES IN Th$_3$Si$_2$/Th MIXTURES

<table>
<thead>
<tr>
<th>(°C)</th>
<th>p(Tb) (atm.)</th>
<th>p(Si) (atm.)</th>
<th>a(Th)</th>
<th>p(Si) (atm.)</th>
<th>a(Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>2.82x10$^{-11}$</td>
<td>6.97x10$^{-11}$</td>
<td>0.405</td>
<td>2.55x10$^{-9}$</td>
<td>1.81x10$^{-8}$</td>
</tr>
<tr>
<td>1527</td>
<td>4.98x10$^{-11}$</td>
<td>1.19x10$^{-10}$</td>
<td>0.420</td>
<td>4.58x10$^{-9}$</td>
<td>1.55x10$^{-2}$</td>
</tr>
<tr>
<td>1560</td>
<td>9.86x10$^{-11}$</td>
<td>2.25x10$^{-10}$</td>
<td>0.439</td>
<td>1.01x10$^{-8}$</td>
<td>2.11x10$^{-2}$</td>
</tr>
</tbody>
</table>

these two studies. As the measurements could be carried out at lower temperatures than with the corresponding silicon compounds, the simple weight loss of the Knudsen cell could be unambiguously interpreted as a germanium loss.

The following free energy equations were calculated from the results.

$$3\text{Th}(s) + \text{Ge}(s) \rightarrow \text{Th}_3\text{Ge}_2(s); \quad \Delta G^0 = -26000 + 0.80T \text{ cal}$$

$$3\text{Th}(s) + 2\text{Ge}(s) \rightarrow \text{Th}_3\text{Ge}_2(s); \quad \Delta G^0 = -47500 + 1.20T \text{ cal}$$

$$\text{Th}(s) + \text{Ge}(s) \rightarrow \text{ThGe}(s); \quad \Delta G^0 = -19400 + 0.70T \text{ cal}$$

$$3\text{Th}(s) + 5\text{Ge}(s) \rightarrow \text{Th}_3\text{Ge}_5(s); \quad \Delta G^0 = -76000 + 3.60T \text{ cal}$$

$$\text{Th}(s) + 2\text{Ge}(s) \rightarrow \text{ThGe}_2(s); \quad \Delta G^0 = -27700 + 1.14T \text{ cal}$$

$$\text{Th}(s) + 3\text{Ge}(s) \rightarrow \text{ThGe}_3(s); \quad \Delta G^0 = -33600 + 2.44T \text{ cal}$$

The germanium pressures of the univariant systems are shown in Fig. 6. It should be noted that the results given above for the compound ThGe$_2$ would, according to Brown and Norreys, relate to the liquid in equilibrium with Th$_{0.9}$Ge$_2$. This in no way affects the thermodynamic results given above for the other compounds. It should also be noted that we have used the formulae "Th$_3$Ge$_5$" which corresponds to the "Th$_2$Ge$_3$" of Tharp, Searcy and Nowotny and "ThGe$_{1.6}$" + "ThGe$_{0.9}$Ge$_2$" of Brown and Norreys.

5. DISCUSSION OF THE THORIUM SYSTEMS

The results given above have been used to construct the two free energy of formation diagrams shown in Figs. 7 and 8. These show a comparison of the results for the silicides at 1700°K and the germanides at 1300°K. In both cases it is clear that the thorium systems are considerably more stable than the uranium systems, by about 3 to 4 kcal/g-atom at the equimolar compositions. Also it is interesting to note that the shapes of these curves,
which indicate the relative stabilities of the compounds in any one system, are very similar. This indicates that the relationship between crystal structure, or co-ordination numbers, and cohesion, which is directly suggested in Kubaschewski's theory, describes the similarity of the general shape of these curves well. Another aspect of this theory which at least qualitatively is correct, is that the thorium compounds are the more stable. This should be related to the larger heat of sublimation of thorium than uranium.

Following this line of thought it should then follow that all thorium compounds are more stable than their isostructural uranium counterparts. Since energies of transformation of compounds from one crystal structure to another are usually small it is probably generally true that all thorium compounds are more stable than their uranium counterparts of the same stoichiometry.

5.1. Melting points of the compounds

From the relatively complete phase diagrams for these four systems it can be seen that, together with the greater stabilities of the thorium compounds we also find higher melting points for these than for the corresponding uranium compounds. Thus U$_3$Si$_2$ melts at 1660°C [23], Th$_3$Si$_2$ at 1850°C [18].
FIG. 7. Integral free energies of mixing per g-at. for the uranium-silicon and thorium-silicon systems at 1700°C.

$\text{U}_5\text{Ge}_3$ melts at 1670°C [24] and $\text{Th}_3\text{Ge}_2$, which is the nearest approximation, to $\text{U}_5\text{Ge}_3$, melts at 1800°C. Thus the old empirical rule that the more stable compounds have the higher melting points is borne out in these systems.

ACKNOWLEDGEMENTS

The authors wish to thank the U.K.A.E.A. for the financial support which has made this work possible.
FIG. 8. Integral free energies of mixing per g-at. for the uranium-germanium and thorium-germanium systems at 1300°K.

REFERENCES

Abstract — Résumé — Аннотация — Resumen

THE VAPOUR PRESSURE OF PLUTONIUM. The vapour pressure of liquid plutonium has been determined over the temperature range 1100 to 1800° К by the Knudsen effusion method. The least-squares equation which fits the data is \( \log_{10} p(\text{atm}) = -17\,420/T(\text{°K}) + 4.913 \). The standard deviation corresponds to about ±10% in the pressures calculated from this equation. The heat of vaporization computed from the temperature dependence of the experimental data is \( \Delta H_{98} = 82.3 \text{ kcal/g-at} \). The heat computed by combining independent entropy and heat capacity data with the present measurements is \( \Delta H_{98} = 82.1 \text{ kcal/g-at} \). Effects of oxygen upon the volatility of liquid plutonium were sought by comparing the vapour pressures observed with the liquid in contact with tantalum, tantalum carbide, magnesia, and plutonium sesquioxide. No differences were found. In addition, the vapour pressure was measured with different degrees of vacuum in the system. No effect was found here either, except that in very poor vacuums a surface film of oxide apparently formed and reduced the volatility by about a factor of 2.

LA TENSION DE VAPEUR DU PLUTONIUM. L'auteur a déterminé la tension de vapeur du plutonium liquide pour des températures de 1100 à 1800° К en appliquant la méthode d'effusion de Knudsen. L'équation aux moindres carrés qui cadre avec les données ainsi obtenues s'énonce comme suit: \( \log_{10} p(\text{atm}) = -17\,420/T(\text{°K}) + 4.913 \). L'écart type est de l'ordre de ±10% pour les tensions déterminées à l'aide de cette équation. En se fondant sur la relation entre la température et les données expérimentales, on obtient une chaleur de vaporisation \( \Delta H_{98} = 82.3 \text{ kcal/at.-g} \). En combinant les données relatives à l'entropie indépendante et à la capacité thermique avec les résultats des mesures actuelles, on obtient pour cette chaleur une valeur de 82.1 kcal/at.-g. L'auteur a essayé de déterminer si l'oxygène avait une influence sur la volatilité du plutonium liquide, en comparant les tensions de vapeur observées pour le liquide en contact avec le tantale, le carbure de tantale, la magnésie et le sesquioxyde de plutonium. Il n'a constaté aucun effet. Il a également mesuré la tension de vapeur en faisant varier le degré de vide dans le système, sans plus de succès, si ce n'est qu'il semblait se former, en présence d'un vide très imparfait, une mince pellicule d'oxyde qui diminuait la volatilité d'un facteur de 2 environ.

ДАВЛЕНИЕ ПАРОВ ПЛУТОНИЯ. Давление паров жидкого плутония было определено в температурном интервале 1 100 — 1 800°К с помощью эффузионного метода Кнудсена. Уравнением наименьших квадратов, отвечающим этим данным, является \( \log_{10} p(\text{атм}) = -17\,420/T(\text{°К}) + 4.913 \). При давлениях, рассчитанных по этому уравнению, стандартное отклонение соответствует примерно ±10%. Теплотой испарения, рассчитанной по температурной зависимости экспериментальных данных, является \( \Delta H_{98} = 82.3 \text{ ккал/г-атом} \). Типичная скорость испарения, рассчитанная по температурной зависимости экспериментальных данных, составляет \( \Delta H_{98} = 82.1 \text{ ккал/г-атом} \). Влияние кислорода на летучесть жидкого плутония было определено путем сравнения давлений паров, наблюдаемых для этой жидкости в контакте с танталом, карбидом тантала, окисью магния и полуторной окисью плутония. Никакой разницы обнаружено не было. Кроме того, давление паров измерялось при различных степенях вакуума в системе. При этом также не было обнаружено никакого эффекта, за исключением того, что при очень слабом вакууме явно образуется поверхностная пленка окиси, и летучесть уменьшается примерно в два раза.

LA TENSION DE VAPOR DEL PLUTONIO. La tensión de vapor del plutonio líquido se determinó en un intervalo de temperaturas de 1100 a 1800° K por el método de efusión de Knudsen. La fórmula de cuadrados mínimos que se ajusta a los datos es \( \log_{10} p(\text{atm}) = -17\,420/T(\text{°K}) + 4.913 \). La desviación tipo es de ±10% aproximadamente para las presiones calculadas a partir de esta ecuación. El calor de vaporización determinado basándose en la variación de los datos experimentales en función de la temperatura es \( \Delta H_{98} = 82,3 \text{ kcal/at.-g} \). El calor calculado combinando los datos independientes relativos a la entropía y a la capacidad calorífica con los resultados de las actuales mediciones es \( \Delta H_{98} = 82,1 \text{ kcal/at.-g} \). La influencia ejercida por el oxígeno...
sobre la volatilidad del plutonio líquido se determinó comparando las tensiones de vapor observadas cuando el líquido estaba en contacto con tántalo, carburo de tántalo, óxido de magnesio, y sesquióxido de plutonio. No se halló ninguna diferencia. Además, la tensión de vapor se midió a diferentes grados de vacío en el sistema. No se observó efecto alguno, salvo que en un vacío muy deficiente parece formarse una película superficial de óxido, reduciéndose la volatilidad a la mitad del valor original.

1. INTRODUCTION

The vapour pressure of elemental plutonium has been determined only once previously, by Phipps et al. [1] in 1944. Phipps' data appeared to be of good quality and gave reasonable values but it was felt desirable to repeat the measurements with purer metal and with attention paid to the possible influences of oxygen on the observed vapour pressure. Rauh and Thorn [2] have found a lowering of the vapour pressure of metallic uranium, apparently caused by oxygen picked up from the vacuum system. Darnell and McCollum [3] have shown the vapour pressure of thorium to be enhanced by the presence of ThO2. The exact explanation of the effect with uranium is currently a somewhat controversial matter but, whatever the explanation, it is clearly desirable to examine as far as possible any effects of oxygen on the vapour pressure of plutonium. In addition, as knowledge of the vapour pressure of an element is primary to all of the high temperature chemistry of that element, at least two independent measurements of this important property should exist.

With these considerations in mind, a new determination of the vapour pressure of plutonium was made. It turned out that no effect attributable to oxygen other than the formation of an oxide skin at very poor vacuums could be found, and that the vapour pressure observed agreed with Phipps' within 2%, more closely than could be reasonably expected from the accuracy of Knudsen vapour pressure measurements in general. The two independent measurements thus provide vapour pressure data in which we believe some confidence can be placed, particularly as there is excellent agreement with independent thermal and spectroscopic data for the condensed and gaseous phases involved.

2. EXPERIMENTAL

2.1. Apparatus

The apparatus used has been described previously [4]. Briefly, the general arrangement was that the Knudsen cell, heated by a close fitting tantalum strip heater through which electric current passed, was supported by a tungsten stem at the centre of a water-cooled shield which surrounded the cell. A collimator hole in the top of the shield was concentric with the cell orifice. The copper target which collected the part of the vapour beam coming out of the collimator was in the form of an annular ring with cooling water on the back side. As many as ten exposures could be made, each on a different sector of the ring, by rotating the target assembly through a vacuum seal. A tantalum shutter between the collimator and target allowed
precise timing of exposures. The above parts were located inside a brass can which was evacuated by a pumping train consisting of a liquid-nitrogen-filled cold trap, a 300 l/s oil diffusion pump using DC-704 silicone oil, and a mechanical pump. A VG1A ionization gauge located close to the cell was used to measure background pressure in the system. A variable leak located between the brass can and the cold trap was used to modify the background pressure as desired by leaking dried air into the system. An ultimate vacuum of $3 \times 10^{-7}$ torr was attainable with the heater and cell at room temperature. Usually, with the cell hot, the vacuum was about $1 \times 10^{-6}$ torr; however, on some occasions, it was possible to make exposures with a vacuum of $5 \times 10^{-7}$ torr.

2.2. Effusion cells and heater

The heater was made from tantalum sheet as described previously [4]. The top half was double thickness to provide more heat at the top end of the cell. Tests with a dummy cell showed that the lid was about 10°C hotter than the cavity. No difference could be detected between the cavity temperature and the temperature read in the sight hole at the bottom of the cell. With this arrangement, no condensation of vapour on the lid or at the orifice was ever observed.

The cylindrical effusion cells were made of tantalum and were 0.375 in diam. by 0.750 in long. The orifice was machined to have a sharp edge with a 15° included angle. The lid was pressed onto a knife-edge seat in the cell body so as to deform the knife edge and make a gas-tight seal. The orifice area was determined by photographing the orifice together with a 0.01 mm scale at 100X magnification, then measuring the orifice diameter on the photograph with the enlarged scale. Cells were assembled, degassed in place at about 2000°C, and then the charge, consisting of short pieces of wire, was added through the orifice.

The cell cavity was 0.250 in in diameter and 0.500 in deep. In some of the measurements the charge was contained in a TaC, ThO$_2$ or MgO cup fitting closely into the cell cavity and having an inside diameter of 0.200 in. A similar cup was formed of plutonium oxide by tamping PuO$_2$ powder into the cell, then firing the assembly in vacuum. The vacuum firing in the tantalum cell partially reduced the PuO$_2$. Heating the cell with the liquid plutonium charge in place completed the reduction of the oxide, which was seen by X-ray analysis to be all hexagonal Pu$_2$O$_3$ after the vapour pressure measurements had been completed. In one series of exposures no cup was used; the plutonium was contained directly in the tantalum cell. This cell had only a short useful lifetime as liquid plutonium wetted the tantalum, climbed the cell walls and crept out of the orifice. The liquid also penetrated the grain boundaries of the tantalum. The cell with a tantalum carbide cup was also short-lived, as TaC is easily wetted by plutonium.

2.3. Temperature measurement

Temperature was measured with a calibrated disappearing-filament optical pyrometer sighted into a 0.070 in diameter threaded hole in the side of the cell. The hole was 0.125 in below the bottom of the cavity. The
observed temperature was corrected for absorption of the fused silica window in the can. It is estimated that the absolute accuracy of temperature determination is ±5°C. Reproducibility, determined largely by ability to read the pyrometer scale, was ±2°C.

Manual temperature control was satisfactory. The power supply, consisting of a step-down transformer fed by a variable autotransformer operating directly off the 440 volt line, maintained the cell temperature constant within 2°C even during two-hour exposures. Most of the time, no temperature drift was detectable during an exposure.

2.4. Determination of target deposits

The amount of plutonium deposited on each target sector during an exposure was determined by counting the alpha emission from the sector. A count of the total alpha activity was made with a 51% geometry proportional alpha counter calibrated for the copper sectors. It was also necessary to determine the fraction of the alpha count which came from plutonium, as the plutonium used contained a small amount of americium-241. The high volatility and the high specific activity of the $^{241}$Am produced alpha count on the targets far out of proportion to the concentration in the charge. However, this difficulty was only encountered when the bare tantalum or tantalum carbide cells were used. The cells in which the charge was contained in an oxide cup gave at most 2 or 3 alpha per cent $^{241}$Am on the targets. Evidently the americium in the charge was absorbed by the oxide and did not volatilize. Nevertheless, every target was pulse-analysed to determine the $^{239}$Pu/$^{241}$Am ratio in the deposit. The pulse analysis was done with an Ortec gold-barrier, silicon solid-state detector and a 400-channel pulse analyser.

2.5. Metal purity

The plutonium used for the measurements was produced by the electrolytic refining process. Spectrographic analysis showed that of 25 metallic elements looked for, all but two were below the limits of detection, these being 30 ppm by weight of tungsten and 20 ppm of iron. Carbon and oxygen analyses gave 15 and 10 ppm by weight, respectively. Micrographic examination showed clean metal with virtually no impurity inclusions discernable. Radiochemical assay showed 28 ppm of $^{241}$Am at the time the metal was received. Purification by evaporation of about 10% of the total weight reduced the $^{241}$Am to 5 ppm. Thus, the impurities analysed for totalled less than 100 ppm.

2.6. Calculations

The vapour pressure in atmosphere was calculated by the usual formula:

$$ P_r = k \frac{m}{1a} \left( \frac{T}{M} \right)^{\frac{1}{2}} \left( \frac{r_2 + r_1}{r} \right) $$

where $k$ is a units constant ($3.760 \times 10^{-8}$), $m$ is the micrograms of plutonium
on a target, $t$ is exposure time in minutes, $a$ is orifice area in mm$^2$, $T$ is the absolute temperature, $M$ is the atomic weight of the effusing species (239.1 in this case), $r$ is the collimator radius, and $I$ is the orifice-to-collimator distance. No correction to the pressures was made for either internal cell geometry or the transmission of the conical orifice, as those corrections do not apply to a collimated beam determination such as the present one.

3. RESULTS

3.1. Primary data

Table I summarizes the data. The exposures are numbered as A1, A2, etc. The letter refers to series on a target during which the vacuum was not broken. The number refers to the chronological order in a series. Cup and cell dimensions are given in section 2.2. Figure 1 shows a plot of the data.

Cells 1 and 2, with no cup and a tantalum carbide cup, failed because of wetting after one heating, as described in section 2.2. Cell 3, with a magnesium oxide cup had a moderately long lifetime. However, after series M, the observed pressure began to decrease with time. The cell was opened and it was seen that all that remained of the plutonium charge was a small droplet in the centre of the oxide cup. The inner surface of the cup had been converted to hexagonal Pu$_2$O$_3$. The targets exposed with cell 3 had visible deposits of metallic magnesium in contrast to the usually invisible plutonium deposits obtained with the other cells. Although the magnesium deposits were thick enough to have a silvery colour, they did interfere with the plutonium determination by alpha counting, i.e. no degradation of the alpha energies by absorption was seen in the pulse analyses.

3.2. Effect of background pressure

To test the effect of the quality of the vacuum on the measured vapour pressure, three series of experiments were done. In the first, the sample was contained in a ThO$_2$ cup within the tantalum cell. A series of three exposures was made with increasing temperature, next the background pressure was increased by leaking dried air into system and the three exposures were repeated. Then the leak was closed, good vacuum restored, and the three exposures repeated. Table II gives the data. Although there is some scatter, no effect of background pressure can be seen.

In the second series, the sample was in a TaC cup. After some exposures at various temperatures, the temperature was held constant, a series of 6 exposures was made at low background pressure giving a constant vapour pressure, next the leak was opened and an exposure was made at high background pressure, then the leak was closed and three more exposures made at low background pressures. The pertinent data are given in the second part of Table II. Again, no effect of background pressure was seen. Any variation is within a random scatter of ±10% which is the standard deviation of all the data.
## TABLE I

Plutonium Vapor Pressure Data

<table>
<thead>
<tr>
<th>Exposure No.</th>
<th>Temperature (°K)</th>
<th>Pu collected (µg)</th>
<th>Time (min)</th>
<th>(P_{Pu}) (atm.)</th>
</tr>
</thead>
<tbody>
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<td><strong>Cell 1 - Bare Ta</strong>, Charge 0.20 g., (a = 0.526 \text{ mm}^2, l = 3.185 \text{ cm}, r = 0.676 \text{ cm})</td>
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<td></td>
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<td>0.047</td>
<td>4.36</td>
<td>4.37</td>
</tr>
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<td>16.02</td>
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<td>83.4</td>
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<td>10.00</td>
<td>4.10</td>
</tr>
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<td><strong>Cell 3 - MgO cup</strong>, charge 0.45 g., (a = 0.503 \text{ mm}^2, l = 3.119 \text{ cm}, r = 0.690 \text{ cm})</td>
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<td>12.0</td>
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<td>10.23</td>
<td>19.3</td>
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<td>9.57 (\times) (10^{-10})</td>
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<td>9.05</td>
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<td>1398</td>
<td>0.032</td>
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<td>24.8</td>
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TABLE I, continued

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<tr>
<th>Exposure No.</th>
<th>Temperature (°K)</th>
<th>Pu collected (μg)</th>
<th>Time (min)</th>
<th>P_Pu (atm.)</th>
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<tbody>
<tr>
<td>Cell 3 - MgO cup, charge 0.45 g., a = 0.503 mm², l = 3.119 cm, r = 0.690 cm</td>
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<td>60.00</td>
<td>1.91 x 10⁻¹⁰</td>
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<td>1.32</td>
<td>2.00</td>
<td>1.42 x 10⁻⁵</td>
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</table>

The third series, F, was run in the same cell with the same charge and ThO₂ cup as was used in series E. Here the temperature was held as constant as possible near 1530°K and the background pressure was varied by a factor of 500. The results are in the third part of Table II. The observed vapour pressure decreased when the background pressure was increased and did not completely recover when good vacuum was restored. Increasing the background pressure (exposure F7) a second time did not appear to affect the vapour pressure. In the poor vacuum of 5 x 10⁻⁴, the tantalum heater oxidized somewhat and changed its resistance, making it difficult to hold a constant temperature throughout the series. After this series, the cell was opened and the charge was seen to be covered with a dark oxide film. Normally the charges had bright surfaces after use.

4. INTERPRETATION AND DISCUSSION OF RESULTS

4.1. Vapour pressure

Forty-five usable measurements listed in Table I were obtained over a temperature range from 1133 to 1792°K. The least-squares fit to these points gave log p(atm.) = -17420/T + 4.913 with a standard deviation of
±0.045 in log p. The maximum deviation of any point was 0.058. This standard deviation is equivalent to ±10% in the absolute vapour pressure. The corresponding standard deviations of slope and intercept are ±100 and ±0.070, respectively.

4.2. Thermodynamics

The enthalpy and entropy of vaporization may be obtained directly from the above equation as $\Delta H_v = 79.70 \text{kcal/g-at.}$ and $\Delta S_v = 22.48 \text{cal/degC g-at.}$ These values apply over the temperature range of the measurements.

To extend the range of usefulness and also to provide a check of the reasonableness of the data, free energy functions are required for the condensed and gaseous phases involved. As these are not available per se in the literature, a discussion of their computation is included here.

Enthalpy increments and free energy functions for monatomic plutonium gas have been calculated by Feber and Herrick [5] from spectroscopic data in the literature. Values appropriate for the present calculations are listed in Table III.

Measurements of the thermal properties of solid plutonium have been made above 298°K by Kay and Loasby [6] as well as by others. Loasby [7] has measured the heat capacity between 17 and 298°K. Loasby's is the most complete set of data available, all from the same laboratory. Other measurements above 298°K are in substantial agreement with Loasby's data. How-

![Graph](image-url)
TABLE II
Effects of Background Pressure

<table>
<thead>
<tr>
<th>Exposure No.</th>
<th>T(°K)</th>
<th>Pu pressure (atm.)</th>
<th>Background pressure (torr)</th>
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<tbody>
<tr>
<td>E1</td>
<td>1451</td>
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<td>1.1 x 10^-6</td>
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<td>E2</td>
<td>1528</td>
<td>2.72 x 10^-7</td>
<td>1.3 x 10^-6</td>
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<td>E3</td>
<td>1673</td>
<td>2.72 x 10^-6</td>
<td>2.9 x 10^-6</td>
</tr>
<tr>
<td>E4</td>
<td>1446</td>
<td>7.11 x 10^-8</td>
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<td>E5</td>
<td>1528</td>
<td>2.82 x 10^-7</td>
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</tr>
<tr>
<td>E6</td>
<td>1679</td>
<td>3.12 x 10^-6</td>
<td>2.6 x 10^-5</td>
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<tr>
<td>E7</td>
<td>1448</td>
<td>8.14 x 10^-8</td>
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<td>E8</td>
<td>1524</td>
<td>2.73 x 10^-7</td>
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<tr>
<td>E9</td>
<td>1683</td>
<td>3.12 x 10^-6</td>
<td>2.5 x 10^-6</td>
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</table>

Above with ThO₂ cup in Ta cell

<table>
<thead>
<tr>
<th>Exposure No.</th>
<th>T(°K)</th>
<th>Pu pressure (atm.)</th>
<th>Background pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E6</td>
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</tr>
<tr>
<td>E7</td>
<td>1531</td>
<td>4.01 x 10^-7</td>
<td>3 x 10^-5</td>
</tr>
<tr>
<td>E8</td>
<td>1533</td>
<td>4.01 x 10^-7</td>
<td>9 x 10^-7</td>
</tr>
</tbody>
</table>

Above with TaC cup in Ta cell

<table>
<thead>
<tr>
<th>Exposure No.</th>
<th>T(°K)</th>
<th>Pu pressure (atm.)</th>
<th>Background pressure (torr)</th>
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</thead>
<tbody>
<tr>
<td>F1</td>
<td>1532</td>
<td>4.06 x 10^-7</td>
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<td>F2</td>
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<tr>
<td>F4</td>
<td>1536</td>
<td>2.43 &quot;</td>
<td>5 x 10^-4</td>
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<td>1531</td>
<td>2.55 &quot;</td>
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<tr>
<td>F8</td>
<td>1527</td>
<td>2.72 &quot;</td>
<td>3 x 10^-6</td>
</tr>
<tr>
<td>F9</td>
<td>1526</td>
<td>2.80 &quot;</td>
<td>2 x 10^-6</td>
</tr>
</tbody>
</table>

Above with ThO₂ cup in Ta cell. Same charge as run E.

ever, Loasby's high and low temperature heat capacity curves fail to match by about 8% at 298°K. An arbitrary smooth join was therefore made between the two heat capacity curves over the range 180 to 320°K. The extrapolation between 17 and 0°K was of the form \( C_p = AT^3 + \gamma T \). The enthalpy increments and free energy functions listed in Table III for solid and liquid plutonium were calculated from the smoothed curve up to 320°K. Loasby's data was used directly for temperatures between 320 and 913°K, and an estimated
for Pu(s,α) \[ H^\circ_{T=298}(s,\alpha) \] for Pu(g) \[ H^\circ_{T=298}(g) \] constant heat capacity of 8.5 cal/degC g-at., for the liquid was used for all temperatures above 913°K.

With the enthalpy increments in Table III, the Second Law heat of vaporization at 298°K may be calculated from the enthalpy of vaporization given above. The result is $\Delta H^\circ_{298} = 82.14$ kcal/g-at. The Third Law heat of vaporization at 298°K may be calculated by combining the free energy functions with the experimental pressures. The result is $\Delta H^\circ_{298} = 82.28$ kcal/g-at. The agreement between Second and Third Law heats is excellent.

We estimate the average heat capacity change for the transition from liquid to gas to be $\Delta C_p = +2$ cal/degC g-at. over a large temperature range. (The heat capacity of the gaseous plutonium atom appears to have an extraordinarily high electronic contribution as calculated from the energy level data.) Extrapolation of our data yields a normal boiling point of 3600°K and an entropy of vaporization at the boiling point of 23.0 cal/degC g-at., which agree well with the Pictet-Trouton rule.

### 4.3. Effect of oxygen

The vapour pressure determinations listed in Table I were obtained with the plutonium charge in contact with tantalum, tantalum carbide, magnesia or plutonium sesquioxide. All these points fit well on the single vapour pressure line and no possible correlation of deviations from the least-squares line with cup material is evident. We believe that any effect of more than a few percent in the vapour pressure, caused by oxygen in the charges, would have been detected. It is conceivable that the plutonium charge was saturated with oxygen in all the cells. However, the solubility of oxygen in liquid
plutonium is only 20 to 30 ppm by weight at 1500°K [8]. This is an atom fraction of 0.0005, hardly sufficient to cause appreciable lowering of vapour pressure without an incredible deviation from the usually accepted solution laws. In addition, data were obtained over a large range of temperature with no deviation from a straight line plot of log p v. 1/T. This is the behaviour expected for a simple vaporization process. If there were two vaporizing species, for example Pu(g) and PuO(g), or if the oxygen solubility were strongly temperature dependent, deviation from a straight line would be expected because it is unlikely that the various equilibrium constants involved would have the same temperature dependence.

The results of the experiments on the effect of background pressure are interpreted as showing that the observed vapour pressure of plutonium is independent of the partial pressure of oxygen in the system at reasonably low partial pressures. In the one case where the vacuum was poor enough to modify the observed vapour pressure, the effect was physical in that a continuous oxide barrier formed over the vaporizing surface and impeded vaporization.

We thus conclude that there is no significant chemical effect of oxygen on the volatility of plutonium up to about 1800°K. A physical effect, in the form of an oxide skin on the liquid metal surface, can be observed under the right conditions.

REFERENCES

THE EVAPORATION BEHAVIOUR, THERMODYNAMIC PROPERTIES AND SYSTEMATIC TRENDS OF ACTINIDE METAL-OXYGEN SYSTEMS

R.J. ACKERMANN AND R.J. THORN
ARGONNE NATIONAL LABORATORY, ILL., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

THE EVAPORATION BEHAVIOUR, THERMODYNAMIC PROPERTIES AND SYSTEMATIC TRENDS OF ACTINIDE METAL-OXYGEN SYSTEMS. Mass effusion measurements and mass spectrometric observations have been combined with existing calorimetric and recent EMF data to yield a consistent thermodynamic description of actinide metal-oxygen systems. Any meaningful description of the evaporation behaviour of a given condensed phase must include a careful specification of either the partial pressure of oxygen in the system or the composition of the condensed phase because all of the solid dioxide phases, for example, exhibit bivariant behaviour due to variation in composition. The solid stoichiometric dioxides increase in total vapour pressure in the somewhat inverted order, ThO₂, PuO₂, NpO₂, and UO₂, and in each case the gaseous dioxide is the predominant vapour species. The ease of reduction in vacuum of these phases increases with increasing atomic number giving rise to a MO₂-x phase and/or metal in the case of Th and U, and to lower oxides in the case of Np and Pu. Reduction of a given dioxide results in an increase of the total vapour pressure due to the rapid increase of the gaseous monoxide which becomes the major vapour species. This behaviour is at present most completely resolved in the case of the uranium oxygen system.

There are two significant systematic trends involving the vapour phase: (1) the gaseous dioxides (plus 4 valence states of metal) become less stable (ΔG° becomes more positive) with increasing atomic number, and (2) the gaseous monoxides (plus 2 valence states of metal) become more stable with increasing atomic number. Other correlations and comparisons of the thermodynamic properties in the solid, vapour and solvated phases of actinide metals and compounds are made with those of lanthanide metals and compounds. The trends in the former case are generally more complex as a result of the more pronounced dual nature of the actinides as transition elements with d-electrons and rare earth elements with f-electrons.

COMPORTEMENT A L’EVAPORATION, PROPRIETES THERMODYNAMIQUES ET TENDANCES SYSTEMATIQUES DES SYSTÈMES ACTINIDE METALLIQUE-OXYGÈNE. Les auteurs ont combiné les résultats de mesures d’effusion massique et les observations par spectrométrie de masse avec les résultats connus des méthodes calorimétriques et f. e. m. pour établir une description thermodynamique cohérente des systèmes actinide métallique-oxygène. Toute description acceptable du comportement à l’évaporation d’une phase condensée donnée doit comprendre la spécification précise de la pression partielle d’oxygène dans le système ou la composition de la phase condensée, car toutes les phases bioxyde solide, par exemple, sont caractérisées par un comportement bivariant dû aux variations de composition. La tension totale de vapeur des bioxydes stoïchiométriques solides augmente dans un ordre à peu près inverse, savoir ThO₂, PuO₂, NpO₂ et UO₂; dans chaque cas, l’espèce vapeur prédominante est le bioxyde gazeux. La facilité avec laquelle ces phases sont réduites sous vide croît à mesure que le numéro atomique augmente, ce qui donne lieu à une phase MO₂-x et/ou au métal dans le cas de Th et U, et à des oxides inférieurs dans le cas de Np et Pu. La réduction d’un bioxyde donné entraîne une augmentation de la tension de vapeur totale par suite de l’accroissement rapide du monoxyde gazeux, qui devient l’espèce vapeur principale. Ce comportement a pu être résolu complètement pour le cas du système uranium-oxygène.

On remarque deux tendances systématiques particulièrement significatives, qui impliquent la phase vapeur, savoir: 1° les bioxydes gazeux (valence du métal; 4°) deviennent moins stables (ΔG° acquiert une valeur positive plus élevée) à mesure que le numéro atomique augmente; 2° les monoxydes gazeux (valence du métal; 2°) deviennent plus stables à mesure que le numéro atomique augmente. Les auteurs ont comparé les propriétés thermodynamiques en phase solide, en phase vapeur et en phase solution des actinides métalliques.
et de leurs composés avec celles des lanthanides métalliques et de leurs composés, et ils ont établi de nouvelles corrélations. Dans le premier cas, on observe généralement des tendances plus complexes du fait que les actinides en tant qu'éléments de transition à électrons d ont un dualisme plus prononcé que les terres rares à électrons f.

ПОВЕДЕНИЕ ПРИ ИСПАРЕНИИ, ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА И СИСТЕМАТИКА КИСЛОРОДНЫХ СОЕДИНЕНИЙ ЭЛЕМЕНТОВ АКТИНИДНОГО РЯДА. Результаты масс-эффектных измерений и масс-спектрометрических наблюдений объединены с имеющимися калориметрическими данными и последними данными по Э.Д.С. для получения непротиворечивого термодинамического описания систем актинидный металл- кислород. Любое имеющее смысл описание поведения данной конденсированной фазы при испарении должно включать точную характеристику или парциального давления кислорода в системе, и образец конденсированной фазы, поскольку все твердые двукиси фазы, например, ведут себя бивариантно вследствие изменения состава. Твердые стехиометрические двукиси увеличивают давление паров в несколько необычном порядке (ThO₂, PuO₂, NpO₂ и UO₃), и в каждом случае газообразная двукись является преобладающим компонентом паров. Восстановление в вакууме этих фаз все более облегчается с увеличением атомного номера, приводя к образованию фазы MO₂₋ₓ, и/или металла в случае Th и U и к образованию низших окислов в случае Np и Pu. Результатом восстановления данной двукиси является повышение общего давления паров вследствие быстрого увеличения газообразной окиси, которая становится основным компонентом паров. В настоящее время это поведение наиболее полно изучено в случае системы уран-кислород.

Имеются две важные тенденции, связанные с паровой фазой: 1) газообразные двукиси (валентные состояния металла +4) становятся менее устойчивыми (ΔG° становится более положительным) с увеличением атомного номера и 2) газообразные моноокиси (валентные состояния металла +2) становятся более устойчивыми с увеличением атомного номера. Производятся другие корреляции и сравнения термодинамических свойств твердой, паровой и сольватированной фаз актинидных металлов и соединений со свойствами лантанидных металлов и соединений. Тенденции в первом случае являются, как правило, более сложными в результате более резко выраженного двойственного характера актинидов как переходных элементов с d-электронами и редкоземельных элементов с f-электронами.

ПОВЕДЕНИЕ ПРИ ИСПАРЕНИИ, ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА И ЭВАПОРАЦИЯ ДРЕМИНХ СИСТЕМАХ АКТИНДИУМ-ОКСИД ОКСИДОВ. Los autores combinaron los resultados de mediciones de efusión mívica y observaciones mediante espectrometría de masas con datos calorimétricos existentes y con valores recientes de fuerzas electromótricas para lograr una descripción termodinámica coherente de sistemas actínico metallo-oxígeno. Toda descripción aceptable del comportamiento de una determinada fase condensada en la evaporação debe especificar con sumo cuidado la presión parcial de oxígeno del sistema, o bien la composición de dicha fase condensada, dado que las fases dióxido sólido suelen caracterizarse por un comportamiento bivariante debido a las variaciones de composición. La presión total de vapor de los dióxidos estequiométricos sólidos aumenta siguiendo un orden algo invertido, a sabóber ThO₂, PuO₂, NpO₂ y UO₂, y en cada caso la especie vapor predominante es el dióxido gaseoso. La facilidad con que se reducen estas fases en el vacío aumenta a medida que crece el número átomico, dando origen a una fase MO₂₋ₓ y/o metal en el caso de Th y U, u a óxidos inferiores en el caso de Np y Pu. La reducción de un dióxido dado hace aumentar la presión total de vapor debido al rápido incremento de la proporción de monóxido gaseoso, que pasa a ser la principal especie vapor. Este comportamiento se ha podido explicar completamente para el caso del sistema uranio-oxígeno.

Se observan dos tendencias sistemáticas significativas relativas a la fase de vapor: 1) los dióxidos gaseosos (valencia del metal: 4⁺) se tornan menos estables (ΔG° se adquiere un valor positivo más elevado) a medida que aumenta el número atómico; 2) los monóxidos gaseoso (valencia del metal: 2⁺) aumentan su estabilidad a medida que crece el número átomico. Se han establecido otras correlaciones y comparaciones de las propiedades termodinámicas de los metales y compuestos actínicos, en fase sólida, de vapor y solvatada, con la de los metales y compuestos lantánidos. En el primer caso, la tendencia es generalmente más compleja, lo que se debe a la dualidad más pronunciada de los actínicos en su calidad de elementos de transición con electrones en la capa d y elementos de las tierras raras con electrones de la capa f.
INTRODUCTION

At the symposium entitled "Thermodynamics of Nuclear Materials" which was held in Vienna in May, 1962, the present authors initiated a critical review of the evaporation and thermodynamic properties of thorium, uranium and plutonium metals and oxides [1] and also a correlation of these properties in terms of the principles of chemical bonding with oxygen of the other elements in the periodic system describable by molecular orbital theory [2]. Since 1962 additional investigations of these materials as well as other actinide metals and oxides make it necessary to amplify, revise, and analyze further the evaporation behavior and thermodynamic properties derivable therefrom, and in particular, to elucidate the systematic behavior and trends in the high temperature chemistry of actinide metal compounds that are becoming apparent. As is becoming more universally recognized the measurements of vapor pressures of "compounds" are not too meaningful in a thermodynamic sense unless the composition of the condensed phase (or phases) is known or even better, controlled. Hence, the accuracy of the evaluation of thermodynamic properties of gaseous molecules in equilibrium with condensed phases requires a rather precise knowledge of the composition and partial molar quantities for both components in the phase. The rapid accumulation of high temperature properties makes it possible to begin a synthesis of the systematic behavior of vapor, solid, and aqueous solution phases in order to discover the fundamental concepts which determine the strength of bonding of actinide metals in a variety of compounds. The discovery of trends in chemical and thermodynamics properties of these materials is interestingly complicated by the dual nature of the metals in that they behave to varying extents as members of a 6-d transition series and as members of a 5-f rare-earth series. Hopefully one would prefer to study the trends in chemical bonding in the vapor phase since the environment is relatively field-free compared with aqueous solutions and solid phases and since the choice of standard states is considerably simplified. However, only the mass spectrometric technique has proved successful in the study of
vapor phase equilibria, and in this case the reliability of estimates of ionization cross-sections and detector efficiencies necessary to make the method absolute is generally unknown. Therefore, heterogeneous equilibria are utilized in the measurement of thermodynamic properties of vapors, and the reliability of such measurements can be greatly enhanced if the composition variable is recognized and properly controlled.

I. The Vapor Pressures of the Dioxide Phases

Since all of the actinide metals from thorium through americium for stable dioxide phases the characterization of the evaporation processes resulting from them are of special importance in deducing the thermodynamic properties of the vapor phase. In Fig. 1 are shown and in Table I are given the results of many investigators in measuring the vapor pressures of the solid dioxide phases. The quantity $p_e$ in the equation in Table I represents the pressure calculated from the effusion equation under the assumption that the vapor is $MO_2$ except for curves e, j, and k wherein the molecular species is $MO$. The vapor pressure of the thoria phase (curve a) has been measured by the effusion method and previously analyzed in terms of $ThO_2(g)$, $ThO(g)$, and $O(g)$ which were identified mass spectrometrically [3]. Quite clearly the vapor pressure of thoria is the lowest of the actinide metal dioxides. The vapor pressures measured for urania by Ackermann et al. (curve b) [4] by Ivanov et al. (curve c) [5], and by Ohse (curve d) [6] agree within a factor of two, and for the plutonia phase the least-squares treatment of the effusion data (cell 1) of Mulford and Lamar (curve h) [7] yield vapor pressures that are approximately 20% higher than those recently measured by Ackermann et al. (curve i) [8]. However, the measurements of Pardue and Keller (curve g) [9] are substantially lower and the results reported here represent the measurements carried out by the transpiration method using 1 atm $O_2$ as the flow gas. Additional series of measurements by these investigators using both air and argon as flow gases yield higher vapor pressures, the latter approaching curve i of Ackermann et al. [8]. In the case of all three flow gases the lack of precision of the data is quite pronounced and.
therefore, the equation given in Table I was fitted to the experimental data for 1 atm \( \text{O}_2 \) by assuming the entropy of sublimation for the process, \( \text{PuO}_2(s) \rightarrow \text{PuO}_2(g) \) is the same as that for \( \text{UO}_2 \), i.e., \( \Delta S^\circ \approx 36 \) e.u. The vapor pressure of the neptunia phase has been measured only quite recently by Ackermann et al. [10]. Inspection of the various results shown in Fig. 1 points to no significant trend in the vapor pressures of the dioxide phases. With the exception of thoria the dioxide phases, urania, neptunia and plutonia appear to have nearly equal apparent vapor pressures as measured by the effusion method in vacuum. One must remember that the vapor pressure is fundamentally related to the difference in the free energies of formation of the vapor and the condensed phases and the thermodynamic analysis which subsequently
### TABLE I. Vapor Pressures of the Actinide Metal Dioxide Phases

<table>
<thead>
<tr>
<th>Curve</th>
<th>Condensed Phase(s)</th>
<th>Least Squares Equation&lt;sup&gt;a&lt;/sup&gt; ( \log p_e(\text{atm}) = )</th>
<th>Remarks</th>
<th>Temperature Range (°K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>ThO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( (8.26 \pm 0.13) - (3.552 \pm 0.031) \frac{10^4}{T} )</td>
<td>vacuum effusion + M.S.&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2170-2860</td>
<td>[3]</td>
</tr>
<tr>
<td>b</td>
<td>UO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( (7.95 \pm 0.20) - (2.997 \pm 0.035) \frac{10^4}{T} )</td>
<td>vacuum effusion, T &lt; 2200°K</td>
<td>1600-2800</td>
<td>[4]</td>
</tr>
<tr>
<td>c</td>
<td>UO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( 9.22 - (3.215) \frac{10^4}{T} )</td>
<td>vacuum effusion</td>
<td>1920-2220</td>
<td>[5]</td>
</tr>
<tr>
<td>d</td>
<td>UO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( (9.18 \pm 0.40) - (3.232 \pm 0.099) \frac{10^4}{T} )</td>
<td>vacuum effusion</td>
<td>2200-2800</td>
<td>[6]</td>
</tr>
<tr>
<td>e</td>
<td>UO&lt;sub&gt;2&lt;/sub&gt;-x+U</td>
<td>( (7.25 \pm 0.14) - (2.702 \pm 0.026) \frac{10^4}{T} )</td>
<td>vacuum effusion+M.S.+L.P.B.&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1540-2320</td>
<td>[11]</td>
</tr>
<tr>
<td>f</td>
<td>NpO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( (8.39 \pm 0.13) - (3.110 \pm 0.030) \frac{10^4}{T} )</td>
<td>vacuum effusion + M.S.</td>
<td>1850-2475</td>
<td>[10]</td>
</tr>
<tr>
<td>g</td>
<td>PuO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( 7.87 - (3.128) \frac{10^4}{T} )</td>
<td>transpiration - 1 atm O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1800-2060</td>
<td>[9]</td>
</tr>
<tr>
<td>h</td>
<td>PuO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( (7.82 \pm 0.23) - (2.970 \pm 0.050) \frac{10^4}{T} )</td>
<td>vacuum effusion</td>
<td>1990-2380</td>
<td>[7]</td>
</tr>
<tr>
<td>i</td>
<td>PuO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( (7.49 \pm 0.15) - (2.926 \pm 0.028) \frac{10^4}{T} )</td>
<td>vacuum effusion</td>
<td>1640-2080</td>
<td>[8]</td>
</tr>
<tr>
<td>j</td>
<td>PuO&lt;sub&gt;2&lt;/sub&gt;-x+Pu&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>( (8.09 \pm 0.27) - (2.780 \pm 0.050) \frac{10^4}{T} )</td>
<td>vacuum effusion, L.P.B. = PuO&lt;sub&gt;1.6&lt;/sub&gt;</td>
<td>1640-2105</td>
<td>[8]</td>
</tr>
<tr>
<td>k</td>
<td>PuO&lt;sub&gt;2&lt;/sub&gt;-x+Pu&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>( 8.13 - (2.791) \frac{10^4}{T} )</td>
<td>same</td>
<td>1790-2075</td>
<td>[12]</td>
</tr>
</tbody>
</table>

<sup>a</sup>The quantity \( p_e \) represents the pressure calculated under the assumption that vapor phase is entirely \( \text{MO}_2(g) \) except for curves e, j, and k in which cases the vapor is assumed to be entirely \( \text{MO}(g) \).

<sup>b</sup>Mass Spectrometric Analysis of Vapor Phase

<sup>c</sup>Lower Phase Boundary of \( \text{UO}_2-x \) phase measured as function of temperature.
follows will begin to elucidate the trends which appear to be
occurring within and between these phases. There are, however,
two very important observations, namely, that the equilibration
of the $\text{UO}_2$ phase with liquid uranium [11] and the $\text{PuO}_2$ phase
with the sesquioxide phase $\text{Pu}_2\text{O}_3$ [8,12] both produce a substantial
increase in the observed pressures as shown by curve e and
by curves j, k, respectively. Similar behavior for the $\text{ThO}_2$
phase saturated with thorium metal has been previously dis-
cussed [1,3]. It is with this observation in mind that we
begin a discussion of the effect of a changing composition
on the partial pressures in equilibrium with the condensed phase.

II. The $\text{M}^{2+\pm x}$ Phases

It is now well recognized that most compounds display a
wide variety of compositions, both hypo- and hyperstoichiometric,
and the discussion of the subject here is not intended to be an
exhaustive compilation but rather the citation of some pertinent
investigations which are illustrative. A recent symposium en-
titled "Nonstoichiometric Compounds" [13] dealt with the effect
of the change of composition variable in homogeneous phases in
a number of chemical and physical properties. More recently a
panel on thermodynamic and transport properties of uranium
dioxide and related phases compiled and examined in detail the
thermodynamic behavior of the $\text{UO}_2^{2+x}$ phase [14]. At the present
time uranium dioxide is rather surprisingly the only actinide
dioxide known to become hyperstoichiometric. The ability of all
the actinide dioxide phases to become hypostoichiometric is
now generally documented. Brewer [15] has compiled the earlier
evidence indicating that the thoria, urania and plutonia can
exist below the stoichiometric composition. Ackermann, et al.
[3] recently demonstrated that thoria heated to 2800°K in
vacuum becomes slightly hypostoichiometric. Anderson et al.
[16] reported that hypostoichiometric urania was produced by
heating in a helium atmosphere above 2800°C. Rothwell [17]
demonstrated that urania heated at 1800°C in a hydrogen atmos-
phere became hypostoichiometric and quite recently Martin and
Edwards [18] have determined the lower phase boundary of the
urania phase from 1600 to 2500°C by equilibration with liquid uranium followed by quenching and chemical analysis of oxide growths which formed between the uranium melts and the oxide crucibles. Ackermann and Chandrasekhariah [11] have also determined the lower phase boundary of urania by a vapor equilibration (isopiestic) method from 1600 to 2200°C. The agreement between the two investigations below 2100°C is excellent but at higher temperatures the results appear to diverge. At 1600°C the lower phase boundary is $UO_{1.95}$ and it decreases nearly linearly to $UO_{1.83}$ at 2100°C. The recent investigations of Chikalla et al. [19] and by Gardner et al. [20] demonstrate that plutonia above approximately 700°C can become hypostoichiometric down to a composition of approximately $PuO_{1.6}$. Ackermann et al. [10] observed the effect of the departure from stoichiometry of the neptunia phase during the investigation of the evaporation behavior. Of the four $MO_2$ phases studied to date, thoria and urania eventually produce the liquid metal phase as they become hypostoichiometric whereas neptunia and plutonia produce the respective sesquioxides.

The effect of composition variable on the evaporation behavior must be recognized if one wishes to analyze further the apparent discrepancies shown in Fig. 1 that exist in the various measurements the vapor pressures of the urania and plutonia. In some of these cases it seems highly improbable that experimental errors in the measured effusion rates and temperatures should account entirely for these discrepancies. The recent mass spectrometric investigation by Ackermann et al. [11] of the dependence of the partial pressures of $U$, $UO$, $UO_2$ and $UO_3$ on the composition of the urania phase is shown in Fig. 2. Quite clearly the total vapor pressure at a constant temperature of 2000°K increases as the condensed phase is oxidized above $UO_2$ due to the rapid increase of the partial pressure of $UO_3(g)$, and similarly, the total vapor pressure increases as the condensed phase is reduced below $UO_2$ due to the rapid increase in the partial pressures of $UO(g)$ and $U(g)$ until the lower phase boundary of urania is reached at which liquid uranium is formed. These results clearly suggest that effusion measure-
ments carried out in "vacuum" (which in general may be either oxidizing or reducing) are not uniquely interpretable unless the composition of the condensed phase is known. The vapor pressure measurements of Ackermann et al. [4] for urania at temperatures below approximately 2200°K correspond very nearly to the stoichiometric composition based on the x-ray and chemical analyses of residues from the evaporation runs. At temperatures above 2200°K a positive deviation from linearity in the vapor pressure plotted in accordance with the Clasius-Clapeyron equation was observed. The re-examination of the vapor pressure of urania from 2200° to 2800°K by Ohse [6] yields values of the vapor pressure in good agreement with the measurements by Ackermann et al. [4] and important evidence of hypo-stoichiometry in the form of a value of the lattice parameter of 5.4714 Å obtained from a residue of urania after successive evaporation runs. This value is significantly larger than the value 5.470 Å normally observed for stoichiometric urania [14].
Hence the positive curvature in the vapor pressure observed by Ackermann et al. [4] at temperatures above 2200° very likely is explained by departure from the stoichiometric composition, although the analysis of x-ray photographs did not indicate any departure from ideal stoichiometry at the higher temperatures. However, an uncontrolled factor such as the rate of cooling of the sample to room temperature could have led to the disproportionation of \( \text{UO}_2^+ \) to nearly stoichiometric urania and a small amount of uranium that was not detected.

In the case of thoria Ackermann et al. [3] observed mass spectrometrically the effect of variable composition in that successive changes in the temperature produced non-parallel response in the ion currents of \( \text{ThO}^+ \) and \( \text{ThO}_2^+ \). The \( \text{ThO}_2^+ \) reached a constant value within 2 minutes or essentially as soon as the temperature attained a constant value whereas the \( \text{ThO}^+ \) exhibited a much slower approach to equilibrium by decreasing toward a limiting value when the temperature was lowered, and increased toward a limiting value when the temperature was raised. Furthermore, the rate of approach to the limiting value was much faster at higher temperatures and for small changes in the temperature.

In the study of the evaporation behavior of neptunia [10] it was observed mass spectrometrically that the \( \text{NpO}^+ \) current increased with time and eventually became comparable to that of \( \text{NpO}_2^+ \) which did not exhibit any variability. Furthermore, the mass effusion data for neptunia indicated an increase by a factor of four or less in the total vapor pressure at lower temperatures once the sample had been heated in excess of approximately 2100°K. The residue of a sample that had undergone a 70% evaporation of 2400°K contained a small amount of an additional phase, tentatively identified as \( \text{Np}_2\text{O}_3 \).

The evaporation behavior of the plutonia phase also appears to depend markedly on the composition variable although no mass spectrometric observations are yet available. Mulford and Lamar [7] reported a lattice parameter of 5.44 Å for their evaporation residues compared with the value 5.396 Å generally accepted for stoichiometric \( \text{PuO}_2 \). Once again the
larger value suggest hypostoichiometry. Ackermann et al. [8] confirm the departure from ideal stoichiometry since they found x-ray evidence of the cubic PuO_{1.6} phase in their residues. If the accuracy of the transpiration measurements (1 atm O_2) of Pardue and Keller [9] is not substantially obscured by the rather large scatter of the data, the vapor in the investigation by Mulford and Lamar [7] and Ackermann et al. [8] must be principally PuO(g) because the total vapor pressure in the former instance (curve g, Fig. 1) is approximately a factor of four less than the latter (curves h and i).

It is, therefore, apparent that the composition variable is a very important parameter in characterizing the system and it is capable of producing rather large changes amounting to several order of magnitude in the overall vapor pressure of a given dioxide phase. It is also apparent that the partial pressure of the MO_2(g) is relatively insensitive to change in the composition of the condensed phase whereas the partial pressures of MO(g), M(g) and O(g) are strikingly dependent as is also the partial pressure of UO_3(g) for the hyperstoichiometric urania phase.

III. Compilation and Trends of Thermodynamic Properties

In Table II are compiled the thermodynamic data for the various gaseous metals, monoxides, dioxides, trioxides and the solid dioxides. The linear equations for the standard free energies of formation given in the second column are generally adequate over the stated temperature range within the precision of the experimental data. In column 3 are given the heats of sublimation of the metals and solid dioxides to the gaseous metal and dioxide respectively along with the standard derivations derived from the precision of the data. In column 4 are tabulated the dissociation energies of the gaseous molecules corresponding to a reference temperature of 2000°K which is common to all of the experimental measurements. Admittedly the more fundamental reference temperature of 0°K is desirable but the reduction of the dissociation energies to this value is not realizable at the present time because of the dearth of information relating to molecular parameters such as interatomic distances, vibrational
<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta G_f^\circ$ ($=\Delta H_f^\circ - T \Delta S_f^\circ$) kcal/mole</th>
<th>$\Delta H_{\text{evap.}}$ kcal/mole</th>
<th>Dissociation Energy (kcal) at 2000°K</th>
<th>Temperature Range (°K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(g)</td>
<td>131,700 - 27.4T</td>
<td>131.7±2.8</td>
<td></td>
<td>1757 - 1956</td>
<td>[22]</td>
</tr>
<tr>
<td>ThO(g)</td>
<td>-10,300 - 14.4T</td>
<td></td>
<td></td>
<td>2000 - 3000</td>
<td>[3]</td>
</tr>
<tr>
<td>ThO₂(g)</td>
<td>-138,600 + 11.4T</td>
<td>157.4±2.5</td>
<td>392.8</td>
<td>2000 - 3000</td>
<td>[3]</td>
</tr>
<tr>
<td>ThO₂(s)</td>
<td>-296,000 + 46.38T</td>
<td></td>
<td></td>
<td>2000 - 3000</td>
<td>[3]</td>
</tr>
<tr>
<td>Pa(g)</td>
<td>+106,620 - 29.0T</td>
<td>106.6</td>
<td></td>
<td>2220 - 2450</td>
<td>[23]</td>
</tr>
<tr>
<td>U(g)</td>
<td>106,800 - 26.09T</td>
<td>106.8±2.2</td>
<td></td>
<td>1630 - 1970</td>
<td>[1,24,25]</td>
</tr>
<tr>
<td>UO(g)</td>
<td>116,800 - 26.8T</td>
<td>116.8±5.6</td>
<td></td>
<td>1775 - 2174</td>
<td>[26]</td>
</tr>
<tr>
<td>UO₂(g)</td>
<td>-121,500 + 4.24T</td>
<td>137.1±1.7</td>
<td>350.8</td>
<td>1600 - 2400</td>
<td>[4,27,28]</td>
</tr>
<tr>
<td>UO₃(g)</td>
<td>-198,500 + 19.0T</td>
<td></td>
<td>360.8</td>
<td>1600 - 2400</td>
<td>[29]</td>
</tr>
<tr>
<td>UO₃(g)</td>
<td>-202,080 + 20.79T</td>
<td></td>
<td>489.0</td>
<td>1230 - 1600</td>
<td>[30]</td>
</tr>
<tr>
<td>UO₂(s)</td>
<td>-258,650 + 40.64T</td>
<td></td>
<td>492.6</td>
<td>1400 - 1800</td>
<td>[27,28]</td>
</tr>
<tr>
<td>Np(g)</td>
<td>94,300 - 23.3T</td>
<td>94.3±5.9</td>
<td></td>
<td>1691 - 1952</td>
<td>[31]</td>
</tr>
<tr>
<td>NpO(g)</td>
<td>(-20,00 - 11.0T)</td>
<td></td>
<td>(175)</td>
<td>1850 - 2475</td>
<td>[10]</td>
</tr>
<tr>
<td>NpO₂(g)</td>
<td>-113,00 + 3.5T</td>
<td>141.2±1.4</td>
<td>329.8</td>
<td>1850 - 2475</td>
<td>[10]</td>
</tr>
<tr>
<td>NpO₂(s)</td>
<td>-251,100 + 40.5T</td>
<td></td>
<td></td>
<td>1500 → 2475</td>
<td>[10]</td>
</tr>
<tr>
<td>Substance</td>
<td>$\Delta G_f^o (=\Delta H_f^o - T\Delta S_f^o)$ cal/mole</td>
<td>$\Delta H_{evap.}$ kcal/mole</td>
<td>Dissociation Energy(kcal) at 2000°K(^a)</td>
<td>Temperature Range (°K)(^b)</td>
<td>Ref.</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------</td>
<td>-----------------</td>
<td>--------------------------------</td>
<td>------------------</td>
<td>-----</td>
</tr>
<tr>
<td>Pu(g)</td>
<td>80,500 - 22.94T</td>
<td>80.5±0.3</td>
<td></td>
<td>1392 - 1793</td>
<td>[32]</td>
</tr>
<tr>
<td>Pu(g)</td>
<td>85,300 - 26.0T</td>
<td>85.3</td>
<td></td>
<td>1691 - 1952</td>
<td>[31]</td>
</tr>
<tr>
<td>PuO(g)</td>
<td>(-30,700 - 10.5T)</td>
<td></td>
<td>(172.4)</td>
<td>1640 - 2125</td>
<td>[8]</td>
</tr>
<tr>
<td>PuO(_2)(g)</td>
<td>(-108,500 ± 4.3T)</td>
<td>(143.1)</td>
<td>(311.5)</td>
<td>1700 - 2100</td>
<td>[9]</td>
</tr>
<tr>
<td>PuO(_2)(s)</td>
<td>-251,600 ± 40.25T</td>
<td></td>
<td></td>
<td>1000 - 1500 $\rightarrow$ 2100</td>
<td>[33]</td>
</tr>
<tr>
<td>Am(g)</td>
<td>51,700 - 18.9T</td>
<td>51.7</td>
<td></td>
<td>1450 - 1820</td>
<td>[34]</td>
</tr>
<tr>
<td>Am(g)</td>
<td>60,230 - 21.4T</td>
<td>60.2</td>
<td></td>
<td>1100 - 1450</td>
<td>[35]</td>
</tr>
<tr>
<td>O(g)</td>
<td>61,245 - 16.07T</td>
<td></td>
<td></td>
<td>2000 - 3000</td>
<td>[36]</td>
</tr>
</tbody>
</table>

\(^a\)Duplicate values results from the use of the two different heats of sublimation of the metal.

\(^b\)The arrows indicate extrapolations.

\(^c\)Recent experimental observations [25] indicate that this equation may yield a vapor pressure too high by at least a factor of 2 at $\sim$ 2000°K.
constants and electronic states for the gaseous oxides which are
needed in the calculation of free energy, and heat content
functions. Only for ThO(g) and ThO$_2$(g) have vibrational con-
stants been measured quite recently by matrix isolation
techniques [21].

In the present compilation the thermodynamic data for the
gaseous dioxides are generally more reliable than those for the
gaseous monoxides for the reason that is apparent in Fig. 2.
Since the gaseous dioxide is generally the predominant vapor
species for the stoichiometric condensed phase and since its
partial pressure is relatively insensitive to the composition
of the solid phase the identification of its partial pressure
with a known composition can be less rigorous. As a first
approximation it can be identified with the nearly stoichiometric
dioxide phase for which the heat and free energy of formation
are known generally from calorimetric data. On the other hand
the gaseous monoxide does not become important until relatively
large hypostoichiometry is produced in the solid dioxide phase
for which the thermodynamic properties are not generally known.
Hence, it is necessary to deduce the thermodynamic properties
of the gaseous monoxides from measurements of univariant systems
of two condensed phases.

From an inspection of the numerical values given in
Table II a number of significant trends are apparent.
1. The vapor pressures of the metals increase and the
heats of vaporization decrease from thorium through
americium. A recent observation of Cunningham [37]
indicates that the vapor pressure of curium is less than
that of americium. It would appear that the vapor
pressures of the actinide metals parallel those of the
lanthanides [38] i.e., the vapor pressure increases with
increasing atomic number up to the (n-2)f$^7$ (n-1)d$^1$ns$^2$
configurations of gadolinium and curium for which the
pressure sharply decreases.
2. The free energies and heats of formation of the solid
dioxide phases become less negative from thoria-to-urania-
to-plutonia. This trend is decreasing stability is mani-
fested by the greater ease of reduction observed for these phases in the vacuum. From the results of the analysis of the urania-liquid uranium system by Ackermann et al. [11] and the measurements of Atlas and Schlehmann [39] it can be shown that the relative partial molar free energy of oxygen at a fixed temperature for a given composition of UO$_2$-$_x$ phase is considerably more negative than that of the same compositions in the PuO$_2$-$_x$ phase.

3. The free energies and heats of formation of the gaseous dioxides become less negative from ThO$_2$(g) to PuO$_2$(g).

4. Although the results are not yet extensive the free energies and heats of formation of the gaseous monoxides appear to become more negative with increasing atomic number of the metal. The trend here appears to be opposite that found in the gaseous dioxides.

5. The dissociation energies of both the gaseous monoxides and dioxides decrease with increasing atomic number of the metal. In the former case the trend seems to parallel that observed by White et al. [40] for the lanthanide monoxides.

The relatively high stability, as well as the increase in stability of the gaseous monoxides with increasing atomic number, suggests an important experimental difficulty associated with the measurements of the vapor pressures of the metals. Small impurities of oxygen (or oxide) will considerably enhance the observed volatility and decrease the apparent heat of vaporization of a given metal due to the presence of gaseous monoxide in the vapor. Hence, the investigator must ascertain the composition of the vapor phase associated with a measured evaporation rate. The lack of agreement between investigations in the cases of uranium, plutonium and americium is undoubtedly influenced by this phenomenon, and hence within the context of this discussion the lower values of the vapor pressure and higher values of the heats of sublimation are presently preferred.
IV. Chemical Systematics of Actinide Elements Based on High Temperature Investigations

In a previously reported study [2] directed principally towards gaseous oxides, we have attempted to recognize the three-fold nature of the transactinium elements to the extent that they are members of the respective a-subgroups, to which they are similar to the rare earth series, and to which they are members of an actinide series. Herein these facets are examined further so as to include the grosser aspects of the chemistries of the vapor and solid states and of the aqueous solutions. For such purposes it is helpful to sketch the various states including where possible the various valencies even though the relative differences in energies have not yet been established extensively with high degrees of accuracy and reliability. Since a correlation is intended, as previously, with the electronic configuration of the ground states of the neutral atoms as a basis, these states are arbitrarily accepted as the reference states. The electronic configurations, as far as they are known, of the elements in the actinide series and of those elements in the rare earth series wherein correspondences are assumed to exist are listed in Table III. In the study of the gaseous molecules evidence [41] was presented suggesting that the low-lying states of the neutral atoms, as measured by the calculated electronic entropy, can contribute significantly through polarization in certain cases to the bonding between two atoms. This effect constitutes a third factor in the ideal resolution of the bonding into effects such as atomic radius and occupied bonding and anti-bonding orbitals. It appears to be the idealized factor which is most important in distinguishing bonding involving the a-subgroup (transition) elements as contrasted with elements in the regular or b-subgroup. The trends observed in the heats of sublimation of the elements in a given chemical group, the one composed of scandium, yttrium, and lanthanum, for instance, suggests that the same factor is operative. In the cases of ionic solids, of covalent solids perhaps, and of aqueous solutions, the factor per se should not be effective because complete ionization par-
## TABLE III. Stabilities of Various Valence States with Reference to Gaseous Atoms

<table>
<thead>
<tr>
<th>Element</th>
<th>Heat of Condensation $\Delta H_{\text{evap}}$ (kcal/mole)</th>
<th>Energy of Solvation for $M^{n+}(\text{aq})$ $\Delta H_{\text{evap}} + nFE^\circ$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th($6d^27s^2$)</td>
<td>-132</td>
<td>+2</td>
</tr>
<tr>
<td>U($5f^36d^17s^2$)</td>
<td>-106 to -117</td>
<td>+3</td>
</tr>
<tr>
<td>Np($5f^96d^17s^2$)</td>
<td>-94</td>
<td>+4</td>
</tr>
<tr>
<td>Pu($5f^67s^2$)</td>
<td>-80 to -86</td>
<td></td>
</tr>
<tr>
<td>Am($5f^77s^2$)</td>
<td>-51 to -60</td>
<td></td>
</tr>
<tr>
<td>Cm($5f^76d^17s^2$)</td>
<td>&lt; Am</td>
<td></td>
</tr>
<tr>
<td>La($5d^16s^2$)</td>
<td>-103</td>
<td></td>
</tr>
<tr>
<td>Ce($4f^15d^16s^2$)</td>
<td>-112</td>
<td></td>
</tr>
<tr>
<td>Pr($4f^36s^2$)</td>
<td>-89</td>
<td></td>
</tr>
<tr>
<td>Nd($4f^46s^2$)</td>
<td>-78</td>
<td></td>
</tr>
<tr>
<td>Sm($4f^66s^2$)</td>
<td>-48</td>
<td></td>
</tr>
<tr>
<td>Eu($4f^76s^2$)</td>
<td>-42</td>
<td></td>
</tr>
<tr>
<td>Gd($4f^75d^16s^2$)</td>
<td>-96</td>
<td></td>
</tr>
<tr>
<td>Tb($4f^96s^2$)</td>
<td>-94</td>
<td></td>
</tr>
<tr>
<td>Dy($4f^{10}6s^2$)</td>
<td>-71</td>
<td></td>
</tr>
<tr>
<td>Ho($4f^{12}6s^2$)</td>
<td>-71</td>
<td></td>
</tr>
<tr>
<td>Er($4f^{12}6s^2$)</td>
<td>-82</td>
<td></td>
</tr>
<tr>
<td>Tm($4f^{13}6s^2$)</td>
<td>-59</td>
<td></td>
</tr>
<tr>
<td>Yb($4f^{11}6s^2$)</td>
<td>-36</td>
<td></td>
</tr>
<tr>
<td>Lu($5d^16s^2$)</td>
<td>-102</td>
<td></td>
</tr>
</tbody>
</table>

*a* See reference [37] for list of configurations.

*b* Values given for actinide elements are at temperatures of measurement. Values at 0°K are approximately 10 kcal larger. Values for lanthanide elements are given for 298°K according to Habermann and Daane [38].

*c* The entropy term corresponding to the condensation process is essentially an additive constant and therefore it is not included in the energy of solvation. The maximum error incurred therefrom is 1.5 kcal between successive elements.
ticularly to higher valence states exists. The actual situation, however, is undoubtedly so complex that some common nuclear property dictates both the low-lying states and the ionization potentials, so that both reflect one property. Such is certainly suggested by the parallisms which one observes by scanning through tables of atomic-energy states.

The three-fold nature of the actinide series makes it particularly difficult to discuss the systematic trends within the series without accomplishing first a rather extensive analysis of all the elements in the a-subgroups. Since such obviously cannot be achieved herein, a superficial examination is attempted with the expectation that some salient and decisive factors which eventually will simplify the complex problem can be discerned. Within this objective potentially significant initial points are comparisons between lanthanum and lutetium and between barium and ytterbium. In each of these two sets the elements have identical electronic configurations of the valence electrons; the two in the former pair are both $5d^16s^2$; the two in the latter pair are both $6s^2$. A comparison of the heat of sublimation of lanthanum, 103 kcal/mole, with that of lutetium, 102 kcal/mole, does suggest a close parallel in the bonding in the two cases. In other compounds such as monoxides and the aqueous $+3$ ion, the agreement appears not to be this close. In the other pair the heats of sublimation are slightly different; barium has a value of 42 kcal/mole; ytterbium has a value of 36 kcal/mole. The significance of this difference is at present obscured, in part because the vapor pressure of barium has not been investigated sufficiently and in part because the $+3$ valence state for ytterbium is more readily observed than the same state for barium. In general though any effect caused by this difference is secondary since the two elements do have very nearly the same heat of sublimation. Certainly one can conclude that the first $5d$-electron contributes significantly, about 60 kcal, to the metallic bond. It is unfortunate that there exists no element with a configuration of $5f^16s^2$ so that a direct comparison between the $d$ and $f$ configurations can be made. A comparison of gadolinium ($4f^75d^16s^2$) with lanthanum and lutetium
indicates that the half filled 4f shell effectively decreases the bonding of the 5d^{16}s^2 configuration by about 7 kcal. Another apparent, partial intercomparison between f and d configurations can be attempted through cerium and the elements in subgroup IVa\((n-1)d^2ns^2\) and through the elements in the 5d transition series and the rare earth or 4f transition series. The heats of sublimation of zirconium, hafnium, and thorium are all at least 30 kcal larger than that for cerium. However, in some way the \(4f^2\) configuration does contribute in cerium because its heat of sublimation is approximately 50 kcal larger than the value for barium. A comparison between the 5d^{16}s^2 series and the \(4f^16s^2\) series demonstrates that whereas the addition of 5d electrons increases the metallic binding to a maximum value of 5d^4, the addition of 4f electrons decreases the binding to a minimum at 4f^7. But it would not be quite correct to assume that these opposite effects are directly a result of the different orbital angular momenta in the two cases. Rather it is possible that such difference reflects the fact that in the first case the principal quantum numbers of the d and s configurations differ by one, whereas in the latter case the principal quantum numbers of the f and s orbital angular momenta differ by two. Likewise the principal "cause" of the difference between the regular elements (np^1ns^4) and the first transition series is undoubtedly part of a pattern in which the higher orbital angular momenta are a direct result of increasing difference between the principal quantum numbers.

The trend observed in the heats of sublimation of the elements in the actinide series is displayed in Table III. In almost all of its chemical behavior thorium can be considered as one of the elements in Group IVA. The elements protactinium, uranium, neptunium, and perhaps plutonium, however, are neither entirely members of the transition metal subgroups nor entirely members of a 5f series comparable to the rare earth series, and particularly they are not the counterparts for praseodymium, neodymium, promethium, and samarium, respectively. Although the heats of sublimation decrease monotonically through americium as f electrons are added to the (n-2) shell, the individual values
are significantly larger than the heats for the assumed corresponding counterparts in the rare earth series. The "replacement" of the 5f-electron by a 6d electron produces an increase in the metallic binding. Of all the actinide elements plutonium at present appears to be the most anomalous because if the configuration of the valence electron is in fact $5f^67s^2$, then one would not expect its heat of sublimation to be higher than that value reported for samarium. However, if the configuration is $5f^56d^17s^2$, then its value is more nearly consistent with the other elements. Whatever the configuration is one recognizes that the valencies in aqueous solutions in excess of +3 for samarium are apparently much less stable than are those for plutonium, so there appears to be a correspondence between the heats of sublimation of these two elements and the valence states in aqueous solutions. The relative values for the heats of sublimation of americium and europium are similar to the preceding members. The situation at curium and gadolinium, however, may be more nearly parallel since the vapor pressure of curium is much lower than that for americium [37]. Hence, there seems to occur an increase in heat of sublimation at curium just as there does at gadolinium.

A comparison among the valancies and their energies in the solid state, in the aqueous solutions, and in the vapor state would be valuable in establishing the systematics of the chemistry of the elements in the a-subgroups. Measurements of the single electrode potentials and the heats of solution of the elements in these groups have been accomplished sufficiently to reveal many of the quantitative aspects of the systematics. Recently, investigations of vapor-solid equilibria have furnished some of the information needed for the vapor phase, however, i.e., the partial pressures of the elements in equilibrium with their various valence states in their respective solids, are almost completely unknown. Indeed, one of the very fruitful areas for investigations at high temperature could be the measurements of these quantities. Until such data as the partial molar enthalpies and entropies of the various metals in in the various crystalline fields of solids are available, much
can be accomplished through studies involving (1) the observed valence states in series of compounds such as oxides, sulfides, selenides, tellurides, etc., (2) the partial pressures of oxygen as functions of compositions as measures of the relative energies of the valence states, (3) the partial molar free energies of the various states observed in aqueous solutions, and (4) eventually the partial molar free energies of the electrons as a unifying concept. An initial attempt is made herein with respect to the first three items.

Pertinent to the chemistry of the solid, vapor, and aqueous states, one of the most convincing initial illustrations of the fact that the elements in the actinide series have a three-fold character is found by examining thorium and uranium. In all three states compounds of these elements resemble the elements in groups IVA and VIA, respectively, more closely than they resemble each other or any elements in the rare earth series. Such obviously has been known since these elements were first characterized. Not so frequently recognized and discussed, however, are the quantitative values for the partial molar quantities such as enthalpies and free energies for the various valences in aqueous solution referred to the gaseous atoms. Accordingly we have tabulated a quantity, the heat of solvation, which in part at least measures the free energy of solvation of gaseous atoms in water in Table III. For the various actinide and lanthanide elements are given the heats of condensation (the negative of the heat of evaporation) and the energies of solvation for the known valence states in aqueous solution. The quantity $F$ is the Faraday (23,060 cal/mole) and the quantity $E^\circ$ is the appropriate standard electrode potential [42]. Due to the inability at the present time to reduce the heats of sublimation of the actinide metals to room temperature, and since a nearly constant term involving the entropy of evaporation for both both actinide and lanthanide elements is not included, the energies of solvation are not absolute values. For the purpose of this discussion, however, the presentation is adequate. The values contained in this table reflect in part at least some features which are known as "chemical" facts. Namely, the
actinide series differs from the rare earth series in that the valence states higher than +3 are, relatively speaking, more stable in the aqueous environment, but these states in the former case become less important with increasing atomic numbers. All the four elements, uranium through americium, have very nearly the same stability in the +3 valence state. Intercomparison between respective members in the two series suggest a close correspondence involving only the +3 valence states. The relative values of the +2 and +3 states in the cases of samarium, europium, and ytterbium are particularly interesting because apparently sulfur is just sufficiently electronegative to reduce these elements to the +2 state but not sufficient to reduce them to the +3 state in the mono-sulfides \[43\]. In all the other rare earth elements, sulfur and the free electrons in the solid monosulfides are sufficiently electronegative to reduce the elements to the +3 state. Hence, comparing the values given in Table III, one predicts that all four of the actinide elements for which the energies of the +3 states are listed should form monosulfides which are metallic conductors.

In a foregoing section the tendency of the actinide dioxides to manifest a hypostoichiometric region of composition is discussed. Such behavior is principally a measure of the relative energies of the +4 and +3 valence states as suggested in item (2) above. It is particularly significant to investigate this aspect of the chemistry of the actinide elements in relation to item (3) given above since eventually quantitative measurements of partial molar free energies will enable one to evaluate the relative energies or forces in the crystalline fields compared with those same factors in the aqueous solution, and thereby one will be able to establish item (4) on a quantitative basis. At present a comparison can be effected which at least demonstrates the parallelism. Thus one represents the relation between the partial pressure of oxygen and the valence states by the reaction:

$$O_2^{+2} + 2M^{+4}_S \rightarrow \frac{1}{2} O_2(g) + 2M^{+3}_S \quad (1)$$
in which the subscript \( \ell s \) represents a lattice site. For this reaction one writes that

\[
\Delta G = -RT \ln \left[ \frac{(M^{+3})^2}{(M^{+4})^2(0^{-2})} \right]
\]

\[
\frac{1}{2} RT \ln p_{O_2} = 2 \left[ \Delta G_f^0(M^{+3}) - \Delta G_f^0(M^{+4}) \right] - \Delta G_f^0(0^{-2})
\]

(2)

The quantity \( \left[ \frac{(M^{+3})^2}{(M^{+4})^2(0^{-2})} \right] \) is a measure of the composition of the dioxide phase. Hence at a given composition one can effect a comparison of the partial pressures of oxygen for a series by comparing the other quantities in equation (2). Thus with respect to uranium as a reference

\[
\frac{1}{2} RT \ln \left[ \frac{P_{O_2}(M)}{P_{O_2}(U)} \right] = 2 \left[ \Delta G_f^0(U^{+3}) - \Delta G_f^0(U^{+4}) \right] - \Delta G_f^0(0^{-2}) - \Delta G_f^0(0^{-2})
\]

(3)

At present, values for the free energies on the right side of equation (3) are not available, but single electrode potentials for aqueous solutions of these valence states of uranium, neptunium, plutonium, and Americium are known [42]. Accordingly, there are tabulated in Table IV the relative stabilities of the +3 and +4 valence states for some of the actinide elements and one rare earth element and the trend in these values is compared with the partial pressures of the oxygen with the hypo-stoichiometric dioxide phase MO\(_{1.96}\). In general one observes that the energy states in the aqueous solution establishes an ordering of these elements which is the same as the order produced on the basis of the relative case with which the dioxides lose oxygen.
TABLE IV. Comparison of Valence States of Some Actinide Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative Stabilities of Valence States</th>
<th>Partial Pressure of $O_2$ for $M_0_{1.96}(s)$ at 1600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In Aqueous Solution</td>
<td>Partial Pressure of $O_2$ for $M_0_{1.96}(s)$ at 1600°C</td>
</tr>
<tr>
<td></td>
<td>Individual$^a$ Values (kcal/mole)</td>
<td>Relative to U (kcal/mole)</td>
</tr>
<tr>
<td>Th</td>
<td>-69 to 0</td>
<td>18 atm [3]</td>
</tr>
<tr>
<td>U</td>
<td>106</td>
<td>0</td>
</tr>
<tr>
<td>Pu</td>
<td>-42</td>
<td>148</td>
</tr>
<tr>
<td>Am</td>
<td>-147</td>
<td>77</td>
</tr>
<tr>
<td>Pr</td>
<td>-207</td>
<td>253</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313</td>
</tr>
</tbody>
</table>

$^a23[3E(M^{+3}) - 4E(M^{+4})]$ $E$ is the electrode potential given by Pourbaix [42], which is the negative of the electrode potential commonly used in the U.S.A.

Obviously more quantitative measurements of the partial pressures of oxygen are needed to establish the quantitative relation between the dielectric and crystalline field environments.

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BIBLIOGRAPHY


VAPORIZATION IN THE LITHIUM FLUORIDE-BERYLLIUM FLUORIDE SYSTEM

A. BÜCHLER AND J. L. STAUFFER
ARTHUR D. LITTLE, INC., CAMBRIDGE, MASS., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

VAPORIZATION IN THE LITHIUM FLUORIDE-BERYLLIUM FLUORIDE SYSTEM. The lithium fluoride-beryllium fluoride system is of interest as a major constituent of the working fluid of certain molten salt reactors. The work reported here forms part of a continuing investigation of the thermodynamics of light metal compounds by means of high temperature mass spectrometry. As a preliminary to work on the mixed system, the sublimation of pure lithium fluoride was re-examined. From the temperature dependence of the Li⁺, Li₂F⁺, and Li₃F⁺ ion intensities the following heats of sublimation at 1000°K were obtained.

\[ \text{LiF}(c) \rightarrow \text{LiF}(g) : \Delta H_{1000} = 64.8 \pm 2 \text{ kcal/mole} \]
\[ 2\text{LiF}(c) \rightarrow \text{Li}_2\text{F}_2(g) : \Delta H_{1000} = 68.3 \pm 2 \text{ kcal/mole} \]
\[ 3\text{LiF}(c) \rightarrow \text{Li}_3\text{F}_3(g) : \Delta H_{1000} = 73.9 \pm 3 \text{ kcal/mole} \]

For the study of the mixed system, a twin-crucible Knudsen effusion cell was designed which permitted the comparison, in a single experiment, of the mass spectra of a solution and of one of its components. With this crucible design it was possible to obtain the activities of LiF and BeF₂ in solution, the composition of the vapour, and the heats of formation of the mixed species LiBeF₃(g) and Li₂BeF₄(g). The LiF-BeF₂ melt in equilibrium with excess solid LiF was studied in the temperature range from 748-978°K, corresponding to melts containing from 66 to 79% LiF. At 900°K the ions observed, in order of abundance, were BeF²⁺, BeF⁺, Li⁺, LiBeF₂⁺, Li₂F⁺, LiF⁺, Li₃F³⁺, and Li₂BeF₄⁺. Comparison of this mass spectrum with that of pure LiF(c) showed that most of the Li⁺ intensity was contributed by the dissociative ionization of the mixed dimer LiBeF₃(g), which is thus the major lithium-containing species in the vapour above the LiF-BeF₂ system. For the reaction LiF(c) + BeF₂(g) \rightarrow LiBeF₃(g); \Delta H_{900} = 4 \pm 2 \text{ kcal/mole} was obtained. Comparison of the mass spectrum of the same melt with that of pure BeF₂(g) showed strong negative deviations from ideality for the activity of BeF₂ in the melt. The mass spectrum of a solution containing 67% BeF₂-33% LiF was also examined. The results obtained confirmed the identification of the Li₂BeF₄ molecule as the precursor of the Li₂BeF₃⁺ ion. The BeF₂ activity in the 67%-BeF₂ solution showed a positive deviation from ideality.

VAPORISATION DU SYSTEME FLUORURE DE LITHIUM-FLUORURE DE BERYLLIUM. Le système fluorure de lithium-fluorure de béryllium présente un intérêt comme élément constitutif important du fluide de service de certains réacteurs à sels fondus. L'étude dont le mémoire rend compte fait partie d'un programme de recherches à long terme sur la thermodynamique des composés de métaux légers au moyen de la spectrométrie de masse à haute température. Avant d'aborder l'étude du système mixte, les auteurs ont fait de nouvelles expériences sur la sublimation du fluorure de lithium pur. Partant du rapport de dépendance entre les intensités des ions Li⁺, Li₂F⁺ et Li₃F³⁺ et la température, ils ont obtenu des chaleurs d'effusion suivantes pour 1000°K:

\[ \text{LiF}(c) \rightarrow \text{LiF}(g) : \Delta H_{1000} = 64.8 \pm 2 \text{ kcal/mole} \]
\[ 2\text{LiF}(c) \rightarrow \text{Li}_2\text{F}_2(g) : \Delta H_{1000} = 68.3 \pm 2 \text{ kcal/mole} \]
\[ 3\text{LiF}(c) \rightarrow \text{Li}_3\text{F}_3(g) : \Delta H_{1000} = 73.9 \pm 3 \text{ kcal/mole} \]

Pour étudier le système mixte, les auteurs ont construit une cellule d'effusion de Knudsen à double creuset qui permettait de comparer en une seule expérience les spectres de masse d'une solution et de l'un
спектра раствора и одного из его компонентов. С помощью этой тигельной конструкции было изучено в диапазоне температур 748 – 978°К, соотношение с избытком твердого LiF-°было изучено в диапазоне температур 748 – 978°К, соотношение с избытком твердого LiF. Полученные результаты подтвердили, что молекула 

диссоциирующей ионизацией смешанного димера LiBeF 

чистого кристаллического LiF показало, что большая часть интенсивности Ы 

ответствующем расплавам, содержащим от 66% до 79% LiF. При температуре 900°К были обнаружены следующие температуры подтверждения, что молекула Li2BeF4 играет роль преобладающего иона в пенетрации в систему. Активность BeF2 в растворе, содержащем 67% BeF2 показала положительное отклонение от идеального случая.

ИСПАРЕНИЕ В СИСТЕМЕ ФТОРИСТЫЙ ЛИТИЙ - ФТОРИСТЫЙ БЕРИЛЛИЙ. Система фтористый литий - фтористый бериллий представляет интерес, так как является основным компонентом рабочей жидкости некоторых реакторов, работающих на распыленной соли. Публикуемая работа является частью постоянных исследований термодинамики соединений легких металлов с помощью высокотемпературной масс-спектрометрии. Прежде чем начать работу над смешанной системой, вновь была изучена сублимация чистого фтористого лития. По температурной зависимости интенсивности Li+, Li3F+ и Li3F+ были получены следующие теплоты сублимации при 1000°К:

\[ \Delta H_{1000} = 64,8 \pm 2 \text{ ккал/моль} \]
\[ \Delta H_{1000} = 65,3 \pm 2 \text{ ккал/моль} \]
\[ \Delta H_{1000} = 73,9 \pm 2 \text{ ккал/моль} \]

Для изучения смешанной системы была сконструирована двухтюбельная эффективная камера Нейсена, которая позволяет производить в одном эксперименте сравнение массового спектра раствора и одного из его компонентов. С помощью этой тигельной конструкции оказалось возможным определить активности LiF и BeF2 в растворе, состав пара и температура образования смешанных систем LiBeF3 (газ) и Li2BeF4 (газ). Расплав LiF - BeF2 в равновесном состоянии с избытком твердого LiF - было изучено в диапазоне температур 748 – 978°К, соответствующем расплаву, содержащем от 66% до 79% LiF. При температуре 900°К были обнаружены следующие ионы (в порядке их относительного содержания): BeF2+, BeF3+, Li+, LiBeF2, Li2F+, Li3F+, Li3F+ и Li3BeF3. Сравнение этого массового спектра с массовым спектром чистого кристаллического LiF показало, что большая часть интенсивности Li+ объясняется диссоциирующей ионизацией смешенного димера LiBeF3 (газ), который, таким образом, является основной содержащейся системой в паре над системой LiF - BeF2. Было установлено, что для реакции LiF(крystalл) + BeF2 (газ) \rightarrow LiBeF3 (газ) \Delta H_{900} = 4 \pm 2 \text{ ккал/моль}. Сравнение массового спектра того же расплава с массовым спектром чистого BeF2 (жидкость) показало наличие сильных отрицательных отклонений от идеального случая для активности BeF2 в этом расплаве. Была также изучена массовый спектр раствора, содержащего 67% BeF2 и 33% LiF. Полученные результаты подтвердили, что молекула Li2BeF4 играет роль преобладающего иона в системе. Активность BeF2 в растворе, содержащем 67% BeF2 показала положительное отклонение от идеального случая.

VAPORIZACION EN EL SISTEMA FLUORURO DE LITIO-FLUORURO DE BERILIO. El sistema fluoruro de berilio reviste interés como constituyente importante del fluido de trabajo de algunos reactores a base de sal fundida. Los estudios de que da cuenta esta memoria forman parte de una investigación continuada sobre la termodínámica de los compuestos de metales ligeros, mediante espectrometría de masas a alta temperatura. Como tarea preliminar al trabajo con el sistema mixto, se volvió a estudiar la sublimación del fluoruro de litio puro. A partir de la relación de dependencia que liga las intensidades de los iones Li+, Li3F+ y Li3F+ con la temperatura, se obtuvieron los siguientes valores de sublimación a 1000°K:

\[ \text{LiF(с) } \rightarrow \text{LiF(г): } \Delta H_{1000} = 64,8 \pm 2 \text{ ккал/моль} \]
\[ \text{2LiF(с) } \rightarrow \text{Li2F3(г): } \Delta H_{1000} = 68,3 \pm 2 \text{ ккал/моль} \]
\[ \text{3LiF(с) } \rightarrow \text{Li3F3(г): } \Delta H_{1000} = 73,9 \pm 3 \text{ ккал/моль} \]
Para estudiar el sistema mixto, se construyó una celda de efusión de Knudsen a crisol doble, que permitió comparar en un solo experimento el espectro de masas de una solución con el de uno de sus componentes. Con este crisol se pudieron obtener las actividades del LiF y del BeF$_2$, en solución, la composición del vapor y los calores de formación de las especies mixtas LiBeF$_3$(g) y Li$_2$BeF$_4$(g). Se estudió la masa fundida LiF-BeF$_2$ en equilibrio con un exceso de LiF sólido en el intervalo de temperatura 748-978°K, correspondiente a mezclas que contienen de 66% a 79% LiF. A 900°K, los iones observados fueron, en orden de abundancia, BeF$_2^+$, BeF$_4^-$, Li$,\text{LiBF}_4^$, Li$_2$F$^+$, Li$_2$F$_2^+$ y Li$_2$BeF$_6^-$. La comparación de este espectro de masas con el de LiF(c) puro puso de manifiesto que la mayor parte de la intensidad del Li$^+$ se debe a la ionización disociativa del dímero mixto LiBeF$_3$(g), que representa por consiguiente la especie que mayor cantidad de litio contiene en el vapor del sistema LiF-BeF$_2$. Para la reacción LiF(c) + BeF$_2$(g) = LiBeF$_3$(g) se obtuvo $\Delta H_{\text{molar}} = 4 \pm 2$ kcal/mol. La comparación del espectro de masas de la misma masa fundida con el del BeF$_2$(g) puro puso de manifiesto una marcada desviación negativa respecto de los valores ideales para la actividad del BeF$_2$ en la mezcla. Se estudió también el espectro de masas de una solución que contiene 67% BeF$_2$-33% LiF. Los resultados obtenidos confirmaron la identificación de la molécula de Li$_2$BeF$_4$ como precursora del ion Li$_2$BeF$_6^-$. La actividad del BeF$_2$ en la solución de BeF$_2$ al 67% presentó una desviación positiva respecto de los valores ideales.

1. INTRODUCTION

The lithium fluoride-beryllium fluoride system is of interest as a major constituent of the working fluid of certain molten salt reactors. The first mass-spectrometric study of this system was carried out by Berkowitz and Chupka of Argonne National Laboratory, who examined briefly a 50 percent LiF - 50 percent BeF$_2$ mixture and identified the gaseous mixed dimer LiBeF$_3$. A re-investigation of this system was undertaken in this laboratory as part of a continuing study of the vaporization thermodynamics of light-metal compounds by means of high-temperature mass spectrometry.

As a preliminary to the study of the mixed system, the vaporization of pure lithium fluoride was examined. Next, the mass spectrum of an LiF-BeF$_2$ melt in equilibrium with excess solid LiF was obtained. It was found that the Li$^+$ ion intensity in this mass spectrum was many times greater than that in the mass spectrum of pure LiF, the excess Li$^+$ ion being obviously produced by the dissociative ionization of a mixed lithium-beryllium fluoride. It thus became clear that careful comparison of the mass spectra of the mixed system and of its components would be required for the correct interpretation of the data in terms of the composition of the equilibrium vapor. In order to increase the reliability of such measurements (which could be significantly affected by relatively small changes in instrument sensitivity from experiment to experiment), a twin-crucible source was designed which permitted the direct comparison, in a single experiment, of the mass spectra of the vapors above a pure compound and a mixture. With this source design it was possible to obtain the fragmentation patterns of the gaseous mixed species LiBeF$_3$ and
Li$_2$BeF$_4$, and hence the composition of the vapor above the lithium fluoride-beryllium fluoride system. Heats of formation of the mixed species were also determined. Finally, the twin-crucible technique provides a useful means of determining thermodynamic activities in the melt, and the results obtained will be discussed very briefly.

2. EXPERIMENTAL

The mass spectrometer used in these experiments is a 12-in. radius, 60° sector magnetic-focusing instrument built by Nuclide Associates. The basic features of apparatus design and experimental procedure have been described by Chupka and Inghram. Vapor molecules emerging from the effusion sources described below enter the ion source where they are bombarded with 60V electrons. The ions formed are accelerated by a 4000V electric field, mass analyzed by magnetic deflection and detected by an electron multiplier. For the experiments on pure lithium fluoride, the effusion source used was a two-piece nickel Knudsen cell designed for accurate second-law heat measurements.

The twin-crucible source used for work with mixed systems is shown in Figure 1. The assembly consists of 2 crucible chambers in a resistively heated block. The samples are contained in platinum cups, each of which has a thermocouple welded to its bottom. Another pair of thermocouples is located near the top of the oven chambers. The oven block can be moved from outside the vacuum chamber so that first one and then the other crucible is brought into the line of sight of the ion source entrance slit. In a typical experiment the crucible block is brought to temperature and mass spectra of first, say, the solution and then of the pure compound are obtained. The design was tested by placing pure lithium fluoride in both chambers. A log $I^+T$ vs $1/T$ plot using data from the two crucibles, and using in each case the temperature given by the bottom thermometer (the temperature of the top being in general about 20° higher) gave a single straight line.

3. RESULTS

3.1 Lithium Fluoride

Data for the two extended heat-of-sublimation experiments on lithium fluoride are given in Table I in terms of the slope of plots of $2.303R \log (I^+T)$ vs $10^3/T$, where $I^+$ is the ion intensity and $T$ the absolute temperature. Data for one of the experiments are shown in Figure 2. For the most abundant
species, $\text{Li}_2F^+$ and $\text{Li}^+$, the results of the two experiments agree within the standard deviation of the slopes; for the other species, the difference between the results of the two runs is slightly greater. From the results of Berkowitz, Tasman and Chupka\textsuperscript{4} on the fragmentation behavior of the various lithium fluoride species, the ions $\text{LiF}^+$, $\text{Li}_2F^+$, and $\text{Li}_3F_2^+$ may be assigned to neutral $\text{LiF}$, $\text{Li}_2F_2$, and $\text{Li}_3F_3$. From the mean of two sets of mass-spectrometric slope
TABLE I

MASS SPECTROMETRIC DATA FOR LITHIUM FLUORIDE SUBLIMATION

<table>
<thead>
<tr>
<th>Species</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>67.4 ± 0.5 (16 points 927°-1113°K)</td>
<td>66.2 ± 0.8 (17 points 860°-1060°K)</td>
</tr>
<tr>
<td>LiF$^+$</td>
<td>65.9 ± 0.6 &quot;</td>
<td>63.7 ± 0.5 &quot;</td>
</tr>
<tr>
<td>Li$_2$F$^+$</td>
<td>68.7 ± 0.6 &quot;</td>
<td>67.9 ± 0.5 &quot;</td>
</tr>
<tr>
<td>Li$_3$F$_2$$^+$</td>
<td>72.1 ± 0.6 &quot;</td>
<td>75.7 ± 1.2 (16 points 897°-1060°K)</td>
</tr>
</tbody>
</table>

TABLE II

HEATS OF SUBLIMATION OF GASEOUS LITHIUM FLUORIDE SPECIES, KCAL/MOLE

<table>
<thead>
<tr>
<th>Species</th>
<th>Hildenbrand, Potter and Ju</th>
<th>Mean Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{1000}$(LiF)</td>
<td>64.8 ± 2</td>
<td>63.6 ± 1</td>
</tr>
<tr>
<td>$\Delta H_{1000}$(Li$_2$F$_2$)</td>
<td>68.3 ± 2</td>
<td>67.1 ± 2</td>
</tr>
<tr>
<td>$\Delta H_{1000}$(Li$_3$F$_3$)</td>
<td>73.9 ± 3</td>
<td>-</td>
</tr>
</tbody>
</table>

Data for LiF$^+$, Li$_2$F$^+$ and Li$_3$F$_2$$^+$, we thus obtain the heats of sublimation of lithium fluoride monomer, dimer and trimer given in the first column of Table II. The heat of dimerization of LiF obtained in this work, -61.3 kcal, is in excellent agreement with the value of 61.4 kcal obtained by Berkowitz et al. The heat of sublimation of Li$_3$F$_3$ obtained here is in good agreement with the only other second-law result reported, the value of 74.9 kcal given by Akishin, Gorokhov and Sidorov. In the second column of Table II we give values of $\Delta H_{1000}$ for monomer and dimer derived from the torsion effusion work of Hildenbrand, Potter, and Ju. These authors analyzed the vapor pressure data using the heat of dimerization given by Berkowitz et al. and a dimer-monomer ratio of 1.5; the values given here were calculated from their
values of $\Delta H_{298}$ and the thermal functions given by JANAF Thermochemical Tables. Agreement between the mass spectrometric and torsion effusion results is very satisfactory. The mean of the two sets of data is given in the last column of Table II and represents our best present estimate of the heats of sublimation of the gaseous lithium fluorides.

3.2 The LiF-BeF$_2$ System: Mass Spectra and Vapor Composition

Three sets of experiments were carried out using the twin-crucible technique. In the first, the mass spectrum of an LiF-BeF$_2$ melt in equilibrium
TABLE III

TWIN CRUCIBLE EXPERIMENTS

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature Range</th>
<th>Sample Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>845°-978°K</td>
<td>Crucible 1: LiF(c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crucible 2: LiF(c) + LiF-BeF$_2$ solution.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Composition range of solution: 70.5% to 79% LiF</td>
</tr>
<tr>
<td>2</td>
<td>748°-875°K</td>
<td>Crucible 1: LiF(c) + LiF-BeF$_2$ solution.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Composition range of solution: 66% to 72% LiF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crucible 2: BeF$_2$(c)(to 815°K); BeF$_2$(g)(above 815°K)</td>
</tr>
<tr>
<td>3</td>
<td>646°-918°K</td>
<td>Crucible 1: BeF$_2$(c)(to 815°K); BeF$_2$(g)(above 815°K)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crucible 2: 67% BeF$_2$-33% LiF solution</td>
</tr>
</tbody>
</table>

The choice of the saturated melt for the major part of the present work deserves some comment, since its composition changes with temperature, and since it is therefore impossible, for instance, to obtain directly partial heats of vaporization from the melt. The LiF-BeF$_2$ melt in equilibrium with solid LiF was chosen for two reasons. First, since BeF$_2$ is the major vaporizing species in this system, LiF will always remain in excess. Thus the
TABLE IV

LiF-BeF₂ TWIN-Crucible Experiments
Mass Spectra at 875°K*

<table>
<thead>
<tr>
<th>Experiment 1</th>
<th>Experiment 2</th>
<th>Experiment 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crucible 1</td>
<td>Crucible 2</td>
</tr>
<tr>
<td></td>
<td>Crucible 1</td>
<td>Crucible 2</td>
</tr>
<tr>
<td></td>
<td>BeF₂⁻</td>
<td>BeF₂⁻</td>
</tr>
<tr>
<td></td>
<td>LiBeF₂⁺</td>
<td>LiBeF₂⁺</td>
</tr>
<tr>
<td></td>
<td>Li₂BeF₃⁺</td>
<td>Li₂BeF₃⁺</td>
</tr>
<tr>
<td></td>
<td>Li⁺</td>
<td>Li⁺</td>
</tr>
<tr>
<td></td>
<td>LiF⁺</td>
<td>LiF⁺</td>
</tr>
<tr>
<td></td>
<td>Li₂F⁺</td>
<td>Li₂F⁺</td>
</tr>
<tr>
<td></td>
<td>Li₃F₂⁺</td>
<td>Li₃F₂⁺</td>
</tr>
<tr>
<td>BeF₂⁻</td>
<td>-</td>
<td>32</td>
</tr>
<tr>
<td>Be₂F₃⁺</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>LiBeF₂⁺</td>
<td>.</td>
<td>1.9</td>
</tr>
<tr>
<td>Li₂BeF₃⁺</td>
<td>.</td>
<td>0.02</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.19</td>
<td>5.7</td>
</tr>
<tr>
<td>LiF⁺</td>
<td>0.17</td>
<td>0.28</td>
</tr>
<tr>
<td>Li₂F⁺</td>
<td>0.38</td>
<td>0.87</td>
</tr>
<tr>
<td>Li₃F₂⁺</td>
<td>0.021</td>
<td>0.020</td>
</tr>
</tbody>
</table>

*Ion current in arbitrary units, summed over all isotopic species
composition of the melt will remain fixed for any given temperature even in
the case of an extended experiment — a decided advantage in exploratory work.

A second, and much more important, advantage of working with the
saturated melt is illustrated by the data for Experiment 1 given in Table IV and
by Figure 3, in which $Li^+$, $LiF^+$, $Li_2F^+$, and $Li_3F_2^+$ ion intensities are plotted
as a function of temperature for the same experiment. For each of the ions
$Li^+$, $LiF^+$ and $Li_2F^+$, a higher intensity is observed in the mass spectrum of
the saturated melt than in the mass spectrum of pure LiF. Since the LiF
activity in the saturated melt is unity, the excess $Li^+$, $LiF^+$, and $Li_2F^+$ ion
intensities must derive from the dissociative ionization of mixed lithium-
beryllium fluorides in the vapor above the melt. That the observed differences
are real is demonstrated rather nicely by the behavior of the $Li_3F_2^+$ ion.
Here there is only a single neutral precursor, the lithium fluoride trimer
$Li_3F_3$, and the points from the melt and from pure LiF fall on a single straight
line.

The data of Table IV may now be used to identify the mixed species
present and to obtain their mass-spectrometric fragmentation patterns. As a
first hypothesis, the ion $LiBeF_2^+$ as well as the excess $Li^+$ and $LiF^+$ ion
intensities obtained in Experiment 1 (and listed in the table as "contribution
of mixed species") may be assigned to the mixed dimer $LiBeF_3(g)$. The data of
Experiment 3 may be used to check this assignment. To a sixty-fold increase
in $BeF_2^+$ activity on going from Experiment 1 to Experiment 3, as measured by
the $BeF_2^+$ ion intensities, there corresponds a four-fold increase in the $LiBeF_2^+$
intensity, and hence, from the equilibrium

$$LiF\text{(solution)} + BeF_2(g) = LiBeF_3(g) \quad (1)$$

a 15-fold decrease in LiF activity. In Experiment 3 therefore, effectively
the entire $Li^+$ and $LiF^+$ ion current is contributed by mixed-species
fragmentation. Since the ratios ($Li^+$, Exp. 3)/(Li$^+$ excess, Exp. 1) and
($LiF^+$, Exp. 3)/(Li$F^+$ excess, Exp. 1) agree very well with the ratio
($LiBeF_2^+$, Exp. 3)/(Li$BeF_2^+$ excess, Exp. 1), the assignment of these three ions
to a single neutral precursor appears justified. Combining the data of
Experiments 1, 2 and 3 we obtain the $LiBeF_3(g)$ fragmentation pattern shown in
Table V.
The excess Li$_2$F$^+$ ion observed in Experiment 1 may be assigned most reasonably to the mixed trimer Li$_2$BeF$_4$, with the structure

\[ \text{Li}_2\text{BeF}_3 \quad \text{Li}^+ \quad 2.9 \]

\[ \text{LiBeF}_2 \quad 1 \]

\[ \text{LiF}^+ \quad 0.06 \]

The excess Li$_2$F$^+$ ion observed in Experiment 1 may be assigned most reasonably to the mixed trimer Li$_2$BeF$_4$, with the structure

\[ \text{LiF(solution)} + \text{LiBeF}_3(g) = \text{Li}_2\text{BeF}_4(g) \quad (2) \]

Evidence for the existence of a mixed trimer through the presence of Li$_2$F$^+$ excess led to the identification of a very small amount of Li$_2$BeF$_3^+$ in the mass spectrum of the melt in Experiment 1. While this ion could correspond to the neutral tetramer Li$_2$(BeF$_3$)$_2$, this assumption would lead, through the equilibrium

\[ 2 \text{LiBeF}_3(g) = \text{Li}_2(\text{BeF}_3)_2(g) \quad (3) \]

to an amount of Li$_2$BeF$_3^+$ in Experiment 3 well above the limit of detectability.
given in Table IV. The absence of this ion in the mass spectrum of Experiment 3 is, however, entirely consistent with its assignment to the trimer Li$_2$BeF$_4$, for which we thus obtain the fragmentation pattern given in Table V.

**TABLE VI**

**VAPOUR COMPOSITION OVER A 26%BeF$_2$ - 74% LiF MELT AT 875°K**

<table>
<thead>
<tr>
<th>p. atm</th>
<th>BeF$_2$</th>
<th>LiBeF$_3$</th>
<th>Li$_2$F$_2$</th>
<th>LiF</th>
<th>Li$_2$BeF$_4$</th>
<th>LiF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 x 10$^{-8}$</td>
<td>2.7</td>
<td>.44</td>
<td>.38</td>
<td>.13</td>
<td>.02</td>
</tr>
</tbody>
</table>

The mass spectra of Table IV and the assignments of Table V may now be used to calculate the composition of the equilibrium vapor above a 26 percent BeF$_2$ - 74% LiF melt at 875°K, Table VI. The pressure of BeF$_2$ above the melt is derived from the vapor pressure of pure BeF$_2$, multiplied by the ratio (BeF$_2$ + melt/BeF$_2$ + pure) of Experiment 2. The pressures of LiBeF$_3$ and Li$_2$BeF$_4$ are derived by means of the equations

\[
P_{\text{LiBeF}_3} = \frac{(\text{Li}^+ \text{ excess} + \text{LiF}^+ \text{ excess} + \text{LiBeF}_2^+)}{(\text{BeF}_2^+ \text{ solution})} \cdot \frac{\sigma_{\text{BeF}_2}}{\sigma_{\text{LiBeF}_3}} \cdot P_{\text{BeF}_2}
\]

\[
P_{\text{Li}_2\text{BeF}_4} = \frac{(\text{Li}_2^+ \text{F}^+ + \text{Li}_2\text{BeF}_3^+)}{(\text{BeF}_2^+ \text{ solution})} \cdot \frac{\sigma_{\text{BeF}_2}}{\sigma_{\text{Li}_2\text{BeF}_4}} \cdot P_{\text{BeF}_2}
\]

where the $\sigma$'s are the relative ionization cross-section calculated from the data of Otvos and Stevenson. Finally, the partial pressures of LiF and Li$_2$F$_2$ were obtained from the total lithium fluoride vapor pressure at 1000°K given by Hildenbrand et al., a dimer-monomer ratio of 1.5 at that temperature and the heats of sublimation given in Table II. The resulting monomer and dimer
pressures are in reasonable accord with the mass spectrometric intensity ratios. The partial pressure of lithium fluoride trimer was estimated from the mass spectrum as one-twentieth of that of lithium fluoride dimer.

3.3 The LiF-BeF$_2$ System: Activities

The data of the present experiments may be used to obtain the thermodynamic activities of LiF and BeF$_2$ in the two melts studied. Considerations
based on activities have, in fact, already been used in Section 3.2 to identify the neutral precursors of the various fragment ions observed. Activity data at 875°K, based on the data of Table IV, are summarized in Table VII. For BeF₂, the ratio of BeF₂⁺ ion currents for the melt and for pure BeF₂ can be used as a measure of the activity. No such simple comparison can be used to obtain the activity of LiF since, particularly at higher BeF₂ concentrations, the contributions of LiF and Li₂F₂ to the Li⁺, LiF⁺ and Li₂F⁺ ion intensities are overwhelmed by the contributions of the mixed dimer and trimer, LiBeF₃ and Li₂BeF₄. However, the LiBeF₃ concentration may be used as a measure of LiF activity by writing the equilibrium constant for equation (1) in the form

\[ K'_1 = \frac{a_{\text{LiF}} I_{\text{BeF}_2}^+}{I_{\text{LiBeF}_2}^+} \]

For a given temperature K' can be evaluated from the data of Experiment 1, for which \( a_{\text{LiF}} = 1 \). The values of \( a_{\text{LiF}} \) at other concentrations can then be derived from BeF₂⁺ and LiBeF₂⁺ ion intensities.

3.4 The LiF-BeF₂ System: Heats of Formation of Mixed Species

The heat of formation of the mixed dimer LiBeF₃(g) may be obtained from the data of Experiment 1 (Figures 3 and 4) by means of the equilibrium

\[ \text{LiF}(c) + \text{BeF}_2(g) = \text{LiBeF}_3(g) \quad (4) \]

The equilibrium constant for this reaction, \( K_4 = \frac{P_{\text{LiBeF}_3}}{P_{\text{BeF}_2}} \), may be written in the form

\[ K'_4 = \frac{I_{\text{LiBeF}_3}^+}{I_{\text{BeF}_2}^+} \]

or

\[ K''_4 = \frac{I_{\text{Li}^+} + \text{excess}}{I_{\text{BeF}_2}^+} \]

Plots of \( \log K'_4 \) and \( \log K''_4 \) against 1/T are shown in Figure 5. Also shown in
Figure 5 are data for log $K'_4$ taken from the first run on the LiF(c)-saturated solution system, which was carried out in a single-crucible source of the type used in the experiments on pure LiF. The second law heats obtained are in good agreement with each other. Since the temperature dependence of the Li$^+$ ion intensity may be subject to kinetic energy effects we have given more weight to the values obtained from $K'_4$ and thus obtain for the heat of reaction (4)

$$\Delta H_{900}(\text{reaction 4}) = 4 \pm 2 \text{ kcal}$$
TABLE VII

BeF$_2$-LiF SOLUTIONS, 875°K
ACTIVITIES (a) AND ACTIVITY COEFFICIENTS (γ)

<table>
<thead>
<tr>
<th>BeF$_2$</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>26%</td>
<td>67%</td>
</tr>
<tr>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>0.017</td>
<td>0.065</td>
</tr>
<tr>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td>0.91</td>
<td>1.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BeF$_2$</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>67%</td>
<td>33%</td>
</tr>
<tr>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>0.073</td>
<td>0.23</td>
</tr>
</tbody>
</table>

TABLE VIII

VAPORIZATION OF BeF$_2$ FROM THE SATURATED SOLUTION

<table>
<thead>
<tr>
<th>Mole Ratio in Melt</th>
<th>2.303R d log p$_{BeF_2}$</th>
<th>d log p$_{BeF_2}$</th>
<th>ΔH$_{fus}$ (LiF)</th>
<th>ΔH$_{vap}$ (BeF$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n$<em>{LiF}$/n$</em>{BeF_2}$</td>
<td>2.017</td>
<td>1.3</td>
<td>48.7</td>
<td>-6.0</td>
</tr>
<tr>
<td>750</td>
<td>2.4</td>
<td>1.3</td>
<td>41.6</td>
<td>-6.15</td>
</tr>
<tr>
<td>850</td>
<td>3.3</td>
<td>1.3</td>
<td>35.9</td>
<td>-6.3</td>
</tr>
</tbody>
</table>

Combining this value with the heat of sublimation of LiF we obtain for the heat of formation of the mixed dimer from the gaseous monomers:

LiF(g) + BeF$_2$(g) → LiBeF$_3$(g) ΔH$_{900}$ = -60 kcal/mole

This value is nearly identical with the heat of dimerization of LiF:

2LiF(g) → Li$_2$F$_2$(g) ΔH$_{900}$ = -61 kcal/mole

The data of Table VI give for reaction (5) an equilibrium constant $K_5 = 4.2 \times 10^7$ atm$^{-1}$ at 875°K, and hence a free energy change ΔF$_{875}$ = -35 kcal.
Combining this value with the heat of formation of the mixed dimer, we obtain...
for the entropy of formation of the mixed dimer the value of -32 eu. This value is within the range of the entropies of dimerization of simple metal halides\textsuperscript{10} and is certainly in accord with the modified alkali-halide dimer structure

$$\text{Li}^+ \text{BeF}_2$$

An attempt was also made to evaluate the heat of formation of the mixed trimer $\text{Li}_2\text{BeF}_4(g)$. For this purpose the equilibrium

$$\text{LiF}(c) + \text{LiBeF}_3(g) = \text{Li}_2\text{BeF}_4(g)$$

may be used. Using the $\text{Li}_2\text{F}^+(\text{excess})$ ion intensity as a measure of $\text{Li}_2\text{BeF}_4(g)$, we can write the equilibrium constant for reaction (6) in the form

$$K'_6 = \frac{I_{\text{Li}_2\text{F}^+(\text{excess})}^+}{I_{\text{LiBeF}_2}^+}$$

From the values of $K'_6$ in the temperature range 860\textdegree-978\textdegree K, we obtain for $\Delta H_{900}$(reaction 6) a least squares value of 10.7 ± 1.3 kcal. Combining this
value (to which a real uncertainty of ± 5 kcal should probably be assigned) with the heat of sublimation of LiF(c), we obtain for

\[ \text{LiF}(g) + \text{LiBeF}_3(g) \rightarrow \text{Li}_2\text{BeF}_4(g) \quad \Delta H_{900} = -53 \text{ kcal/mole} \]

This may be compared to the value for the corresponding reaction in the pure lithium fluoride system:

\[ \text{LiF}(g) + \text{Li}_2\text{F}_2(g) \rightarrow \text{Li}_3\text{F}_3(g) \quad \Delta H_{900} = -59 \text{ kcal/mole} \]

The temperature dependence of the BeF\(^+\) ion intensity (Figure 4) over the saturated melt in Experiments 1 and 2 may be used as a further check on the consistency of the present data. For the vapor pressure of BeF\(_2\) in a solution saturated with excess solid LiF we have

\[
2.303R \frac{d \log p_{\text{BeF}_2}}{d(1/T)} = \Delta H_{\text{vap, BeF}_2} - \frac{n_{\text{LiF}}}{n_{\text{BeF}_2}} \Delta H_{\text{fus, LiF}}
\]

where \(n_{\text{LiF}}\) and \(n_{\text{BeF}_2}\) are the moles of LiF and BeF\(_2\) in solution, \(\Delta H_{\text{vap, BeF}_2}\) is the heat of vaporization of one mole of BeF\(_2\) from the melt, and \(\Delta H_{\text{fus, LiF}}\) is the heat of fusion of LiF(c) to give one mole of supercooled LiF(l) at its concentration in the solution. The \(I^+T\) data for BeF\(_2\)^+ in solution of Figure 4 were fitted to a parabola and slopes determined at three temperatures. Assuming as a first approximation that \(\Delta H_{\text{fus, LiF}}\) has the ideal value, we obtain the values of \(\Delta H_{\text{vap, BeF}_2}\) given in Table VIII. As should be expected, these values are all above the heat of vaporization of BeF\(_2\) at the temperatures involved.

4. SUMMARY AND CONCLUSIONS

The present experiments show that the molten-salt system LiF-BeF\(_2\) is quite non-ideal, the BeF\(_2\) activity coefficient going from less than 0.1 to greater than 1 in a concentration range from 26%-67% BeF\(_2\). In the vapor phase we note the great stability of the mixed dimer LiBeF\(_3\), which is underlined by the fact that its heat of formation from the gaseous monomers is nearly identical with the heat of dimerization of lithium fluoride. From a mass-spectrometric point of view, the high degree of fragmentation of the mixed
dimer LiBeF$_3$ and particularly of the mixed trimer Li$_2$BeF$_4$ is notable. Analysis of the vapor composition shows that the LiBeF$_3$ (g) is the predominant lithium-containing vapor species in the LiF-BeF$_2$ system.

REFERENCES


[7] JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, December 1964. The thermal functions for Li$_2$F$_2$ given there are nearly identical to those used by HILDENBRAND, POTTER, and JU.


[11] The temperature ranges of Experiments 2 and 3 bracket the melting point of BeF$_2$, 815°K. No attempt was made to derive separate heats of vaporization and sublimation for the data of pure BeF$_2$. However, a straight line through the points for pure BeF$_2$ in Figure 4 gives a slope of 52.2 ± 2
kcal, which may be compared to the heat of sublimation of 53.1 kcal/mole at 800°K and the heat of vaporization of 50.5 kcal/mole at 900°K.  

The preparation and thermodynamics of europium dicarbide

R.E. GEBELT* and H.A. EICK
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

The preparation and thermodynamics of europium dicarbide. Europium dicarbide has been prepared by the reaction of europium metal and graphite in a stainless steel bomb. Chemical analysis indicates an average composition of the product of EuC₂₀₀ ± 0.07. X-ray powder diffraction analysis shows the compound to be of body-centred tetragonal symmetry, space group D₂₁₄/mmm, with lattice parameters: a₀ = 4.045 Å; c₀ = 6.645 Å. Vapour phase chromatographic analysis indicates that 98% of the gaseous product of acid hydrolysis of europium dicarbide is the hydrocarbon acetylene. These analytical data, together with the lattice parameters, indicate that europium dicarbide resembles alkaline earth dicarbides more than it resembles the other lanthanide dicarbides. The vaporization of europium dicarbide over the temperature range 1130 to 1600°K was investigated by the Knudsen effusion method. The effusate was either collected and analyzed chemically or observed with a time-of-flight mass spectrometer. The data presented here are based predominantly on the mass spectrometric observations since they yielded more reproducible data than the collection technique. Gaseous europium dicarbide and europium, in concentrations of 1 and 99% respectively, were found in the effusate. Instrument limitations prevented determination of the concentration of the gaseous dicarbide as a function of temperature. Calibration of the mass spectrometer with silver permitted the calculation of the pressures corresponding to the observed ion intensities. An empirical equation was fitted to the data for europium by the method of least squares. From the second law of thermodynamics the following values were calculated for the reaction:

\[ \text{EuC}_2 = \text{Eu}(g) + 2\text{C} \text{(graphite)}; \Delta H^\circ_{\text{f298}} = 51.09 \pm 1.42 \text{kcal/mole}; \Delta S^\circ_{\text{m298}} = 18.43 \pm 1.75 \text{e.u.} \]

Values of the free energy function for EuC₂(g) were estimated and combined with published data to yield for the same reaction, from the third law of thermodynamics, the value of ΔH^\circ_{\text{f298}} = 51.22 ± 6.80 kcal/mole. The enthalpies obtained for the dissociation reaction were combined with published data on the enthalpy of vaporization of europium to yield for the standard enthalpy of formation of EuC₂ the value ΔH^\circ_{\text{f298}} = -9.17 ± 1.15 kcal/mole.

Preparation et thermodynamique du bicarbure d'europium. Les auteurs ont préparé du bicarbure d'europium par réaction entre l'europium métallique et le graphite dans une bombe en acier inoxydable. L'analyse chimique indique EuC₁₀₀ ± 0.07 comme composition moyenne du produit. D'après l'analyse au moyen de la diffraction des rayons X par les poudres, le composé présente une symétrie quadratique centrée (groupe spatial de Schoenflies D₂₁₄/mmm) avec les paramètres de réseau a₀ = 4.045 Å et c₀ = 6.645 Å. Il ressort de l'analyse chromatographique de la phase vapeur que 98% du produit gazeux de l'hydrolyse acide du bicarbure d'europium sont constitués par de l'acétylène. Les résultats de ces opérations d'analyse et les paramètres de réseau indiquent que le bicarbure d'europium présente plus d'analogie avec les bicarbures des métaux alcalino-terreux qu'avec les bicarbures des autres lanthanides. Les auteurs ont étudié, par la méthode d'effusion de Knudsen, la vaporisation du bicarbure d'europium dans l'intervalle de température compris entre 1130 et 1600°K. L'effusate a été rassemblé et analysé chimiquement ou observé à l'aide d'un spectromètre de masse à temps de vol. Les valeurs données dans le mémoire se fondent avant tout sur les observations faites au moyen de cet appareil; en effet, ces observations fournissent des valeurs plus aisément reproductibles que la méthode du rassemblement. Il a été constaté que l'effusate contenait du bicarbure d'europium et de l'europium gazeux, dont les concentrations étaient respectivement de 1 et 99%. Les limitations dues à l'appareil n'ont pas permis de déterminer la concentration du bicarbure gazeux en fonction de la température. Après avoir étalonné le spectromètre de masse au moyen de l'argent, il a été possible de calculer les pressions correspondant aux intensités ioniques observées. Une équation empirique a été ajustée aux données relatives à l'europium par la méthode de régression.
En appliquant le deuxième principe de la thermodynamique à la réaction, on a calculé les valeurs suivantes:

\[
\text{EuC}_2 = \text{Eu(g)} + 2\text{C(graphite)}; \quad \Delta H^0_{298} = 51,09 \pm 1,42 \text{ kcal/mole}; \quad \Delta S^0_{298} = 18,43 \pm 1,75 \text{ u.e.}
\]

Les auteurs ont déterminé des valeurs estimées de la fonction d'énergie libre pour \( \text{EuC}_2 \) et les ont combinées avec les données publiées; ils ont ainsi obtenu pour la même réaction, en se fondant sur le troisième principe de thermodynamique, la valeur \( \Delta H^°_{98} = 51,22 \pm 0,80 \text{ kcal/mole} \). Ils ont combiné les enthalpies obtenues pour la réaction de dissociation avec les données publiées sur l'enthalpie de vaporisation de l'europium et ont ainsi obtenu la valeur ci-dessus pour l'enthalpie type de la formation de \( \text{EuC}_2 \):

\[
\Delta H^0_{(98)} = -9,17 \pm 1,15 \text{ kcal/mole.}
\]

**POLYCHÈRE ET TÉРMODINAMIČESKIE SVOJSTVA DİКАРБИДА ЕВРОПИЯ.** Дикарбид европия получен в результате реакции металлического европия и графита в бомбе из нержавеющей стали. Данные химического анализа указывают, что средний состав продукта составляет \( \text{EuC}_1,87\pm0,07 \). Результаты анализа рентгенограмм типа Дебая-Шеррера свидетельствуют о наличии объемно-центрированной тетрагональной симметрии в структуре соединения и пространственной группе \( D_{4h}^1 = 14/mmm \) с параметрами решетки: \( a_0 = 4,045 \) Å; \( c_0 = 6,645 \) Å. Данные хроматографического анализа фазы пары указывают на то, что девяносто восемь процентов газообразного продукта кислотного гидролиза дикарбид европия составляет углеводород, ацетилен. Эффузат либо собирался и анализировался химическим путем, либо изучался с помощью масс-спектрометра по времени пролета. Представленные здесь данные основаны главным образом на результатах наблюдений с помощью масс-спектрометра, поскольку эти результаты привели к облучению более воспроизводимых данных, чем при методе сбора.

В эффузате обнаружены газообразные дикарбид европия и европий в концентрациях соответственно 1 и 99%. Возможности приборов не позволили определить концентрацию газообразного дикарбид как функцию температуры. Калибрование масс-спектрометра серебром позволило рассчитать давления, соответствующие отмеченной интенсивности ионов. Эмпирическое уравнение соответствовало данным по европию, полученными методом наименьших квадратов.

На основании второго закона термодинамики

\[
\text{EuC}_2 = \text{Eu(gaz)} + 2\text{C(графит)}
\]

были вычислены следующие данные:

\[
\Delta H^0_{298} = 51,09 \pm 1,42 \text{ ккал/моль};
\quad \Delta S^0_{298} = 18,43 \pm 1,75 \text{ эд. энт.}
\]

**PREPARACION Y TERMODINAMICA DEL DICARBURO DE EUROPIO.** Se preparó dicarburo de europio por reacción entre europio metálico y grafito, en una bomba de acero inoxidable. Los análisis químicos indican que la composición media del producto puede representarse por la fórmula \( \text{EuC}_{1,87}\pm0,07 \). El examen mediante difracción de rayos X por polvos muestra que el compuesto posee una simetría tetragonal centrada en el cuerpo (grupo espacial \( D_{4h}^1 = 14/mmm \)) con parámetros del reticulado \( a_0 = 4,045 \) Å y \( c_0 = 6,645 \) Å. El análisis cromatográfico en fase vapor indica que el 98% del producto gaseoso proveniente de la hidrólisis ácida del dicarburo de europio está formado por acetileno. Estos datos analíticos, juntamente con los parámetros del reticulado,
indican que el dicarburo de europio se asemeja más a los dicarburos de elementos alcalino-térreos que a los de lantánidos. Empleando el método de efusión de Knudsen, se estudió la vaporización del dicarburo de europio en el intervalo de temperaturas 1130 - 1600°K. El producto efundido se recogió y se analizó químicamente, o bien se observó con un espectrómetro de masas por el método del tiempo de vuelo. Los resultados presentados en la memoria se basan fundamentalmente en las observaciones efectuadas con este último aparato, pues los datos suministrados son más reproducibles que los obtenidos con la técnica de recolección. En el producto efundido se halló dicarburo de europio y europio gaseosos, en concentraciones de 1 y 99% respectivamente. Las limitaciones del instrumental impidieron determinar la concentración del dicarburo gaseoso en función de la temperatura. La calibración del espectrómetro de masas con plata permitió calcular las presiones correspondientes a las intensidades iónicas observadas. Una ecuación empírica fue adaptada a los datos del europio usando el método de los cuadrados mínimos. Partiendo del segundo principio de la termodinámica se obtuvieron los siguientes valores para la reacción

\[
\text{EuC}_2 \rightarrow \text{Eu}(g) + 2\text{C} \text{(grafito); } \Delta H_{298} = 51,09 \pm 1,42 \text{ kcal/mol; } \Delta S_{298} = 18,43 \pm 1,75 \text{ u.e.}
\]

Se estimaron los valores correspondientes a la función de energía libre para el \( \text{EuC}_2(g) \) y se combinaron con los datos publicados alcanzando para la misma reacción y aplicando el tercer principio de la termodinámica, el valor \( \Delta H_{298} = 51,22 \pm 0,80 \text{ kcal/mol.} \)

Las entalpas obtenidas para la reacción de disociación se combinaron con los datos publicados sobre la entalpia de vaporización del europio, obteniéndose para la entalpia tipo de formación del \( \text{EuC}_2 \) el valor \( \Delta H_f(298) = -9,17 \pm 1,15 \text{ kcal/mol.} \)

INTRODUCTION

All the lanthanide dicarbides, except that of europium, have been prepared and studied extensively [1-4]. However, none of the reports contains either data or statements about europium dicarbide, leaving doubt as to whether it could not be prepared or whether its preparation was even attempted. Europium binary compounds differ frequently from their analogous neighbouring species; thus, an understanding of the properties of the europium-carbon system would be most desirable. This paper discusses the preparation, identification, and some of the thermodynamics of the vaporization of a europium dicarbide phase.

EXPERIMENTAL

Preparation

Preliminary studies [5] indicated that when a mixture of either europium sesquioxide or europium metal and graphite was heated in a graphite or tantalum crucible, elemental europium distilled from the container. For this reason a mixture of europium metal and graphite was inserted into a bomb machined from 25 mm diameter stainless steel bar stock. The rim of the threaded bottom half of the bomb was machined to a sharp point (an inverted "V") which cut into a platinum gasket (about 0.1 mm thick) when the matching top was screwed on tightly. The cavity in the 100 mm long bomb was 9.5 mm in diameter and 17.2 mm deep. Before use the halves of the bomb were heated to 1100°C in a high vacuum to out-gas the metal. The bomb, which was charged in a helium atmosphere, confined a pressure of about 5 atm at the reaction temperature. Although "parting" compounds such as graphite were
used, the threads were frequently damaged severely when the bomb was opened and it was usually necessary to machine a new top after each use. The most successful bombs — those which could be used more than once — were machined from different types of stainless steel.

The charged and sealed bomb was placed in a resistance-heated tube furnace through which helium flowed constantly, and was heated for about twelve hours at 1050°C. After the reaction was complete, the bomb was cooled slowly (although the data indicated the products were independent of the cooling rate) and was transferred to the helium-filled glove box where it was opened and the contents were removed and stored. Some preparations were made in bombs machined from molybdenum bar stock. The temperature was monitored with a chromel-alumel thermocouple whose output was measured with a Rubicon portable potentiometer. Reaction temperatures were varied from about 950°C to 1125°C to check for completeness of reaction.

**Target collection: effusion studies**

For target collection Knudsen effusion studies, an apparatus similar to that reported by Ackermann, Gilles, and Thorn [6] was used. The effusion cell, machined from molybdenum and shown schematically in Fig. 1, was 1.5 cm in diameter and 2.0 cm high. The orifice was 0.711 mm in diameter. The cell was machined so that once the two halves had been fitted together, they could not be separated. After they had been out-gassed, a graphite liner was inserted into the cavity and the halves were fitted together under pressure. Subsequently, the assembly was heated to 2000°C to weld the top and bottom into a leakproof unit. The cell was loaded in a helium atmosphere with a finely ground sample inserted through the orifice.

Since this cell was designed to be used in the mass spectrometer, it was impossible to drill a separate black body hole in its base. Therefore, the temperature of the inductively-heated cell was measured with a Leeds and Northrup disappearing-filament type optical pyrometer calibrated at the National Bureau of Standards (and compared to another standardized pyrometer which is used for reference only) by sighting onto the bottom surface of the effusion cell. This apparent temperature was corrected to the true cavity temperature (obtained by sighting into the cell through the orifice) by use of a correction equation determined in separate experiments. The temperatures were corrected in the usual manner for window and prism absorption errors.

The effusate was collected on platinum discs 25 mm in diameter and 0.1 mm thick held by phosphor bronze springs in aluminium cassettes confined in an assembly which was cooled by liquid nitrogen. Experiments to determine the degree of condensation on the targets were performed by drilling a small hole (2-3 mm) in two targets ("a" and "b") located in the same cassette. The target facing the cell ("a") collected all of the beam passing through the collimator, except that fraction of it which passed through the hole drilled in the target. Effusate which passed through this hole struck a target held in the second cassette, and most of the atoms which did not condense but "bounced" were collected on the backing target ("b"). By determining the europium content on the backing target ("b"), the fraction condensing on the cooled targets could be calculated.
Mass spectrometric studies

The crucible (illustrated in Figure 1), described and loaded as indicated above, was inserted into the mass spectrometer heating chamber (Fig. 2). This chamber and the associated power supply are similar to those used by Mr. Everett G. Rauh of the Argonne National Laboratory.

The mass spectrometer, which is similar to the Bendix Model 12-101, was constructed in our laboratory using the electronic chassis purchased from the Bendix Corporation. The spectrometer is fitted with a 167 cm drift tube instead of the normal one metre unit. The output of two modified analogue units was recorded on Bausch and Lomb VOM-5 strip chart recorders, and the intensity of a peak was assumed to be proportional to the recorded peak height.

The high temperature Knudsen inlet source, again modelled after that used at the Argonne National Laboratory, and constructed in our shops, was pumped by a 15 l/s Varian Vac-Ion pump which served also as a pressure gauge for the source region. During operation the pressure in this chamber was maintained always below $5 \times 10^{-5}$ torr. The pressure in the main vacuum system, monitored with a Veeco high vacuum gauge, varied between $1 \times 10^{-1}$ and $6 \times 10^{-7}$ torr during operation. Since the reaction proceeded at a rather low temperature, the loaded cell was out-gassed at about 900°C until the residual pressure in the system was at the background level.

Cell temperatures were measured with the pyrometer described above by sighting into the orifice of the effusion cell. They were constant to within the limits of error associated with the reading of the pyrometer over the range of temperatures used in these experiments. The data were corrected for window and prism absorption errors. In each experiment data were collected first at increasing and then at decreasing temperatures.
Although in most of the experiments only EuC₂ and graphite were inserted in the effusion cell, a weighed quantity of silver was inserted along with the samples in two experiments to calibrate the mass spectrometer. The time required for complete vaporization of the silver and its ion intensity were recorded. These data were used to calculate the silver pressure within the cell and to calibrate the instrument.

After an ionization efficiency curve had been determined experimentally, a value of 18 eV was chosen for the intensity measurements. The energy of the ionizing electrons, monitored continuously with a digital voltmeter, was maintained manually at this value and the electron current was regulated automatically at approximately one microampere. At 18 eV residual gases in the spectrometer were not visible in the spectrum.

**Analyses**

Platinum targets on which small amounts of the condensate from the effusion cell had collected were treated with 1N perchloric acid to dissolve the europium. The resulting solution was analysed spectrophotometrically using a method described by Rinehart [7].

The composition of the EuC₂ specimens was determined by dissolving samples in 6N HCl. The solution was filtered to remove free carbon and the europium was precipitated as an oxalate and determined gravimetrically. The free carbon was dried at 110°C and weighed. Other samples were burned in air to the sesquioxide and from the weight difference the total carbon content was determined. Bound carbon was assumed to be the difference between total and unbound (free) carbon. The product was checked for the presence of foreign substances such as iron and nickel by standard qualitative tests.

The gases produced by hydrolysis of some of the samples were swept with helium into a U-tube which was packed with glass wool and suspended in liquid nitrogen. Those gases which condensed were analysed using a flame-ionization type gas chromatographic unit which had been standardized with welding grade acetylene and natural gas.

X-ray powder diffraction analyses were performed using either CuKα (λ = 1.5418 Å) or FeKα (λ = 1.9373 Å) using both 114.59 mm Debye-Scherrer powder cameras and Siemens powder diffractometers. X-ray powder diffraction photographs were taken of the samples used for effusion studies both before and after the experiments.

**RESULTS**

The percentages of europium and bound carbon, the latter determined by difference, indicate that the composition of the specimens was EuC₁.₈⁷ ± 0.₀₇. The gas chromatographic analyses of the hydrolysis product indicated it to be principally acetylene, with traces of methane and other hydrocarbons. A typical chromatographic spectrum is illustrated in Figure 3.

The X-ray powder diffraction patterns could be indexed on the basis of a body-centred tetragonal cell, space group D₄h - 14/mmm, identical to that exhibited by other lanthanide dicarbides, the lattice parameters of which are
TABLE I

ENTHALPY OF VAPORIZATION OF EUROPIUM DICARBIDE  
(Units: kcal/gfw)

<table>
<thead>
<tr>
<th>Experiment (No)</th>
<th>$\Delta H_{\text{vap}}^{151\text{Eu}}$</th>
<th>$\Delta H_{\text{vap}}^{153\text{Eu}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS - 26</td>
<td>+50.31 ± 1.35$^a$</td>
<td>+51.68 ± 1.71$^a$</td>
</tr>
<tr>
<td>MS - 3</td>
<td>52.10 ± 0.51</td>
<td>53.92 ± 1.22</td>
</tr>
<tr>
<td>MS - 5</td>
<td>48.81 ± 0.53</td>
<td>49.53 ± 0.56</td>
</tr>
<tr>
<td>Average</td>
<td>50.41 ± 1.04</td>
<td>51.71 ± 1.45</td>
</tr>
<tr>
<td>Final value</td>
<td>51.06 ± 1.25$^a$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Standard deviation

$a_0 = 4.045\text{"A}$ and $c_0 = 6.645\text{"A}$ with an estimated error of ± 0.005\text{"A}. In the powder diffraction photographs some weak lines were present in addition to the lines attributable to this phase and graphite. The quantity of this minor impurity could neither be decreased nor increased appreciably by altering the preparatory conditions. The low angle lines of this impurity could be indexed using a computer programme [8] on the basis of an orthorhombic cell whose dimensions are $a_0 = 8.76\text{"A}$, $b_0 = 11.23\text{"A}$, and $c_0 = 7.19\text{"A}$, but the high angle lines could not be indexed satisfactorily.

A logarithmic graph of the europium concentration on the targets exposed to the Knudsen cell times the square root of the temperature versus $10^4/T$ indicated considerable scatter in the data. This scatter was found to result both from "bouncing" of the europium atoms from the target and from errors in the spectrophotometric analysis scheme. The "bouncing experiments" indicated that only 55 to 75% of the atoms striking the target adhered. In addition, errors of up to ± 50% resulted from the analytical scheme.

The mass spectrometric data indicated that at 1450°K about 99% of the effusate was elemental europium – about 1% was gaseous europium dicarbide. Since the percentage of gaseous EuC$_2$ was so low, its temperature dependence could not be measured with our instrument. A typical spectrum of the mass region of interest is illustrated in Figure 4.

In Figure 5, the logarithm of the ion intensity times temperature data of a three day experiment is graphed against $10^4/T$. The logarithm IT versus reciprocal temperature data (I = ion intensity) of this and two different experiments were fitted by the method of least squares and the average second law heat of vaporization was calculated to be 51.06 ± 1.25 kcal/gfw. The individual heats calculated for each of the two europium isotopes, their standard deviations, and the best second law value of the heat and its standard deviation, are listed in Table I.
FIG. 2 The mass spectrometer heating assembly

FIG. 3 Vapour phase chromatogram of the hydrolysis product of europium dicarbide
FIG. 4  The mass spectrum of europium and europium dicarbide

FIG. 5  The temperature dependence of the europium ion intensity
The sensitivity factor, \( k \), determined from the time necessary to vaporize a known weight of pure silver, was \( 2.488 \times 10^2 \text{nA/atm of } ^{107}\text{Ag} \). The silver pressure, calculated to be \( 4.06 \times 10^{-5} \text{atm} \) at a temperature of 1370°C may be compared with the value of \( 3.77 \times 10^{-5} \text{atm} \) computed from the data in Stull and Sinke [9]. The ionization efficiency curves of masses 151 (europium), 28, and 18, extrapolated linearly to zero ion intensity to permit appearance potential determination, are illustrated in Figure 6.

DISCUSSION

The phase prepared, although contaminated always with a minor constituent which contained only europium and carbon, was unquestionably a dicarbide. Although its structure is similar to that reported for other lanthanide dicarbides, the lattice parameters are similar to those reported for strontium dicarbide \( (a_0 = 4.11\text{Å}, c_0 = 6.68\text{Å}) \) [10] and are considerably larger than those expected for a lanthanide species. In addition, the hydrolysis product, which is principally acetylene, indicates a difference, since the other lanthanides evolve a mixture of hydrocarbons upon hydrolysis [11]. Europium behaves very much like the alkaline earth dicarbides which hydrolyse only to acetylene. Furthermore, unlike the other lanthanides, europium apparently hydrolyses to europium(II) (as do the alkaline earth dicarbides), and since the europium(II) oxidizes slowly to europium(III), only traces of methane and other reduced hydrocarbons are observed in the spectrum.

The concentration of the minor phase present in all samples was altered little, if any, when either the composition of the reactants or the temperature was changed. We think this minor phase may be a different crystalline modification of the same phase. Calcium dicarbide has been reported to exist in four different crystalline modifications [12-15], and the similarity of this phase to CaC\(_2\) would make allotropy quite probable. The allotropic modifications reported for calcium dicarbide are:

- CaC\(_2\) (II), monoclinic, \( a_0 = 8.36\text{Å}, b_0 = 4.20\text{Å}, c_0 = 11.25\text{Å}, \beta = 96.3^\circ \)
- CaC\(_2\) (III), triclinic, \( a_0 = 8.42\text{Å}, b_0 = 11.84\text{Å}, c_0 = 3.94\text{Å}, \alpha = 93.4^\circ, \beta = 92.5^\circ, \gamma = 89.9^\circ \)
- CaC\(_2\) (IV), cubic, \( a_0 = 5.880 \pm 0.005\text{Å} \), stable only above 450°C.

Phase II is reported to be stable only in the presence of cyanide ions.

The lines present in the X-ray powder diffraction data which could not be assigned to either EuC\(_2\) or graphite were indexed partially with an orthorhombic cell whose lattice parameters are quite close to those of both forms (II) and (III). Since the angles in these two forms do not differ appreciably from 90°, such partial orthorhombic indexing of low angle lines should be possible if the unit cells are similar. It seems likely, therefore, that the extra lines belong to an allotropic modification of europium dicarbide.

The target collection effusion data were converted into pressures by use of the familiar Knudsen equation:

\[
P_{\text{atm}} = 0.022557 \frac{w}{\text{at}} \left(\frac{T}{M}\right)^{\frac{1}{2}} \left(1 + \frac{d^2}{r^2}\right)
\]

in which \( w \) is the mass of the collected effusate expressed in grams, \( a \) is the orifice area expressed in \( \text{cm}^2 \), \( t \) is the time (expressed in seconds), \( T \) is the
temperature (°K), M is the atomic weight of elemental europium, r is the radius of the collimator, and d is the collimator to orifice distance. Both r and d had the same units, cm.

A third law heat was calculated from these pressures using the free energy functions of europium and carbon listed in Stull and Sinke [9] and an estimated free energy function for solid EuC₂ computed according to the following equation:

\[
\Delta \text{f}_{\text{EuC}_2} = \text{f}_{\text{CaC}_2} - \text{f}_{\text{Ca}} + \text{f}_{\text{Eu}}
\]  

using data from Kelley [16] and Kelley and King [17]. Since EuC₂ seems to be similar to the alkaline earth dicarbides, this estimate is probably quite accurate. The free energy function calculated for EuC₂(s) is listed in Table II along with \( \Delta \text{f}_{\text{f}} \) for the reaction:

\[
\text{EuC}_2(s) = \text{Eu}(g) + 2\text{C(graphite)}
\]  

The \( \Delta \text{f}_{\text{f}} \) for reaction (3) is illustrated graphically in Fig.7 also. (The non-stoichiometry of the dicarbide phase was not considered in these calculations.) The third law heat obtained from the treatment of the best set of experimental data are compiled in Table III. The average heat together with its standard deviation is 56.29 ± 3.84 kcal/gfw, a value which must be somewhat high since the pressures used in its calculation are low. In addition, the heats show a slight dependency upon temperature. Although additional experiments were performed, third law heats were not calculated from them since the data obtained from the mass spectrometer are more accurate.

The ionization efficiency curves obtained with the mass spectrometer were treated by the method described by White and co-workers [18]. From the appearance potentials of 18.6, 16, 0, and 80 eV determined for masses 28, 18, and 151 respectively, by extrapolation to zero ion intensity, 3.0 eV were subtracted, since the accepted ionization potential of nitrogen (28) is 15.6 eV [19]. The experimental values for mass 18 and 151 then become 13.0 and 5.0 eV, respectively, in good agreement with the reported ionization potential of water (12.9 eV) and europium (5.6 eV). From this we conclude that the europium observed in the spectrometer is the primary product of the vaporization described by Eq.(3) above and is not produced by fragmentation.

This curve indicates also that operation at 18 eV is not on the plateau portion of the ionization efficiency curve, but on a shoulder. However, when the ion intensity was monitored as a function of time, it was found to remain constant for periods of 30 min or more. In addition, when the temperature was returned to an initial value after 16 h of vaporization, the europium ion intensity returned to the value recorded previously at that temperature. This reproducibility, which resulted in part from the extremely stable power supply, indicates that, in any given experiment, the choice of 18 eV was not detrimental.

From the ion intensity data of one experiment a pressure was calculated for each isotope by the following equation [20] relating the pressure of a standard substance (s) – in this case, silver vapour – to that of an unknown (x),
TABLE II

FREE ENERGY FUNCTIONS OF EuC₂(s) AND Δfef FOR THE REACTION
EuC₂(s) → Eu(g) + 2 C (graphite)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Δfef for EuC₂(s) (cal/°K·gfw)</th>
<th>Δfef for reaction (cal/°K·gfw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>-33.794</td>
<td>20.776</td>
</tr>
<tr>
<td>1200</td>
<td>-35.017</td>
<td>20.473</td>
</tr>
<tr>
<td>1300</td>
<td>-36.133</td>
<td>20.177</td>
</tr>
<tr>
<td>1400</td>
<td>-37.174</td>
<td>19.916</td>
</tr>
<tr>
<td>1500</td>
<td>-38.183</td>
<td>19.707</td>
</tr>
<tr>
<td>1600</td>
<td>-39.122</td>
<td>19.508</td>
</tr>
</tbody>
</table>

\[
P_x = \frac{(\sigma_x) (T_x) (S_x) I_x}{k(r_x) (T_s) (S_x) (\sigma_x)} \tag{4}
\]

In this equation \( P_x \) = partial pressure of unknown species \( x \), \( r = \) isotopic fraction of the ion observed, \( T = \) temperature in °K, \( \sigma = \) ionization cross-section, \( S = \) sensitivity of the ion detector to the ion measured, \( k = \) sensitivity of the mass spectrometer in units of ion intensity/atm of vapour of \( (s) \), and \( I = \) ion intensity. We assumed that \( S_{Ag}/S_{Eu} = 1 \), and that the ratio of the ionization cross-section would be proportional to the metal-metal distance in the crystal. Using metal-metal distances given by Pauling [21] we calculated \( \sigma_{Ag}/\sigma_{Eu} = 0.4768 \). The other values used were:

\[ r_{151} = 0.4782; \quad r_{155} = 0.5218 \]

\[ k = 2.448 \times 10^2 \text{ nA/atm of } ^{107}\text{Ag} \]

\[ T_s = 1369°K \]

Collecting the terms assigned numerical values and substituting \( k^* \) for them Eq.(4) becomes:

\[
P_x = k^* I_x T_x \tag{5}
\]

where \( k^* \) has the value of \( 2.932 \times 10^{-6} \text{ atm/nA °K for } ^{151}\text{Eu} \) and \( 2.685 \times 10^{-6} \text{ atm/nA °K for } ^{153}\text{Eu} \).

Using these values of \( k^* \), pressures were calculated for all data collected in one experiment (MS-5) and fitted by the method of least squares to determine the intercept and slope. Because a number of approximations are involved, the errors associated with the pressure (and concentrated in the intercept term) are greater than the standard deviation of the intercept.
**TABLE III**

THIRD LAW VALUES OF THE ENTHALPY OF VAPORIZATION OF EUROPium DICARBIDE CALCULATED FROM TARGET COLLECTION DATA

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$\Delta H^0$ (kcal/gfw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1246</td>
<td>49.67</td>
</tr>
<tr>
<td>1321</td>
<td>53.69</td>
</tr>
<tr>
<td>1358</td>
<td>52.79</td>
</tr>
<tr>
<td>1404</td>
<td>54.61</td>
</tr>
<tr>
<td>1405</td>
<td>59.15</td>
</tr>
<tr>
<td>1486</td>
<td>57.34</td>
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<tr>
<td>1503</td>
<td>58.51</td>
</tr>
<tr>
<td>1542</td>
<td>59.75</td>
</tr>
<tr>
<td>1578</td>
<td>54.39</td>
</tr>
<tr>
<td>1609</td>
<td>61.49</td>
</tr>
<tr>
<td>1625</td>
<td>53.10</td>
</tr>
<tr>
<td>1661</td>
<td>61.28</td>
</tr>
<tr>
<td>1672</td>
<td>57.71</td>
</tr>
</tbody>
</table>

Average 56.27 ± 3.84$^a$

---

$^a$ Standard deviation

indicates. The principal error is probably the estimate of the ionization cross-section which we believe to be in error by less than a factor of two. Since the errors in the other quantities estimated or measured for Eq. (3) are relatively small compared to this error, we have assumed that the $k^*$ is in error by a factor of two. When this error is combined with the statistical error in the intercept obtained from the log $I/T$ versus $10^4/T$ graph (Fig. 4), the calculated error becomes ± 0.38, or ± 1.75 entropy units. Thus the standard entropy of vaporization of EuC$_2$, assuming that heat capacity corrections are negligible, is

$$\Delta S^0_{298} = 18.43 \pm 1.75 \text{ cal/°K gfw}$$

When this intercept, with its associated error, is combined with the slope of the line illustrated in Fig. 4, the following equation is obtained for the logarithm
FIG. 6 Ionization efficiency curves

FIG. 7 $\Delta$ef for the reaction: $\text{EuC}_2(s) = \text{Eu}(g) + 2\text{C(graphite)}$
of the pressure of europium in equilibrium with europium dicarbide:

\[ \log P_{\text{Eu( atm)}} = \frac{(-10,745 \pm 249)}{T} + 4.03 \pm 0.38 \]  

(6)

If the average enthalpy calculated from the data listed in Table I is combined with the entropy calculated as indicated above, again assuming heat capacity corrections to be negligible, the free energy of vaporization may be expressed as:

\[ \Delta G^0_{298} = 51.06 \pm 1.25 - T(18.43 \pm 1.75) \]  

(7)

and the corresponding equation describing the partial pressure of europium in equilibrium with the dicarbide becomes:

\[ \log P_{\text{Eu( atm)}} = \frac{(-11,163 \pm 273)}{T} + 4.03 \pm 0.38 \]  

(8)

Although the two equations agree within their limits of error, equation (8) is probably more accurate.

The pressures of identical isotopes measured at the same temperature were averaged and from this average pressure a third law heat was calculated to compare with the second law value listed previously. These data are listed in Table IV. The average third law heat, with its associated standard deviation, is 51.24 ± 0.41 kcal/gfw. However, we feel that the actual uncertainty is probably ± 1.5 kcal/gfw.

The reasonably good agreement between this third law value calculated from the data collected in one experiment, the average second law heat (51.06 ± 1.25 kcal/gfw) calculated from all the experiments, and the third law heat calculated from the effusion data whose pressures were known to be low, indicates that this value is the actual enthalpy of vaporization of the dicarbide.

Combination of this enthalpy of vaporization of europium dicarbide with the enthalpy of sublimation of europium \([22]\) (\(\Delta H_{\text{sub}}^0 = 42.066 \pm 0.075 \text{ kcal/g-at.}\)) permits calculation of the heat of formation of \(\text{EuC}_2\): \(\Delta H_f^0 = -9.15 \pm 1.8 \text{ kcal/gfw}\). From the vapour pressure equation, an entropy of sublimation of europium of 24.16 ± 0.12 cal/°K g-at. can be calculated. When this value is combined with the entropy of decomposition of \(\text{EuC}_2\), an entropy of formation of \(\text{EuC}_2\) of \(\pm 5.63 \pm 1.76 \text{ cal/°K gfw}\) is calculated. Combination of these values leads to a free energy of formation of \(\text{EuC}_2\):

\[ \Delta G_f^0 = -7.47 \pm 1.87 \text{ kcal/gfw} \]  

(9)

It is interesting to compare the heat of formation of europium dicarbide with heats of other lanthanide and alkaline earth dicarbides. Chupka et al. \([1]\) determined the heat of formation of \(\text{LaC}_2\) to be -44 kcal/gfw. Jackson et al. \([23, 24]\) determined the heat of formation of \(\text{CdC}_2\) to be -26 kcal/gfw and Deane et al. \([25]\) determined the heat of formation of \(\text{HoC}_2\) to be -19.6 kcal/gfw. Even omitting lanthanum dicarbide - the first member of the series which may be different from the others - we see that the heat of formation of europium dicarbide is significantly lower than that of either holmium or gadolinium.
TABLE IV

THIRD LAW VALUES OF THE ENTHALPY OF VAPORIZATION OF EUROPIUM DICARBIDE

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$\Delta H^o_{298}^{151} Eu$ (kcal/gfw)</th>
<th>$\Delta H^o_{298}^{153} Eu$ (kcal/gfw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1139</td>
<td>51.668</td>
<td>51.861</td>
</tr>
<tr>
<td>1190</td>
<td>51.072</td>
<td>51.230</td>
</tr>
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<td>1214</td>
<td>51.712</td>
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<td>1263</td>
<td>51.925</td>
<td>52.022</td>
</tr>
<tr>
<td>1280</td>
<td>51.942</td>
<td>51.586</td>
</tr>
<tr>
<td>1298</td>
<td>51.485</td>
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<td>51.512</td>
</tr>
<tr>
<td>1339</td>
<td>51.492</td>
<td>50.806</td>
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<td>51.000</td>
<td>51.066</td>
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<td>1356</td>
<td>51.456</td>
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<td>50.895</td>
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<td>1518</td>
<td>51.032</td>
<td>50.932</td>
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<td>1520</td>
<td>51.346</td>
<td>51.272</td>
</tr>
<tr>
<td>1536</td>
<td>51.873</td>
<td>51.982</td>
</tr>
<tr>
<td>1537</td>
<td>50.822</td>
<td>50.620</td>
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<td>1554</td>
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<td>51.216</td>
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<tr>
<td>1568</td>
<td>51.009</td>
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</tr>
<tr>
<td>1587</td>
<td>51.170</td>
<td>51.234</td>
</tr>
</tbody>
</table>

Average $51.25 \pm 0.38$ $51.23 \pm 0.45$

Best value $51.24 \pm 0.41$ kcal/gfw

The only alkaline earth dicarbide for which data are available is CaC$_2$, whose heat of formation is -15.0 kcal/gfw [19]. By comparing the enthalpies of formation [26] of the hydrides, oxides, nitrides, and sulphides of calcium, strontium and barium (Table V), we conclude that the enthalpies of formation
TABLE V

ENTHALPIES OF FORMATION, OF SELECTED ALKALINE EARTH BINARY COMPOUNDS

<table>
<thead>
<tr>
<th></th>
<th>Hydride</th>
<th>Oxide</th>
<th>Nitride</th>
<th>Sulphide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>-45.1</td>
<td>-151.9</td>
<td>-103.2</td>
<td>-115.3</td>
</tr>
<tr>
<td>Sr</td>
<td>-42.3</td>
<td>-141.9</td>
<td>93.4</td>
<td>-108.1</td>
</tr>
<tr>
<td>Ba</td>
<td>-40.9</td>
<td>-133.4</td>
<td>86.9</td>
<td>-106.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Average increase in enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>4.4 kcal/gfw</td>
</tr>
</tbody>
</table>

of strontium and barium dicarbide should be about -10 and -5 kcal/gfw, respectively. If these estimates are correct, we can see again a similarity between SrC₂ and EuC₂ — substantiating further the original hypothesis that europium dicarbide is much more like the alkaline earth dicarbides than the lanthanide dicarbides.

ACKNOWLEDGEMENTS

The support of the United States Atomic Energy Commission, (COO-716-0013) is gratefully acknowledged. We wish to thank also Messrs. Rauh and Johansson of the Argonne National Laboratory for their assistance in the construction and alignment of the mass spectrometer, the heating assembly, and its power supply. The use of Mr. P. E. Werner's Computer Programme, PR-2, and time made available on the computer, FACIT EDB, by the Swedish Board of Computing Machinery are acknowledged gratefully.

REFERENCES

A MASS SPECTROMETRIC STUDY OF THE VAPOUR PRESSURE OF U(g) AND UC2(g) OVER VARIOUS COMPOSITIONS IN THE URANIUM-CARBON SYSTEM*  

E.K. STORMS  
UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY,  
N. MEX., UNITED STATES OF AMERICA  

Abstract — Résumé — Аннотация — Resumen  

A MASS SPECTROMETRIC STUDY OF THE VAPOUR PRESSURE OF U(g) AND UC2(g) OVER VARIOUS COMPOSITIONS IN THE URANIUM-CARBON SYSTEM. The pressure of U(g) and UC2(g), and the resulting partial heats of vaporization of U(g) and C(g) have been measured as a function of composition from UC + U(ℓ) to UC2 + C. An abrupt pressure change with composition was found near UC1.0 and a much lesser change within the UC1 region. The partial heat of vaporization of U(g) at ~2200°K shows a similar rapid change in value through UC1.0 with a maximum near UC1.2 at 167±2 kcal/mole. Another maximum occurs in the UC2 region at 147±2 kcal/mole and UC1.85. The heat of vaporization based on the UC1 + C region is too low since the UC2 phase changes composition with temperature. The measured pressures are consistent with congruent vaporization near UC1.1.  

Evidence is presented supporting a value for the heat of vaporization of uranium near 126 kcal/mole. Using this value, the measured pressures in the U-C system show excellent agreement with the other thermodynamic measurements. A re-evaluation has been made of the high temperature thermal functions of U, UC, and UC2 with the result that significant changes must be made in the currently used values. Several areas of the phase diagram have been determined both directly and from the pressure measurements and are compiled into a phase diagram of the system.  

* Work done under the auspices of the USAEC
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Теплота испарения, основанная на области UC<sub>2</sub> + C, является слишком небольшой, поскольку фаза UC<sub>2</sub> изменяет состав с изменением температуры. Измеренные давления согласуются с соответствующим испарением около UC<sub>1.1</sub>. Приводятся данные, подтверждающие величину теплоты испарения урана около 126 ккал/моль. С учетом этой величины измеренные давления в системе U - C показывают превосходное согласие с результатами других термодинамических измерений. Были произведены новая оценка высокотемпературных тепловых функций U, UC и UC<sub>2</sub>, в результате которой должны быть внесены существенные изменения в используемые в настоящее время величины. Несколько областей фазовой диаграммы были определены как непосредственным путем, так и по результатам измерений давления, и была составлена фазовая диаграмма системы.

ESPECTROMETRÍA DE MASAS APLICADA AL ESTUDIO DE LA TENSION DE VAPOR DE U(g) Y UC<sub>2</sub>(g) EN DIVERSOS COMPOSTOS DEL SISTEMA URANIO-CARBONO. La tensión de vapor del U(g) y del UC<sub>2</sub>(g), y los calores parciales resultantes de la vaporización del U(g) y del C(g), se midieron en función de la composición en el intervalo UC + U(1) a UC<sub>2</sub> + C. Cerca de C<sub>i0</sub> se observó un cambio brusco de presión, y otro mucho menor en la región de UC<sub>2</sub>. El calor parcial de vaporización del U(g) a 2200°K sufre un análogo cambio rápido en UC<sub>1.0</sub>, con un máximo de 167 ± 2 kcal/mol cerca de UC<sub>1.2</sub>. Hay otro máximo, en la región de UC<sub>2</sub> de 147 ± 2 kcal/mol para UC<sub>4.85</sub>. El calor de vaporización basado en los datos correspondientes a la región UC<sub>2</sub> + C es demasiado bajo, puesto que la composición de la fase UC<sub>2</sub> cambia con la temperatura. Las presiones medidas concuerdan con la vaporización congruente cerca de UC<sub>1.1</sub>.

Se presentan pruebas según las cuales el calor de vaporización del uranio es de 126 kcal/mol aproximadamente. Aplicando este valor, las presiones medidas en el sistema U-C concuerdan satisfactoriamente con los resultados de otras mediciones termodinámicas. El nuevo examen de las funciones térmicas del U, UC y UC<sub>2</sub> a temperaturas elevadas ha exigido introducir cambios importantes en los valores utilizados corrientemente. Se han determinado, directamente y basándose en las mediciones de la presión, varias áreas del diagrama de fase que se utilizan para compilar un diagrama de fases del sistema.

1. INTRODUCTION

There have been numerous vapour pressure measurements of the uranium-carbon system, all in sufficiently poor agreement so that the actual vaporization behaviour is in some dispute. In the two phase region consisting of UC + C, six Knudsen effusion studies using target collection [1-6]; a measurement by weight loss from a cell [7]; and one mass spectrometric study [8] have been reported. In addition, two laboratories have reported studies at a composition near UC, one using Langmuir evaporation [9,10] and the other using target collection techniques [2]. The results of measurements using UC<sub>2</sub> + C are shown in Fig. 1 as equilibrium evaporation rates. By comparing these to the equilibrium evaporation rate of carbon, as presented by Stull and Sinke [11], one can see that all except two investigations predict a preferential loss of carbon from UC<sub>2</sub> + C. This is consistent with observations of a congruently vaporizing composition near UC<sub>1.1</sub> [5, 10, 12]. However, the thermodynamic values adopted by the Vienna Panel [13] predict that uranium will be lost faster than carbon from all compositions in this system. Support for this view has been presented in papers by Alcock, Eick, Rauh and Thorn [14] in which they suggest that the measured uranium pressure over UC<sub>2</sub> is too low because of its slow diffusion through a graphite layer which forms on the surface, and that the congruent composition was obtained because of an excessive loss of carbon as CO. On the other hand, Alexander and co-workers [2] have argued that the congruent composition is dictated by the kinetics of vaporization and not by the equilibrium pressures.
Figure 1. A comparison between the "equilibrium" evaporation rates of \( U(g) \) from \( UC_2 \) and of carbon from graphite.
Therefore, the pressure of U(g) and UC₂(g) were re-measured over UC₂ + C as well as over eighteen other compositions within the system.

Recently, Drowart, Pattoret and Smoes [15] have re-determined the heat of vaporization of pure uranium using a mass spectrometer. From this work, and previous mass spectrometer studies [16, 17], with supporting arguments based on thermodynamic cycles within several uranium systems, they conclude that the value reported by Rauh and Thorn [18] is too low. Because of this conflict, measurements were made which set limits to the heat of vaporization and pressure of uranium. This included a determination of the solubility of carbon in liquid uranium.

An additional problem, not specific to this system, is that in a two phase region the composition of the phases will change with temperature. Unless the magnitude of this change is known to be small, the thermodynamic values have no simple significance. All of the vapour pressure measurements using UC₂ + C suffer from this uncertainty. Consequently, the composition of the β-UC₂ + C phase boundary was determined.

2. EXPERIMENTAL

2.1. Sample preparation and analysis

Samples of various compositions were prepared by arc-melting uranium and graphite rods together using a graphite electrode and a copper hearth. All of the samples were analysed for uranium by ignition at 800°C and some were analysed for carbon, nitrogen and oxygen and various other elements. The results are listed in Table I. As a check, some samples were analysed repeatedly for uranium by a gravimetric technique\(^1\). The agreement between the methods was excellent and gave an uncertainty in the C/U atomic ratio of ± 0.005.

X-ray diffraction examination of the important samples was made using a 114.6 mm Debye-Scherrer camera with copper radiation and a nickel filter. Metallographic examination of certain samples was also undertaken.

2.2. Vapour pressure determination

A 60° sector, 12 in radius, differentially-pumped mass spectrometer was used for these studies. Electron bombardment heating was used but several important improvements were made in the conventional oven design. To control or eliminate the axial temperature gradient within the crucible, three independently controlled tungsten filaments were used as the electron source. This arrangement is shown in Fig. 2. The top and centre filaments surrounded the top and bottom of the crucible, respectively, while the bottom filament heated mainly the base. By changing the filament temperature, the amount of bombardment current to these regions could be changed, with a resulting change in the temperature gradient. The radiation shield was

---

\(^1\) The carbide was converted to U₃O₈ by ignition in air, dissolved in acid, purified in a cell using a Hg cathode, oxidized and titrated with cerium sulphate.
### Composition of Samples Before and After Vapour Pressure Measurements

<table>
<thead>
<tr>
<th>Comp.</th>
<th>C/U</th>
<th>O&lt;sup&gt;a&lt;/sup&gt; ppm</th>
<th>N&lt;sup&gt;b&lt;/sup&gt; ppm</th>
<th>Si&lt;sup&gt;c&lt;/sup&gt; ppm</th>
<th>Cu&lt;sup&gt;c&lt;/sup&gt; ppm</th>
<th>Comp.</th>
<th>C/U</th>
<th>O&lt;sup&gt;a&lt;/sup&gt; ppm</th>
<th>Phases present at room temp.</th>
<th>Lattice Parameter λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>575</td>
<td></td>
<td>U + UC</td>
<td>4.9564 ± 0.0001</td>
</tr>
<tr>
<td>V-1</td>
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<td>30</td>
<td>&lt;200</td>
<td>200</td>
<td>6</td>
<td>0.930</td>
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<td>UC</td>
<td>4.9555 ± 0.0003</td>
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<td>V-2</td>
<td>0.968</td>
<td>30</td>
<td>&lt;200</td>
<td>80</td>
<td>200</td>
<td>0.946</td>
<td>100</td>
<td></td>
<td>UC</td>
<td>4.9555 ± 0.0003</td>
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<td>V-3</td>
<td>0.968</td>
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<td>&lt;200</td>
<td></td>
<td></td>
<td>0.973</td>
<td>&lt;225</td>
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<td>&lt;5</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1.276</td>
<td>65</td>
<td></td>
<td>UC &gt; UC&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4.9616 ± 0.0003</td>
</tr>
<tr>
<td>V-9</td>
<td>1.286</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.286</td>
<td></td>
<td></td>
<td>UC &gt; UC&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4.9616 ± 0.0003</td>
</tr>
<tr>
<td>V-10</td>
<td>1.492</td>
<td>115</td>
<td>&lt;200</td>
<td>150</td>
<td>15</td>
<td>1.487</td>
<td></td>
<td></td>
<td>UC&lt;sub&gt;2&lt;/sub&gt; = UC</td>
<td>4.9616 ± 0.0003</td>
</tr>
<tr>
<td>V-11</td>
<td>1.665</td>
<td>50</td>
<td>&lt;50</td>
<td></td>
<td></td>
<td>1.599</td>
<td>25</td>
<td></td>
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<tr>
<td>V-12</td>
<td>1.665</td>
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<td></td>
<td></td>
<td></td>
<td>1.646</td>
<td>80</td>
<td></td>
<td>UC&lt;sub&gt;2&lt;/sub&gt; &gt; UC</td>
<td>4.9616 ± 0.0003</td>
</tr>
<tr>
<td>V-13</td>
<td>1.776</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.713</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-14</td>
<td>1.776</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.781</td>
<td>25</td>
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<tr>
<td>V-15</td>
<td>1.848</td>
<td>45</td>
<td>&lt;200</td>
<td>70</td>
<td>10</td>
<td>1.846</td>
<td>50</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>V-16</td>
<td>1.890</td>
<td>210</td>
<td></td>
<td>70</td>
<td>10</td>
<td>1.877</td>
<td>130</td>
<td></td>
<td>Equilibrated with C at 1795°C</td>
<td>4.9616 ± 0.0003</td>
</tr>
<tr>
<td>V-17</td>
<td>1.890</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.884</td>
<td>140</td>
<td></td>
<td>Equilibrated with C at 1903°C</td>
<td>4.9616 ± 0.0003</td>
</tr>
<tr>
<td>V-18</td>
<td>2.08</td>
<td>40</td>
<td>&lt;200</td>
<td>15</td>
<td>15</td>
<td>2.080</td>
<td></td>
<td></td>
<td>UC + C</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> One determination

<sup>b</sup> Although no N<sub>2</sub> was detected, the reported value is an upper limit because of the small sample available.

<sup>c</sup>Spectroscopic analysis (V, Nb, Ta, W, Mo - not detected)

---

*Notes:*
- Comp. = Composition
- C/U = Carbon to Uranium ratio
- Lattice Parameter λ = Lattice constant λ
- UC = Uranium Carbide
- UC<sub>2</sub> = Uranium Carbide
- Equilibrated with C at 1795°C
- Equilibrated with C at 1903°C
- Values in <200 ppm indicate detection limits.
allowed to float electrically. Elimination of the gradient was found to be no easy task, especially when uranium compounds were used. At low temperatures (< 1500°C) equal power to each filament produced a slight gradient, but as the temperature was increased the gradient between the ends became increasingly worse. Adjustment of the relative filament power could keep this gradient small until the top filament was essentially off and control was lost. The temperature at which this occurred depended on the amount of uranium activation the top filament had experienced and was the upper limit to the measurements. If the radiation shield was grounded, this limit was much lower. In addition to the problem of keeping the ends of the crucible at the same temperature, it was found that above 1500°C the temperature at the position of the evaporating surface increased over the end temperature. The magnitude of this effect was determined by measuring the temperature in holes drilled at various levels in an empty crucible. This gave a correction factor which was subsequently applied to the measured top and bottom temperature. A complete study of the gradient effect was made and reported previously [20]. The results of this study indicate that if the temperature at the evaporating surface is known, temperature and pressure are uniquely related regardless of the temperature in the remainder of the cell. This generalization is complicated somewhat if condensation is occurring within the cell.

As a further check on the temperature, pieces of metal-carbide eutectic compositions were placed in the cell and, after cooling from various temperatures, an indication of melting was determined by visual inspection. This temperature was compared to measurements made in a special black-body crucible using induction heating and the "Rupert" thermal analysis apparatus [21]. The Rh-RhC eutectic melting point, at 1650 ± 2°C, showed no more than a 5°C difference between that observed in the spectrometer and the thermal arrest method. A similar comparison with the Mo-Mo₅C eutectic temperature at 2208 ± 5°C also gave agreement within 5°C. The Pyro Micro Optical pyrometers used in both studies were compared to a NBS-calibrated pyrometer and band lamp. As a result of this effort, a measurement of
### TABLE II

**SUMMARY OF LEAST-SQUARES EQUATIONS**

\[
\log P_u \text{ (atm)} = A - \frac{B}{T}
\]

<table>
<thead>
<tr>
<th>Comp., c/u</th>
<th>Slope $\Delta H_u$ (kcal/mole)</th>
<th>A</th>
<th>$-B \times 10^{-x}$</th>
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</thead>
<tbody>
<tr>
<td>V-0</td>
<td>5.039 ± 0.051</td>
<td>2.499 ± 0.011</td>
<td>114.4 ± 0.5</td>
</tr>
<tr>
<td>V-1</td>
<td>4.527 ± 0.054</td>
<td>2.410 ± 0.011</td>
<td>110.3 ± 0.5</td>
</tr>
<tr>
<td>V-2</td>
<td>4.662 ± 0.136</td>
<td>2.376 ± 0.029</td>
<td>113.3 ± 1.3</td>
</tr>
<tr>
<td>V-3</td>
<td>4.170 ± 0.089</td>
<td>2.404 ± 0.018</td>
<td>110.0 ± 0.8</td>
</tr>
<tr>
<td>V-4</td>
<td>6.769 ± 0.215</td>
<td>3.121 ± 0.049</td>
<td>142.8 ± 2.2</td>
</tr>
<tr>
<td>V-5</td>
<td>8.040 ± 0.204</td>
<td>3.501 ± 0.046</td>
<td>160.0 ± 2.1</td>
</tr>
<tr>
<td>V-6</td>
<td>8.378 ± 0.132</td>
<td>3.608 ± 0.031</td>
<td>165.1 ± 1.4</td>
</tr>
<tr>
<td>V-7</td>
<td>7.238 ± 0.081</td>
<td>3.374 ± 0.019</td>
<td>154.4 ± 0.9</td>
</tr>
<tr>
<td>V-8</td>
<td>6.758 ± 0.368</td>
<td>3.267 ± 0.085</td>
<td>149.5 ± 3.9</td>
</tr>
<tr>
<td>V-9</td>
<td>6.671 ± 0.098</td>
<td>3.256 ± 0.023</td>
<td>149.0 ± 1.1</td>
</tr>
<tr>
<td>V-10</td>
<td>5.911 ± 0.070</td>
<td>3.101 ± 0.017</td>
<td>141.9 ± 0.8</td>
</tr>
<tr>
<td>V-11</td>
<td>5.806 ± 0.077</td>
<td>3.077 ± 0.018</td>
<td>140.8 ± 0.8</td>
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<tr>
<td>V-12</td>
<td>6.271 ± 0.087</td>
<td>3.195 ± 0.020</td>
<td>146.1 ± 0.9</td>
</tr>
<tr>
<td>V-13</td>
<td>6.253 ± 0.126</td>
<td>3.228 ± 0.029</td>
<td>147.7 ± 1.3</td>
</tr>
<tr>
<td>V-14</td>
<td>5.699 ± 0.070</td>
<td>3.139 ± 0.016</td>
<td>143.6 ± 0.7</td>
</tr>
<tr>
<td>V-15</td>
<td>5.881 ± 0.143</td>
<td>3.165 ± 0.033</td>
<td>144.8 ± 1.5</td>
</tr>
<tr>
<td>V-16</td>
<td>4.808 ± 0.094</td>
<td>2.939 ± 0.022</td>
<td>134.5 ± 1.0</td>
</tr>
</tbody>
</table>

**Ideal Solution**

<p>| | | | |</p>
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<th></th>
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<tbody>
<tr>
<td></td>
<td>5.529</td>
<td>2.583</td>
<td>118.2</td>
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<table>
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<tr>
<th>$\bar{\nu}$ (26)</th>
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</thead>
<tbody>
<tr>
<td>7.219 ± 0.773</td>
<td>3.291 ± 0.171</td>
<td>150.6 ± 7.8</td>
<td>UC$_{1\cdot o_3}$</td>
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<table>
<thead>
<tr>
<th>Vozzella and co-workers$^c$ [10]</th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>8.358 ± 0.722</td>
<td>3.676 ± 0.173</td>
<td>168.2 ± 7.9</td>
<td>Congruent</td>
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<table>
<thead>
<tr>
<th>$\theta$</th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>5.227 ± 0.652</td>
<td>3.018 ± 0.143</td>
<td>138.1 ± 6.5</td>
<td>$\beta\cdot$UC$_2$ + C</td>
</tr>
</tbody>
</table>

**UC$_2$ pressure**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>V-6 to</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>7.399 ± 0.188</td>
<td>3.725 ± 0.045</td>
<td>170.5 ± 2.1</td>
</tr>
<tr>
<td>V-5</td>
<td>8.381 ± 0.812</td>
<td>3.993 ± 0.189</td>
<td>182.7 ± 8.6</td>
</tr>
<tr>
<td>V-4</td>
<td>10.89 ± 2.77</td>
<td>4.628 ± 0.644</td>
<td>211.8 ± 29.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\theta$</th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>7.235 ± 0.016</td>
<td>3.394 ± 0.037</td>
<td>155.3 ± 1.7</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Absolute calibration not obtained.

$^b$Average of 3 independent runs.

$^c$Corrected for UC$_2$($g$) evaporation.

$^d$Points eliminated as described in the text. Corrected for UC$_2$ collected.
Au(l) over three pressure decades (1474-1838°C) gave \( \Delta H_{Au}^{\text{298K}} \) (2nd Law) = 87.0 ± 0.9 kcal/mole compared to a 3rd Law value of 88.3 ± 0.9 kcal/mole obtained by Hildenbrand and Hall [23]. In addition, a determination of Mo(g) pressure over Mo between 1830 and 2080°C gave a slope which differed from measurements of Vozzella and co-workers [22] by 2.2% (See Table II). In all of the pressure measurements most of the points differed from the least-squares line by no more than 5°C. Everything considered, the temperature error is probably no more than 7°C throughout the measurement range.

The crucible consisted of a tantalum shell and an inner graphite cell having a conical shaped interior. Black-body holes were located at the top and bottom. A cross-section drawing is shown in Fig. 3. Most studies were made using a 1.0 mm diam. orifice. When compositions below UC_{1.9} were examined, a Ta or TaC cup was placed in the crucible well to prevent the diffusion of carbon into the material. Over the temperature range of these measurements, this was the only significant source of carbon to the sample. A comparison of the composition before and after a run (Table I) shows that, if anything, the material lost carbon due to the loss of surface oxide as CO.
This occurred as the material was heated through 1600°C with a characteristic evolution of gas.

Knudsen conditions might not have existed within the cell when low carbon samples were used. Although this problem was minimized by the $\text{UC}_2 + \text{UC}$ diffusion barrier which formed on the graphite surface, the measured pressures could be too low if the evaporation coefficient is much less than unity.

The crucible assembly was designed to allow the crucible to be moved in any direction externally. Thus, compensation could be made for any sagging of the supports and the crucible position could be re-established after disassembly.

Each crucible was calibrated initially using molten gold. The spectrometer was then vented with helium, and the gold was replaced by the carbide sample. This consisted of several grams of coarse fragments, broken from an arc-melted button. The presence of powder or fine pieces caused an exceptionally large evolution of CO as the temperature was raised and a pronounced decrease in the stoichiometry. Frequently, a series of compositions were run in the same crucible after the initial calibration. Appropriate, previously measured samples ($\text{UC}_2 + \text{C}$ or $\text{UC} + \text{UC}_2$) were then interspersed to check the calibration consistency. In general, the machine calibration did not change significantly during this procedure. Data were taken over several temperature cycles following an anneal at the highest temperature. The final values were based on at least two temperature cycles which showed agreement within the temperature error.

The calculation of pressure was based on the following constants. The pressure of gold at 1667°K was assumed to be $1.04 \times 10^{-5}$ atm [23], and its relative ionization cross-section was taken as 35 from the measurement by Ackerman, Stafford and Drowart [24]. A cross-section of 50 for uranium was based on a measurement by DeMaria, Burns, Drowart and Inghram [16], and the value for carbon was taken from the paper by Ötvos and Stevenson [25]. The cross-section of $\text{UC}_2$ was assumed equal to the sum of uranium and twice the carbon values. Measurements of the multiplier gain showed that the U/Au current ratio is inversely equal to the square root of the atomic weight ratio. $\text{UC}_2$ was assumed also to follow this relationship. Since an ionization energy of 100 V was used, 11% of the gold ions, 23% of the uranium ions and <3% of the UC ions were multicharged. All of the ions were included when calculating the beam intensity. The small amount of Au$^+$ was neglected. No U$^+$ was observed, but it is interesting that when uranium and gold were mixed, small amounts of UA$^+$ appeared.

A least-squares fit of the final pressure data was made using an IBM7094 and was based on a weighting scheme which depended on the meter range used to measure the current. The uncertainty in the current precision varied from 1% to 10%.

3. EXPERIMENTAL RESULTS

The various compositions and the range over which they were studied are shown on the phase diagram in Fig.4. Beginning with $\text{UC}_2 + \text{C}$, the uranium pressure measurement of each region will be discussed separately.
3.1. UC₂ + C

The two determinations made in this study were based on separate gold calibrations using different crucibles. The consistency is within the temperature error. Samples of UC₂ + C showed no detectable UO⁺ and, except for a peak at UC⁺ and UC₄ at very high temperatures, nothing unexpected was seen in the spectrum. No reluctance to reach pressure equilibrium was observed. Data taken during heating and cooling showed excellent agreement, and an anneal at 2170°C for 3 h produced only a small increase in pressure. No change in pressure was observed when the orifice area was changed from 0.011 cm² to 0.021 cm².

Besides comparing this study, in Fig. 5, to the previous measurements, it is instructive to examine these measurements in light of what is now known about the reactive properties of the system.

The data reported by Leitnaker and Witteman [5] was obtained by total collection using < 325 mesh UC₂ + C powder in a graphite cell. Within a

As explained later, the UC⁺ is probably a decomposition fragment of UC₄⁺, but the UC₄⁺ appears to be real. At 2450°K the UC₄⁺/UC₄⁺ ratio was ~70. One would expect UC₄⁺ to become a more important species at higher temperatures.
given series the material was not exposed to air. The first series (E) was started after considerable time at temperature and shows good agreement with this study except for a point taken just before the window was cleaned. Therefore, this point (42E) was omitted from the recalculation. During the early part of the second series (EE), in spite of a pre-treatment at 1900°C for 6 h, the pressure started high and dropped with time. This suggests that all of the oxide had not been eliminated and UO was evaporating. Therefore, the points (47EE, 48EE, 49EE) which showed this trend were omitted. With these changes, a correction for the collected UC₂(g), and the omission of all points below the α-β transition temperature, the 2nd Law apparent heat of vaporization increased by 4.7 kcal/mole over the value originally reported. (These changes were made with the concurrence of W. Witteman).

Lonsdale and Graves [6] used partial collection from a graphite cell containing powdered carbide. Their procedure consisted of grinding the charge after each measurement, then pretreating the cell at 200°C below the collection temperature for 20 to 60 min. As a result, their sample would have been re-contaminated with oxide after each run, and this would not have been removed by such a short pre-treatment unless the temperature was above ~2000°C. Thus, one would expect the measured pressures below
~2500°K to have become progressively higher than the correct values as the collection temperature was reduced.

The mass spectrometric measurements by Norman and Winchell [8] give pressures which deviate slightly toward higher temperatures as the temperature is raised. Considering the arrangement of their electron bombardment furnace and that the temperature was measured only at the midplane of a bare graphite crucible, there is little doubt that a temperature gradient existed which would have become worse as the temperature increased. However, at low temperatures the agreement is excellent.

The results of Eick, Rauh and Thorn [3] are in slight disagreement, but the reasons are harder to understand. They observed that the data appeared to fall into two groups, depending on the temperature and sample size. Also there appeared to be a slowness in reaching equilibrium. If the composition of their sample is correct (UC\textsubscript{1.7840.05}), it was either not in equilibrium with graphite, which is unlikely at the measurement temperature, or more likely the sample contained some undetected impurity which, in addition to the 0.1% Ta, lowered the activity of uranium.

The very limited measurements by Alcock and Grieveson [7] gave pressures which are higher than most of the other studies and which would predict preferential loss of uranium from UC\textsubscript{2} + C. However, since the pressures were obtained from total weight-loss measurements, the effusion of both CO and UO would add to the apparent uranium pressure. Without some knowledge of the sample purity, these values are best ignored.

The work of Alexander, Ward and Ogden [2], in addition to giving high uranium pressures also showed a rather pronounced orifice effect. This is in contrast to the absence of such an effect in the work of Lonsdale and Graves [6] and in this study. In the absence of experimental details, the reasons for this are hard to determine.

After correcting for the UC\textsubscript{2} collected, the effusion measurements of Fujishiro [4] give a slope which agrees well with this study, but the pressures are about 10 times higher. The carbide was prepared by heating metallic uranium in graphite at 2400°C for 10 h and it would have been oxide free if it were not subsequently powered. In any case, since the carbide would have equilibrated with graphite at 2400°C, it would have contained very little free carbon at the collection temperatures. In the absence of a final analysis, there is no assurance that the evaporating material was in equilibrium with carbon.

By considering these possible sources of error, good agreement can be obtained between the various measurements. In other words, most of the differences are not due to errors in basic technique but are due to an unfortunate combination of chemical properties.

### 3.2. Single phase UC\textsubscript{2}

Single phase compositions near the UC\textsubscript{2} + C phase boundary were obtained by equilibrating a solid piece of carbon-deficient UC\textsubscript{2} with carbon above the $\alpha$-$\beta$ transition temperature. Because the boundary moves to higher carbon contents as the temperature is raised, samples prepared in this way were single phase throughout the range of measurement. The other
compositions were obtained from fragments of an arc-melted button. A TaC cup was used to contain the material. The resulting pressures, compared in Fig. 6, show clearly the effect of the composition change when graphite was present.

3.3. UC$_2$ + UC

Measurements in this two-phase region are shown in Fig. 7. Three different compositions and five samples were used and each run was based on a separate gold calibration. A check on the machine calibration was made by Krupka [26] using a total-collection effusion apparatus with a TaC cell containing UC$_{1.49}$ (same material used for V-10, Table I). A vacuum of 10^{-8} to 10^{-9} torr was maintained. This result and others which will be discussed later, give excellent support to the pressures measured by the spectrometer.

The Langmuir measurements of Vozzella and co-workers [10] using UC$_{1.1}$ are also shown in Fig. 7. Since this composition is in the single phase UC region, the pressures should actually be higher than those measured for UC$_2$ + UC. The fact that the values are lower suggests either that a
temperature error existed in the inductively heated plugs used in their study or the accommodation coefficient for uranium evaporation is not unity at this composition. In addition, the slope has no significance unless the congruent composition is independent of temperature, i.e., unless the partial heats of vaporization of uranium and carbon are equal. More will be said of these possibilities later.

3.4. UC single phase

The data obtained in this region are shown in Figs. 7 and 8. Because of the rapid change in pressure with composition, some difficulty was experienced in obtaining constant pressure when a TaC cup was used to contain the sample. This problem was solved by using a tantalum cup which had been previously equilibrated with the UC composition. Most samples showed a high uranium pressure during the initial heating which rapidly approached an equilibrium value as the temperature was increased. Additional tempera-
ture cycles produced no further changes in the pressure. Apparently the removal of the oxide film during the early stages of heating produced a deficiency of carbon at the evaporating surface. Gradually, as the temperature was raised, the loss of uranium and the diffusion of carbon returned the surface to the interior composition. Although some UO(g) was observed initially, its final pressure dropped to near the limit of detection.

Krupka [26], using the same effusion apparatus described previously, measured the uranium pressure over UC_{1.03} as part of an earlier study. His values, as will be seen, again show excellent agreement. Recent mass spectrometric measurements of UC_{1.04} by Drowart [19] give pressures and a slope which agree closely with this study.

Measurements of UC by Alexander and co-workers [2] gave pressures which would agree with this work if their material had a composition of about UC_{0.96}. Unfortunately, they did not report the final composition.
3.5. \( \text{U}(l) + \text{UC} \)

Pressures in this region, shown in Fig. 8, were obtained by placing a solid piece of clean uranium rod in the crucible well and heating it to the desired temperature. Subsequent examination showed that the molten uranium was contained in a shell consisting of solid UC\(_2\) and UC. Although the molten uranium saturated rapidly, the growth of solid UC\(_2\) and UC was slow. As a result, samples could be examined for several hours without losing the liquid phase. The presence of \( \text{UO}^+ \) was always observed initially but after a heating cycle it dropped to a small fraction (0.01) of the uranium peak without affecting the uranium pressure.

Since gas phase equilibrium is impossible to achieve under these conditions, it is possible that the measured uranium pressure is too low. As a check, the graphite crucible top was replaced by one made from TaC. Although equilibrium still might not be realized, one would expect the conditions to be improved. However, no significant difference in pressure was noticed. If, on the other hand, the evaporation coefficient of uranium from the liquid is unity, the absence of vapour phase equilibrium should not affect the measured pressure. When the UC\(_2\) - UC surface layer on a well-covered graphite top was removed, the apparent pressure was reduced initially by one half. Thus, the coefficient is apparently slightly less than one and, to the extent that equilibrium between the vapour and the walls was not achieved, the measured pressures in this region might be slightly low.

As part of the following study, the effect of tungsten saturation in this region was measured and found to be negligible.

3.6. Single phase uranium liquid

Some preliminary measurements were made using a tungsten cup to contain the molten uranium. Various amounts of carbon were added (as UC\(_{1.9}\)) and the pressure was studied as a function of carbon content. Although these studies are inconclusive, the following observations can be made:

(a) During a run, a change in \( \text{UO} \) pressure from twice to one tenth of the uranium pressure made no significant change (< 5%) in the uranium pressure.

(b) The pressure of uranium did not change rapidly with carbon content.

3.7. Measurement of the UC\(_2\)(g) pressure

The UC\(_2\) (g) pressure was obtained from the beam current ratio, \( I_{\text{UC}_2}/I_U \), by applying the cross-section ratio (0.858) and multiplying by the uranium pressure. The results from the various compositions are shown in Fig. 9. Essentially no change in pressure occurs between UC\(_2\) + C and UC\(_{1.087}\), but it drops rapidly with composition below UC\(_{1.078}\).

The possible errors in measuring the UC\(_2\) pressure are more difficult to evaluate than those affecting the uranium pressure. Aside from the uncertainty in the cross-section, there is the possibility that a significant amount might decompose after being ionized. The presence of some UC\(^+\) in the spectrum added support to this suspicion. Because of its small intensity, neither the heat of vaporization nor the appearance potential could be
measured accurately, however, the UC²⁺/UC⁺ ratio was essentially the same over UC₁₁ and UC₂ + C. Therefore UC⁺ is probably a fragment of UC₂. Nevertheless, the possible error in the UC₂ pressure from this source is negligible. The appearance potential curves for U⁺ and UC₂ were examined carefully to determine if any breaks could be associated with the decomposition reaction UC₂ → U⁺ + C₂. A hump in the U⁺ curve was observed both in the presence and absence of UC₂ and, therefore, cannot be due to this reaction³. It was found that the IUC₂/IU ratio changes appreciably with ionization voltage. Thus, measurements of this ratio by Eick, Rauh and Thorn [3] at 25 V and by Norman and Winchell [8] at 8 V would give values which are lower than those found at 100 V.

The pressures reported by Norman and Winchell [8] are compared to this work in Fig. 9. Their pressures are much lower, probably due to the difference in ionization voltage used, and show an 8% greater slope.

³ It is interesting that a similar hump was observed by Mann [27] in the presence of UO⁺ and was blamed on the dissociation of the UO⁺ ion. The complete absence of UO⁺ in this study eliminates this explanation.
3.8. Phase boundary studies

To better understand the pressure measurements, several features of the phase diagram were determined.

The composition of the UC$_2$-C phase boundary was measured as a function of temperature by equilibrating a solid piece of carbon deficient UC$_2$ with carbon at a fixed temperature, cooling and analysing for uranium by ignition. Equilibrium was assumed when samples heated for much different times (Table III) gave the same composition. The surface carbon was removed previous to analysis by an S.S. White abrasive unit using $\text{Al}_2\text{O}_3$. All of the remaining carbon, regardless of its form at room temperature, would have been dissolved in the cubic UC$_2$ phase at temperature and, therefore, represents the phase composition at this temperature. An upper limit of UC$_{1.89}$ to the composition of UC$_2$ at the $\alpha$-$\beta$ transition, and a lower limit of UC$_{1.94}$ to the composition at the eutectic temperature reported by Witteman and Bowman [29] are in good agreement.

The saturation limit of carbon in liquid uranium was determined by heating a clean uranium rod in a graphite crucible to the desired temperature. Studies with the spectrometer showed that equilibrium was rapidly attained. The graphite was broken from the metal plug, and any UC$_2$ or UC on its surface was removed by a combination of dilute $\text{HNO}_3$ and an S.S. White abrasive unit. Since UC turns dark brown in nitric acid, it was easy to tell when the surface had been cleaned. An analysis for total carbon and uranium was made, and the material was examined metallographically. The results, in Fig.4 and Table III, show excellent agreement with similar measurements by Mallett, Gerds and Nelson [28].

4. DISCUSSION

An internal comparison of the data will be made first at the measurement temperature starting with a plot of $\log$ (uranium pressure) v. composition in Fig.10. As was expected, the large change in uranium pressure was found in the UC region. Here the values can be fitted best if slope of the curve is allowed to maximize at UC$_{1.0}$. This behaviour is consistent with the idea that two competing reactions are operating, i.e. that sub-stoichiometric UC is produced by vacancies in the carbon lattice while higher compositions result when the carbon atoms are replaced by C$_2$ groups. Also shown are the results of the collection study by Krupka [26]. Between UC and UC$_2$ a miscibility gap exists below $\sim$2100°C. The boundaries of this region were determined from the vapour pressure and are indicated in Fig.4. Values for the upper temperature limit of this gap have ranged up to 2100°C [29,30]. This value is not inconsistent with the pressure measurements. In the UC$_2$ region the pressure changes rather slowly with composition. However, as the temperature is raised, the change becomes especially rapid at the high carbon phase boundary. The implication of this behaviour is best seen in Fig.11 where the partial heat of vaporization of uranium ($\Delta\mathcal{H}_U$), obtained from the slope of the pressure data, is plotted as a function of composition. Apparently $\Delta\mathcal{H}_U$ becomes a maximum at about UC$_{1.84}$ and
TABLE III
PHASE BOUNDARY STUDIES

UC₂ + C phase boundary

<table>
<thead>
<tr>
<th>Composition, C/U</th>
<th>Temperature, °C</th>
<th>Time at Temperature, hr.</th>
<th>Oxygen, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.927</td>
<td>2384</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>1.921</td>
<td>2364</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>1.909</td>
<td>2301</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>1.909</td>
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<td>1.923</td>
<td>2250</td>
<td>1.3</td>
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<td>1.915</td>
<td>2146</td>
<td>1.5</td>
<td></td>
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<td>2138</td>
<td>5.0</td>
<td></td>
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<td>2044</td>
<td>5.0</td>
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</tr>
<tr>
<td>1.901</td>
<td>2028</td>
<td>15.5</td>
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<tr>
<td>1.903</td>
<td>1992</td>
<td>15.0</td>
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</tr>
<tr>
<td>1.890 (v-17)</td>
<td>1903</td>
<td>20.0</td>
<td></td>
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<tr>
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<td>1837</td>
<td>18.5</td>
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<tr>
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<td>1815</td>
<td>87.0</td>
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<td>1587</td>
<td>148.0</td>
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</table>

U₄ + UC phase boundary

<table>
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<tr>
<th>Composition, C/U</th>
<th>Temperature, °C</th>
<th>Oxygen, ppm a</th>
<th>Nitrogen, ppm b</th>
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<td></td>
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<td></td>
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<td>1898</td>
<td>850</td>
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<tr>
<td>0.347</td>
<td>2001</td>
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<td></td>
</tr>
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<td>2007</td>
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<td>&lt;500</td>
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<td>2106</td>
<td>790</td>
<td>&lt;500</td>
</tr>
<tr>
<td>0.560</td>
<td>2250</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a One determination
b No N₂ detected

147 kcal/mole, then drops to 142 kcal/mole at UC₁,₉₀. Because the composition of UC₂ changes with temperature when excess carbon is present, the two-phase material shows a significantly lower value. Near the boundaries of the miscibility gap, the values are somewhat erratic due probably to a difficulty in reaching equilibrium. In the UC region another maximum near 167 kcal/mole is indicated, but the upper temperature limit prevented an examination of the single phase region above the gap to define its position. Presumably, a behaviour indicated by the dashed line would be found if this
region could be studied. As the composition is reduced through UC$_{1.0}$ there is a drastic drop in $\Delta H$ followed by a much smaller change throughout the defect region. This behaviour should be reflected in the other thermodynamic
quantities such as heat capacity and heat of formation. Unfortunately these measurements have not, as yet, been made as a function of composition.

4.1. Carbon activity

If U(g), C(g) and UC\(_2\)(g) are in equilibrium, the UC\(_2\)/U pressure ratio is proportional to the carbon activity squared. Since the activity is unity at the UC\(_2\) + C phase boundary, \(a_C^2\) can be obtained at any composition simply by dividing its UC\(_2\)/U pressure ratio by that measured over UC\(_2\) + C at the same temperature. The results of this calculation are shown in Fig. 12 at 2100 and 2300\(^\circ\)K, and the values and equations are given in Table IV.

An extrapolation to the UC phase boundary allows the carbon activity in the carbon saturated liquid uranium phase to be determined. The effect of this negative deviation from ideal on the uranium activity will be discussed later. In any case, at lower temperatures, where the carbon content is smaller, the solution should approach ideal behaviour.

At the other end of the phase diagram, the carbon activity at the UC\(_2\) + C eutectic temperature (2700\(^\circ\)K) extrapolates to unity at UC\(_1,96\). This is, therefore, the maximum solubility of carbon in UC\(_2\).

The manner in which the activity of carbon changes with temperature shows that \(\Delta H_C\) is \(\approx 5.5\) kcal/mole less than the heat of vaporization of graphite throughout the range of UC\(_2\). Within the UC region, \(\Delta H_C\) reaches
### TABLE IV

**ACTIVITY OF CARBON AND URANIUM**

<table>
<thead>
<tr>
<th>Composition, C/U</th>
<th>Activity</th>
<th>( \Delta H_c^\circ - \Delta H_c ) kcal/mole</th>
<th>Activity</th>
<th>( \log \alpha_u = A + B/T ) Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A )</td>
<td>( B \times 10^{-3} )</td>
<td>2100°K</td>
<td>2300°K</td>
</tr>
<tr>
<td>( U(\ell) + UC )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.930</td>
<td>0.946</td>
<td>0.973</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.930</td>
<td>0.946</td>
<td>0.973</td>
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<td></td>
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<tr>
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<td>-1.124</td>
<td>1.470</td>
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<td>0.64</td>
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<td>2.175</td>
<td>0.66</td>
<td>0.54</td>
</tr>
<tr>
<td>( UC_2 + UC )</td>
<td>-0.932</td>
<td>1.587</td>
<td>0.67</td>
<td>0.57</td>
</tr>
<tr>
<td>1.713</td>
<td>-0.499</td>
<td>0.690</td>
<td>0.68</td>
<td>0.63</td>
</tr>
<tr>
<td>1.781</td>
<td>-0.722</td>
<td>1.270</td>
<td>0.75</td>
<td>0.66</td>
</tr>
<tr>
<td>1.846</td>
<td>-0.491</td>
<td>1.000</td>
<td>0.97</td>
<td>0.88</td>
</tr>
<tr>
<td>1.877</td>
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<td>1.130</td>
<td>1.00</td>
<td>0.90</td>
</tr>
<tr>
<td>( UC_2 + C )</td>
<td></td>
<td>--</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>( U(\ell) + UC )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \Delta H_u^\circ = 126 \text{ kcal/mole} \]

\[ \Delta H_u^\circ = 117 \text{ kcal/mole} \]

a minimum near UC_{1.087} and becomes equal to ΔH_{graphite} at UC_{1.083}. Near UC_{1.1} the values for ΔH_C and ΔH_J become equal. This means that the congruent composition will change little with temperature and accounts for the
agreement between this work and the measurements of Vozzella and co-workers [10] (see Fig. 11).

It is important to realize that the activity of carbon obtained from the UC$_2$/U ratio is independent not only of the spectrometer calibration, but also of the ionization cross-section, the possible loss of UC$_2$ ions due to decomposition, and it is very insensitive to temperature errors.

4.2. Congruent vaporization

Assuming that the only evaporating species, U, UC$_2$, C$_1$ and C$_3$, are in equilibrium and have equal evaporation coefficients, the total molar evaporation rates for uranium and carbon were calculated. These are plotted in Fig. 13 as log (evaporation rate ratio) against C/U in the solid. The vapour pressure of graphite was based on the compilation by Stull and Sinke [11]. The figure shows that below ~ 2200°C the congruent composition lies in the UC$_2$ region and that it moves toward the UC$_2$ + C boundary as the temperature is lowered. If the evaporation coefficient for carbon should be less than that for uranium at this composition, below ~ 2200°C a plug of UC$_2$ could lose uranium preferentially and acquire a layer of carbon as was observed by Alcock and co-workers [14]. However, above 2200°C the congruent composition moves to UC$_{1.11}$ and thereafter is fairly independent of temperature. This agrees with numerous [5, 10, 12] observations of a congruent composition near UC$_{1.10}$ and with the observation by Witteman and Krupka [32] that a plug of UC$_{2.2}$ loses carbon preferentially when heated at 2300°C. At still higher temperatures, the composition apparently moves to UC$_{1.3}$ [31] at the melting point.

On the other hand, a comparison between the Langmuir measurements of Vozzella and co-workers [10] and this work suggests that the evaporation coefficient for uranium could be about 0.44 at UC$_{1.1}$. If this assumption is made, the calculated congruent composition remains at UC$_{1.08}$ between at least 2100 and 2300°C. Unfortunately, this composition is sufficiently close to the direct measurements that no conclusions can be made from it concerning the evaporation coefficient.

4.3. Heat of vaporization of uranium metal

Before a further analysis of the data is made it is necessary to choose a value for the heat of vaporization of uranium. The value reported by Rauh and Thorn [18], which has been used extensively in the past, has been recently disputed by Drowart and co-workers [15, 17]. For this reason, an effort was made to add more evidence to the argument.

The pressure of U(g) over U(ℓ) + UC and its change with temperature give a means to obtain limits for the heat of vaporization. Since this measurement does not suffer from the presence of oxygen nor does the liquid creep out of the crucible, as is the case with tantalum and tungsten crucibles, it is probably less prone to error than the direct measurements. The major uncertainty, however, is the effect of the dissolved carbon. One would expect that this carbon would lower the pressure of uranium and that there would be a negative deviation from ideal behaviour. As the temperature is
lowered and the solubility of carbon drops, the pressure should approach that over an ideal solution. Thus, by calculating the pressure over the ideal solution (Fig. 8) a minimum uranium pressure or, in other words, a maximum value for $\Delta H_0^\circ$ can be obtained. In addition, the second law treatment would give a minimum value for $\Delta H_0^\circ$. This reasoning leads to $\Delta H_0^\circ (298^\circ K, 3rd \text{ Law}) = 130.7 \text{ kcal/mole}$ as the maximum and $\Delta H_0^\circ (298^\circ K, 2nd \text{ Law}) = 127.9 \text{ kcal/mole}$ as the minimum value.

Using the same thermal data as above, the measurements of Rauh and Thorn [18] give $\Delta H_0^\circ (298^\circ K, 3rd \text{ Law}) = 117.6 \text{ kcal/mole}$ and $\Delta H_0^\circ (298^\circ K, 2nd \text{ Law}) = 116.3 \text{ kcal/mole}$, and the measurements of Drowart and co-
workers [17] give 125.8 ± 0.2 kcal/mole and 122.4 ± 3.6 kcal/mole, respectively. As can be seen, the values of Rauh and Thorn do not fall near these limits. Furthermore, if their value is used the activity of uranium in the carbon-saturated solution would increase as the temperature is raised and more carbon is dissolved. If their value is indeed correct, the behaviour of this solution is certainly very unusual. In addition, as pointed out by Drowart and co-workers [15], this value is inconsistent with thermodynamic cycles in the U-C and U-O systems, but is consistent with the behaviour of U(ε) + UO₂.

For these reasons ΔH₀(298°K) = 126.0 ± 1 kcal/mole will be used in subsequent calculations. This gives the following equation for the pressure of uranium:

$$\log P_U (\text{atm}) = -2.554 \times 10^4/T + 5.890.$$  

This results in an activity coefficient of 0.33 for uranium in the saturated liquid between 2100 and 2300°K.

4.4. Free energy of formation between 2100 and 2400°K

The free energy of formation was calculated from the relation

$$\Delta F_f^0 = RT(\ln a_U + C/U \ln a_C)$$

and is plotted in Fig. 14 at 2300°K as a function of composition. A decrease in temperature causes $\Delta F_f^0$ in the UC region to become more negative while just the opposite effect occurs in the UC₂ region. In fact, the curve pivots around a composition near UC₁.₁, which has essentially a zero temperature coefficient. This can be seen in Table V where the free energy equations are listed. It is interesting to note that the $\Delta f_{ef}$ values also have a minimum temperature coefficient near this composition. The reduced stability of UC₂ as the temperature is dropped is consistent with its eventual decomposition into UC or U₂C₃ and carbon near 1500°C.

4.5. Evaluation of the thermal measurements

The published high temperature heat content measurements have been re-examined and fit to an equation having the form

$$H_T - H_{298.15} = A + BT + CT^2 + DT^3 + E/T$$

In addition, the equation was made to equal zero at $T = 298.15°K$ and the resulting $C_p$ at 298.15°K was made equal to a value obtained by Westrum and co-workers [33]. The results are shown in Figs. 15, 16, 17, and 18 as plots of $H_T - H_{298.15}$ and $C_p$ for UC₁.₀₂ and UC₁.₉. A similar analysis was made for pure uranium, shown in Fig. 19. The values and equations are also listed in Table VI.

The two UC measurements, in Fig. 15, show excellent agreement with each other and are fitted well by the equation. However, the resulting $C_p$ values are much different than the estimations. UC₂ is particularly notable.
in this respect. It is, of course, possible that the data are in error, but it is more likely that the standard "Kelley" equation which was used for the estimations is not a satisfactory way to fit enthalpy measurements at high temperatures\(^4\). Since no thermal measurements have been made as a function of composition, it was assumed that \(S^0\), \(\Delta H\) and \(\Delta f_{ef}\) divided by \((1 + C/U)\) are a linear function of mole fraction. On such a basis, these values change by only \(\sim 5\%\) between UC\(_{1.92}\) and UC\(_{1.90}\).

\(^4\) ZrC and TiC also show an increased heat capacity above 1500°K.
<table>
<thead>
<tr>
<th>Composition, C/U</th>
<th>Δ£F°(kcal/mole) = ΔT-B</th>
<th>Δ£H°(298°, 2nd Law) kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.995</td>
<td>0.087</td>
<td>-22.9</td>
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<tr>
<td>1.078</td>
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<tr>
<td>9.567</td>
<td>9.581</td>
<td>+59.1</td>
</tr>
<tr>
<td>9.787</td>
<td>9.801</td>
<td>+61.1</td>
</tr>
<tr>
<td>10.00</td>
<td>10.02</td>
<td>+63.1</td>
</tr>
</tbody>
</table>

TABLE V
FREE ENERGY AND HEATS OF FORMATION
-Δ£F° (298°, 3rd Law) kcal/mole
-Δ£H° (298°, 2nd Law) kcal/mole

STORMS
4.6. Heat of formation at 298.15°K

\[ \Delta H_f^0(298\text{°K}, \text{3rd Law}) \] was obtained from \( \Delta F_f^0 \) at 2100 and 2400°K using the equations for \( \Delta F_f^0 \) listed in Table V and \( \Delta \text{fef} \) values obtained as described.
The 2nd Law heat of formation was calculated from the relationship

\[ \Delta H_f^0 = -\Delta H_U + C/U(\Delta H_C^0 - \Delta H_C) + \Delta H_U^0 \]

where \( \Delta H_U \) was obtained from the slope of \( \log P_U \) v. \( 1/T \), \( (\Delta H_C^0 - \Delta H_C) \) was calculated from the slope of \( \log ac \) v. \( 1/T \), and the heat of vaporization of uranium \( (\Delta H_U^0) \) was obtained as described previously. Since \( \Delta C_p \) (vaporization) has not been measured as a function of composition, it was assumed that the partial heats of vaporization were typical of a temperature at the centre of the measured range. The results are listed in Table V.

The UC region is not so clear cut. A trend of \( \Delta H_f^0 \) (3rd Law) with temperature exists which becomes worse as the composition is reduced. In addition, the agreement between the 2nd and 3rd Law values also becomes worse.
There are several errors which could lead to this result, such as an error in the U- or UC2-pressure slopes, but this would also result in inconsistencies elsewhere in the data. Therefore, the error is probably mainly in the 2nd Law values. Such a discrepancy would result if the heat content had a minimum in the region near UC1.08. The 3rd Law values are independent of composition at -23.8 kcal/mole down to a composition near UC1.0, but
**TABLE VI**

<table>
<thead>
<tr>
<th>Temperature, °K</th>
<th>$H_T - H_{298}$</th>
<th>$S^0_T$</th>
<th>$f_{298}$</th>
<th>$C_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal/mole</td>
<td>cal/mole</td>
<td>cal/mole-deg</td>
<td>cal/mole-deg</td>
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<td>1500</td>
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<td>1700</td>
<td>17.15</td>
<td>30.71</td>
<td>20.62</td>
<td>11.45</td>
</tr>
<tr>
<td>1800</td>
<td>18.30</td>
<td>31.56</td>
<td>21.19</td>
<td>11.45</td>
</tr>
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<td>1900</td>
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<td>2000</td>
<td>20.59</td>
<td>32.57</td>
<td>22.28</td>
<td>11.45</td>
</tr>
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<td>33.15</td>
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</tr>
<tr>
<td>2200</td>
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<td>23.25</td>
<td>11.45</td>
</tr>
<tr>
<td>2300</td>
<td>24.02</td>
<td>34.14</td>
<td>23.69</td>
<td>11.45</td>
</tr>
</tbody>
</table>

$(H_T - H_{298})_o = 2.43 - 8.00 \times 10^{-3} + 1.672 \times 10^{-5}T^2 - 6.56 \times 10^{-7}T^3 - 4.582 \times 10^{-9}T^{-1}$

(kcal/mole, 298° - 939.1°K)

$(H_T - H_{298})_\beta = 1.28 \times 10^{-2}T - 5.83$

(kcal/mole, 939.1° - 1044.9°K)

$(H_T - H_{298})_\gamma = 1.038 \times 10^{-2}T - 2.46$

(kcal/mole, 1044.9° - 1390°K)

$(H_T - H_{298})_{11q} = 1.145 \times 10^{-2}T - 2.32$

(kcal/mole, above m.p.)

<table>
<thead>
<tr>
<th>Temperature, °K</th>
<th>$H_T - H_{298}$</th>
<th>$S^0_T$</th>
<th>$f_{298}$</th>
<th>$C_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal/mole</td>
<td>cal/mole</td>
<td>cal/mole-deg</td>
<td>cal/mole-deg</td>
</tr>
<tr>
<td>1700</td>
<td>20.78</td>
<td>39.12</td>
<td>26.90</td>
<td>16.78</td>
</tr>
<tr>
<td>1800</td>
<td>22.47</td>
<td>40.09</td>
<td>27.61</td>
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</tr>
<tr>
<td>1900</td>
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<td>41.03</td>
<td>28.29</td>
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</tr>
<tr>
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<td>28.94</td>
<td>17.86</td>
</tr>
<tr>
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<td>29.59</td>
<td>18.26</td>
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<td>43.67</td>
<td>30.20</td>
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<tr>
<td>2300</td>
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<td>44.51</td>
<td>30.81</td>
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<tr>
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<td>45.34</td>
<td>31.40</td>
<td>19.38</td>
</tr>
<tr>
<td>2500</td>
<td>35.43</td>
<td>46.15</td>
<td>31.96</td>
<td>19.74</td>
</tr>
</tbody>
</table>

$k_T - H_{298} = -4.625 + 1.410 \times 10^{-2}T - 2.56 \times 10^{-6}T^2 + 3.261 \times 10^{-10}T^3$

+1.852 \times 10^{8}T^{-1}$

(kcal/mole, 298° - 2500°K)

<table>
<thead>
<tr>
<th>Temperature, °K</th>
<th>$H_T - H_{298}$</th>
<th>$S^0_T$</th>
<th>$f_{298}$</th>
<th>$C_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal/mole</td>
<td>cal/mole</td>
<td>cal/mole-deg</td>
<td>cal/mole-deg</td>
</tr>
<tr>
<td>2100</td>
<td>43.09</td>
<td>57.03</td>
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<tr>
<td>2600</td>
<td>57.81</td>
<td>63.32</td>
<td>41.09</td>
<td>29.44</td>
</tr>
</tbody>
</table>

$\alpha$-UC$_2$ $H_T - H_{298} = -8.091 + 2.240 \times 10^{-2}T - 4.50 \times 10^{-6}T^2 + 2.31 \times 10^{-10}T^3$

+5.225 \times 10^{8}T^{-1}$

(kcal/mole, 298° - 2038°K)

$\beta$-UC$_2$ $H_T - H_{298} = -18.73 + 2.944 \times 10^{-2}T$

(kcal/mole, 2038°-2600°K)
within the defect region they drop rapidly with composition. Attempts to compare this value to the results of combustion measurements are difficult because both Farr and co-workers [47], and Droge and co-workers [48] used UC which was in equilibrium with uranium. The former study was based on UC$_{0.96}$ and gave a value of $-21.7 \pm 1.0$ kcal/mole. Since $\Delta H_f^0$ is changing rapidly with composition in this region, one can only conclude that their value is in the proper relationship to the results of this study.

5. COMMENTS

There is now considerable reason to believe that the measured pressures over the U-C system are essentially correct. Within a reasonable evaluation of the possible errors, there is good consistency between the various studies and, if a value of $126 \pm 1$ kcal/mole is adopted for the heat of vaporization of uranium metal, there is excellent agreement with the heat of combustion measurements. It is believed that the apparent inconsistencies were due primarily to the use of impure materials in the pressure measurements, the reliance on a heat of vaporization for uranium which was too low, and the use of inaccurate high temperature thermal functions. In addition, too little attention has been given to using materials of fixed and characterized composition. It is this final point which needs emphasis. Measurements made using two-phase samples can be severely compromised by a change in phase composition as the temperature is changed, even if this change is known to be small. The effect of a small change in composition can be unexpectedly magnified by a steep change in properties near the phase boundary, as was found at the UC$_2 +$ C boundary. Furthermore, the use of congruently vaporizing material does not guarantee a fixed composition at all temperatures either unless the partial heats of vaporization of the evaporating species are equal. One would expect this to be a rare coincidence. In the U-C system the problem is further complicated by the unavoidable presence of combined oxygen. Its loss as CO(g) and UO(g) can change the composition, but, far worse, it can add to the apparent uranium pressure if collection or weight-loss techniques are used. Agreement between measurements will not be obtained until this problem is taken into account.

Between UC and UC$_2$ there is a common crystal structure and, at a sufficiently high temperature, there is a continuous change from the one compound to the other. This results from the replacement of C by C==C groups in the regular cubic lattice sites. The substitution does not go to completion, however, since UC$_{1.96}$ is the upper limit to the UC$_2$ phase. No gross changes in the chemical or physical properties occur in this region although the lattice is weakened slightly in going from UC to UC$_2$. There is, however, a reversal in the temperature coefficient of $\Delta F_f^0$ which correctly predicts that UC$_3$ becomes less stable with respect to UC as the temperature is lowered. On the other hand, near UC$_{1.6}$ an entirely different phenomenon occurs which has a profound effect on all of the measured properties. In this region vacancies are formed in the normal carbon lattice with the result that as the stoichiometry is reduced the melting point, the lattice parameter and all of the thermodynamic measurements show a pronounced decrease
in value. It is to be expected that the other properties would show a similar drastic change in this region and, therefore, great care must be taken when measurements are made. This behaviour pattern is shared with the other defect compounds, of which the carbides are extreme examples.

ACKNOWLEDGEMENTS

The author wishes to thank Mr. W. G. Witteman and Dr. M. C. Krupka for sharing their ideas and unpublished data, Drs. A. L. Bowman and A. Goldman for providing the computer programmes, and Dr. M. G. Bowman for encouragement and support. Messrs. J. Buchen and D. Court deserve special acknowledgement since without their help the spectrometer would have been a far poorer instrument. The various chemical analyses were made by Messrs. B. Baca, J. Hansel and Mrs. J. Pena and the author.

REFERENCES

[19] DROWART, J., A communication reported in the discussions to Session III, these Proceedings 1 (1965).
[26] KRUPKA, M. C., unpublished information, Los Alamos Scientific Laboratory.
[37] WITTEMAN, W. W., WALLACE, T., to be published.
[39] HARRINGTON, L. C., ROWE, G. H., Pratt and Whitney Aircraft, Canel, PWAC-426 (1964), see also Ref. [10].
[40] BOETTCHER, A., SCHNEIDER, G., Proc. 2nd UN Int. Conf. PUA6 6 (1958) 561.
VAPOUR PRESSURES AND MOLECULAR ASSOCIATION OF THE VAPOURS OF MOLTEN POTASSIUM CHLORIDE AND BROMIDE. The work presents a new technique for determining vapour pressures by the transport method. This method is applied to pure, molten potassium chloride and bromide. Using transport data we had obtained previously, and knowing the vapour pressures, which had been determined by a static method, we calculated the average molecular weight of the vapours. From mass-spectrometric, magnetic resonance and velocity distribution studies on a molecular cluster of alkali halides, it is known that the vapours of KCl and KBr are composed exclusively of monomers and dimers. It has thus been possible to calculate the molar fractions of the monomer and the dimer in equilibrium with the liquid from the average molecular weight obtained experimentally, using a relation of the following type:

$$\bar{M} = x_1 M + 2x_2 M$$

where $\bar{M}$ is the average molecular weight of the vapours, $x_1$ and $x_2$ are the molar fractions of the monomer and the dimer and $M$ is the molecular weight of the monomer. Knowing the molar fractions of the monomer and the dimer for the vapours of KCl and KBr, we have calculated their partial pressure and heat of vaporization as well as the dissociation constant and the heat of dissociation of the dimer.
М - средний молекулярный вес паров, \textit{x} \textsubscript{1} и \textit{x} \textsubscript{2} - молярная концентрация мономера и димера, \textit{M} - молекулярный вес мономера. Зная молярную концентрацию мономера и димера паров KCl и KBr, мы рассчитали парциальное давление и теплоту испарения последних, а также константу и теплоту диссоциации димера.

**ТENSIONES DE VAPOR Y ASOCIACION MOLECULAR DE VAPORES DE CLORURO Y BROMURO DE POTASIO FUNDIDOS.** Los autores presentan una nueva técnica para determinar tensiones de vapor por el método de transporte. Aplican este método al cloruro y al bromuro de potasio puros y fundidos. Según los datos de transporte obtenidos por los autores y conociendo el valor de las tensiones de vapor determinadas por un método estático, obtuvieron los pesos moleculares medios de los vapores. Los datos obtenidos aplicando la espectrometría de masas, la resonancia magnética y la distribución de las velocidades en una asociación molecular de haluros alcalinos, revelan que los vapores de KCl y KBr están constituidos exclusivamente por monómeros y diméros. A causa de ello, y sobre la base del peso molecular medio obtenido experimentalmente, los autores pudieron calcular las fracciones molares de monómero y de dímero en equilibrio con el líquido, empleando para ello una relación de la forma:

\[ \bar{M} = x_1M + 2x_2M \]

donde \( \bar{M} \) es el peso molecular medio de los vapores, \textit{x} \textsubscript{1} y \textit{x} \textsubscript{2} son las fracciones molares de monómero y de dímero, \( M \) es el peso molecular del monómero. Conociendo las fracciones molares de monómero y de dímero en los vapores de KCl y KBr, los autores calcularon las tensiones parciales y los calores de vaporización de esos compuestos, así como la constante y el calor de disociación del dímero.

Des recherches effectuées récemment ont révélé la présence d'espèces polymères dans les vapeurs des halogénures alcalins. Diverses méthodes ont été utilisées: l'analyse de la distribution des vitesses dans un fascicule moléculaire d'halogénures alcalins [1]; la spectrométrie de masse [2-6]; la détermination de la masse molaire des vapeurs de quelques halogénures alcalins [7, 8]. D'autres études sur les vapeurs des sels fondus ont été effectuées en combinant les données fournies par la mesure des pressions de vapeur par une méthode absolue avec les données fournies par la méthode du transport [9-11].

Dans ce mémoire, nous présentons une nouvelle technique pour la détermination des pressions de vapeur par la méthode du transport appliquée au chlorure et au bromure de potassium; nous en décrivons également les avantages.

La détermination de l'intensité relative des ions dans les vapeurs des halogénures alcalins au moyen de la spectrométrie de masse a montré la présence de monomères, dimères et trimères, ces derniers ne se trouvant en quantités appréciables que dans les vapeurs de LiF, LiCl, LiBr et NaF [12]. Ainsi, en considérant que les vapeurs de KCl et de KBr sont formées d'un mélange de monomères et de dimères, nous avons pu, à l'aide des résultats que nous avons obtenus pour les pressions de vapeur par la méthode du transport et de ceux qui ont été obtenus par une méthode absolue, déterminer la masse molaire de la vapeur, la chaleur de vaporisation du monomère et du dimère, la constante de dissociation et la chaleur de dissociation du dimère.
APPAREILLAGE ET MÉTHODE DE TRAVAIL

C'est la méthode du transport, dont nous avons modifié la technique, que nous avons utilisée. Dans la méthode classique appliquée aux sels fondu [13-15], on travaillait en système horizontal; l'extraction d'un volume connu de vapeur était effectuée en l'entraînant par un gaz inerte. Puisque la capsule contenant la substance se trouvait dans un tube horizontal ayant un grand gradient de température d'un bout à l'autre, il était possible que le sel évaporé se condensât dans la partie plus froide du tube, ce qui détruisait l'équilibre liquide-vapeur. Afin de réduire l'espace où se produit l'évaporation et où s'établit l'équilibre liquide-vapeur, d'éviter la circulation de la vapeur dans les parties froides du tube horizontal, et d'uniformiser la température, on a utilisé des écrans de nickel [16]. Pour les mêmes raisons, Wagner et Stein [17], et récemment Beusman [18], ont utilisé une cellule de quartz munie d'un tube horizontal rotatif où l'on introduit le condenseur. Bien que les résultats ainsi obtenus soient bons, ces cellules de quartz ne permettent pas de travailler à des températures plus élevées et avec des halogénures alcalins qui exercent une forte action corrosive sur le quartz. La réalisation expérimentale d'une cellule étanche, capable de résister à des températures élevées ainsi qu'à l'action corrosive des sels fondu tout en laissant circuler un gaz inerte, est très difficile. Aussi avons-nous décidé d'employer une nouvelle technique.

Nous avons utilisé des creusets en matières réfractaires résistant à des températures atteignant 1500°C, munis de deux orifices latéraux opposés par lesquels on a introduit le thermocouple et le condenseur de platine (dont le diamètre intérieur était d'un millimètre). Ces creusets étaient convenablement fermés au moyen d'autres creusets, placés plus bas, par l'intermédiaire d'une garniture d'asbeste. La tension de vapeur des halogénures alcalins étant élevée et l'espace disponible après fermeture du creuset étant petit, l'équilibre liquide-vapeur a été vite établi. Dans ces conditions, le prélevement d'une quantité connue de vapeur - qui ne nécessitait plus la circulation d'un gaz inerte pour l'entraîner - s'effectuait tout simplement en reliant directement le condenseur à un tube rempli d'eau. En laissant s'écouler un volume déterminé d'eau, le condenseur était automatiquement rempli par le même volume de vapeur de sel (compte tenu de la pression de la vapeur d'eau). Le volume d'eau était déterminé par pesée, compte tenu de la densité de l'eau et de la température ambiante.

Lorsqu'on effectue ces déterminations par la méthode classique du transport, deux sources d'erreurs possibles doivent être prises en considération: - la non-saturation du gaz inerte par la vapeur; - la diffusion de la vapeur dans le condenseur.

Pour éliminer les erreurs dues à la non-saturation du gaz d'entraînement, Jellinek [13] propose d'utiliser diverses vitesses d'écoulement du gaz inerte et d'extrapoler pour la vitesse nulle la quantité de substance entraînée. Au cours des travaux effectués par la méthode du transport [11, 18-20], on a cependant montré que, la saturation étant atteinte à des vitesses d'écoulement assez élevées du gaz inerte, l'extrapolation pour la vitesse nulle n'est pas nécessaire. La quantité de substance dans le condenseur ne dépend donc pas de la vitesse à laquelle le gaz est entraîné.
Dans le cas de la nouvelle technique que nous proposons, on constate en outre que la saturation est atteinte à des vitesses assez grandes d'extraction de l'échantillon de vapeur de l'enceinte contenant la substance fondue (tableaux I et II).

En ce qui concerne la diffusion de la vapeur, on a montré qu'elle est en général négligeable [18-20], pourvu que le diamètre intérieur de l'orifice du condenseur soit petit (1 mm) [18].

Dans les déterminations que nous avons faites de la façon décrite ci-dessus, nous avons pourtant constaté la diffusion dans le condenseur d'une quantité non négligeable de substance, bien que le diamètre du condenseur ne dépasse pas 1 mm. Au cours des mesures, nous avons déterminé cette quantité en introduisant le condenseur, par l'orifice du creuset, dans l'enceinte à vapeur et en l'y laissant un certain temps. Les quantités de substance diffusant (par minute ainsi que durant la détermination) aux diverses températures sont données aux tableaux I et II.

Nos mesures, portant sur KCl et KBr, ont été effectuées dans un four vertical alimenté par un autotransformateur à courant stabilisé. Le chauffage était fait des barres de carbure de silicium. La température était maintenue constante à ± 2° près au moyen d'un régulateur à photorésistance. Les températures étaient mesurées avec un thermocouple joint à un potentiomètre de précision. La technique de travail était la suivante:

Le creuset contenant la substance était introduit, bien fermé, dans le four froid muni de deux orifices latéraux par lesquels on introduisait le thermocouple et le condenseur; ceux-ci pénétraient aussi à l'intérieur du creuset, par les orifices qui y étaient ménagés. L'échauffement du four était rapide; une tige de quartz remplaçait le condenseur jusqu'à ce que la température de travail soit atteinte. A cette température, on introduisait le condenseur de platine, à travers lequel on faisait passer un courant d'azote purifié, afin d'empêcher la diffusion de la vapeur dans le condenseur avant le commencement de la détermination. Lorsque la température était stabilisée, le courant d'azote était coupé et le condenseur était relié au tube rempli d'eau. Après extraction d'un volume connu de vapeur par écoulement d'une certaine quantité d'eau du tube, le condenseur était enlevé et lavé, et la quantité de substance déposée était dosée par la méthode de Volhard.

La méthode que nous proposons offre certains avantages par rapport aux méthodes employées jusqu'ici, à savoir:
- La petite enceinte (le volume libre du creuset est d'environ 25 cm³) où se produit l'équilibre liquide-vapeur permet:
  a) de maintenir tout le système à la même température.
  Dans le cas du système horizontal, où le gradient de température le long du tube est grand, la vapeur pouvait se condenser dans ses parties plus froides, ce qui entraînait la destruction de l'équilibre liquide-vapeur et, dans le cas des mélanges de sels fondus, le changement même de leur composition.
  b) de saturer le volume extrait avec la vapeur du sel utilisé.
- L'extraction d'un volume connu de vapeur n'étant pas fait par entraînement au moyen d'un gaz inerte, il n'est plus nécessaire d'avoir un système étanche, en général très difficile à réaliser aux températures élevées, surtout avec des halogénures alcalins.
RESULTATS EXPERIMENTAUX

La précision de la technique proposée a été vérifiée par les mesures faites sur KCl; on a encore fait des déterminations de masses molaires en combinant les données de transport avec les données fournies par une méthode absolue [18, 21], ainsi que la mesure de la pression absolue exerçée par une quantité connue de sel complètement vaporisé, contenu dans un vase isotherme de volume connu [22](tableau III).

La méthode du transport permet de calculer la pression de vapeur \( p \) d'un sel pur par la relation

\[
p = \left[ \frac{\frac{g}{M}}{n_A + \frac{g}{M}} \right] P
\]

où

- \( g \) désigne le poids du sel extrait dans le condenseur,
- \( M \) est la masse molaire moyenne de la vapeur du sel respectif,
- \( n_A \) est le nombre de moles du gaz inerte entraînant le sel, ou, dans notre cas, le nombre de moles d'air saturé de vapeur qui ont été extraites,
- \( P \) est la pression totale dans le système - dans notre cas, la pression atmosphérique.

Nous avons substitué à \( p \) la pression de vapeur déterminée par une méthode statique [21, 23] et obtenus ainsi, au moyen de la relation (1), la masse molaire de la vapeur

\[
M = \frac{g}{n_A} \left[ \frac{P}{P_s} - 1 \right]
\]

Le nombre de moles d'air extraites \( n_A \) a été déduit de la loi des gaz parfaits, suivant la relation

\[
n_A = \frac{(P_{\text{atm}} - P_{H_2O}) \rho_{H_2O}}{R(273 + t) \rho_{H_2O}}
\]

où

- \( P_{\text{atm}} \) désigne la pression atmosphérique en mm Hg durant les déterminations,
- \( P_{H_2O} \) la pression de la vapeur d'eau à la température ambiante,
- \( \rho_{H_2O} \) la quantité en grammes de l'eau qui s'est écoulée du tube pendant une détermination,
- \( \rho_{H_2O} \) la densité de l'eau à la température ambiante,
- \( t \) la température ambiante,
- \( R \) la constante des gaz en \( \text{cm}^3\cdot\text{mm/deg}\cdot\text{mole} \).

Toutes les grandeurs nécessaires pour le calcul de la masse molaire moyenne de la vapeur à diverses températures pour KCl et KBr sont données aux tableaux I et II, à savoir: la vitesse d'extraction de la vapeur en \( \text{cm}^3/\text{min} \),
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<th>Température (°C)</th>
<th>Poids de H₂O (g)</th>
<th>Moles d'air</th>
<th>Poids de substance condensée (mg)</th>
<th>Poids de substance diffusée total (mg/min)</th>
<th>Masse molaire moyenne (mmHg)</th>
<th>Masse molaire moyenne (g/mol)</th>
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**Tableau I**

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TABLEAU II
DONNEES DE TRANSPORT POUR KBr A DIVERSES TEMPERATURES

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<th>Moles d'air</th>
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</table>
TABLEAU III

VALEURS DE LA MASSE MOLAIRE MOYENNE DE LA VAPEUR DE KCl, DÉTERMINÉES PAR DIVERSES MÉTHODES

<table>
<thead>
<tr>
<th>Température (°C)</th>
<th>Masse molaire moyenne $\overline{M}$</th>
<th>Méthode</th>
<th>Références</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100 - 1200</td>
<td>93,6</td>
<td>Ebullition + transport</td>
<td>Ce mémoire</td>
</tr>
<tr>
<td>962 - 1099</td>
<td>91,6</td>
<td>Quasi-statique + transport</td>
<td>[18]</td>
</tr>
<tr>
<td>1037 - 1131</td>
<td>93,2</td>
<td>Pression exercée par une quantité de sel vaporisé</td>
<td>[22]</td>
</tr>
<tr>
<td>977 - 1143</td>
<td>96,1</td>
<td>Ebullition + transport</td>
<td>[21]</td>
</tr>
<tr>
<td>1153 - 1352</td>
<td>95,6</td>
<td>Ebullition + transport</td>
<td>[19]</td>
</tr>
</tbody>
</table>

la pression atmosphérique en mm Hg, le nombre de grammes de H$_2$O extraits, le nombre de grammes de substance entraînée et condensée dans le condenseur, le nombre de grammes de substance diffusée dans le condenseur par minute ainsi que durant la détermination, la pression statique et la masse molaire moyenne de la vapeur déduits des données ci-dessus à diverses températures.

Puisque, dans la phase vapeur, il n'y a que des monomères et des dimères, nous avons

$$x_1 + x_2 = 1$$

et

$$\overline{M} = x_1M + 2x_2M$$  \hspace{1cm} (4)

où

$x_1$ et $x_2$ désignent les fractions molaires du monomère et du dimère dans la phase vapeur, et

$M$ désigne la masse molaire et l'espèce monomère.

La pression partielle d'une espèce $p_i$ sera

$$p_i = x_i p_s$$  \hspace{1cm} (5)

où

$x_i$ désigne la fraction molaire de l'espèce $i$ de vapeur, et

$p_s$ la pression totale qui, dans notre cas, est la pression statique.

En utilisant les relations (2), (3), (4) et (5), nous avons déterminé la masse molaire moyenne des vapeurs de KCl et KBr, les fractions moléculaires, ainsi que les pressions partielles du monomère et du dimère (tableau IV). En représentant graphiquement log $p_1$ et log $p_2$ en fonction de
1/T et en utilisant la méthode des moindres carrés, nous avons trouvé la chaleur de vaporisation du monomère et du dimère, ce qui nous a permis de déterminer la chaleur de dissociation du dimère et la chaleur de sublimation du monomère et du dimère:

\[
H_{\text{dis}} = H_{2\text{vap}} - 2H_{1\text{vap}}
\]

\[
H_{1\text{sub}} = H_{1\text{vap}} + H_{\text{fus}}
\]

\[
H_{2\text{sub}} = H_{2\text{vap}} + 2H_{\text{fus}}
\]

Afin de déduire les chaleurs de vaporisation de la pente de la droite logp en fonction de 1/T, nous avons tenu compte des capacités caloriques pour KCl [18]. Nous avons obtenu pour les chaleurs de vaporisation du monomère et du dimère de KCl les relations

\[
\Delta H_{1\text{vap}} = 52,7 - 7 \cdot 10^{-3}T
\]

et

\[
\Delta H_{2\text{vap}} = 56,08 - 13 \cdot 10^{-3}T
\]

Le tableau V permet de comparer nos résultats avec ceux obtenus par d'autres auteurs, par diverses méthodes, pour les enthalpies de vaporisation et de sublimation du monomère et du dimère de KCl, ainsi que l'enthalpie de dissociation du dimère.

Pour KBr, nous avons obtenu, dans l'intervalle de températures compris entre 1100 et 1200°C, une masse molaire moyenne de la vapeur de 154,2. En considérant \(C_{p_k} = 8,74\) cal pour KBr [25], 9 cal pour le monomère, et 19,86 cal pour le dimère, nous avons obtenu, pour les chaleurs de vaporisation du monomère et du dimère, les formules

\[
\Delta H_1 = 46,6 - 7,7 \cdot 10^{-3}T
\]

\[
\Delta H_2 = 52,6 - 13,54 \cdot 10^{-3}T
\]

A 1100°K, on a donc \(\Delta H_1 = 38,1\) kcal/mole et \(\Delta H_2 = 37,7\) kcal/mole; les résultats obtenus par d'autres chercheurs sont respectivement 42,6 et 41,4 [9].

A 1000°K, \(\Delta H_{\text{dis}} = 38,7\) kcal/mole (résultat obtenu par d'autres chercheurs: 41 kcal/mole [26]).

Pour les chaleurs de sublimation, à 1007°K, on a obtenu les valeurs suivantes:

\[
\Delta H_{1\text{sub}} = 44,95\text{ kcal/mole}; \quad \Delta H_{2\text{sub}} = 51,2\text{ kcal/mole}
\]

(autres résultats: 47,8 kcal/mole et 54,6 kcal/mole [26]).
### TABLEAU IV

**FRACTIONS MOLAIRES ET PRESSIONS PARTIELLES DU MONOMÈRE ET DU DIMÈRE DE KCl ET DE KBr, À DIVERSES TEMPERATURES**

<table>
<thead>
<tr>
<th>Température (°C)</th>
<th>Fraction molaire du monomère</th>
<th>Fraction molaire du dimère</th>
<th>Pression partielle du monomère $P_1$ (mmHg)</th>
<th>Pression partielle du dimère $P_2$ (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>0,71</td>
<td>0,29</td>
<td>33,63</td>
<td>13,74</td>
</tr>
<tr>
<td>1130</td>
<td>0,75</td>
<td>0,25</td>
<td>52,43</td>
<td>17,48</td>
</tr>
<tr>
<td>1150</td>
<td>0,76</td>
<td>0,24</td>
<td>64,74</td>
<td>20,44</td>
</tr>
<tr>
<td>1170</td>
<td>0,74</td>
<td>0,26</td>
<td>77,40</td>
<td>27,19</td>
</tr>
<tr>
<td>1200</td>
<td>0,76</td>
<td>0,24</td>
<td>98,72</td>
<td>31,18</td>
</tr>
<tr>
<td><strong>KBr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>0,69</td>
<td>0,31</td>
<td>55,62</td>
<td>21,82</td>
</tr>
<tr>
<td>1130</td>
<td>0,70</td>
<td>0,30</td>
<td>66,55</td>
<td>28,52</td>
</tr>
<tr>
<td>1150</td>
<td>0,69</td>
<td>0,31</td>
<td>79,52</td>
<td>35,73</td>
</tr>
<tr>
<td>1170</td>
<td>0,73</td>
<td>0,27</td>
<td>101,47</td>
<td>37,53</td>
</tr>
<tr>
<td>1200</td>
<td>0,72</td>
<td>0,28</td>
<td>131,90</td>
<td>51,28</td>
</tr>
</tbody>
</table>
**TABLEAU V**

**VALEURS DE LA CHALEUR DE DISSOCIATION DU DIMERE ET DES CHALEURS DE VAPORISATION ET DE SUBLIMATION DU MONOMÈRE ET DU DIMÈRE DE KCl FOURNIES PAR DIVERS CHERCHEURS**

<table>
<thead>
<tr>
<th>Température (°K)</th>
<th>$\Delta H_{\text{vap}}$ (kcal/mole)</th>
<th>$\Delta H_{\text{vap}}$ (kcal/mole)</th>
<th>$\Delta H_{\text{dis}}$ (kcal/mole)</th>
<th>$\Delta H_{\text{subl}}$ (kcal/mole)</th>
<th>$\Delta H_{\text{subl}}$ (kcal/mole)</th>
<th>Références</th>
</tr>
</thead>
<tbody>
<tr>
<td>1043</td>
<td>45,4</td>
<td>42,5</td>
<td>48,3</td>
<td>51,7</td>
<td>55,2</td>
<td>Ce mémoire</td>
</tr>
<tr>
<td>1043</td>
<td>45,1</td>
<td>42,3</td>
<td></td>
<td>51,2</td>
<td>54,5</td>
<td>[18]</td>
</tr>
<tr>
<td>1043</td>
<td>43,6</td>
<td>43,8</td>
<td></td>
<td>49,8</td>
<td>56,0</td>
<td>[18]</td>
</tr>
<tr>
<td>842-1001</td>
<td></td>
<td></td>
<td></td>
<td>50,0</td>
<td>60,8</td>
<td>[24]</td>
</tr>
<tr>
<td>774-999</td>
<td></td>
<td></td>
<td></td>
<td>48,9</td>
<td>57,2</td>
<td>[24]</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ce mémoire</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>1300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[19]</td>
</tr>
</tbody>
</table>
REFERENCES

VAPOUR PRESSURE OF URANIUM MONOCARBIDE. The partial vapour pressures of uranium and carbon over uranium monocarbide have been studied in the temperature range 1900–2400°K by a differential Knudsen method. The following equations were obtained for the temperature dependences of the vapour pressures (mm Hg):

\[
\log P_U = 10.054 - \frac{2.809 \times 10^4}{T}
\]

\[
\log P_C = 2.515 - \frac{1.324 \times 10^4}{T}
\]

The partial heat of sublimation of uranium (\(\Delta H_{298}\)) assessed by the second- and third-law methods was 132.6 and 123 kcal/mol respectively. Up to a temperature of \(\sim 2100^\circ K\) mainly carbon atoms vaporized, and above this temperature uranium atoms.

* Доклад представлял А.А. Бабад-Захряпин
ESTUDIO DE LA TENSION DE VAPOR DEL MONOCARBURO DE URANIO. Se han estudiado las tensiones de vapor parciales del uranio y del carbono en el monocarburo de uranio, en el intervalo de temperaturas 1900 - 2400°C, por el método diferencial de Knudsen. Se han obtenido las siguientes ecuaciones de variación de las tensiones de vapor (mm de Hg) en función de la temperatura:

\[
\log p_U = 10,054 - \frac{2,809 \cdot 10^4}{T}
\]

\[
\log p_C = 2,515 - \frac{1,324 \cdot 10^4}{T}
\]

El calor parcial de sublimación del uranio (ΔH°) calculado por medio de los principios 2° y 3° de Termodinámica es, respectivamente, 132,6 y 123 kcal/mol. Hasta ~ 2100°C predomina la vaporización de los átomos de carbono y por encima de esta temperatura la de los átomos de uranio.

Исследованию испарения монокарбида урана посвящены работы [1-3], результаты которых представлены в табл. 1. Эти данные довольно резко отличаются друг от друга. Анализ результатов [2, 3] затруднителен, поскольку в докладах, представленных на Харуэлльский симпозиум по карбидам, подробности экспериментальной методики, как правило, не сообщались. В связи с возрастающим интересом к монокарбиду урана казалось целесообразным уточнить имеющиеся сведения по упругости пара этого соединения, определить парциальные теплоты сублимации и другие термодинамические характеристики.

Мы исследовали испарение монокарбида урана дифференциальным вариантом метода Кнудсена [4] в интервале температур 1900-2400°C. В качестве исходных препаратов были использованы две серии образцов (I и II), изготовленных трехступенчатым синтезом порошков урана и углерода в вакууме 10⁻⁵ - 5 • 10⁻⁶ мм рт. ст. (950°C - 2 часа; 1250°C - 3 часа; 1650 - 1700°C - 4 часа). Образцы одной из серий (II) содержали изотоп углерода C¹⁴ с удельной активностью около 2 мккюри/г. Количество связанного углерода в образцах составляло 4,8 (I) и 4,7 (II) вес. %; содержание свободного углерода - 0,1%; азота - 0,01%; урана - 95,1%(I) и 95,2%(II). По данным рентгеноструктурного анализа все образцы были однофазными с периодами решетки a ≈ 4,961 Å (I) и a ≈ 4,958 Å (II).

Опыты проводили в установке, схема нагревательного устройства которой приведена на рис. 1. Кнудсеновская вольфрамовая камера 3 нагревалась с помощью цилиндрического танталового нагревателя 1, обеспечивающего равномерный нагрев на длине около 40 мм. Температура измерялась оптическим пирометром через отверстие 6. Точность измерения температуры ±5° - 7°C.

Испаряемое вещество конденсировалось на интенсивно охлаждаемых медных мишениях 4; температура мишени во время опытов не превышала 50 - 100°C. Конструкция установки позволяла проводить смену мишени без нарушения вакуума. Во время экспериментов вакуум составлял 1 • 10⁻⁴ - 1 • 10⁻⁵ мм рт. ст. Конструкция камеры позволяла использовать смешные тигли из различных материалов (Ta, BeO, W и др.), которые ставились в камеру Кнудсена.

Площадь эфузийного отверстия в вольфрамовой диафрагме во всех опытах составляла 1,52 • 10⁻³ см²; поправочный коэффициент Клаузинга при
Рис. 1. Схема нагревательного устройства: 1 — танталовый нагреватель; 2 — экраны; 3 — кнудсеновская камера; 4 — кассета; 5 — кассетодержатель; 6 — отверстие для измерения температуры.

Таблица 1

РЕЗУЛЬТАТЫ ИЗУЧЕНИЯ ИСПАРЕНИЯ МОНОКАРБИДА УРАНА.

<table>
<thead>
<tr>
<th>№</th>
<th>Метод исследования</th>
<th>Интервал температур,°К</th>
<th>Вид зависимости lg P(мм) = ( \frac{1}{T} )</th>
<th>Теплота сублимации, ккал/моль</th>
<th>Источник</th>
<th>Примечание</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Кнудсеновский</td>
<td>1 948 - 2 133</td>
<td>lg P = 21.3 - ( \frac{49.2 \cdot 10^4}{T} )</td>
<td>225</td>
<td>[1]</td>
<td>Испарение из длинного тигра; весовой метод.</td>
</tr>
<tr>
<td>2</td>
<td>Кнудсеновский</td>
<td>1 910 - 2 660</td>
<td>lg P = 8.98 - ( \frac{27.8 \cdot 10^4}{T} )</td>
<td>126</td>
<td>[2]</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>Ленгмюровский</td>
<td>2 250 - 2 524</td>
<td>lg P = 9.33 - ( \frac{36.9 \cdot 10^4}{T} )</td>
<td>168</td>
<td>[3]</td>
<td>Весовой метод</td>
</tr>
</tbody>
</table>

толщине диафрагмы 0.06 мм был равным 1.07. Отношение площади эффи- зионного отверстия к площади камеры составляло 0.001. Предварительными опытами на двуокиси и карбиде урана было показано, что увеличение площади отверстия до 1 \( \cdot 10^{-2} \) см\(^2\); т.е. примерно в 8 раз, не влияло на результаты измерений, поэтому поправка Россмана-Ярвула в расчетах не использовалась.

Упругость пара рассчитывалась по известной формуле

\[
P = G \sqrt{\frac{2\pi RT}{M}},
\]

где P — давление пара; G — скорость эфузии; M — молекулярный вес пара;
СКОРОСТЬ ИСПАРЕНИЯ И ДАВЛЕНИЕ ПАРА ДВУОКИСИ УРАНА.

<table>
<thead>
<tr>
<th>Т°K</th>
<th>t, секунды</th>
<th>Скорость испарения г·см·сек^-1</th>
<th>Давление пара, мм рт.ст.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2063</td>
<td>6,64·10^3</td>
<td>1,052·10^-5</td>
<td>4,99·10^-4</td>
</tr>
<tr>
<td>2148</td>
<td>3,6·10^3</td>
<td>3,285·10^-5</td>
<td>1,589·10^-3</td>
</tr>
<tr>
<td>2228</td>
<td>1,8·10^3</td>
<td>9,47·10^-5</td>
<td>4,615·10^-3</td>
</tr>
<tr>
<td>2328</td>
<td>3,2·10^2</td>
<td>1,955·10^-4</td>
<td>7,94·10^-3</td>
</tr>
<tr>
<td>3308</td>
<td>6,3·10^2</td>
<td>2,67·10^-4</td>
<td>1,341·10^-2</td>
</tr>
</tbody>
</table>

R — газовая постоянная; Т — абсолютная температура. Коэффициент конденсации на мишени принимался равным 1.

Как видно из рис.1, в наших опытах верхняя часть нагревателя служила отражателем для эффундирующих атомов. Для учета этого дополнительного отражения были поставлены специальные опыты, в которых на нагреватель устанавливался конический полый коллиматор, исключающий влияние дополнительного отражения от стенок нагревателя. Для условий наших опытов (расстояние от центра эффузионного отверстия до мишени — 115 мм, длина выступающей части нагревателя — 75 мм, внутренний диаметр нагревателя — 38 мм, диаметр кассеты — 42 мм) количество конденсирующихся на мишени атомов составляло 0,33 от общего числа эффундирующих атомов.

Радиометрический анализ напыленных мишеней, а также а- и β- эталонов проводили на сцинтилляционных датчиках и торцовых счетчиках. Благодаря использованию препаратов моноокарбида с неактивным (I) и активным (II) углеродом удалось выделить долю урана и С<sup>14</sup> в общем излучении. Максимальная ошибка в определении давления паров составляла около 12%.

Для проверки надежности результатов, получаемых на установке, была измерена упругость пара двуокиси урана. Опыты проводились в танталовых тиглях; перед измерениями двуокись урана длительное время отжигалась при температуре 2100°С. Результаты измерений для нагрева и охлаждения хорошо совпадали между собой. Данные представлены в табл.2 и на рис.2.

Температурная зависимость \( \lg P \) имела вид:

\[
\lg P(\text{мм рт.ст.}) = 10,025 - \frac{2,757 \cdot 10^4}{T};
\]

теплота сублимации \( \Delta H \) оказалась равной 126 ккал/моль. Эти данные удовлетворительно согласуются с результатами работ [1, 5].

В табл.3, а также на рис.3 представлены результаты измерения парциальных давлений пара урана и углерода над моноокарбидом урана. Температурные зависимости \( \lg P(\text{мм рт.ст.}) \) имеют вид

\[
\lg P_u = 10,054 - \frac{2,809 \cdot 10^4}{T},
\]

\[
\lg P_c = 2,515 - \frac{1,324 \cdot 10^4}{T}.
\]
Рис. 2. Температурная зависимость давления пара двуокиси урана: 1 — наши данные; 2 — результаты работы [1]; 3 — результаты работы [3].

Таблица 3

СКОРОСТЬ ИСПАРЕНИЯ И ДАВЛЕНИЕ ПАРА УГЛЕРОДА НАД МОНОКАРБИДОМ УРАНА.

<table>
<thead>
<tr>
<th>T°К</th>
<th>t, секунды</th>
<th>Количество испарившегося вещества, г</th>
<th>Скорость испарения, г·см²·сек⁻¹</th>
<th>Давление пара, мм рт. ст.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1878</td>
<td>4,260·10⁴</td>
<td>1,057·10⁻⁵</td>
<td>1,623·10⁻⁷</td>
<td>3,482·10⁻⁵</td>
</tr>
<tr>
<td>1993</td>
<td>4,896·10⁴</td>
<td>2,161·10⁻⁵</td>
<td>2,905·10⁻⁷</td>
<td>6,240·10⁻⁵</td>
</tr>
<tr>
<td>2118</td>
<td>1,710·10⁴</td>
<td>2,034·10⁻⁵</td>
<td>7,830·10⁻⁷</td>
<td>1,781·10⁻⁴</td>
</tr>
<tr>
<td>2283</td>
<td>9,0·10⁵</td>
<td>2,507·10⁻⁵</td>
<td>1,834·10⁻⁶</td>
<td>4,335·10⁻⁵</td>
</tr>
<tr>
<td>5358</td>
<td>1,980·10⁵</td>
<td>1,137·10⁻⁵</td>
<td>4,156·10⁻⁶</td>
<td>1,0·10⁻³</td>
</tr>
</tbody>
</table>

Парциальные теплоты сублимации (ΔHₜ), рассчитанные по методу наименьших квадратов, оказались равными для урана 128,5 и для углерода 60,6 ккал/моль. Расчеты парциальной упругости пара углерода проводились в предположении моноатомного испарения по схеме

\[ UC_{T}B \rightarrow U_{T} + C_{T} \]  \hspace{1cm} (4)

Определенное нами значение ΔHₜ для урана хорошо совпадает с результатами работы Александера и сотрудников [2], однако абсолютные величины давления паров отличаются примерно на порядок. В работах [1, 3] весовым методом определялись не парциальные теплоты сублимации, а суммарные значения теплот сублимации соединений. Если принять, что ΔH = ΔHₜ + ΔHₖ, то полученные нами значения теплоты сублимации карбида урана составляют 199,1 ккал/моль, что по абсолютной величине больше значений, полученных в работе [3], и меньше результатов [1] (см. табл.1).
Рис. 3. Температурные зависимости давления паров монокарбида урана: 1 - результаты работы [1]; 2 - наши данные по парциальной упругости пара урана (● образцы серии I, X - образцы серии II); 3 - результаты работы [2]; 4 - наши данные по парциальной упругости пара углерода.

Отметим также, что расчеты $P_{c_3}$ по схеме

$$\text{UC}_7 \to \text{U}_7 + \text{C}_3,$$

принятой в работе [3] не внесут никаких коррективов в приведенные значения $\Delta H_T$; уменьшается лишь в $\sqrt{3}$ раз абсолютные величины парциального давления паров углерода над монокарбидом урана. Дальнейшие масс-спектрометрические исследования должны уточнить моно- или полиатомный характер испарения углерода из карбида урана.

Используя полученные результаты по парциальным давлениям углерода и урана над монокарбидом урана, мы рассчитали некоторые термодинамические характеристики. Для изменения парциальной молярной свободной энергии сублимации были получены следующие выражения

$$\Delta F_{(u)} = 128500 - 32.8T,$$

$$\Delta F_{(c)} = 60600 + 1.67T.$$  

Значения парциальных молярных энтропий сублимации составили для урана +32,8 кал/моль·°C. С учетом теплоты сублимации ($\Delta H^0$) урана, равной, по данным [6], 105,6 ккал/моль, относительная парциальная молярная теплота сублимации ($\Delta H^m$) оказалась равной около 23 ккал/моль.

Парциальная теплота сублимации урана, приведенная к 298*К, рассчитывалась по известным формулам:

$$\Sigma = \frac{\Delta H_{298}}{T} + \varphi. $$
\[ \Delta H_{298} = \Delta \left[ T \left( \frac{F^0_T - H^0_{298}}{T} \right) \right] - 4,575 \lg P , \]  
(9)

где \( \Sigma = 4,575 \lg P - \Delta C_P \lg T \); \( \Delta C_P \) – разность теплоемкостей для реакции \( \text{UC}_{298} = \text{U}_T + \text{C} \) (графит); \( \Delta \left[ T \left( \frac{F^0_T - H^0_{298}}{T} \right) \right] \) – разность приведенных термодинамических потенциалов для той же реакции; \( \mathcal{J} \) – постоянная интегрирования.

Значения теплоемкостей и приведенных термодинамических потенциалов для графита и газообразного урана принимались по данным [7], а для теплоемкости монокарбида урана была принята зависимость

\[ C_P = 13,40 + 1,02 \cdot 10^{-3} T - 1,46 \cdot 10^{5} T^{-2} , \]  
(10)

предложенная на Венском совещании экспертов по термодинамике [8].

Величина приведенного термодинамического потенциала для карбида была вычислена обычным образом; значение \( S_{298} \) принималось равным 14,2 [8]. Расчет по второму закону, проводимый по формуле [8] в предположении \( \Delta C_P = \text{const}^1 \), привел к значению \( \Delta H_{298} \), равному 132,6 ккал/моль. Расчет по третьему закону дал величину \( \Delta H_{298} = 123,1 \pm 1 \) ккал/моль.

Отличие в результатах расчетов по II и III законам в опытах по испарению наблюдается довольно часто (например, [9]). Это объясняется как систематическими ошибками в опытах по испарению, так и не совсем точными данными для расчетов приведенных термодинамических потенциалов. Если, по данным [10], принять теплоту испарения урана (\( \Delta H^6_{298} \), равной 115,2 ккал/моль, то теплота образования для карбида урана при 298°К получается равной \(-17,4 \) и \(-7,9 \) ккал/моль для расчетов по II и III закону. Последняя величина \( \Delta H_{298} \) явно занижена по сравнению с рекомендуемыми значениями теплоты образования \( \text{UC} \) (\(-21,7 \pm 1,0 \) ккал/моль [8]). Помимо отмеченных ранее обстоятельств, осложняющих точное определение \( \Delta H_{298} \) и соответственно теплоты образования, можно указать и на то, что такая расчеты правильное было бы проводить, имея в виду схему испарения (4) или (5). Однако отсутствие сведений о характере испарения углерода из монокарбидца урана и не совсем точные сведения об испарении чистого углерода (например, [4]) не позволяют это сделать достаточно корректно. Из рис. 3 видно, что по абсолютной величине при всех исследованных температурах, за исключением 1 878°К, давление пара урана выше давления пара углерода. Целесообразно оценить атомное соотношение углерода и урана в парах. На рис.4 приведена температурная зависимость параметра \( \lambda \), равного отношению \( G_{C}M_{U}/M_{C}G_{U} \), где \( G_{i} \) – парциальные скорости испарения углерода и урана, \( M_{i} \) – их атомные веса. Как следует из этих данных, до температуры \(~2100^\circ K\) наблюдается преимущественное испарение атомов углерода, выше этой температуры монокарбид урана обедняется ураном и обогащается углеродом. Последнее обстоятельство отмечается также в работах [3, 11], в которых было установлено, что длительные выдержки в

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1 В исследованном интервале температур разность теплоемкостей колебалась от 2,72 до 2,92. В расчетах было принято \( \Delta C_P = 2,8 \).
вакууме при температурах 2 250 – 2 540°К приводят к обогащению карбида углеродом до состава UC1._1._
Таким образом конгруэнтное испарение монокарбида урана без изменения состава (λ = 1) наблюдается только при одной температуре. Это вполне понятно, если учесть, что парциальные теплоты сублимации урана и углерода отличаются примерно на 70 ккал/моль. В этой связи результаты изучения испарения монокарбида урана методом Лэнгмюра [3] представляются нам неверными. Представляет интерес изучить кинетические закономерности изменения состава карбида урана в широком интервале температур.
Авторы выражают благодарность О.Л.Ижванову, В.С.Смирнову и Ю.Ф.Хромову за помощь в проведении опытов.

ЛИТЕРАТУРА
[3] DE CRESCENTE M. A. et al., ibid, paper С8В.
C. B. ALCOCK (Discussion Leader): One of the aspects of vaporization measurements which I think should be discussed is second law heats. What in fact can we do to break down measured free energies into heats and entropies? Judging by the discussion at Session 1 of this Symposium, the trend in calorimetry is towards higher temperatures, and calorimetrists may therefore encounter problems similar to those which have been complicating vapour pressure interpretation for some years. I think a possible result may be that they will find it more difficult to obtain the heats than we do now.

Paper SM-66/72 (P. W. Gilles)

There was no discussion of this paper.


J. DROWART: I should like to comment on the possible presence of Ga₂O in the gallium. I think the species is there, at least in Ga₂O₃ or in the system gallium plus gallium oxide; it has been detected mass-spectrometrically, and as far as we can judge from our data and other data in the literature, the results of Cochran and Foster (Ref. [13] in the paper) are correct. It should therefore be possible, if there is equilibrium, to calculate the importance of this molecule in a system such as SiO₂ plus gallium.

C. B. ALCOCK (Discussion Leader): I do not agree that the results of Cochran and Foster are correct. I think Dr. Edwards can confirm my view.

R. K. EDWARDS: Yes. A student of mine has obtained results on the vapour pressures of gallium and indium which agree well with those of Dr. Alcock¹.

E. BONNIER: I should like to comment on Dr. Alcock's suggestion at the end of his oral presentation to the effect that it may be possible to learn more about the solid by studying the liquid.

Such a step may seem surprising, but two observations may be made which tend to cancel each other out. On the experimental level, measure-

ment of the co-ordination number is considerably more difficult in liquids, while on the theoretical level, critical study of the models proposed - and this is particularly true for the "surrounded atom" model suggested by Mathieu and Durand - shows that the co-ordination number is not often a very important parameter.

Paper SM-66/75 (R. N. R. Mulford)

There was no discussion of this paper.


There was no discussion of this paper.

Paper SM-66/26 (A. Büchler and J. L. Stauffer)

J. DROWART: In connection with Dr. Büchler's results on the stability of ternary gaseous halides, I should like to mention that ternary gaseous oxides also have surprisingly high stabilities. This is the case, for example, for the gaseous molybdates and tungstates of magnesium, calcium and strontium, for which the stability has recently been published. These molecules are the main species in the gas phase when the corresponding compounds are vaporized or when the binary alkaline earth oxides are placed in molybdenum or tungsten crucibles.

Other analogous cases are those of NaReO₄ and KReO₄ recently studied in Brussels by Dr. K. Skudlarski. The main vaporizing molecules in this case are NaReO₄ and Na₂(ReO₄)₂, or KReO₄ and K₂(ReO₄)₂.

A. BÜCHLER: Ternary gaseous halides and oxides constitute in fact a large group of stable compounds which in general have not been systematically studied. In the presentation of our paper I mentioned briefly our recent work on the LiF-AlF₃ and NaF-AlF₃ systems, where the mixed dimer (LiAlF₄ or NaAlF₄) is the most abundant species over the entire composition range. In addition we were able to demonstrate the existence of gaseous Li₃AlF₆ and Li₂Al₂F₆, as well as the analogous Na compounds to the molybdates, one ought to add In₂MoO₄, found at the University of Chicago, and Li₂MoO₄, identified in our laboratory. In the vapour over the alkali nitrates and nitrates we have identified the gaseous species (LiNO₂)₂, LiNO₃, (LiNO₃)₂, as well as the corresponding sodium species.

L. MARTA: Table VI of your paper shows the vapour pressures of different molecular species. I should like to know if you calculated these figures simply by using the indirect relationships given in your paper, or if you also calibrated to determine the absolute vapour pressure values.

2 VERHAEGEN et al., Trans. Faraday Soc. 61 (1965) 1372.
3 BÜCHLER, A., STAUFFER, J. L., unpublished results.
Also, do you think it possible to determine by this method the small discrepancies in thermodynamic activity of systems which do not form complex combinations?

A. BÜCHLER: All the pressures in Table VI were obtained using the published vapour pressure of pure BeF$_2$ as a reference point. The BeF$_2^+$ peak height corresponding to pure BeF$_2$ essentially corresponds to the pressure calibration.

My answer to your second question is, it would probably be very difficult. On the one hand, differences of 10% in the mass spectrometric signals would push the experimental method to its limit from the point of view of uncertainties in the resulting activities; on the other, in, say, a NaCl-NaBr mixture, Na$^+$ could come in equivalent amounts from NaCl, NaBr, Na$_2$Cl$_2$, Na$_2$Br$_2$, and Na$_2$ClBr.

C. BECKETT: Could you comment on the structure and molecular properties of the binary vapour molecules (LiF-BeF$_2$)? Recent experimental data on some of the simpler polyatomic molecules occurring in high-temperature vapour have revealed significant differences from estimates used only a few years ago to obtain ideal gas functions. The latter are used in the so-called "third law treatment" of vaporization data. Both configurations and bending vibrational frequencies have been found to be quite different from the estimates. The bending vibrations observed in the far infra-red region are much lower than estimated. These changes result in large increases in the entropy and Gibbs energy function.

A. BÜCHLER: For LiBeF$_3$, we have an "entropy of dimerization" of 32 e.u., which would agree with the halide-dimer structure

\[
\begin{align*}
\text{Li} & \quad \text{Be-F} \\
& \quad \text{F}
\end{align*}
\]

For Li$_2$BeF$_4$(g) we feel that the fragment ion Li$_2^+$ suggests the gas-phase structure

\[
\begin{align*}
\text{Li} & \quad \text{Li} \\
& \quad \text{F} \\
& \quad \text{F}
\end{align*}
\]

It may be noted that in this condensed phase, Li$_2$BeF$_4$ probably contains the tetrahedral BeF$_4^-$ ion. At the same time, we find in the LiF-AlF$_3$ system the alkali-halide type of fragmentation pattern

\[M_2X_2 + e \rightarrow M_2^+ + X + 2e,\]
when $X = A1F_4$, i.e.

$$\text{Li}_2\text{AlF}_5 \rightarrow \text{Li}_2\text{F}^+$$

$$\text{Li}_2\text{Al}_2\text{F}_8 \rightarrow \text{Li}_2\text{AlF}_4^+$$

and I do not really know how to write a structure for $\text{Li}_2(\text{AlF}_4)_2$. We must perhaps be very much more sophisticated (or imaginative?) in writing structures. For rhenium trichloride we were able to show that at 300°C more than 99% of the vapour consisted of $\text{Re}_3\text{Cl}_9$ (cf. also a mass spectrum by Rinke and Schoefer, Angew. Chemie (1965)). Here one has the binding

$$\text{Cl} - \text{Re} - \text{Cl}$$

and no monomer is present. Another problematic case is molybdenum oxide, where the trimer is traditionally written as a six-membered ring

$$\text{Mo} \quad \text{O} \quad \text{OE} \quad \text{O} \quad \text{Mo} \quad \text{Mo}$$

but where one also has $\text{MoO}_3$, $\text{Mo}_2\text{O}_6$, $\text{Mo}_3\text{O}_{12}$, and $\text{Mo}_6\text{O}_{15}$. I am afraid I must return the question to Dr. Beckett.

Paper SM-66/58 (R. E. Gebelt and H. A. Eick)

E. GLUECKAUF: The authors have drawn attention to the great similarity between europium dicarbide and the dicarbides of the alkaline earths. In the experiments with the Pluto loop at Harwell, carried out for the Dragon Project, we have found a comparable similarity in the kinetics of diffusion of fission-product europium through pyrolytic carbon. Here we found that europium diffuses very much faster than other rare earths; the only other fission products which show similar diffusion rates are the alkaline earths barium and strontium. This would seem to indicate that the stability of $\text{EuC}_2$ within the excess carbon of the pyrolytic coating could be the rate-determining factor in the diffusion process at 1100-1500°C.

H. A. EICK: I cannot comment specifically on your statement, other than to say that we too observed that europium diffused quite rapidly through graphite.
J. DROWART: I would like to ask Dr. Eick if he calculated the stability of the gaseous molecule EuC\(_2\) from its partial pressure and estimated thermodynamic functions, based for example on a hypothetical model of this molecule.

H.A. EICK: No, we did not undertake this calculation, but I agree that it should be done.

G. De MARIA: What was the temperature at which you started to observe the EuC\(_2\) species? Was it the maximum temperature of the range explored?

H.A. EICK: I do not know the exact temperature, but it was near the maximum temperature of the observations. The EuC\(_2\) species seemed to increase in concentration as the temperature was raised, as would be expected.

G. De MARIA: In connection with the question raised by Dr. Drowart and your answer to my previous question, one can estimate an approximate value of about 160 kcal/mole for the Eu-C\(_2\) bond energy, taking as a basis the pressure-independent reaction Eu(g) + 2C(s) \rightarrow EuC\(_2\)(g) and using for \(-\Delta G^0\) an average value of 14 entropy units. This leads to the conclusion that EuC\(_2\) is a molecular species of high physical stability.

In addition, I should like to mention that the correlation between the bond energy of gaseous dicarbides and the dissociation energy of corresponding monoxides for Group IIIa elements and for the first three elements of the lanthanide series is now well established. Their differences lie within one electron volt, the dissociation energies of the monoxides being always higher. On this basis the above estimate for Eu-C\(_2\) bond energy would lead to the prediction that EuO is a physically stable gaseous species.

I also have another question. The third law heat of vaporization values obtained in the effusion experiments show a significant temperature trend, which, I think, cannot be attributed to uncertainties associated with the estimation of free energy functions. I wonder whether temperature measurements or temperature gradients along the cell might be responsible for the temperature dependence observed.

H.A. EICK: The temperature of the cell interior, as measured through the orifice, was compared with the temperature measured at the base of the cell, and the difference was found to be slight - of the order of 10°C or so. The deviation cannot therefore be the result of a temperature gradient.

The temperature trend in the third law heats derived from the effusion data has two causes: the analytical scheme used to analyse the collection targets, and the bouncing from the targets.

Experiments were performed to determine the degree of condensation on the platinum targets, and the results indicated that only about 60-70% of the effusate striking the targets adhered. In addition, some large errors resulted from the analysis of targets on which a small quantity of europium was condensed. We believe the temperature trend results from these two known errors, and rather than attempt to refine the experimental procedure to eliminate them, we relied upon the mass spectrometric data. The effusion data are presented simply as supplementary evidence.

W.L. WORRELL: In a similar study of the thermodynamic properties of Al\(_4\)C\(_3\), a graphite layer was observed to form around the carbide; this
could have caused the measured aluminium pressures to deviate from the true equilibrium ones. Dr. Storms has also mentioned that he suspected that a similar problem occurs with vanadium carbide. Did you observe any graphite-layer formation around EuC$_2$?

H.A. EICK: We did not observe such a graphite layer in our work, although we were concerned about its existence, and looked for it. Figure 5 of our paper shows the reproducibility which we observed over a three-day period. Such reproducibility would not be likely if a layer of carbon was building up, so we concluded that one was not present. The foregoing remarks by Dr. Glueckauf may provide a possible explanation for this absence.

J. DROWART: I would like to mention that during the mass spectrometry study of the reaction B$_4$C(s) $\rightarrow$ 4B(g) + C(graphite) we obtained evidence for the formation of a carbon layer which apparently reduces the rate of vaporization of boron.

Paper SM-66/70 (E.K. Storms)

G. W. CUNNINGHAM: I should like to make a few comments about some of our own unpublished data. Two years ago we found that by varying the charge and the orifice site we could obtain uranium vapour losses comparable to any one of the eight vapour pressures taken from the literature by Dr. Storms. Since we used graphite cells, high-purity arc-cast UC$_{2+x}$, and a tungsten resistance furnace capable of reaching vacuums of 10$^{-8}$ torr, we did not expect any contamination effects and therefore attributed the orifice effect to a preferential loss of uranium and a build-up of carbon near the surface. In our method the total uranium effused is measured, and since we did not have mass spectrometric data, the uranium-oxygen vapour phase observed by Dr. Storms may be a possible explanation for those results.

However, we have also used a modified Langmuir technique to measure vapour loss as a function of time, temperature and thermal cycling. In this procedure, the effusate is collected from a graphite crucible with no lid. In general we show a high initial loss followed by steady-state conditions which permit us to obtain consistent and reproducible values for the vapour loss of uranium over UC$_2$. Although we still have some additional work to perform before we are satisfied with our results, the work to date still suggests that uranium is preferentially lost from UC$_{2+x}$.

I would also comment that we are very interested in seeing the controversy on vapour pressure of pure uranium settled, since the conclusions about UC$_2$ are dependent upon the vapour pressure of uranium selected.

E.K. STORMS: We find that in addition to the possible evaporation of UO(g), the evolution of CO(g) can deplete the surface of carbon resulting in an increased uranium pressure. This can lead to an abnormally high pressure, even after all the oxygen has left the sample and UO(g) is no longer an important species.

R.N. R. MULFORD: I note that you have obtained both uranium activities and carbon activities directly from your experimental data. I would
like to ask if you have done a Gibbs-Duhem integration of the uranium activity in order to check the internal consistency of the data?

E. K. STORMS: No, a Gibbs-Duhem integration has not yet been made. This and other calculations relating the pressure measurements to features of the phase diagram will eventually be made and reported in subsequent papers.

G. De MARIA: You have mentioned that you observed the UC\(_4^+\) species in addition to UC\(_2^+\) ions. From your measurements can you give an estimate of the partial pressure of the relative molecular species? Were you able to attribute the UC\(_4^+\) ions to direct ionization of the tetracarbide molecule by measuring the ionization potential, the isotopic distribution and the intensity distribution in the molecular beam?

E. K. STORMS: No, the pressure of UC\(_4^+\) could not be studied in detail because its intensity was too near the sensitivity limit of the spectrometer. As mentioned in the paper, the UC\(_2^+\)/UC\(_4^+\) ratio at 2450°K was about 70. This would lead to a pressure of perhaps 1.4 \times 10^{-10} \text{ atm} at this temperature.

G. De MARIA: I should like to emphasize that tetracarbide molecules have been unambiguously identified in the vapour over cerium-graphite and holmium-graphite systems, by means of mass spectrometric investigations recently carried out by my group at the University of Rome. PtC\(_4\) was tentatively identified. Typical relative ion intensities measured at 17 eV and 2273°K for Ce, CeC\(_2\) and CeC\(_4\) were 1:7.7 \times 10^{-1}:1.8 \times 10^{-2}, and for Ho, HoC\(_2\) and HoC\(_4\) at 2360°K 1:4 \times 10^{-3}:6 \times 10^{-5}. Calculated dissociation energies show these species to have a high physical stability. The correlation between dicarbide and monoxide species could be extended to the tetracarbide and dioxide molecules. With reference to the paper by R.J. Ackermann and R.J. Thorn (paper SM-66/80), I might say that tetracarbide molecules will also probably be important species at very high temperatures in actinide-carbon systems.

Paper SM-66/19 (I. G. Murgulescu and Letitia Marta)

There was no discussion of this paper.

Paper SM-66/107 (V. V. Khromonojkin and R. A. Andrievsky: Presented by A. Babad-Zakhryapin)

E. K. STORMS: The vaporization behaviour of UC you have described differs in many respects from the other data reported in this Symposium. Since these properties depend on the composition and purity of the material, I would like to ask what was the composition (stoichiometry) of the samples during the measurement? In addition, would you elaborate further on the technique used?

A. BABAD-ZAKHRYAPIN: The uranium carbide was produced from graphite of nuclear purity and vacuum-melted uranium. I cannot give exact information on the amount of impurity, but it was probably not more than 0.1%.

The equipment used was of the Knudsen-effusion-cell type. The crucible was made of ThO\(_2\), and the temperature of the condenser-type trap did not
DISCUSSION TO SESSION 3

exceed 50°C. Since reflection of the vapour atoms from the surface of the tantalum heater was possible, we ran tests both with and without a conical collimator, and were thus able to take this effect into account.

M. H. RAND: How did you obtain the separate uranium and carbon pressure?

A. BABAD-ZAKHRYAPIN: We used two series of samples, one with and one without 14C. The partial pressure was determined from the difference in activity.

General Discussion

P. W. GILLES: Could the discussion leader comment on the relative advantages of the EMF and vaporization methods for studying thermodynamic properties?

C. B. ALCOCK (Discussion Leader): Are there in fact any data available where both techniques have been brought together on oxides? We can obtain the vapour pressure of UO₂ going up to UO₂ gas from vaporization measurements, but we cannot yet obtain the free energy of formation of UO₂ using cells, because of the electron transport problem in the electrolytes, so that we are not measuring the same thing by these two techniques. The iron-oxygen system has been studied by EMF, but while the vapour pressure might give the FeO vapour species, no-one has measured the oxygen dissociation pressure directly, which would give the free energy of formation for comparison.

C. WAGNER: For the coexistence of Cu and Cu₂O, the equilibrium oxygen partial pressure at 1000°C is of the order of 10⁻⁷ atm, which has been determined both directly and using EMF measurements. If the volumes around the two electrodes of a galvanic cell are not separated from each other, transfer of gaseous O₂ from one electrode to the other may affect the EMF of the cell if the oxygen partial pressure at one electrode is more than about 10⁻⁷ atm. Under these conditions, EMF measurements can be expected to yield significant results only if gas-tight compartments around the electrodes are provided.

C. B. ALCOCK (Discussion Leader): That is quite true. I think we may soon see these two techniques overlapping in the application of electrolytes to activities in binary alloy phases, and this would afford an excellent opportunity for comparison.

R. J. ACKERMANN: Dr. M. H. Rand and Mr. R. L. Faircloth of Harwell and I have used the results of Dr. Markin's EMF study of the plutonium-oxygen system in order to explain the variety of evaporation behaviours observed for the plutonium oxides. The use of both the EMF and the vapour pressure data enable us to arrive at thermodynamic properties of the vapour molecules, but unfortunately they cannot each be examined for internal consistency until a calorimetric measurement of the heat of formation of Pu₃O₇ becomes available.

O. KUBASCHIEWSKI: Although generalizations of this nature can be misleading, I am inclined to give preference to the EMF method, at least in the field of alloy thermodynamics. Provided the component metals differ
sufficiently in electronegativity, free energies can usually be obtained at, say, 1000°C with an accuracy of ±1 mV or even better, corresponding to ±46 cal/gram-ion for a divalent ion. Activities obtained as differences of vapour pressures at a similar temperature carry an uncertainty of about ±7%, at best. Quite a number of examples are available where EMF and vapour pressure measurements have been made on the same alloy systems, and these support the claim for a greater accuracy of the EMF method, but one would probably find exceptions, and there are of course many systems to which only the one or the other method is applicable.

M.H. RAND: There has been a comparison of results obtained by vaporization and EMF methods on a number of uranium-intermetallic systems - for example with gallium, indium, lead and zinc. The agreement is very good except for the gallium system.

Moreover, Dr. Egan has recently measured the free energy of formation of UC₂ by an EMF method, with results which, I think, imply a rather less negative heat of formation at 298°K than that suggested by Dr. Storms.

J.J. EGAN: Yes. Work has been carried out on the cell

$$U, UF_3(s)|CaF_2(s)|UF_3(s), UC_2, C$$

and the free energy of formation of UC₂ determined between 700°C and 900°C. Since it is difficult to obtain accurate entropy values from the temperature coefficient of these cells, it might not be useful to calculate $\Delta H^{\circ}_{298}$ of UC₂ from results of the above cell. However the values of $\Delta G^{\circ}(UC_2)$ should be accurate to ±0.5 kcal.

Cells have also been operated on U₂C₃ and it was found that, in the temperature region 700 to 900°C, U₂C₃ is more stable than UC₂, as predicted by the phase diagram.

A. BÜCHLER: To turn to another subject, Dr. Alcock has asked for comments concerning second-law determinations. In our very first mass spectrometric work⁸ we had to deal with a tetrameric system. We found that the errors introduced by having to estimate molecular parameters were at least as large as the errors conventionally associated with second-law work. We felt that careful crucible design and good temperature calibrations could yield satisfactory second-law results. There are two points which must be made. First, it is not enough to calibrate at a single temperature. Assume, for instance, that one works over a 200°C range. Then, if the temperature is off by +10°C at one end of the range and -10°C at the other, the second-law slope will be 10% in error, even though a temperature calibration at the centre of the range would show no error. Secondly, in a system such as NaF-AlF₆, the more complex species (in this case Na₂Al₂F₈) may increase in importance at higher temperatures, and I see no way of dealing with them except through second-law measurements⁹.

C.B. ALCOCK (Discussion Leader): I have noticed that in current published work on vapour pressure measurements there is an increasing

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⁷ BEHL, W., EGAN, J.J., Abstracts of Electrochemical Society Meeting of May 1965 at San Francisco, Calif., USA.
⁹ BÜCHLER, A., STAUFFER, J.L., unpublished results.
tendency to use gold as a standard, which enables one to calibrate up to say 1500°C. I was very interested in Dr. Storms' remarks on molybdenum, which I feel would be a useful second standard from 1600 to say 2000°C. Perhaps he could give us more details.

E. K. STORMS: The molybdenum pressures measured in the spectrometer were compared with those obtained by Vozzella, Miller and De Crescente (Ref. [22] in my paper Sm-66/70) from Langmuir measurements and with unpublished values of Fries obtained by the same technique. The agreement between the three studies is excellent. Molybdenum metal would, indeed, make a good secondary standard for spectrometer calibration. It is especially useful in a graphite cell since the very small solubility of carbon has essentially no effect on the pressure.

R. N. R. MULFORD: If I may make a comment in connection with third law heats, I feel that there is a great lack of data on the heat capacities of liquid metals. This means that one can get almost any third law heat value one likes by appropriate choice of a heat capacity for the liquid metal.

O. J. KLEPPA: I should like to offer the observation that inverse drop calorimetry offers the possibility of obtaining good heat content and heat capacity data for liquid metals in the temperature range where precise calorimetry is possible. For liquid tin this has already been done by Hultgren et al. We should look forward to similar data for more high-melting metals as suitable calorimeters are developed.

J. DROWART: Other difficulties with molten metals are the interactions with the container, even when they do not lead to the formation of additional gaseous species, and the approximations used to estimate the activity of the metal studied in the solution formed.

In many cases, such difficulties probably cause uncertainties equivalent to or larger than those introduced by estimating or extrapolating thermodynamic functions.

It would therefore seem to me that no generally valid prescription can be given as to when to use the second or the third law approach, since comparable discrepancies between the true and the measured quantity can appear in either of these. Rather we should carefully examine in each case whether differences in the results obtained by the two methods can be attributed to specific causes, and which of the two procedures leads to the result more likely to be correct.

(Dr. Drowart was invited to give a summary of some mass spectrometry results obtained by Pattoret, Smoes and himself, and this is given as an Appendix to this Discussion)
APPENDIX

MASS SPECTROMETRY ON THE URANIUM-OXYGEN AND URANIUM-CARBON SYSTEMS

A. PATTORET, S. SMOES AND J. DROWART

Previous experimental work [1, 2] and discussions of the influence of oxygen on the vapour pressure of uranium [3] and of the consistency [4] between the value $\Delta H_{298}^0 = 126$ kcal/g-at. [1, 2, 5] for the heat of sublimation of this element with the thermochemical data for the vaporization of uranium oxides and carbides available early in 1964 were already reported.

The work I wish to summarize here concerned mainly the determination of the vapour pressure and heat of sublimation of uranium and of UO$_2$. Studies of the partial pressures in the UO$_2$ single phase and a determination of the uranium pressure over UC$_{1.04}$ were further made.

Tungsten and tantalum Knudsen cells were used for uranium. As a result of the presence of oxygen, the U-UO$_2$ two-phase system was simultaneously studied, at least in the initial part of most of the experiments. In addition to the alloy formation, sintered tungsten and tantalum gave rise to serious problems of inter-boundary migration. These difficulties were markedly reduced by using crucibles made from tungsten single crystals and especially re-molten tantalum. Remaining difficulties due to creeping were overcome by retaining only those points for which careful measurements of the intensity distribution in the molecular beam showed the latter to originate from the effusion orifice. These intensity measurements were made using two mutually perpendicular slits in a rotary sector, which also made it possible to intercept the molecular beam completely. Further, to make as direct a comparison as possible of the different compositions, twin Knudsen cells inserted in a single tantalum shell and mounted on an externally adjustable support [2] were used. The vaporization of UO$_2$ and the partial pressures in the UO$_2$ single phase were studied in tungsten cells. For UC$_{1.04}$ a Knudsen cell entirely made out of this material was placed in a ZrC cylinder surrounded by a molybdenum shell. The movable assembly was used here to mass analyse molecular beams issuing one inside the cell, one from the surface of the UC$_{1.04}$ cover. These beams were formed with a tantalum collimator, carrying two identical orifices placed about 2 mm above the cell.

The absolute values of the pressures of the uranium-containing species were derived from the ion intensities by calibrating the mass spectrometer by quantitative evaporation of known amounts of silver. The relative ionization efficiency cross-sections previously established by De Maria, Burns, Drowart and Inghram [5] were used. For UO and UO$_2$, these were independently verified by quantitatively vaporizing known amounts of UO$_2$ or by condensing a known fraction of the effusate in the U-UO$_2$ system. To avoid the contribution of fragmentation to the measured ion intensities, the energy of the ionizing electrons was held between 8 and 14 eV for U, UO and UO$_2$. For UO$_3$, which is one of the main gaseous species in the UO$_{2+x}$ region, but
The uranium vapour pressures were measured in the temperature interval 1720-2340°K in thirteen different experiments. They are given by the relation \( \log p(\text{U}) \text{ (atm)} = 5.77 - 2.54 \times 10^4 / T \). The average third law value for the heat of sublimation is \( \Delta H^0 = 126.1 \text{ kcal/g-at} \). This value was obtained with the free energy functions given by Stull and Sinke [7] which are practically identical with those calculated from the heat of fusion and the heat capacity of liquid uranium measured by Levinson [8]. Activity corrections in the U-Ta and U-W alloys [9] were made by assuming both to be perfect solutions. The standard deviation in the \( \Delta H^0 \) value is ±0.9 kcal/g-at. The overall estimated uncertainty, which further takes into account uncertainties in the temperature, in the pressure calibration, in the relative ionization crosssections, in the activity corrections and in the free energy functions is ±2 kcal/g-at.

The comparison of the uranium pressures in the two phase system and in the single phase after de-oxygenation as well as the direct comparison of the intensities in the molecular beam issuing from twin Knudsen cells, one of which contained the U-Ta alloy, the other the U-\( \text{UO}_2 \)-Ta system, showed oxygen not to affect the uranium activity by more than a factor of 1.6 around 2000°K and probably by less.

The \( \text{UO}_2 \) pressure [1, 2] in the two phase system \( \text{U}(\ell) + \text{UO}_2(s) \) is given by the relation \( \log p(\text{UO}_2) \text{ (atm)} = 7.85 - 2.76 \times 10^4 / T \). It leads to a third law enthalpy \( \Delta H^0 = 134.0 \pm 4.0 \text{ kcal/mole} \) for the reaction \( \frac{1}{2} \text{U}(\ell) + \frac{1}{2} \text{UO}_2(s) \rightarrow \text{UO}(g) \) and a dissociation energy \( D^0(\text{UO}) = 180.3 \pm 4.5 \text{ kcal/mole} \) (free-energy functions: \( \text{U}(\ell) \) se above; \( \text{UO}_2(s) \): Kelley and King [10]; \( \text{UO}(g) \): De Maria et al. [5]).

The study of the \( \text{UO}_2 \) single phase included the measurement of the heat of sublimation of \( \text{UO}_2 \) and of the variation of the U, \( \text{UO}_2 \), \( \text{UO}_3 \) and oxygen partial pressures with composition. These results will be presented later. It is mentioned here that from the weight loss calculated by integrating the flux of each of these species with time, the composition of the phase limit was deduced to be \( \text{UO}_2 \) at 2300°K. At the same temperature, under conditions of effusive evaporation, the congruently vaporizing composition, approached both from the uranium rich side (mainly by preferential vaporization of gaseous \( \text{UO} \)) and from the oxygen rich side (mainly by preferential vaporization of gaseous \( \text{UO}_3 \)) was similarly established as \( \text{U} \frac{1.94 \pm 0.04}{2} \). This composition changes to lower O/U ratios with increasing, and to higher O/U ratios with decreasing temperatures, as was also observed in other reports presented at this symposium.

In the interval 1890-2420°K, the molecule \( \text{UO}_2 \) remains the predominant gaseous species at compositions O/U<2.0. Its pressure varies by less than 25% between the lower phase limit and \( \text{UO}_2 \) at 2300°K. In the interval 1890-2420°K, the pressures measured in this investigation are given by the relation \( \log p(\text{UO}_2) \text{ (atm)} = 8.60 - 3.09 \times 10^4 / T \), in agreement with the equations summarized by Ackermann and Thorn [11]. The second law heat of sublimation, \( \Delta H_{2160}^0 = 141.4 \pm 2.5 \) or \( \Delta H_{2160}^0 = 152.6 \pm 3.5 \text{ kcal/mole} \) is further...
in agreement with the third law value $\Delta H^0 = 157.3 \pm 4.0$ kcal/mole calculated with the free energy functions estimated by De Maria, Burns, Drowart and Inghram [5]. The corresponding atomization energy is $\Delta H^0_{\text{at}}(\text{UO}_3) = 345.1 \pm 5.0$ kcal/mole.

The atomization energy of the molecule UO$_3$ was deduced from the iso-molecular exchange reaction $\text{UO}(g) + \text{UO}_3(g) \rightarrow 2\text{UO}_2(g)$. It is $\Delta H^0_{\text{at}}(\text{UO}_3) = 507 \pm 8$ kcal/mole compared with earlier values [5] for the same molecule obtained in an analogous way but corrected for fragmentation, $\Delta H^0 = 503 \pm 7$, or from pressure measurements by the transport method using oxygen [12], $\Delta H^0 = 499 \pm 6$, or water [13] as carrier gas, $\Delta H^0 = 504 \pm 7.0$ kcal/mole, all evaluated with the same free-energy functions [5].

The vaporization of UC$_{1.04}$ was investigated in the temperature interval 2230-2510°K. The uranium partial pressure and its variation with temperature, given by the relation $\log p(\text{U}) \text{ (atm)} = 7.61 - 3.35 \times 10^4 / T$ are in agreement with those interpolated from Storms' data [14]. The $p(\text{UC}_2)/p(\text{U})$ ratio is however somewhat different. It is 1/400 at 2500°K for 20 eV electrons. If equilibrium inside the cell is established (ratio effusion to vaporizing areas = 1/50) and if the variation of the $I(\text{UC}_2^+)/I(\text{U}^+)$ ratio with the energy of the ionizing electrons is neglected and the ratio $I(\text{UC}_2^+)/I(\text{U}^+)$ taken as 1/4 [14, 15] at 2500°K in the two phase system UC$_2(s) + \text{C (graphite)}$, the resulting carbon activity in this experiment would be a(C) $> 0.1$ at 2500°K, compared to a(C) $= 0.2$ calculated from Storms' data. Although it is believed that some carbon pick-up from the Knudsen cell assembly could have occurred in the latter measurements, it is felt that the difference can well be due to the hypotheses that have been made to arrive at the result.

The comparison in the same experiment of the pressure in the Knudsen cell and the flux from its surface at 2500°K showed the latter to decrease rapidly with time from a value identical to that inside the cell to a steady state value $\log p(\text{U}) \text{ (atm)} = -6.35$, in good agreement with the flux measured by Vozella, Miller and De Crescente [16] for the congruently vaporizing composition UC$_{1.10 \pm 0.3}$. This agreement and the simultaneous constancy of the flux from the inside of the cell tend to indicate that, at this temperature and for a wall about 1 mm thick, a sufficient concentration gradient can be established to have a surface composition near the congruently vaporizing one. The fact that the flux from the surface and from the cell were initially identical indicate that, at least for UC$_{1.04}$, the vaporization coefficient of uranium is close to unity at 2500°K. Whether the vaporization coefficient remains unity or decreases in the steady state can not be concluded from this experiment. It is however of interest to mention that for the steady state vaporization from the surface the ratio $I(\text{UC}_2^+)/I(\text{U}^+)$ was less than 1/800 compared to 1/400 for the Knudsen cell and to the approximate value 1/110 expected from the change in carbon activity between UC$_{1.04}$ and UC$_{1.1}$. The molecule UC$_2$ therefore probably has a vaporization coefficient below unity.

REFERENCES

DISCUSSION TO SESSION 3

Session 4

THERMODYNAMICS OF THE LIQUID STATE
Chairman: M. DIAZ-PEÑA

SPAIN
THERMODYNAMICS OF FUSED SALTS AND FUSED SALT MIXTURES

O.J. KLEPPA
UNIVERSITY OF CHICAGO,
ILL., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

THERMODYNAMICS OF FUSED SALTS AND FUSED SALT MIXTURES. Broadly speaking the liquids which are available for technological applications at elevated temperatures are either metallic or ionic in character. The present survey will cover the ionic state only. To a first approximation the behaviour of ionic liquids may be described in terms of simple models which incorporate features known from the chemistry of ionic solids. This forms the background for the corresponding states approach, which has had considerable success in rationalizing the thermodynamic properties both of pure ionic liquids and of mixtures formed by them.

Simple fused salt mixtures may be classified according to the following scheme:

1. Mixtures of salts with similar charge structure containing a common ion. This ion may be an anion as in NaCl-KCl or a cation as in NaCl-NaBr.

2. Mixtures of salts with different charge structure but with a common ion, e.g. NaCl-CaCl₂ or NaCl-Na₂O.

3. Mixtures of salts containing two different cations and two different anions (reciprocal systems). These may be charge symmetrical as in NaCl-KBr or charge unsymmetrical as in NaCl-CaBr₂.

This list outlines, in the order of increasing complexity, a series of fundamental problems in the chemistry of fused salt mixtures: how do the thermodynamic properties of each type of mixed system depend on the size, charge and structure of the participating ions? During recent years these problems have been the subject of systematic investigations. As a result it has become possible to rationalize the behaviour of certain classes of fused salt solution systems. Some of these developments will be reviewed.
стояние. Весьма приближенно поведение ионных жидкостей можно описать с помощью простых моделей, включающих характеристики, известные из химии твердых ионных тел. Это является предпосылкой соответствующего подхода к состояниям, который был довольно успешно применен для рационалистического объяснения термодинамических свойств чистых ионных жидкостей, так и смесей, образованных ими.

Простые смеси расплавленных солей могут быть классифицированы в соответствии со следующей схемой:
1. Смеси солей с одинаковой структурой заряда, содержащие общий ион. Этот ион может быть анионом, как в NaCl-KCl, или катионом, как в NaCl-NaBr.
2. Смеси солей с различной структурой заряда, но с общим ионом, например, NaCl-CaCl₂ или NaCl-Na₂O.
3. Смеси солей, содержащие два различных катиона и два различных аниона (равновесные системы). Они могут быть заряжены симметрично, как в NaCl-KBr, или асимметрично, как в NaCl-CaBr₂.

Этот список намечает, в порядке возрастания сложности, ряд основных проблем химии смесей расплавленных солей, например: как термодинамические свойства каждого типа смешанной системы зависят от размера, заряда и структуры участвующих ионов. В последние годы эти проблемы были предметом систематических исследований. В результате стало возможным дать рационалистическое объяснение поведению определенных классов систем растворов расплавленных солей. Рассматриваются некоторые результаты этих исследований.

TERMODINAMICA DE SALES FUNDIDAS Y MEZCLAS DE LAS MISMAS. En términos generales, los líquidos de que se dispone para aplicaciones tecnológicas a temperaturas elevadas son de carácter metálico o iónico. La presente memoria se refiere exclusivamente al estado iónico. En primera aproximación, el comportamiento de los líquidos iónicos puede describirse según modelos sencillos que presentan características conocidas en la química de los sólidos iónicos. Esto constituye el antecedente para el enfoque basado en los estados correspondientes, que ha permitido racionalizar las propiedades termodinámicas, tanto de los líquidos iónicos puros como de sus mezclas.

Las mezclas simples de sales fundidas pueden clasificarse con arreglo al siguiente esquema:
1. Mezclas de sales con análoga estructura de cargas, con un ion común. Este puede ser un anión, como en el NaCl-KCl, o un catión como en el NaCl-NaBr.
2. Mezclas de sales con distintas estructuras de cargas pero con un ion común, por ejemplo, NaCl-CaCl₂ o NaCl-Na₂O.
3. Mezclas de sales con dos cationes y dos aniones distintos (sistemas recíprocos). La estructura de cargas puede ser simétrica como en el NaCl-KBr, o asimétrica como en el NaCl-CaBr₂.

Esta lista esboza, en orden creciente de complejidad, una serie de problemas fundamentales en la química de las mezclas de sales fundidas: ¿Cuál es la relación entre las propiedades termodinámicas de cada tipo de sistema mixto y el tamaño, carga y estructura de los iones que forman parte del mismo? En los últimos años, estos problemas se han investigado de forma sistemática. Como resultado de ello, se ha podido racionalizar el comportamiento de algunas clases de sistemas a base de soluciones de sales fundidas. En la memoria se pasa revista a algunas de las mencionadas investigaciones.

1. Introduction. The liquid ionic state

On theoretical grounds we are led to recognize in simple ionic liquids several contributions to the pair potential acting between two ions, i and j, of charge \( z_i \) and \( z_j \), and of polarizability \( \alpha_i \) and \( \alpha_j \), as a function of the interionic distance \( r \) [Stillinger (1)]

\[
\phi_{ij}(r) = A_{ij} e^{-Br} + \frac{z_i z_j e^2}{r} - \frac{\{z_i e\}^2 \alpha_j + (z_j e)^2 \alpha_i}{2r^4} - \frac{C_{ij}}{r^6} + \text{higher order terms} \tag{1}
\]
The terms on the right-hand side represent:

(a) Short range repulsive potential.
(b) Charge-charge interaction.
(c) Charge-dipole interaction.
(d) Dipole-dipole interaction. The coefficient $C_{ij}$ may be approximated by the London formula for the dispersion energy [2]

$$C_{ij} = \frac{(3/2)\alpha_i\alpha_jI_iI_j}{(I_i + I_j)}$$

where $I_i$ is the ionization potential of the ion.
(e) Higher order terms, such as dipole-quadrupole terms, etc.

In order to obtain the total cohesive energy of the ionic melt a summation must be carried out over all the pair interactions in the system. The summation of terms (a), (b) and (d) is expected to be essentially additive. However, the charge-dipole interaction (c) involves the field created by the charges and induced dipoles surrounding a given ion. Thus this quantity has the character of a many-body term. This introduces an element of great complexity in any rigorous theoretical treatment of even a very simple fused salt. In approximate treatments this difficulty usually is side-stepped through the introduction of a dielectric constant, $\kappa$.

Additional complexity arises if the salt in question is not a simple ionic medium. This presumably is the case for many salts which have proved particularly attractive from an experimental point of view, such as, e.g., the salts of the highly polarizable ions silver, thallium, lead, cadmium, etc. Evidence for this is provided, e.g., by the recent nuclear magnetic resonance work on the thallium salts of Hafner and Nachtrieb [3], and by the lattice energies of these salts, which cannot be fully accounted for in terms of ionic and dispersion interactions alone. This latter point is illustrated in Fig. 1, in which we plot the lattice energies of the monovalent halides against the reciprocal of interionic distance. For further information see the recent review by Ladd and Lee [4].

The rigorous theories of fused salts have not yet been developed to a point where they provide a basis for the prediction and correlation of thermodynamic information. For this purpose the most successful theoretical approach has been based on the methods of corresponding states theory [Pitzer (5)]. For ionic
liquids this approach was developed by Reiss and co-workers [6, 7].

Reiss, Mayer and Katz [7] assume that the equilibrium properties of a fused salt can be related to those of a model ionic melt. This melt is defined through the following assumptions:

(a) The role of the long-range Coulomb forces is to generate a locally ordered structure, in which, on the average, a negative ion is surrounded by positive ions and vice versa.

(b) Because of the local structure and the Coulomb repulsion between ions of the same sign, short-range interactions between ions of like sign are neglected.

(c) The pair potential between ions $i$ and $j$ is taken to be of the form

$$
\phi_{ij} = \begin{cases} 
\infty ; & r \leq d \\
(z_i e)(z_j e)/\kappa r ; & r > d
\end{cases}
$$

where $\kappa$ is a dielectric constant. With this choice of potentials each salt is fully characterized by the specification of a single parameter of length, $d$. A convenient choice for this parameter is the sum of the ionic radii, $r_+ + r_-.$

Reiss, Mayer and Katz find the following expressions for the reduced pressure, $\pi$, the reduced temperature, $\mathcal{C}$, and reduced volume, $\Theta$, for a charge-symmetrical salt, $|z_i| = |z_j|$

$$
\pi = \kappa d^4 p/z^2
$$
$$
\mathcal{C} = d \kappa T/z^2
$$
$$
\Theta = V/d^3
$$

One can write a reduced equation of state for any salt for which the stated assumptions are valid.

Based on the provisional assumption of $\kappa = 1$, Reiss et al. find their theory to be confirmed in several ways. For example, they show that the reduced melting points for the simple alkali halides, $\mathcal{C}_m = d T_m/z^2$, all fall near the value $3 \times 10^{-5}$ deg cm. Among these salts the only significant deviations are found for the lithium halides, which have values near $2.2 \times 10^{-5}$ deg cm. This is interpreted to reflect that the size relations between cations and anions in these salts are such that assumption (b)
above may be violated. Other confirmations of the corresponding states theory are found for the vapor pressures and surface tensions, thermal expansion, etc. The theory of Reiss et al. as expected fails to account for the behavior of salts of the highly polarizable ions silver, thallium, etc., for which dispersion interactions and small covalent contributions to interionic bonding must be included.

2. Mixtures of fused salts

As a consequence of the electrostatic forces between the ions in a fused salt there will, at ordinary temperatures, be no mutual randomization of the cations and anions. This led Temkin [8] to postulate that in an ideal fused salt mixture the different types of anions will be randomly distributed among the anions (i.e., on the anion "sub-lattice"), while similarly the different types of cations will be randomly distributed among the cations.

In a mixture containing $n_A$ moles of cation $A$, $n_B$ moles of cation $B$, $n_X$ moles of anion $X$ and $n_Y$ moles of anion $Y$, the inte-
gral entropy of mixing will, according to Temkin, be

$$\Delta S = -R(n_A \ln N_A + n_B \ln N_B + n_X \ln N_X + n_Y \ln N_Y)$$  \hfill (4)$$

In this expression $N$ represents the ionic fractions, defined through

$$N_A = n_A/(n_A + n_B), \text{ etc.}$$

For the ideal fused salt mixture we also have $\Delta H = \Delta U = \Delta V = 0$, while, of course

$$\Delta G = -T\Delta S$$

In real mixtures deviations from these relations generally will be found. It is the general objective of experimental work on fused salt mixtures to obtain information on these deviations.

From a phenomenological point of view simple mixtures of fused salts may be classified according to the following scheme:

(a) Systems with symmetrical charge structure containing a common ion. This ion may be either the anion, as in NaCl-KCl, or the cation as in NaCl-NaBr.

(b) Systems with unsymmetrical charge structure containing a common ion. Again, this ion may be the anion as in NaCl-CaCl$_2$ or the cation as in NaCl-Na$_2$O.

(c) Systems containing two cations and two anions. These systems may be further described as charge-symmetrical (Na$^+$, K$^+$, Cl$^-$, Br$^-$), or charge-unsymmetrical (e.g., Na$^+$, Ca$^{++}$, Cl$^-$, Br$^-$).

We may now ask: How do the excess thermodynamic properties in each class of mixed systems depend on the size, charge and structure of the participating ions?

A great deal of new information relating to this question has become available during the past few years. Some of this information has been discussed in recent review articles by Førland [9] and by Blander [10]. The present survey will in the main stress developments which have occurred since these reviews were completed. However, in view of the limitations of space and time we will make no attempt to give encyclopedic coverage. Instead we will select for special attention those aspects of fused salt solution chemistry which are most well developed in a quantitative sense.
2.1 Charge-symmetrical mixtures containing a common ion

2.1.1 General and theory. Until very recently the most comprehensive quantitative data on fused salt mixtures were the data of Kleppa and co-workers [11-14], who measured the enthalpies of mixing for the binary system formed by the monovalent nitrates. For the alkali nitrates it was found that the enthalpy of mixing obeys the following approximate, empirical relation

$$\Delta H^M = -N_1N_2 \ 140 \ \delta^2 \ \text{kcal/mole}$$  \hspace{1cm} (5)

Here $N$ is the molefraction, while $\delta = (d_1-d_2)/(d_1+d_2)$, where $d_1$ and $d_2$ are the interionic distances characteristic of the two pure salts.

Originally the data for the binary alkali nitrates were rationalized on the basis of very crude models, proposed by Førland [15] and by Blander [16]. In Førland's model one considers only a linear assembly of three hard sphere ions, two cations and a common anion. Blander extended this by considering a single solute cation in an infinite linear chain of the solvent salt. Both models, while grossly oversimplifying the physical picture, were in agreement with experiment in indicating a decrease in potential energy on mixing. This arises in large measure from the reduction in the Coulomb repulsion between next nearest neighbor cations.

A different point of view was adopted by Lumsden [17] who assumed that the principal source of the energy of mixing is the interaction of the anion with the polarization field in which it is placed. This field was considered to be zero in the pure molten salt, and to have a calculable value in the mixture. While Lumsden's method of calculating the polarization energy may be criticized, his work was significant in drawing attention to the polarization interactions.

Later a modified, conformal solution theory for the heats of mixing of fused salts was developed by Reiss, Katz and Kleppa [18], based on the model ionic melt of Reiss, Mayer and Katz [7].

Application of the methods of conformal solution theory [Longuet-Higgins (19), Brown (20)] to charge-symmetrical fused salt mixtures gives the following result: The first order term cancels. The second order term gives a functionally simple
expression for the enthalpy of mixing

\[ \Delta H^M = N_1 N_2 \bigg\langle \frac{1}{T,P} \bigg( \frac{d_1 - d_2}{d_1 d_2} \bigg)^2 \bigg\rangle = N_1 N_2 \delta_{12}^2 \]  

(6)

Here \( \bigg\langle (T,P) \bigg\rangle \) is a so far unevaluated complicated integral which is a negative function of temperature and pressure, while \( d_1 \) and \( d_2 \) are the interionic distances which characterize the two salts. Note that this expression is closely related to the empirical one found for the alkali nitrates [Equation 5].

Recently an extension of the conformal solution theory has been given by Davis and Rice [21]. They assume the same model ionic melt, but their model includes also short-range dispersion interactions as a perturbation to the pair potential of the original theory of Reiss et al. In the theory of Davis and Rice the general form of the pair potential between the ions is written as

\[ \varphi = \frac{1}{d} f\left(\frac{r}{d}\right) + \frac{s}{2} V(r) \]  

(7)

The first term is a generalized form of the interionic potential [Blander (22)], while \( \frac{s}{2} \) represents the coupling parameter for the particular van der Waals type interaction considered. \( V(r) \) is defined as \( V(r) = -r^{-n} \). Examples of \( \frac{s}{2} \) and \( n \) pertinent to the ion-ion interactions are [see Eqs. (1) and (2) above]:

(a) Induced dipole-ion interaction: \( n = 4 \);
   \[ \frac{s}{2} = e^2 (\alpha_i + \alpha_j) / 2 \], where \( \alpha_i \) and \( \alpha_j \) are the polarizabilities of ions \( i \) and \( j \), respectively, and \( e \) is the ionic charge.

(b) Van der Waals-London (dipole-dipole) interaction: \( n = 6 \), \( \frac{s}{2} = C_{ij} \), where \( C_{ij} \) may be determined by various approximate expressions such as that given by London [2].

According to Davis and Rice the thermodynamic properties of the fused salt mixture depend both on the parameter of length, \( d \), and on the coupling parameter \( \frac{s}{2} \). The latter takes into account those properties of the cations and anions, such as polarizability and charge, which are important for the dispersion interactions. The following expression is derived for the enthalpy of mixing

\[ \Delta H^M = N_1 N_2 \left( U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2 \right) \]  

(8)

The unevaluated coefficients \( U_0 \), \( U_1 \) and \( U_2 \) are complicated functions of \( \frac{s}{2} \). However, they may be described qualitatively in
terms of the types of interactions on which they depend as follows:

(a) $U_0$: This term is positive and determined largely by the change in van der Waals interactions between next nearest neighbor cations. Terms of this type were previously calculated for fused salt mixtures by Blander [23] and by Lumsden [17].

(b) $U_1$: The leading term in the expression for this coefficient depends on the difference between the nearest neighbor anion-cation dispersion interactions in each of the two components of the mixture.

(c) $U_2$: This coefficient, while primarily represented by the coefficient $\int (T,P)$ of the theory of Reiss et al. includes also a term which depends on the sum of the anion-cation dispersion interactions in the two components of the mixture.

For systems in which the dispersion interactions described by $\frac{1}{2} V(r)$ are negligibly small compared to the Coulomb potential energy, the theory of Davis and Rice reduces to that of Reiss et al. This appears to be the situation in the binary alkali nitrates. However, in systems which contain highly polarizable cations such as Ag$^+$ and Tl$^+$ the dispersion interactions are of greater importance. This is reflected in increased importance of the terms that contain $U_0$ and $U_1$ in Eq. (8).

2.1.2 Binary alkali halides. For many reasons it has proved extremely difficult to study the binary alkali halides by electrochemical methods. Therefore, until recently, the only thermodynamic information on these liquid systems consisted of phase diagram data and scattered cryoscopic measurements. The data were inadequate to provide the basis for a deeper understanding of these important solution systems. However, since 1960 calorimetric data have become available through the works of Aukrust et al. [24], of Gilbert [25], and in particular through a very recent comprehensive study of the binary alkali chlorides, bromides and iodides by Hersh and Kleppa [26].

In Fig. 2 we present a graph of the experimental values of $4\Delta H^M_{0.5}$ plotted against $\sum_{12}^{2}$ taken from reference [26]. Clearly, the systems fall into two groups. On the one hand we find that systems with large values of $\sum_{12}^{2}$ show large negative enthalpies of mixing and do not depart significantly from the trend established by the alkali nitrates. On the other
hander we note that for systems with small values of $\sigma_{12}^2$ we have both positive and negative mixing enthalpies.

Hersh and Kleppa showed that the enthalpies of mixing for all the binary alkali halides, as well as for the previously
studied alkali nitrates, to a first approximation can be represented by the following semi-empirical relation:

$$\Delta H^M = N_1 N_2 \left( U_0^{++} - 340 \delta_{12}^2 \right) \text{kcal/mole} \quad (9)$$

In this expression the second term on the right-hand side, which is Coulombic in origin, corresponds to the term $U_2 \delta_{12}^2$ in Eq. (8). The first term on the right-hand side ($U_0^{++}$) differs from system to system. It represents a theoretical estimate of the contribution to the mixing enthalpy arising from the dispersion energy between next nearest neighbor cations [Lumsden (17), Blander (23)].

For large differences in size between the two cations the Coulomb term predominates, and the enthalpy of mixing is negative. However, for small values of $\delta_{12}$ the term $U_0^{++}$ may predominate, in which case the sign of the enthalpy of mixing may be positive. We give in Fig. 3 a plot of $\Delta H^M_{0.5} - U_0^{++}$ plotted against $\delta_{12}^2$, taken from reference [26]. Although the uncertainties associated with the calculation of $U_0^{++}$ are quite large, it is indicated that all the studied systems, with the possible exception of (Li-K)F [Gilbert (25)], are reasonably well represented by Eq. (9).

Hersh and Kleppa found no evidence in their data on the binary alkali halides for a term linear in $\delta_{12}$. This suggests that in these solutions the term $U_1 \delta_{12}$ in 9 is relatively small. However, this cannot be considered proved, since it is not at the present time known how to make a realistic numerical estimate of the contributions to the mixing enthalpy which may arise from nearest neighbor dispersion interactions.

### 2.1.3 Mixtures involving silver and thallium halides.
Information on the solution behavior of the liquid silver bromide - alkali bromide systems has been available since the pioneering e.m.f. investigation by Hildebrand and Sals'trom [27]. Unfortunately, the lack of corresponding data for the alkali halide systems has prevented a full interpretation of these early results. This situation is improved through the recent publication by Hersh et al. of calorimetric data on some binary liquid systems involving silver, thallium and alkali-halides [26, 28].

Hersh finds that it is not possible to rationalize the thermodynamic properties of these mixtures in terms of the Coulombic and next-nearest-neighbor van der Waals interactions alone. On
the other hand, he shows that to a first approximation the enthalpy data may be represented by expressions of the type

$$\Delta H^M = N_1N_2 (U_0^{++} + U_1 \delta_{12} - 340 \delta_{12}^2) \text{ kcal/mole} \quad (10)$$

The first and third terms on the right-hand side are the same as in Eq. (9), while the second term, $U_1 \delta_{12}$, is new. Formally, Eq. (10) is of the form predicted by Davis and Rice (Eq. (8)). However, the experimentally determined values of $U_1$ differ significantly from system to system, being about 12 kcal for (Ag-Alk)NO$_3$, 40 kcal for (Ag-Alk)Cl, 52 kcal for (Ag-Alk)Br, and about 20 kcal for (Tl-Alk)Cl. Hersh et al. argue that these values cannot be accounted for on the basis of the dispersion interactions. On the other hand, they find a clear correlation with the covalent contributions to the lattice energy in the non-alkali salts. According to Ladd and Lee [4] this contribution amounts to 9 kcal/mole for TlCl, 15 kcal/mole for silver chloride and 18 kcal/mole for silver bromide (see Fig. 1).

2.1.4 Mixed anion-common cation systems. It has been known for some time that simple mixed anion-common cation systems tend to show relatively small departures from ideality. For example, on the basis of a pioneering application of the oxygen electrode in a fused salt medium Flood et al. [29] found that the liquid system Na$_2$CO$_3$-Na$_2$SO$_4$ is essentially ideal. For many other systems near ideal behavior can be inferred from phase diagram information. However, not until the past two years have systematic data become available which permit a somewhat more detailed discussion of this type of solution system. The new information consists in part of calorimetric measurements, in part of exchange equilibrium data.

The calorimetric investigations of Kleppa and co-workers [30-32] have covered two categories of mixtures. On the one hand this work has consisted of solution and dilution experiments on higher melting chlorides, bromides and other salts dissolved in the corresponding nitrates at temperatures below 500°C. On the other it has involved more preliminary work on alkali halide-halide systems at temperatures up to about 800°C. The results may be summarized as follows:

All the investigated alkali nitrate-chloride and nitrate-bromide mixtures have small positive enthalpies of mixing, with
FIG. 3. Dependence of the "corrected" enthalpy of mixing, $\Delta H_{\text{mix}}^M - U_0^+$, for the binary alkali nitrates and halides on the parameter $\delta_{ij}$. The indicated limits of error principally reflect the uncertainty in the calculation of $U_0^+$; data from Ref. [26].
the largest values observed for the sodium systems. The positive enthalpies tend to decrease as the size of the alkali ion increases in the sequence Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$. The data for the liquid alkali chloride-bromide systems show even smaller positive enthalpies of mixing than the corresponding nitrate-halide systems.

The exchange investigations are due to Førland and co-workers [33, 34], and are based on exchange equilibria between HCl(g), HBr(g), and Me(Cl,Br)(l), where Me is Li, Na, K, Rb, Cs, Ca, Mg. From the dependence of the apparent equilibrium constant for the exchange equilibrium on the composition of the melt, one can derive information on the excess free energy of mixing in the liquid mixture. It is found that Mg(Cl,Br) and Ca(Cl,Br) have small negative deviations from ideality, while all the alkali chloride-bromide mixtures show small positive deviations. In particular it is found that these deviations increase somewhat in the sequence Li(Cl,Br) < Na(Cl,Br) < K(Cl,Br). The data for the rubidium and cesium systems are less accurate, but show smaller positive deviations than the potassium system.

For these mixed anion-common cation systems which have been investigated in some detail the two anions differ little in size. Therefore, the negative Coulomb term, which often tends to dominate the solution behavior of the mixed cation-common anion systems, undoubtedly will be quite small. For combinations of anions of more widely different size, say fluoride-chloride, fluoride-bromide, or fluoride-iodide mixtures, this situation may be different. In this event negative deviations from ideality may be expected, even in mixed anion systems. In some cases this is indicated by available phase diagram data, an example being the LiF-LiCl system.

Otherwise, small positive deviations from ideality are expected to be a common occurrence in mixed anion systems. In some cases the magnitude of the positive deviations may perhaps be estimated from the van der Waals-London interaction between next nearest neighbor anions, as outlined above for the mixed cation case. In addition, it has been suggested [Flood (35)] that, due to the size relations between the (usually) large anions and the (usually) small cations a significant positive contribution may often arise from the packing of the two anions on the anion "sub-lattice".

Finally, it should be noted that covalency effects related to those indicated for the silver halide - alkali halide mixtures
undoubtedly may occur also in mixed anion systems. This may possibly account for the negative enthalpies of mixing in the silver nitrate - silver halide systems [30].

2.2 Charge-unsymmetrical mixtures containing a common ion

This is a large and as yet not well understood area of fused salt solution chemistry. Formally it extends from relatively simple mixtures (e.g., alkali plus alkaline earth salts, halides plus sulfates, etc.) to quite complex systems, such as those formed by the borates, silicates, and phosphates. While these two categories may be considered to represent two extremes in a fairly continuous spectrum, we will restrict the present discussion to the simpler types of mixtures.

During the past decade a great many equilibrium and e.m.f. investigations of simple charge-unsymmetrical mixtures have been reported. A number of these have been due to Russian workers, who have made extensive use of the formation and decomposition cell methods pioneered by Hildebrand and Salstrom [27]. References to the Russian work may be found in the book by Delimarskil and Markov [36], and in the review by Blander [10]. Other data on charge-unsymmetrical systems have been obtained through vapor pressure measurements on systems containing volatile species such as PbCl₂, CdCl₂ (see e.g., Bloom [37]) and FeCl₂ (Beusman [38]), and also by the study of decomposition pressures, as in the work by Fyrland on systems containing calcium carbonate [15]). Finally, significant contributions in this area have been made by phase diagram analysis, see, e.g., the review by Fyrland [9], and in the recent cryoscopic studies of solutions in liquid sodium fluoride by Cantor et al. [39-42]. As a result of these investigations certain general statements can be made regarding the behavior of simple charge-unsymmetrical systems containing a common anion.

(a) When a salt of a simple divalent ion, e.g., Ca²⁺, is mixed with the corresponding alkali salts, the systems will show increasing negative departures from ideality with increasing size of the alkali metal ion.

(b) For a given alkali metal cation the negative deviation from ideality tends to increase as the size of the divalent ion is reduced.

(c) If the alkali ion is replaced by another singly charged ion of comparable size (i.e., Na⁺ by Ag⁺, or Rb⁺ by Tl⁺) the negative deviation from ideality is reduced (or the positive deviation increased).
FIG. 4. Limiting enthalpies of solution of undercooled liquid alkaline-earth nitrates in alkali nitrates plotted against the parameter $\delta_{12} = (d_1 - d_2)/d_2^2$: Ref. [43].

(d) If the divalent alkaline earth ion is replaced by a more polarizable ion of comparable size (i.e., Sr$^{++}$ by Pb$^{++}$) the negative deviation from ideality is increased.

In a phenomenological sense these observations are well established. Qualitatively they may be rationalized in terms of the competition between the two cationic species for the common anion. This competition is aided by a small size, a high charge and a high polarizability of the cation.

Very recently a theory for simple charge-unsymmetrical fused salt mixtures has been given by Davis [43]. In this theory
mixtures of the type \((P^+ - Q^{Z+})X^-\) are considered, and the analysis represents an extension of the conformal solution theory of Reiss et al. [18] to this more complicated case.

According to the Davis theory there should, for charge-unsymmetrical mixtures with the same values of \(\mathcal{I}\) and \(\Theta\), be a first order contribution to the excess thermodynamic properties which depends roughly linearly on the previously defined parameter 
\[
\delta_{12} = \frac{(d_1 - d_2)}{d_1 d_2}.
\]
This is in agreement with available calorimetric data on the limiting heats of solution of the alkaline earth nitrates in the alkali nitrates as illustrated in Fig. 4.

Davis concludes that the mixing properties of simple charge-unsymmetrical nitrate mixtures are adequately described in terms of the Coulomb-plus-hard-core interaction potential. This is consistent with the success of Reiss et al. [18] in accounting for the heats of mixing of the binary alkali nitrates, and amounts to a neglect of polarization and dispersion forces. For systems containing anions other than the nitrate ion, one clearly should consider also these additional terms. Also, in mixtures of salts with highly polarizable cations (Ag\(^+\), Tl\(^+\), Pb\(^{++}\), Cd\(^{++}\), etc.) one may also have covalent bonding contributions.

2.3 Systems containing two cations and two anions

2.3.1 Thermodynamics and theory. As an illustration of the special problems presented by these reciprocal fused salt systems we will take the mixed system which contains the four ions Na\(^+\), K\(^+\), Cl\(^-\) and Br\(^-\). This is a three component system in the sense of thermodynamics; i.e., a mixture of any composition may be prepared by bringing together suitable amounts of any three of the four salts NaCl, NaBr, KCl and KBr. Let us now consider the formation (at constant P, T) of one mole of the ternary mixture Na\(_x\)K\(_{1-x}\)Cl\(_y\)Br\(_{1-y}\) (1) from the three components NaCl (l), NaBr (l) and KBr (l):

\[
yNaCl + (x-y)NaBr + (1-x)KBr = Na\(_x\)K\(_{1-x}\)Cl\(_y\)Br\(_{1-y}\)
\]

This process may be broken down into a series of consecutive steps, which when added will yield the overall mixing reaction. We will demonstrate this by reversing the mixing procedure. Schematically, the various steps are illustrated in Fig. 5.
FIG. 5. Schematic diagram showing the formation of the ternary fused-salt mixture $Na_{x}K_{1-x}Cl_{y}Br_{1-y}$ from the pure salts.

$$x = N_{Na^+} = \frac{n_{Na^+}}{n_{Na^+} + n_{K^+}} \quad ; \quad y = N_{Cl^-} = \frac{n_{Cl^-}}{n_{Cl^-} + n_{Br^-}}$$

$$(l-x) = N_{K^+} = \frac{n_{K^+}}{n_{Na^+} + n_{K^+}} \quad ; \quad (l-y) = N_{Br^-} = \frac{n_{Br^-}}{n_{Cl^-} + n_{Br^-}}$$

$$Na_{x}K_{1-x}Cl_{y}Br_{1-y} = xNa(Cl_{y}Br_{1-y}) + (l-x)K(Cl_{y}Br_{1-y}) \quad (12)$$

$$xNa(Cl_{y}Br_{1-y}) = xyNaCl + x(l-y)NaBr \quad (13)$$

$$(l-x)K(Cl_{y}Br_{1-y}) = (l-x)yKCl + (l-x)(l-y)KBr \quad (14)$$

$$(l-x)yKCl + (l-x)yNaBr = (l-x)yNaCl + (l-x)yKBr \quad (15)$$

Alternatively we may unmix along a different path:

$$Na_{x}K_{1-x}Cl_{y}Br_{1-y} = yCl(Na_{x}K_{1-x}) + (l-y)Br(Na_{x}K_{1-x}) \quad (16)$$

$$yCl(Na_{x}K_{1-x}) = xyNaCl + y(l-x)KCl \quad (17)$$

$$(l-y)Br(Na_{x}K_{1-x}) = (l-y)xNaBr + (l-y)(l-x)KBr \quad (18)$$
Clearly

\[(11) + (12) + (13) + (14) + (15) = (11)\]

\[+ (16) + (17) + (18) + (15) = 0\]  

Let \(X\) be any extensive thermodynamic quantity, let us denote the molar change in \(X\) according to Eq. (11) with \(\Delta X^M_{134}\), and let the symbol \(\Delta X^M_{ij}\) represent the corresponding molar change for the binary or quasi-binary mixing processes starting from \(i\) and \(j\) in Fig. 5. Finally, let \(\Delta X^o\) be the standard change in \(X\) associated with the metathetical reaction

\[\text{NaCl (1) + KBr (1) = NaBr (1) + KCl (1)}\]  

In view of 19, we have

\[\Delta X^M_{134} = (1-x)y\Delta X^o_{13} + x\Delta X^M_{14} + (1-x)\Delta X^M_{23} + \Delta X^M_{68}\]  

\[= (1-x)y\Delta X^o_{13} + y\Delta X^M_{12} + (1-y)\Delta X^M_{34} + \Delta X^M_{57}\]  

We now define a molar ternary excess quantity, \(\Delta X^E_{1234}\) through the following relations

\[\Delta X^E_{1234} = \Delta X^M_{68} - y\Delta X^M_{12} - (1-y)\Delta X^M_{34}\]

\[= \Delta X^M_{57} - x\Delta X^M_{14} - (1-x)\Delta X^M_{23}\]  

Introducing this quantity and rearranging terms in 21 we may write

\[\Delta X^M_{134} = (1-x)y\Delta X^o_{13} + x\Delta X^M_{14} + (1-x)\Delta X^M_{23} + y\Delta X^M_{12}\]

\[+ (1-y)\Delta X^M_{34} + \Delta X^E_{1234}\]  

Thus, we have reduced the thermodynamic problem associated with simple reciprocal mixing processes to the sum of a metathetical term, four binary terms plus a ternary excess term \(\Delta X^E_{1234}\). Only this last term is a novel feature. It should be the principal
objective of work on reciprocal mixtures to provide information on this quantity, and to relate it to the characteristic properties of the component species.

We want to emphasize that there are four possible ways of forming the mixture \( \text{Na}_x \text{K}_{1-x} \text{Cl}_y \text{Br}_{1-y} \) from a combination of three of the four salts NaCl, NaBr, KCl, KBr. Depending on the combination selected, the coefficient of the metathetical term in Eq. (23) will be different, while all other terms will remain unchanged.

This purely thermodynamic analysis provides a convenient starting point for a review of recent theoretical and experimental work on simple reciprocal fused salt solutions.

The appropriate thermodynamic equations for an ideal reciprocal mixture were given already by Temkin (see Eq. (4) above). For this case we clearly have \( \Delta X_{1234}^E = 0 \) for all extensive properties \( X \).

The first detailed theory of non-ideal reciprocal fused salt mixtures was given by Flood, Førland and Grjotheim [44]. This theory is a quasi-thermodynamic one, based on a cycle related to the one given above. However, it involves a mass-action approach and emphasizes activities and activity coefficients, rather than the integral thermodynamic quantities. As a consequence the derived expressions appear in a very different form. For convenience in comparing their theory with experiments Flood, Førland and Grjotheim introduce simplifying assumptions. These are equivalent to neglecting the binary terms and the ternary excess term in Eq. (23). This inadequacy was rectified by Førland [15], who re-introduced the binary terms on an ad hoc basis.

Last year a general theory of reciprocal fused salt mixtures was published by Blander and Yosim [45], who applied the methods of conformal solution theory to the special case of reciprocal mixtures. Blander and Yosim show that the first five terms on the right-hand side of Eq. (23) follow directly from a straightforward application of this theory. The term for the metathetical step is first order, while the four binary terms are the second order terms already derived by Reiss et al. [18]. In addition conformal solution theory provides a new second order ternary excess quantity. The leading term in this quantity depends on composition through the product of the four ionic fractions, \( x(1-x) y(1-y) \), as might also be expected from its definition through Eqs. (21a) and (21b) above. In the theory of Blander and Yosim the proportionality constants for \( \Delta X_{1234}^E \) represent the difference between two complicated and unevaluated integrals.
As in the case of simple binary systems the non-ideal reciprocal fused salt mixtures are expected to exhibit deviations from random distribution of the ions. This problem was recognized already by Flood et al., who suggested a treatment along the lines of the quasi-chemical theory of Guggenheim [46]. More explicit calculations of the influence of departures from random mixing on the solution properties have been made by Blander and Braunstein on the basis of a quasi-lattice model [47-49]. These calculations have been discussed in considerable detail in the recent review article by Blander [10].

2.3.2 Comparison with experiment. The original theory of Flood et al. has proved useful in approximate treatments of a variety of different fused salt solution problems. However, since this theory neglects all terms other than that associated with the metathetical step, it cannot be expected to yield truly quantitative agreement with experiment.

A strong point in the Flood theory is that it can readily be generalized so that it can be applied to mixtures which contain more components than three. This requires only the introduction of one additional metathetical term for each additional component. As a consequence this theory offers a basis for the treatment of very complicated multi-component systems, such as those encountered in the chemistry of silicates and slags. A recent example is the work of Flood and Toguri [50] on the application of the law of mass action to metal-slag equilibria.

The significance of the binary terms in Eq. (23) is well illustrated in some recent studies by Blander et al. [51, 52]. These investigations involve e.m.f. measurements of solubility products and heats of solution for silver halides in liquid alkali nitrates according to processes of the following type:

\[ \text{AgX(s)} + \text{MeNO}_3(l) = \text{Dil. Solns. in MeNO}_3 \]  

Blander analyses this overall process in terms of a metathetical step

\[ \text{AgX(s)} + \text{MeNO}_3(l) = \text{MeX(l)} + \text{AgNO}_3(l) \]  

plus two binary steps

\[ \text{MeX(l)} + \text{MeNO}_3(l) = \text{Inf. Dil. Soln. in MeNO}_3 \]

\[ \text{AgNO}_3(l) + \text{MeNO}_3(l) = \text{Inf. Dil. Soln. in MeNO}_3 \]
He finds that his experimentally determined heats of solution for the overall process, $\Delta H_a$, are well represented by the sums $\Delta H_b + \Delta H_c + \Delta H_d$, calculated from data reported in the literature. The dominant term in these sums is $\Delta H_b$, which in the considered cases represents about 95 per cent of $\Delta H_a$. It follows that for these examples the treatment of Flood et al. is a very reasonable first approximation.

So far there have been no comprehensive tests of the conformal solution theory for reciprocal mixtures of Blander and Yosim [45]. However, first steps have been taken by Blander and Topol [53] and by Kleppa and Toguri [54].

Blander and Topol have examined available equilibrium and electro motive force data for the LiF-KCl and NaNO$_3$-AgCl systems. They conclude that the experimental data can be explained only if the ternary excess terms are taken into account. For concentrated solutions in the simple ionic system LiF-KCl the ternary excess terms are of significant magnitude and relatively insensitive to temperature. Even for dilute solutions of AgCl in NaNO$_3$ the ternary excess terms are found to be quite large, but also strongly temperature dependent. Blander and Topol relate these observations, on the one hand, to departures from random mixing, and on the other to the known tendency of the ions Ag$^+$ and Cl$^-$ to form well characterized complex species in nitrate melt solvents.

Kleppa and Toguri have carried out a detailed calorimetric study of the ternary system Na$^+$, K$^+$, Cl$^-$, Br$^-$. Their data allow a quantitative evaluation of the small ternary excess enthalpy, $\Delta H_{1234}$, near the composition Na$^+_{0.5}$ K$^+_{0.5}$ Cl$^-$ Br$^-_{0.5}$. Their results are in excellent agreement with a value of $\Delta H_{1234}$ calculated from the assumed small deviations from random mixing.

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4. References

THE CHEMISTRY AND THERMODYNAMICS OF MOLTEN-SALT-REACTOR FLUORIDE SOLUTIONS*  

C. F. BAES, Jr.,  
OAK RIDGE NATIONAL LABORATORY,  
TENN., UNITED STATES OF AMERICA  

Abstract — Résumé — Аннотация — Resumen  

THE CHEMISTRY AND THERMODYNAMICS OF MOLTEN-SALT-REACTOR FLUORIDE SOLUTIONS. A solvent of lithium and beryllium fluorides (about 2 moles of LiF per mole of BeF₂) is used in the fuel salt, the coolant salt, and the flush salt of the Molten Salt Reactor Experiment. As a result of the chemical development work done for this reactor concept, considerable chemical and thermodynamic information has been acquired concerning this solvent and its solutions with actinide, lanthanide, and structural metal fluorides. It is the purpose of this paper to review this information, much of which is not yet generally available. The data were obtained mainly by measurements of heterogeneous equilibria, i.e. by equilibration of melts with gaseous mixtures containing hydrogen, hydrogen fluoride or water and by determinations of solid-liquid phase equilibria.  

The results of these measurements gave direct information about such important chemical problems as: (1) the corrodibility of structural metals and the reducibility of the structural metal ions, Ni²⁺, Fe²⁺, Cr²⁺; (2) reactions with water vapour to form oxide and hydroxide ions, and the removal of these ions; (3) the precipitation, solubility, and tendency toward solid-solution formation of the oxides of beryllium, uranium, zirconium, thorium and the rare earths; (4) the stability of uranium(IV) toward reduction to the trivalent state and possible subsequent disproportionation; and (5) the solubilities and solid solution formation of rare earth fluorides. Equally important has been the wider usefulness of this information when the methods of thermodynamics are brought to bear. Thus the data obtained could be used to: (1) correlate, revise, and extend existing thermochemical data on fluorides and oxides; (2) determine activity coefficients of the components LiF, BeF₂, UF₄, ZrF₄, and NiF₂ in these molten salt solutions; (3) revise the generally accepted phase diagram for UO₂-ZrO₂; and (4) estimate solubilities and reactivities of compounds not directly investigated. Thus the chemical development programme for the Molten Salt Reactor concept provides a number of interesting examples of the interrelationship between thermodynamics and problems in reactor chemistry and engineering.  

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ХИМИЯ И ТЕРМОДИНАМИКА РЕАКТОРНЫХ ФТОРИСТЫХ РАСТВОРОВ РАСПЛАВЛЕННОЙ СОЛИ. Растровитель, состоящий из фтористого лития и бериллия (около 2 молей LiF на моль BeF₂), используется в топливной соли, и в соля охладителя и в качестве промывной соли в реакторных экспериментах с расплавленной солью. В результате химических разработок для этой реакторной концепции была получена значительная химическая и термодинамическая информация относительно самого растворителя и его растворов с актинидом, лантаноидом и структурными металлическими фтористыми соединениями. Настоящий доклад имеет целью рассмотреть эту информацию, которая в большей части еще не имеет широкого распространения. Данное в основном было получено путем измерений гетерогенных равновесий, то есть посредством уравновешивания расплавленных соединений с газообразными смесями, содержащими водород, фтористый водород или воду, и путем определения фаз равновесия твердого тела с жидкостью.

Результаты этих измерений дают непосредственную информацию о таких важных химических проблемах, как: 1) коррозия структурных металлов и восстановлением ионов окисных и гидрокисных ионов и удаление этих ионов; 2) осаждение, растворимость и тенденция к образованию твердого раствора окисей берилия, урана, циркония, титана и редкоземельных элементов; 4) устойчивость урана (IV) к восстановлению в трехвалентное состояние и возможной последующей диспропорции; и 5) растворимость и образование твердых растворов фторидов редкоземельных металлов. В равной степени важное значение имела полезность этой информации для случаев, когда методы термодинамики применяются к металлическим опорам. Полученные данные могут использоваться для: 1) корреляции, пересмотра и расширения существующих термодинамических данных по фторидам и окислам; 2) определения коэффициентов активности таких соединений как LiF, BeF₂, UF₄, ZrF₄ и NiF₂ в этих растворах расплавленных солей; 3) пересмотра общепринятых фазовых диаграмм для UO₂ - ZrO₂; и 4) вычисления растворимости и реактивности соединений, не подвергавшихся исследованию непосредственно. Таким образом программа химических разработок для концепции реактора на расплавленных солях дает целый ряд интересных примеров связи между термодинамикой и проблемами реакторной химии и технологии.

QUIMICA Y TERMODINAMICA DE LAS SOLUCIONES DE FLUORUROS PARA REACTORES DE SAL FUNDIDA. En el reactor experimental de sal fundida se usa un solvent de fluoruros de lítio y de berilio (unos 2 moles de LiF por mol de BeF₂) en la sal combustible, la sal refrigerante y la sal depuradora. Como resultado de los trabajos de perfeccionamiento químico realizados para este concepto de reactor, se ha adquirido una considerable información química y termodinámica acerca de este solvente y de sus disoluciones con fluoruros de actínidos, lantánidos y metales estructurales. Es finalidad de esta memoria pasar revista a dicha información, gran parte de la cual no se ha dado todavía a conocer en forma general. Los datos se obtuvieron principalmente por medición de equilibrios heterogéneos, es decir, equilibrando masas fundidas con mezclas gasosas que contienen hidrógeno, ácido fluorhídrico o agua, y determinando equilibrios de fases sólido-líquido.

Los resultados de estas mediciones suministraron información directa sobre problemas químicos tan importantes como: 1) susceptibilidad a la corrosión de los metales estructurales y capacidad de reducción de los iones metálicos estructurales Ni^2+, Fe^3+, Cr^3+; 2) reacciones con vapor de agua para formar iones óxido e hidróxido, y eliminación de dichos iones; 3) precipitación, solubilidad y tendencia a la formación de soluciones sólidas, de los óxidos de berilio, uranio, circonio, torio y tierras raras; 4) estabilidad del U(IV) ante la reducción al estado trivalente y la posible dismutación subsiguiente; 5) solubilidad y formación de soluciones sólidas, de los fluoruros de tierras raras. Igualmente útiles resultan los datos de esa índole cuando se hacen intervenir los métodos de la termodinámica. Así, por ejemplo, los datos obtenidos podrán usarse para: 1) correlacionar, revisar y ampliar los datos termoquímicos disponibles acerca de los fluoruros y óxidos; 2) determinar coeficientes de actividad de los componentes LiF, BeF₂, UF₄, ZrF₄ y NiF₂ en estas soluciones de sales fundidas; 3) revisar el diagrama de fases generalmente aceptado para UO₂-ZrO₂; 4) estimar solubilidades y reactividades de los compuestos que no se han estudiado directamente. Así, pues, el programa de perfeccionamiento químico para el concepto de reactor de sal fundida brinda una serie de ejemplos interesantes de la relación existente entre la termodinámica y los problemas vinculados a la química y a la ingeniería de reactores.
1. Introduction

The Molten Salt Reactor Experiment (MSRE), which went critical at ORNL in June, 1965, is fueled by a molten LiF-BeF$_2$-ZrF$_4$-UF$_4$ mixture and moderated by graphite. This reactor experiment is intended to show, as an important step toward the goal of a thermal breeder, the engineering reliability and the chemical stability of the system. The reactor and the extensive development work which led to its design, construction, and operation have been described in a recent collection of papers [1].

In considering possible materials which could serve as constituents in such a thermal breeder reactor, Grimes [2] reached the conclusion that the choice of major salt components is largely limited to mixtures of Li$^7$F and BeF$_2$ by the need for neutron economy, low volatility, and chemical stability. While in the LiF-BeF$_2$ system (Fig. 1) mixtures with melting points below 500°C occur in the range 0.33 - 0.73 mole fraction BeF$_2$ [3], compositions near 0.33 BeF$_2$ appear the most suitable. (Here, and elsewhere, numbers preceding a salt component denote mole fraction).

The composition of the MSRE fuel salt is 0.65 LiF, 0.291 BeF$_2$, 0.05 ZrF$_4$, 0.009 UF$_4$. That of the coolant and flush salt is LiF - 0.34 BeF$_2$.

As part of the development of the MSRE, a considerable amount of chemical and thermodynamic information has been gathered about LiF-BeF$_2$ melts near this composition. Most such information has been gained by the use of heterogeneous equilibria involving reactions of gases or solids, or both, with the liquid phase. In general, these studies gave fairly direct information about important chemical questions related to the MSRE.

It is the present purpose to review this information, much of which is not yet generally available, and to indicate its application to the chemistry of the MSRE. It will then be summarized by thermodynamic methods as a means of extending its usefulness. This seems fitting and proper at this stage in the development of the molten salt reactor concept. Future such reactors evidently will employ salt mixtures similar to those of the MSRE considered here; hence, a knowledge of the thermodynamics of these solutions should prove generally useful.

2. Reactions in LiF - 0.33 BeF$_2$

Table I lists the reactions studied, the form of the equilibrium constants, and values of $a$ and $b$ in the following expression
FIG. 1. The system LiF-BeF₂.

which gives the numerical value of the equilibrium constants in LiF - 0.33 BeF₂

\[ \log K = a + b(10^3/T) \]

This expression, implying a constant heat (\( \Delta H = -2.3 R_b \)) and entropy (\( \Delta S = 2.3 R_a \)) of reaction, adequately approximates the measured values in the temperature range studied (usually 500 - 700°C). The concentration scale is the mole fraction; e.g.,

\[ X_{MF} = n_{MF}/(n_{MF} + n_{LiF} + n_{BeF_2}) \]

Gas pressures are expressed in atmospheres, and at the low pressures and high temperatures involved, gases are assumed ideal.

The standard states for reactants and products generally can be seen from the form of \( K \). Here and elsewhere for most solutes the standard state is the hypothetical one mole fraction solution. Exceptions are LiF, BeF₂, Be\(^{2+}\), Li\(^{+}\), and F\(^-\), for which the solvent composition LiF - 0.33 BeF₂ is taken as the standard state. The notations (s), (d), and (g) denote, respectively, solid, dissolved, and gaseous states. In the majority of reactions listed, F\(^-\) is the only anion involved, and for simplicity the dissolved components are written in the molecular form, though this is not intended to imply the actual species present in solution. When anions other than F\(^-\) appear in the reaction,
ionic species are written. In some cases this is done to avoid the choice of a neutral component in the liquid phase and in others to indicate that complete dissociation of an anion (e.g., $O^{2-}$) and a cation (e.g., $Zr^{4+}$) is assumed.

Estimates of activity coefficients as a function of solvent composition and solute concentration are discussed in Section 3. On the basis of these estimates, the values of $K$ indicated in Table I include, where necessary, a correction of the original measurements to a melt composition of $LiF - 0.33 BeF_2$.

2.1 Hydrogen Reduction Reactions

The reduction of the bivalent fluorides of nickel, iron and chromium by hydrogen in $BeF_2-0.38LiF$ was investigated by Blood [4] in a series of careful transpiration experiments. The equilibrium quotients which were measured for the reaction

$$H_2(g) + MF_2(d) \rightleftharpoons M(s) + 2HF(g) \quad (3)$$

were found to be independent of $x_{MF_2}$ at the low concentrations studied. These concentrations were limited by the solubilities of the fluorides. The reduction of $UF_4$ dissolved in $LiF-BeF_2-UF_4$ melts by hydrogen as well as the reduction of $UF_4$ solid to $UF_3$ solid has recently been investigated by Long [5]. He summarized his results by the following expressions: For the reduction of $UF_4$ to $UF_3$ in solution

$$\log(x_{UF_3}P_{HF}/x_{UF_4}P_{H_2}^{1/2}) = 3.995 - 9.329 (10^3/T) + 3.77x_{UF_4} + 2.09(x_{BeF_2} - .30) \quad (4)$$

For the reduction of $UF_4$ solid to $UF_3$ solid

$$\log(P_{HF}/P_{H_2}^{1/2}) = 3.57 - 6.87 (10^3/T) \quad (5)$$

While the reduction of $BeF_2$ in $LiF-0.33BeF_2$ by hydrogen is inaccessible to direct measurement, recently Dirian [6] and Romberger [7] have made measurements on the following cell

$$Pd, H_2, HF, LiF-0.33BeF_2 | Be$$

The cell reaction was taken to be

$$H_2(g) + BeF_2(d) \rightleftharpoons Be(s) + 2HF(g) \quad (6)$$

With $P_{HF}$ and $P_{H_2}$ corrected to 1 atm, the potential was found to be

$$E = -2.436 + 0.715(T/10^3) \ v. \quad (7)$$
Table I
Reactions in LiF-0.33BeF₂

\[ \log K = a + b \left( 10^3/T \right) \]

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction</th>
<th>( K_a )</th>
<th>( a )</th>
<th>( b )</th>
<th>Est. ± Error in ( \log K )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction Reactions Involving Hydrogen (^a)</td>
<td>( \text{H}_2(g) + \text{NiF}_2(d) \rightarrow \text{Ni(s)} + 2\text{HF(g)} )</td>
<td>8.37</td>
<td>-3.60</td>
<td>0.04</td>
<td>Ref. 4</td>
<td></td>
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<tr>
<td></td>
<td>( \text{H}_2(g) + \text{FeF}_2(d) \rightarrow \text{Fe(s)} + 2\text{HF(g)} )</td>
<td>5.20</td>
<td>-5.31</td>
<td>0.02</td>
<td>Ref. 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2(g) + \text{CrF}_2(d) \rightarrow \text{Cr(s)} + 2\text{HF(g)} )</td>
<td>5.12</td>
<td>-9.06</td>
<td>0.06</td>
<td>Ref. 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{1}{2}\text{H}_2(g) + \text{UF}_4(d) \rightarrow \text{UF}_3(d) + \text{HF(g)} )</td>
<td>4.07</td>
<td>-9.33</td>
<td>0.02</td>
<td>Ref. 5</td>
<td></td>
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<tr>
<td></td>
<td>( \text{H}_2(g) + \text{BeF}_2(d) \rightarrow \text{Be(s)} + 2\text{HF(g)} )</td>
<td>7.21</td>
<td>-21.56</td>
<td>0.1</td>
<td>Refs. 6,7</td>
<td></td>
</tr>
<tr>
<td>Metathesis Reactions Involving Gases</td>
<td>( \text{H}_2O(g) + \text{BeF}_2(d) \rightarrow \text{BeO(s)} + 2\text{HF(g)} )</td>
<td>4.23</td>
<td>-5.67</td>
<td>0.02</td>
<td>Ref. 9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 2\text{H}_2O(g) + \text{ZrF}_4(d) \rightarrow 2\text{ZrO}_2(s) + 4\text{HF(g)} )</td>
<td>11.21</td>
<td>-10.66</td>
<td>0.04</td>
<td>Ref. 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2O(g) + 2\text{F}^- (d) \rightarrow 0^2^-(d) + 2\text{HF(g)} )</td>
<td>4.20</td>
<td>-8.64</td>
<td>0.08</td>
<td>Ref. 9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2O(g) + \text{F}^- (d) \rightarrow \text{OH}^-(d) + \text{HF(g)} )</td>
<td>-1.03</td>
<td>-2.08</td>
<td>0.04</td>
<td>Ref. 9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2S(g) + 2\text{F}^- (d) \rightarrow \text{S}^2^-(d) + 2\text{HF(g)} )</td>
<td>( \log K(873°K) &lt; -4 )</td>
<td>---</td>
<td></td>
<td>Ref. 12</td>
<td></td>
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<td></td>
<td>( \text{H}_2I(g) + \text{F}^- (d) \rightarrow \text{I}^-(d) + \text{HF(g)} )</td>
<td>( \log K(763°K) &lt; -3 )</td>
<td>---</td>
<td></td>
<td>Ref. 13</td>
<td></td>
</tr>
<tr>
<td>Metathesis Reactions Involving Solid Oxides</td>
<td>( \text{ZrO}_2(s) + 2\text{BeF}_2(d) \rightarrow \text{ZrF}_4(d) + 2\text{BeO(s)} )</td>
<td>( x_{\text{ZrF}_4} )</td>
<td>-2.75</td>
<td>-0.69</td>
<td>0.05</td>
<td>6,7; Ref. 15</td>
</tr>
<tr>
<td></td>
<td>( \text{UO}_2(s) + 2\text{BeF}_2(d) \rightarrow \text{UF}_4(d) + 2\text{BeO(s)} )</td>
<td>( x_{\text{UF}_4} )</td>
<td>-2.07</td>
<td>-1.74</td>
<td>0.07</td>
<td>12,14; Ref. 15</td>
</tr>
<tr>
<td></td>
<td>( \text{ZrO}_2(s) + \text{UF}_4(d) \rightarrow \text{ZrF}_4(d) + \text{UO}_2(s) )</td>
<td>( x_{\text{ZrF}<em>4} )/( x</em>{\text{UF}_4} )</td>
<td>-0.67</td>
<td>1.05</td>
<td>0.05</td>
<td>Ref. 15</td>
</tr>
<tr>
<td></td>
<td>( \text{ThO}_2(s) + \text{UF}_4(d) \rightarrow \text{ThF}_4(d) + \text{UO}_2(s) )</td>
<td>( x_{\text{ThF}<em>4} )/( x</em>{\text{UF}_4} )</td>
<td>( \log K(1023°K) \approx 1.2 )</td>
<td>---</td>
<td>Ref. 18</td>
<td></td>
</tr>
<tr>
<td>Solubility Reactions</td>
<td>$\mu^b$</td>
<td>a</td>
<td>b</td>
<td>Est. ± Error in log K</td>
<td>Source$^c$</td>
<td></td>
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<tr>
<td>----------------------</td>
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<tr>
<td>16 BeO(s) = $\text{Be}^{2+}(d) + \text{O}^{2-}(d)$</td>
<td>$x_{\text{O}^{2-}}$</td>
<td>-0.04</td>
<td>-2.96</td>
<td>0.08</td>
<td>6,8</td>
<td></td>
</tr>
<tr>
<td>17 ZrO$_2$(s) = $2\text{Zr}^{4+}(d) + 2\text{O}^{2-}(d)$</td>
<td>$(x_{\text{Zr}^{4+}})(x_{\text{O}^{2-}})^2$</td>
<td>-2.82</td>
<td>-6.62</td>
<td>0.09</td>
<td>7,8</td>
<td></td>
</tr>
<tr>
<td>18 UO$_2$(s) = $\text{U}^{4+}(d) + 2\text{O}^{2-}(d)$</td>
<td>$(x_{\text{U}^{4+}})(x_{\text{O}^{2-}})^2$</td>
<td>-2.15</td>
<td>-7.66</td>
<td>0.1</td>
<td>14,17</td>
<td></td>
</tr>
<tr>
<td>19 ThO$_2$(s) = $\text{Th}^{4+}(d) + 2\text{O}^{2-}(d)$</td>
<td>$(x_{\text{Th}^{4+}})(x_{\text{O}^{2-}})^2$</td>
<td>log $K(1023^\circ\text{K}) ≈ -8.6$</td>
<td>---</td>
<td>15,18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 NiO(s) = $\text{Ni}^{2+}(d) + \text{O}^{2-}(d)$</td>
<td>$(x_{\text{Ni}^{2+}})(x_{\text{O}^{2-}})$</td>
<td>-2.58</td>
<td>-4.39</td>
<td>---</td>
<td>Eqs. 25, 26, Ref. 32</td>
<td></td>
</tr>
<tr>
<td>21 FeO(s) = $\text{Fe}^{2+}(d) + \text{O}^{2-}(d)$</td>
<td>$(x_{\text{Fe}^{2+}})(x_{\text{O}^{2-}})$</td>
<td>-0.52</td>
<td>-4.12</td>
<td>---</td>
<td>Eqs. 25, 26, Ref. 32</td>
<td></td>
</tr>
<tr>
<td>22 NiF$_2$(s) = NiF$_2$(d)</td>
<td>$x_{\text{NiF}_2}$</td>
<td>0.30</td>
<td>-2.07</td>
<td>0.01</td>
<td>Ref. 4</td>
<td></td>
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<tr>
<td>23 FeF$_2$(s) = FeF$_2$(d)</td>
<td>$x_{\text{FeF}_2}$</td>
<td>2.45</td>
<td>-3.05</td>
<td>0.01</td>
<td>Ref. 4</td>
<td></td>
</tr>
<tr>
<td>24 LaF$_3$(s) = LaF$_3$(d)</td>
<td>$x_{\text{LaF}_3}$</td>
<td>1.58</td>
<td>-3.38</td>
<td>0.02</td>
<td>Ref. 20</td>
<td></td>
</tr>
<tr>
<td>25 CeF$_3$(s) = CeF$_3$(d)</td>
<td>$x_{\text{CeF}_3}$</td>
<td>1.64</td>
<td>-3.38</td>
<td>0.02</td>
<td>Ref. 20</td>
<td></td>
</tr>
<tr>
<td>26 SmF$_3$(s) = SmF$_3$(d)</td>
<td>$x_{\text{SmF}_3}$</td>
<td>1.97</td>
<td>-3.38</td>
<td>0.02</td>
<td>Ref. 20</td>
<td></td>
</tr>
<tr>
<td>27 PuF$_3$(s) = PuF$_3$(d)</td>
<td>$x_{\text{PuF}_3}$</td>
<td>1.30</td>
<td>-3.15</td>
<td>Ref. 19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The notations (s), (d), and (g) indicate respectively the solid, dissolved, and gaseous states.

\(^b\) $P_1$ is expressed in atmospheres; $x_1$ is the mole fraction and, for $\text{LaF}_3$-$0.33\text{BeF}_2$, is equal to moles of $i$/kg of salt/30.03.

\(^c\) Numbers other than reference numbers and numbers of equations in text refer to reactions in this table.
FIG. 2. Oxidation-reduction reactions in LiF-0.33BeF₂. Left; reaction of Cr, Fe, Ni, and U³⁺ with HF (1 atm) and H₂ (1 atm); right; mole fractions of FeF₂, NiF₂ and the x(UF₃)/x(UF₆) ratio in equilibrium with 10⁻⁴ mole fraction CrF₂ and chromium metal.

From this the equilibrium constant expansion in Table I has been calculated. The two electrodes — Be²⁺|Be and Pd,H₂, HF|F⁻ — were judged to be reversible from polarization measurements.

These results show that nickel is the most noble of the three structural metals studied, Ni²⁺ being readily reduced by hydrogen (Fig. 2). Chromium was the least noble, Cr²⁺ being reduced by hydrogen with difficulty. The sparging of molten fluorides with hydrogen to reduce structural metal impurities is routinely used as a purification step. The concentrations of Ni²⁺, Fe²⁺ and Cr²⁺ and the ratio U⁴⁺/U³⁺ in LiF-0.33BeF₂ expected under two sets of conditions are indicated in Fig. 2. On the left of the figure, wherein the equilibrium constants are plotted, it...
appears that only Ni\textsuperscript{2+} is extensively reduced by a mixture of H\textsubscript{2} and HF, both at unit activity (1 atm). Nickel is a relatively inert container material for LiF-BeF\textsubscript{2} melts in the presence of excess hydrogen. On the right of Fig. 2 are much more reducing conditions which approximate those in the MSRE. The concentration of Cr\textsuperscript{2+} is set at 100 ppm in equilibrium with the pure metal. It is seen that Fe\textsuperscript{2+} and Ni\textsuperscript{2+} should be reduced essentially completely to the metals and some U\textsuperscript{4+} should be reduced to U\textsuperscript{3+}. The reaction of U\textsuperscript{4+} in the MSRE fuel with the container metal (INOR-8, a nickel-base alloy containing about 7% Cr, 5% Fe and 16% Mo)

\[
Cr(\text{in INOR-8}) + 2UF_4(d) \rightleftharpoons 2UF_3(d) + CrF_2(d), \log K (873^\circ) \approx -9.0
\]  

(8)
is the only corrosion reaction expected, and the extent of this reaction should be small [8]. In the absence of UF\textsubscript{4} e.g., in the coolant salt) no reaction between the salt and the container metal is expected.

2.2 Metathesis Reactions Involving HF and H\textsubscript{2}O

Extensive equilibrium measurements of reactions between water in hydrogen carrier gas with LiF-BeF\textsubscript{2} melts were made by Mathews and Baes [9]. Equilibrium quotients for the reaction

\[
H_2O(g) + BeF_2(d) \rightleftharpoons BeO(s) + 2HF(g)
\]  

(9)

(wherein beryllium oxide was present as a saturating solid phase) were measured from 500 to 700°C over the composition range x\textsubscript{BeF\textsubscript{2}} = 0.3 - 0.8, limited at one extreme by the LiF liquidus (Fig. 1) and at the other by rapidly increasing viscosity. The results were summarized by the expression

\[
\log \left( \frac{P_{HF}}{P_{H_2O}} x_{BeF_2} \right) = a + b x_{LiF}^2 + c x_{LiF}^4
\]  

(10)

wherein a, b and c all were linear functions of 1/T\textsuperscript{OK}

\[
a = 3.900 - 4.418(10^3/T),
b = 7.819 - 5.440(10^3/T),
c = -12.66 + 5.262(10^3/T).
\]

From this expression the activities of BeF\textsubscript{2} and, by a Gibbs-Duhem integration, the activities of LiF were estimated (Fig. 5). In the same investigation, measurements were made upon melts not saturated with BeO. In addition to the reaction

\[
H_2O(g) + 2F^-(d) \rightleftharpoons O^2-(d) + 2HF(g)
\]  

(11)

for the formation of oxide ion, it became evident, both from these measurements and from those upon BeO saturated melts, that
hydroxide ion also was formed

$$H_2O(g) + F^-(d) = OH^-(d) + HF(g)$$  (12)

Because of limitations inherent in the transpiration method used, the equilibrium quotients for these two reactions were less accurately determined than was the previous one for BeO saturated melts (ca. ±10% respectively compared to ±5%). They were sufficient to show, however, that both oxide and hydroxide increase in stability with increasing temperature. The stability of hydroxide with respect to oxide, however, decreases with increasing temperature and it is low enough that hydroxide can be readily decomposed in these fluoride melts by sparging with an inert gas (e.g., hydrogen).

$$OH^- + F^- = HF(g) + O^{2-}, \log K = 5.23 - 6.56(10^3/T)$$  (13)

Similar measurements have also been made by Baes and Hitch [10] in which the LiF-0.33BeF$_2$ contained added ZrF$_4$. With $x_{ZrF_4} > \sim 3 \times 10^{-4}$, ZrO$_2$ is the stable saturating oxide solid, and hence the following equilibrium may be written

$$2H_2O(g) + ZrF_4(d) = ZrO_2(s) + 4HF(g)$$  (14)

From these measurements the activity coefficient of ZrF$_4$ could be estimated (Fig. 5) as well as the solubility of ZrO$_2$ (Sect. 2.5). It was also found that the equilibria (11 and 12) for the formation of oxide and hydroxide ions were shifted to the right with increasing $x_{ZrF_4}$; i.e., in the direction of greater stability of these ions.

These results are generally consistent with previous observations that LiF-BeF$_2$ melts are readily freed of oxide contamination by treatment with gaseous mixtures of H$_2$ and HF, another routinely used purification step. The measured equilibrium quotients in LiF-0.33BeF$_2$ were used to calculate the efficiency of HF utilization in such a treatment as a function of temperature and HF partial pressure with the assumption that equilibrium is maintained between the gas stream, the molten salt, and any BeO solid present. This calculation (Fig. 3) shows that the efficiency in the removal of oxide to a final value of 16 ppm ($x_{O_2} = 3.3 \times 10^{-5}$) is quite high over a wide range of conditions. The removal of oxides from LiF-0.33BeF$_2$ melts by H$_2$-HF sparging during the preparation of flush salts and coolant salts for the MSRE [11] was performed on 100 kg batches in cylindrical vessels with a single gas delivery line. It appeared that about 2/3 of
In the presence of ZrF$_4$ and ZrO$_2$ the increased stability of oxide and hydroxide render more difficult the removal of oxide from such melts than is the case with the solvent salt. Because of this, in the purification of LiF-BeF$_2$-ZrF$_4$ melts it was found expedient to decant the molten salt away from the precipitated ZrO$_2$ as a simple means of removing most of the oxide before HF-H$_2$ treatment.

2.3 Metathesis Reactions Involving HF-H$_2$S and HF-HI

An attempt has been made to study the removal of sulfide from LiF-0.33BeF$_2$ melts by HF-H$_2$ sparging [12]

$$2\text{HF}(g) + S^2-(d) = F^-(d) + \text{H}_2\text{S}(g), \log K > 10^5 \quad (15)$$

but, unfortunately, the effluent H$_2$S-H$_2$ mixture reacted with the relatively cooler surfaces of the nickel exit tubing used. It was also found that sulfide was precipitated from the melt, presumably as BeS, though no direct evidence of this was obtained. In tests on the removal of iodide by HF-H$_2$ sparging [13]

$$\text{HF}(g) + I^-(d) = F^-(d) + \text{HI}(g), \log K > 10^5 \quad (16)$$

there was also interference caused by reaction of the effluent gases with the metal surfaces in the gas exit lines. Because of these difficulties it is possible, at present, only to assign
lower limits to the equilibrium constants of reactions (15) and (16).

These preliminary results do serve to confirm, however, observations that the HF-H₂ treatment used in purifying molten salts seems to remove any sulfide, as well as oxide, which may be present as an impurity. The use of HF sparging also may prove a valuable means of removing the iodine precursor of the important fission product, Xe¹³⁵, in an operating reactor.

2.4 Metathesis Reactions Involving Solid Oxides

By combination of reactions 9 and 14, it is possible to calculate that both BeO and ZrO₂ will co-exist at equilibrium with LiF-0.33BeF₂ containing oxide ion

\[ \text{ZrO}_2(s) + 2\text{Be}^{2+}(d) \rightleftharpoons \text{Zr}^{4+}(d) + 2\text{BeO}(s) \]  (17)

when ZrF₄ is present at concentration of approximately 3 x 10⁻⁴ mole fraction. With larger amounts of added ZrF₄, ZrO₂ becomes the less soluble (stable) oxide.

It was decided to include ZrF₄ in the MSRE fuel composition to prevent the precipitation of UO₂ which otherwise would result from inadvertent oxide contamination of the fuel. Measurements of the metathesis reaction

\[ \text{ZrO}_2(s) + \text{UF}_4(d) \rightleftharpoons \text{ZrF}_4(d) + \text{UO}_2(s) \]  (18)

have shown that the mole ratio of ZrF₄ to UF₄ at equilibrium with both UO₂ and ZrO₂, while varying somewhat with temperature and melt composition, remains well below that chosen for the fuel salt [14,15]. As a consequence, a considerable amount of Zr⁴⁺ — an amount easily detected by chemical analysis of the fuel salt — would be precipitated by oxide contamination before any UO₂ should precipitate.

In connection with these studies, it was ascertained that, contrary to published UO₂-ZrO₂ phase diagrams [16], (U-Zr)O₂ solid solutions are not formed in the temperature range 500 - 700°C. Because of the obvious importance of this to the MSRE, experiments have been carried out in which both UO₂-ZrO₂ mixtures and (U-Zr)O₂ solid solutions prepared by fusion were equilibrated with LiF-BeF₂ melts. At the present writing, no solid solution formation has been detected below 1100°C [17].

The metathesis equilibrium in Table I involving UO₂ and ThO₂ is an estimate from results of Shaffer et al, in LiF-0.4 NaF [18].
2.5 Oxide Solubilities

The oxide concentration in LiF-0.33BeF$_2$ saturated with BeO was estimated by combining the equilibrium results for reactions (9) and (11). The solubility increased with temperature, but no strong dependence on $x_{\text{BeF}_2}$ was found. In these measurements [9], the mole fraction of oxide at BeO saturation probably was less than 0.002. Hence, the activities of BeF$_2$ and LiF which were derived from them are probably not appreciably different from the corresponding activities in oxide-free mixtures.

From the similar measurements in ZrF$_4$-containing melts [10] the solubility product of ZrO$_2$ could be estimated. With increasing $x_{\text{ZrF}_4}$, the concentration of oxide at ZrO$_2$ saturation at first falls as would be expected from the equilibrium

$$\text{ZrO}_2(s) = \text{Zr}^{4+}(d) + 2\text{O}_2^-(d)$$

(19)

However, it then levels off and subsequently rises with further increases in $x_{\text{ZrF}_4}$ (Fig. 4). This could be caused, at least in part, by the formation of a complex ion, ZrO$_2^+$

$$\text{Zr}^{4+}(d) + \text{O}_2^-(d) = \text{ZrO}_2^+(d)$$

(20)

or it could be caused entirely by the influence of the changing melt composition on the activity coefficients of the species Zr$^{4+}$ and O$_2^-$. The plot in Fig. 4 indicates approximately the "oxide tolerance" of MSRE fuel salt-flush salt mixtures; i.e., the amount of dissolved oxide these mixtures can contain without oxide precipitation. It is seen that the oxide tolerance increases rapidly with temperature, especially near the fuel composition ($x_{\text{ZrF}_4} \approx 0.05$), indicating that any excess oxide present might be removed by collecting ZrO$_2$ on a relatively cool surface in the MSRE system.

The solubility products of NiO and FeO, indicated in Table I, were estimated from the previously cited equilibrium results (Sect. 4.3).

2.6 Fluoride Solubilities

Table I also summarizes the solubility measurements by Blood [4] of FeF$_2$ and NiF$_2$, those by Barton [19] of PuF$_3$, and those by Ward, et al [20] of rare earth trifluorides. These last investigators found fluoride solid solution formation and pointed out that this could provide a useable method for removing rare-earth fission products from a reactor fuel stream by exchange reactions.
3. Effect of Melt Composition Upon Activity Coefficients

In several of the investigations cited above the effect of melt composition on equilibrium was studied and from these results the corresponding variation of a number of activity coefficients can be determined. The curves shown in Fig. 5 represent these variations as a function of the solvent composition (left-hand figure) and as a function of the mole fraction of solute added to LiF-0.33BeF$_2$ (right-hand figure). The standard states remain the same; i.e., for the solvent components it is LiF-0.33BeF$_2$ and for the solutes it is the hypothetical mole fraction solution in LiF-0.33BeF$_2$.

The curves (Fig. 5, on the left) for LiF and for BeF$_2$ are derived from Eqn. 10, $\gamma_{\text{BeF}_2}$ being obtained directly and $\gamma_{\text{LiF}}$ being obtained by a Gibbs-Duhem integration. The curves for PuF$_3$ and CeF$_3$ are based on the solubility measurements of Barton [19] and of Ward, et al [20]. The curves for UF$_4$ are based on Long's results (Eqn. 4) with the assumption that $\gamma_{\text{UF}_3}$ is similar to $\gamma_{\text{CeF}_3}$ and $\gamma_{\text{PuF}_3}$. The curve for ZrF$_4$ is from the preliminary measurements of Baes and Hitch (Eqn. 14). The curve for NiF$_2$ is an estimate based on the observation that $\gamma_{\text{NiF}_2}$ in NaF-ZrF$_4$, (as indicated by reaction 3 [4]) varies less with ZrF$_4$ in this solvent than does $\gamma_{\text{CeF}_3}$ (as indicated by its solubility [20]).

These activity coefficient curves were used, where necessary, to correct equilibrium measurements to the reference composition.
LiF-0.33 PuF$_3$. It is seen that the variation of activity coefficients with composition is not large and that, in general, the various curves are ordered according to the ratio of charge to ion radius ($z/r$) for the cation. As more data become available, it will be of considerable interest to test the correlation of $\gamma_{MF}$ with $z/r$, since it could provide a simple basis for estimates of activity coefficients where data on the effect of melt composition are lacking.

4. Thermodynamic Correlations

4.1 Heats and Free Energies of Formation ($\Delta H^f$ and $\Delta G^f$).

From the equilibrium measurements (Table I) and published values of $\Delta H^f$ and $\Delta G^f$ for HF(g) and H$_2$O(g) [21], formation heats and free energies may be calculated for BeO(s), BeF$_2$(s), NiF$_2$(s), and FeF$_2$(s) in the temperature range of interest here (Table II). In addition, Long has calculated $\Delta H^f$ and $\Delta G^f$ for UF$_3$ from his measurements (Eqn. 5), adopting the corresponding values given by Rand and Kubaschewski [22] for UF$_4$(s). In general, the agreement of these calculations with previous estimates is
satisfactory, except in the case of NiF₂(s). Grimes has previously indicated [23] that the present values for NiF₂(s), based on Blood's measurements, differ considerably from — and are probably more nearly correct than — previous estimates for NiF₂(s) based on measurements of Jellinek and Rudat [24]. Long's values for UF₃(s) agree with a previous estimate by Brewer [25] but differ considerably from estimates by Glassner [26] and Rand and Kubaschewski [22].

Included in Table II are other heats and free energies of formation from the literature [27,28]. These were used in the calculation of \( \Delta H_f \) and \( \Delta G_f \) values for dissolved components (Table III); i.e., the partial molal heats and free energies of formation for the components in the solution standard states defined previously.

The \( \Delta H_f \) and \( \Delta G_f \) values in Table III for LiF(d), BeF₂(d), NiF₂(d), FeF₂(d) and CrF₂(d) come most directly from the equilibrium measurements, with \( \Delta H_f \) and \( \Delta G_f \) for HF(g), H₂O(g), and LiF(s) only being required from the literature. In the case of the tetravalent fluorides, literature values of \( \Delta H_f \) and \( \Delta G_f \) for the corresponding oxides were utilized, but these in general are more accurately known than are those for the fluorides. The values of \( \Delta H_f \) and \( \Delta G_f \) for the rare earths are based on the solubility measurements [20] and on Brewer's estimates for the solids [28].

The partial molal free energies of formation (Table III) indicate the relative stabilities of the dissolved fluorides. In terms of \( \Delta G_f \) per g atom of fluoride LiF is the most stable, followed by the rare earths. BeF₂ and ThF₄ next fall together, then UF₄ and ZrF₄. Least stable are the structural metal fluorides.

4.2 Electrode Potentials

The results in Table III are expressed perhaps in a more familiar way in Table IV as electrode potentials for various half cell reactions with

\[
\text{HF(g)} + e \rightleftharpoons F^-(d) + \frac{1}{2} \text{H}_2 \text{O(g)}, \quad E^0 = 0
\]  

(21)

The standard states remain the same. The manner in which these are calculated is most easily shown by pointing out that any combination of half cell reactions which gives a complete reaction of the form

\[
M(s) + zF_2(g) \rightleftharpoons MF_{2z}(d), \quad E^0 = -\frac{\Delta G_f}{znF}
\]  

(22)
Table II
Formation Heats and Free Energies of Fluorides and Oxides
(700-1000°K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( -\Delta H^f ) kcal</th>
<th>( -\Delta G^f ) (1000°K), kcal</th>
<th>Est. ± Error, kcal</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 HF(g)</td>
<td>65.19</td>
<td>66.20</td>
<td>0.4</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>2 H(_2)O(g)</td>
<td>59.07</td>
<td>46.04</td>
<td>0.1</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>3 LiF(s)</td>
<td>146.50</td>
<td>123.39</td>
<td>0.7</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>4 BeO(s)</td>
<td>145.47</td>
<td>118.84</td>
<td>0.6</td>
<td>5,6,(2)</td>
</tr>
<tr>
<td>5 BeF(_2)(l)</td>
<td>237.00</td>
<td>207.57</td>
<td>1</td>
<td>5,6,(1),Eq. 10</td>
</tr>
<tr>
<td>6 ZrO(_2)(s)</td>
<td>260.4</td>
<td>216.0</td>
<td>0.4</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>7 UF(_4)(s)</td>
<td>448.5</td>
<td>381.1</td>
<td>5</td>
<td>Ref. 22</td>
</tr>
<tr>
<td>8 UO(_2)(s)</td>
<td>258.0</td>
<td>218.0</td>
<td>0.8</td>
<td>Ref. 22</td>
</tr>
<tr>
<td>9 UF(_3)(s)</td>
<td>351.9</td>
<td>299.8</td>
<td>5</td>
<td>(7),(1),Eq. 5</td>
</tr>
<tr>
<td>10 ThO(_2)(s)</td>
<td>293</td>
<td>250</td>
<td>4</td>
<td>Ref. 27</td>
</tr>
<tr>
<td>11 LaF(_3)(s)</td>
<td>421</td>
<td>360</td>
<td>7</td>
<td>Ref. 28</td>
</tr>
<tr>
<td>12 CeF(_3)(s)</td>
<td>416</td>
<td>355</td>
<td>7</td>
<td>Ref. 28</td>
</tr>
<tr>
<td>13 SmF(_3)(s)</td>
<td>405</td>
<td>344</td>
<td>7</td>
<td>Ref. 28</td>
</tr>
<tr>
<td>14 NiF(_2)(s)</td>
<td>156.33</td>
<td>118.69</td>
<td>0.8</td>
<td>1,22,(1)</td>
</tr>
<tr>
<td>15 FeF(_2)(s)</td>
<td>168.62</td>
<td>135.64</td>
<td>0.8</td>
<td>2,23,(1)</td>
</tr>
</tbody>
</table>

\( a \) The notations (s), (l), and (g) indicate respectively the solid, liquid, and gaseous states.

\( b \) Numbers not in parentheses refer to \( \Delta G \) values for reactions in Table I. Numbers in parentheses refer to \( \Delta G \) values in this table.

will yield the \( \Delta G^f \) value given in Table III (\( u \) is the number of equivalents of charge and \( F \) is the Faraday).

The positions of the various cations in the electrochemical series in LiF-0.33BeF\(_2\) is seen to be quite similar to that in aqueous solutions. This is illustrated on the left side in Fig. 6, wherein the \( E^0 \) values in LiF-0.33BeF\(_2\) at 1000°K are plotted vs the \( E^0 \) values for the same half-cell reaction in aqueous solutions at 25°C [29]. It is notable from this comparison that the structural metals are relatively more noble in the molten fluoride than
Table III
Formation Heats and Free Energies for Solutes in LiF-0.33BeF₂
(773-1000°K)

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\Delta H^r$ (kcal)</th>
<th>$\Delta G^r$ (1000°K), kcal</th>
<th>Est. ± Error, kcal</th>
<th>Source^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Li$^+$ + F$^-$</td>
<td>142.70</td>
<td>124.79</td>
<td>0.8</td>
<td>(3), Eq. 10</td>
</tr>
<tr>
<td>2 La$^{3+}$ + 3F$^-$</td>
<td>405.5</td>
<td>351.8</td>
<td>7</td>
<td>24, (11)</td>
</tr>
<tr>
<td>3 Cr$^{3+}$ + 3F$^-$</td>
<td>400.5</td>
<td>347.0</td>
<td>7</td>
<td>25, (12)</td>
</tr>
<tr>
<td>4 Sm$^{3+}$ + 3F$^-$</td>
<td>389.5</td>
<td>337.5</td>
<td>7</td>
<td>26, (13)</td>
</tr>
<tr>
<td>5 Be$^{2+}$ + 2F$^-$</td>
<td>242.75</td>
<td>211.80</td>
<td>1</td>
<td>5, (1)</td>
</tr>
<tr>
<td>6 Th$^{4+}$ + 4F$^-$</td>
<td>-</td>
<td>424.0</td>
<td>5</td>
<td>19,(10],[5],[13]</td>
</tr>
<tr>
<td>7 Zr$^{4+}$ + 4F$^-$</td>
<td>451.85</td>
<td>386.21</td>
<td>1.7</td>
<td>17,(6],[5],[13]</td>
</tr>
<tr>
<td>8 U$^{4+}$ + 4F$^-$</td>
<td>444.61</td>
<td>386.48</td>
<td>1.8</td>
<td>18,(8],[5],[13]</td>
</tr>
<tr>
<td>9 U$^{3+}$ + 3F$^-$</td>
<td>336.73</td>
<td>296.19</td>
<td>1.8</td>
<td>4,(1),(8)</td>
</tr>
<tr>
<td>10 Cr$^{2+}$ + 2F$^-$</td>
<td>171.82</td>
<td>150.41</td>
<td>0.9</td>
<td>3,(1)</td>
</tr>
<tr>
<td>11 Fe$^{2+}$ + 2F$^-$</td>
<td>154.69</td>
<td>132.92</td>
<td>0.8</td>
<td>2,(1)</td>
</tr>
<tr>
<td>12 Ni$^{2+}$ + 2F$^-$</td>
<td>146.37</td>
<td>110.61</td>
<td>0.8</td>
<td>1,(1)</td>
</tr>
<tr>
<td>13 Be$^{2+}$ + O$^2-$</td>
<td>131.91</td>
<td>105.10</td>
<td>0.6</td>
<td>16,(4)</td>
</tr>
<tr>
<td>14 Be$^{2+}$ + 2OH$^-$</td>
<td>170.54</td>
<td>159.35</td>
<td>0.7</td>
<td>8,9,(2],[13]</td>
</tr>
<tr>
<td>15 Be$^{2+}$ + 2I$^-$</td>
<td>-</td>
<td>≪66 (763°K)</td>
<td></td>
<td>11,(1),[5], $\Delta G_f$(HI)</td>
</tr>
<tr>
<td>16 Be$^{2+}$ + S$^2-$</td>
<td>-</td>
<td>&lt;79 (873°K)</td>
<td></td>
<td>10,(1),[5], $\Delta G_f$(H₂S)</td>
</tr>
</tbody>
</table>

^a The standard state of the ions is the hypothetical mole fraction solution in LiF-0.33BeF₂, with the exception of Li$^+$, Be$^{2+}$, and F$^-$, for which the standard state is LiF-0.33BeF₂.

b Numbers not in parentheses, numbers in parentheses, and numbers in brackets refer respectively to items listed in Tables I, II, and in this table.
Table IV
Calculated Electrode Potentials in LiF-0.33BeF$_2^a$
(773-1000°K)

<table>
<thead>
<tr>
<th>Half Cell Reactions$^b$</th>
<th>$E^0$ (1000°K), v.</th>
<th>Temperature Coefficient $\theta$/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$ + e $\rightarrow$ Li(s)</td>
<td>-2.541</td>
<td>0.821</td>
</tr>
<tr>
<td>La$^{3+}$ + 3e $\rightarrow$ La(s)</td>
<td>-2.21</td>
<td>0.821</td>
</tr>
<tr>
<td>Ce$^{3+}$ + 3e $\rightarrow$ Ce(s)</td>
<td>-2.14</td>
<td>0.817</td>
</tr>
<tr>
<td>Sm$^{3+}$ + 3e $\rightarrow$ Sm(s)</td>
<td>-2.01</td>
<td>0.795</td>
</tr>
<tr>
<td>Be$^{2+}$ + 2e $\rightarrow$ Be(s)</td>
<td>-1.721</td>
<td>0.715</td>
</tr>
<tr>
<td>Th$^{4+}$ + 4e $\rightarrow$ Th(s)</td>
<td>-1.73</td>
<td>-</td>
</tr>
<tr>
<td>Zr$^{4+}$ + 4e $\rightarrow$ Zr(s)</td>
<td>-1.316</td>
<td>0.755</td>
</tr>
<tr>
<td>U$^{4+}$ + 4e $\rightarrow$ U(s)</td>
<td>-1.319</td>
<td>0.694</td>
</tr>
<tr>
<td>U$^{3+}$ + 3e $\rightarrow$ U(s)</td>
<td>-1.410</td>
<td>0.630</td>
</tr>
<tr>
<td>U$^{4+}$ + e $\rightarrow$ U$^{3+}$</td>
<td>-1.044</td>
<td>0.807</td>
</tr>
<tr>
<td>Cr$^{2+}$ + 2e $\rightarrow$ Cr(s)</td>
<td>-0.390</td>
<td>0.505</td>
</tr>
<tr>
<td>Fe$^{2+}$ + 2e $\rightarrow$ Fe(s)</td>
<td>-0.011</td>
<td>0.516</td>
</tr>
<tr>
<td>Ni$^{2+}$ + 2e $\rightarrow$ Ni(s)</td>
<td>+0.473</td>
<td>0.830</td>
</tr>
<tr>
<td>HF(g) + e $\rightarrow$ F$^-$ + $\frac{3}{2}$H$_2$(g)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\frac{1}{2}$I$_2$(g) + e $\rightarrow$ I$^-$</td>
<td>&lt;0.45</td>
<td>-</td>
</tr>
<tr>
<td>$\frac{1}{2}$S$_2$(g) + 2e $\rightarrow$ S$^{2-}$</td>
<td>&lt;0.10</td>
<td>-</td>
</tr>
<tr>
<td>$\frac{1}{2}$O$_2$(g) + 2e $\rightarrow$ O$^{2-}$</td>
<td>0.558</td>
<td>0.134</td>
</tr>
<tr>
<td>$\frac{1}{2}$O$_2$(g) + $\frac{3}{2}$H$_2$(g) $\rightarrow$ OH$^-$</td>
<td>1.734</td>
<td>0.472</td>
</tr>
<tr>
<td>$\frac{1}{2}$F$_2$(g) + e $\rightarrow$ F$^-$</td>
<td>2.871</td>
<td>0.044</td>
</tr>
</tbody>
</table>

$^a$ Calculated from $\Delta G$ values in Table III.

$^b$ Standard states for ions are defined in footnote (a) of Table III.

the relative stability of U$^{4+}$ with respect to U$^{3+}$ — tend to favor LiF-0.33BeF$_2$ as a reactor fuel solvent. The correlation in Fig. 6 could prove a useful means of estimating the $E^0$ values ($\Delta G$ values) of reactions for which data are lacking.
FIG. 6. Electrode potentials in LiF-0.33BeF$_2$ (versus HF/H$_2$F$^-$ electrode) at 1000°C compared (left) to aqueous electrode potentials at 25°C and compared (right) to electrode potentials in LiCl-KCl eutectic (versus Ag$^+/Ag$) at 450°C.
A number of other observations, in part evident from the equilibrium measurements, are more clearly apparent from the $E^\circ$ values in Table IV. The stability of the trivalent rare earth cations is such that direct reduction to the metals as a means of removing rare-earth fission products would be accompanied by reduction of $\text{Be}^{2+}$ as well as $\text{U}^{4+}$. Trivalent uranium should disproportionate.

$$4\text{UF}_3(d) \Leftrightarrow 3\text{UF}_4(d) + \text{U}(s), \quad E^\circ(873^\circ\text{K}) = -0.086 \text{ v.} \quad (23)$$

However, the difference in $E^\circ$ values for the $\text{U}^{4+}/\text{U}^{3+}$ and the $\text{Cr}^{2+}/\text{Cr}$ couples is so large that the amount of $\text{U}^{3+}$ produced by reaction with the container metal should be small (Eqn. 8) and, in fact, the reduction of $\text{U}^{4+}$ to $\text{U}^0$ by chromium

$$2\text{Cr}(s) + \text{U}^{4+} \rightarrow 2\text{Cr}^{2+} + \text{U}(s), \quad E^\circ(873^\circ\text{K}) = -0.950 \text{ v.} \quad (24)$$

should not be significant [8]. The strongest reducing agent which can be used in LiF-0.33BeF$_2$ without reducing the solvent components is beryllium metal, which indeed has been used as a reducing agent during purification of such melts [11]. With ZrF$_4$ present, a weaker reducing agent (e.g., zirconium metal) must be used.

4.3 Estimated Solubilities of Other Oxides

From the equilibrium data, the free energy change associated with the following reaction is known

$$\text{F}^- + 1/4 \text{O}_2(g) = 1/2 \text{O}^{2-} + 1/2 \text{F}_2(g), \quad \Delta G(1000^\circ\text{K}) = 53.34 \text{ kcal} \quad (25)$$

By combining this with $\Delta G^f$ values for the fluorides in Table III, $\Delta G^f$ values for the corresponding dissolved oxides are obtained. These values in turn may be compared to published values for $\Delta G^f$ of the solid oxides to yield an estimate of the corresponding solubility products

$$\log K_{sp} = -(\Delta G^f - \Delta G^f)/2.3 \text{ RT} \quad (26)$$

Such calculations show that, aside from the oxides already considered ($\text{BeO}$, ZrO$_2$, UO$_2$, ThO$_2$) the oxides of Ni$_{2+}$ and Fe$_{2+}$ are the only others of the cations listed in Table III which are predicted to have low solubility (Table I). The less soluble of these two is NiO. The predicted value of $x_{\text{NiF}_2}$ in LiF-0.33BeF$_2$ saturated with BeO and NiO is $\approx 10^{-4}$ at 1000$^\circ$K. This is higher than is expected for a typical reactor system, i.e., neither
NiO (nor FeO) is expected as a stable solid phase under normally reducing conditions.

Less exact but useful estimates of the solubilities of other oxides can be made from the following reaction

\[
\frac{1}{z} MF_z(s) + \frac{1}{2} O^2^-(d) = F^-(d) + \frac{1}{z} MO_{z/2}(s) \quad (27)
\]

\[
\Delta G = \frac{1}{z} G^f(MO_{z/2}) - \frac{1}{z} AG^f(MF_z) - \Delta G \left(\frac{1}{2} O^2^- - F^-\right) \quad (28)
\]

wherein the last \( \Delta G \) term corresponds to reaction (25) above. A survey of available \( \Delta G^f \) data for oxides and fluorides of Group I, II, III, and IV cations, and of the bivalent first transition metal cations indicates that aside from the oxides already considered only Al\(^{3+}\) and perhaps Sc\(^{3+}\) should be significantly insoluble. This scarcity of insoluble oxides is caused by the relative greater stability of fluorides. It offers little help in the search for refractory materials which might prove useful agents for ion exchange or precipitation reactions which could be made the basis for fuel reprocessing schemes. For example, an attractive possibility would be the removal of rare earth fission products by ion exchange reactions involving rare-earth oxides of suitably low neutron capture cross section, but these oxides are expected to be too soluble in a LiF-0.33BeF\(_2\) and should cause the precipitation of BeO (or UO\(_2\), if UF\(_4\) is present).

4.4 Formation of Carbides

Direct reactions between constituents of the MSRE fuel and graphite to form carbides may be represented by the following general reaction for which chromium metal was chosen as the reducing agent.

\[
\frac{2}{z} MF_z(d) + \frac{2y}{z} C(s) + Cr(s) \rightleftharpoons CrF_2(d) + \frac{2}{z} MCy \quad (29)
\]

\[
\Delta G = \Delta G^f(CrF_2(d)) - \frac{2}{z} \Delta G^f(MF_z(d)) + \frac{2}{z} \Delta G^f(MCy(s)) \quad (30)
\]

Values for the free energy change associated with this reaction at 1000\(^{0}\)K are listed in Table V. They indicate that Zr, U, and Th carbides should not be formed.

5. Conclusions

The mutually re-enforcing relationship between chemistry and thermodynamics in a reactor development program is, I think, well illustrated in the case of the molten salt reactor program. The chemical information most urgently needed in order that
Table V
Carbide Formation

\[
\frac{2}{3} \text{MF}_2(d) + \frac{2}{3} \text{C}(s) + \text{Cr}(s) \rightleftharpoons \text{CrF}_2(d) + \frac{2}{3} \text{MC}\]

<table>
<thead>
<tr>
<th>Carbide</th>
<th>(\Delta G^f(1000^\circ K)^a), kcal</th>
<th>(\Delta G) (Reaction, 1000(^\circ)K), kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrC(s)</td>
<td>-38</td>
<td>24</td>
</tr>
<tr>
<td>UC(_2)(s)</td>
<td>-42</td>
<td>22</td>
</tr>
<tr>
<td>ThC(_2)(s)</td>
<td>-48</td>
<td>39</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 27, page 587.

development of the MSRE might proceed was obtained by direct experiment. But, by conducting these experiments in a sufficiently controlled manner that the chemical equilibria involved could be identified and the associated equilibrium constants measured, each experiment could contribute to a growing knowledge of the thermodynamics of the pertinent molten salt systems. This knowledge, in turn, has been useful in several ways. It has extended the significance of the chemical information upon which it is based, it has indicated where new chemical problems may arise and how to deal with them, and it provides a growing structure which will continue to grow in extent as more data are acquired, and in usefulness as more problems appear which require solutions.

References

8. GRIMES, W. R., In: ref. 1, Chemical Basis for Molten-Salt Reactors, 1964, p. 235-244.


CATION-EXCHANGE EQUILIBRIA WITH FUSED SALTS*

E.C. FREILING
US NAVAL RADIOLOGICAL DEFENSE LABORATORY,
SAN FRANCISCO, CALIF., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

CATION-EXCHANGE EQUILIBRIA WITH FUSED SALTS. Solute distributions of alkali metal, alkaline-earth, transition metal, and actinide ions have been studied in fused salt-cation exchanger systems. The fused salts employed were alkali halides and nitrates. The cation exchangers used were natural zeolites, synthetic zeolites, high-porosity glasses, and molten oxide mixtures. The molten exchangers were composed of Na$_2$O and B$_2$O$_3$ in various proportions. The relative quantities not only determined the exchanger capacity and electrolyte penetration but also produced distribution coefficients for a given solute which varied over several orders of magnitude. Moreover, they produced marked reversals in the selectivity series. Additional studies on the anion distributions, miscibility diagrams, vapour pressures and diffusion rates in these systems have elucidated the mechanisms involved and the relation of selectivity to solute properties, system thermodynamics, exchanger structure and available functional groups. In the region of high Na$_2$O composition, the distribution coefficients for mono-, di- and trivalent cations in NaCl have not only the same order of selectivity found in Dowex 50-HCl systems but also similar values for the distribution coefficients. The results are summarized qualitatively and compared to behaviour in aqueous systems (Table VII).

EQUILIBRES D’ÉCHANGE DE CATIONS AVEC DES SELS FONDUS. L’auteur a étudié la distribution des ions de métaux alcalins, de métaux alcalino-terreux, de terres rares, de métaux de transition et d’actinides en solution dans des systèmes échangeurs de cations-sel fondu. Les sels fondues employés étaient surtout des halogénures et des nitrates alcalins ; les échangeurs de cations étaient des zéolithes naturels, des zéolithes synthétiques, des verres à forte porosité et des mélanges d’oxydes fondues. Les échangeurs fondues se composaient de Na$_2$O et B$_2$O$_3$ dans des proportions diverses. Les quantités relatives non seulement déterminaient la capacité de l’échangeur et la pénétration de l’électrolyte, mais encore donnaient des coefficients de distribution pour un soluté déterminé, qui variaient de plusieurs ordres de grandeur. En outre, il en résultait des inversions prononcées dans la série des sélectivités. En procédant à des études complémentaires sur les distributions d’anions, les diagrammes de miscibilité, les pressions de vapeur et les vitesses de diffusion de ces systèmes, l’auteur a pu élucider les mécanismes qui interviennent et la relation entre la sélectivité et les propriétés du soluté, la thermodynamique du système, la structure de l’échangeur et les groupes fonctionnels disponibles. Dans la région de forte teneur en Na$_2$O, les coefficients de distribution des cations mono-, bi- et trivaux dans NaCl présentent non seulement le même ordre de sélectivité que les systèmes Dowex 50-HCl, mais aussi des valeurs analogues pour les coefficients de distribution. L’auteur résume les résultats du point de vue qualitatif et les compare au comportement dans les systèmes aqueux (Tableau VII).

КАТИОНООБМЕННЫЕ РАВНОВЕСИЯ С РАСПЛАВЛЕННЫМИ СОЛЯМИ. Распределение ионов растворенных щелочных, щелочноземельных, редкоземельных, переходных металлов и актинидов изучалось в системах расплавленная соль-катионообменник. В качестве солей использовались галогениды и нитраты щелочных металлов. Использованными катионообменниками были природные и искусственные цеолиты, высокопористое стекло и смеси расплавленных окислов. Расплавленные обменники были составлены из Na$_2$O и B$_2$O$_3$ в различных пропорциях. Относительное содержание их не только определяло обменную способность обменника и электролитическое проникновение, но и давало также коэффициенты распределения для данного растворенного вещества, величина которых колебалась в пределах нескольких порядков. Кроме того, они вызывали заметное реверсирование в ряду селективности. Дополнительное изучение распределения анионов, диаграмм смесимости, давлений паров и скоростей диффузии в этих системах позволило понять механизмы этих процессов и отношение селективности к свойствам растворенных веществ, термодинамике системы, структуре обмен-
1. INTRODUCTION

Molten salt reactors offer immediate promise for slow-neutron breeding in the thorium-uranium cycle and for eventual fast-neutron breeding in the uranium-plutonium cycle [1]. Fluoride salts are being used in the former case; chloride salts are under consideration in the latter. Continuous removal of fission products from the fuel salt and of bred material from the blanket salt are attractive possibilities, and the possibility of processing by ion exchange or immiscible melt extraction comes naturally to mind. Ion exchangers for such applications must meet a number of obvious requirements such as thermal and radiation stability, immiscibility with the fuel or blanket salts, appropriate selectivities, etc. Because complete immiscibility is unlikely under the operating conditions, additional demands of neutron economy restrict the exchanger compositions to elements and isotopes of tolerable cross-sections. Since O, F, 7Li, 11B, Si, Al, Ca, Na and 31Cl are among such elements and isotopes, borates, silicates and inorganic zeolites are likely candidates for processing materials.

By ion exchange, subsequent separations and concentrations of carrier-free, long-lived fission products for SNAP devices might also be possible. Solution of waste-disposal problems could be facilitated. A more remote possibility is the use of such materials for in situ concentration of product isotopes from an underground nuclear detonation in a salt dome, an event being considered by the USAEC's Plowshare programme.

The development of ion-exchange techniques for molten salt technology has additional fundamental applications to the basic chemistry of molten salt systems and the study of species present in them.

We have accumulated a considerable amount of basic data on the equilibrium ion-exchange distributions of various fission products and actinides in molten salt systems. The salts studied were alkali-metal halides and...
nitrates. The cation exchangers used were natural zeolites, synthetic zeolites, high-porosity glasses and molten oxide mixtures.

2. MOLTEN EXCHANGERS

The major part of our effort has been devoted to the study of the exchanger properties of molten alkali borates. These properties vary markedly with the exchanger composition, i.e. the ratio of acid (B₂O₃) to base (alkali oxide or alkali borate, depending upon the manner of presentation). To aid the reader in interpreting our results in terms of present thinking on the structure of molten borates, some background material is necessary. The reader must bear in mind, however, that no general agreement has yet been reached on the structures proposed by various investigators.

2.1. Borate glasses

Biscoe and Warren [2] have proposed that boric oxide is a random network of trigonal $B\phi_3$ groups. The structure is shown schematically in Fig. 1. Added oxide ions can either form additional bridges by making the boron atoms negative and tetrahedrally co-ordinated:

$$2B\phi_3 + O^- \rightarrow 2B\phi_4^-$$

or they can break bonds to form negatively charged, non-bridging oxygens:

$$2B\phi + O^- \rightarrow 2B\phi_2O^-$$

Biscoe and Warren postulated that added oxygens built bridges until about 16 mole % alkali oxide. Further addition broke bridges. The formation of tetrahedral borons was based upon X-ray diffraction studies which have since been confirmed by nuclear magnetic resonance [3-4], but there is no general agreement on when it ceases. Krogh-Moe believes it continues up to 33.3 mole % [5].

2.2. Liquid borates

In liquid borates, the density rises and the viscosity decreases with added alkali oxide. The former indicates bridge formation, and the latter indicates bridge destruction as suggested by Shartsis et al. [6]. We can visualize an equilibrium between the fourfold and threefold co-ordinated borons:

$$B\phi_4^+ = B\phi_2O^-$$

Bonding considerations favour adjacent fourfold groups, while steric considerations favour the non-bridging arrangements. As addition of oxide ions

---

1 Here the convention $\phi$ indicates a bridging oxygen atom, i.e. one shared between two boron atoms, only one of which is shown.
increases, steric factors become more important, and non-bridging groups predominate.

The vapour pressure measurements of Adams and Quan [7] indicate that Bischoe and Warren's considerations can be applied to the liquid state if one considers vapour pressure to be related to the fraction of non-bridging oxygens. Using a transpiration method, Adams and Quan measured the vapour pressure of Rb$_2$O-B$_2$O$_3$ mixtures from 0 to 50 mole % Rb$_2$O and over a 450°C temperature range. At 1050°C they found the activity of the vapour species (RbBO$_2$), related to the 50 mole % composition as a standard state, to be 0.01 or less until some composition between 12 and 20 mole % Rb$_2$O (i.e. near the M$_2$O.5B$_2$O$_3$ composition) is reached, after which it rises in a rather linear fashion. Their results are shown in Fig. 2.

This model of liquid alkali borates indicates that alkali borates are bifunctional cation exchangers. They have replaceable alkali metal ions which are coulombically bound to the negatively charged sites of a network structure. The capacity of these exchangers is proportional to their basicity and their cross linking goes through a maximum at 20 ± 10 mole % of M$_2$O (M = alkali metal). At 50 mole % they become completely converted to the polyelectrolyte (BO$_2$O)$_3$. Before presenting the experimental evidence to substantiate this view, however, it will be well to consider the behaviour of molten alkali borates in contact with fused salts.

2.3. Alkali borate-alkali halide systems

Fig. 3 shows the miscibility diagrams for the ternary systems Na$_2$O-NaX-B$_2$O$_3$ (X = Cl, Br or I) at 980°C. These results were obtained by
FIG. 2. RbBO$_2$ activity as a function of composition. (The theoretical line is obtained on the assumption that the activity is proportional to the fraction of oxygen atoms which are non-bridging.)

Dunicz and Scheidt [8] using closed graphite containers sealed in evacuated quartz capsules. The diagrams show increasing miscibility in going from NaI to NaCl (NaF is completely miscible with B$_2$O$_3$). The important feature of this diagram for the subject at hand is that the miscibility gaps fall into two regions and this is indicated by both the behavior of the tie lines and the shape of the curves. For brevity, we will call the region of low alkali oxide content (the acidic region) region A. This region extends over borate compositions ranging from pure boric oxide to approximately M$_2$O.5B$_2$O$_3$. In this region there is appreciable alkali halide solubility (i.e. electrolyte penetration) in the oxide (exchanger) phase. The convergence of the tie lines at the alkali halide corner shows that the solubility of the oxide (exchanger) in the halide phase (co-phase) is slight. Rowell obtained similar data for the NaCl case at 830°C using platinum crucibles open to the atmosphere and mechanical stirring. From careful analyses of the phases he determined the formula of the soluble species in the sodium chloride system to be B$_2$O$_3$ and the solubility to be 0.04 mole % [9].

Region B, the basic region, extends from the M$_2$O.5B$_2$O$_3$ composition to the plait point. It shows increasing electrolyte penetration but is characterized better by the sharply increasing borate solubility. Rowell found that in the NaCl system the species NaBO$_2$ appears to be dissolving at compositions between M$_2$O.5B$_2$O$_3$ and M$_2$O.4B$_2$O$_3$: At still higher alkali oxide contents the presence of polyborate species was in evidence. The solubility of alkali borates in alkali halides thus resembles their volatility. The resemblance cannot be expected to go too far, however, since the substantial quantities of alkali halide dissolved in the former case are absent in the latter.
In region A, no Na$_2$O dissolves in the halide phase, and only a fraction of a mole % of B$_2$O$_3$ dissolves. The halide phase may therefore be considered as having unit thermodynamic activity throughout this region. The halide dissolved in the borate phase will also be at unit thermodynamic activity with respect to the same standard state. The activity coefficients for the alkali halides in the borate phase in region A are therefore the reciprocals of their equilibrium concentrations.

2.4. Evidence for ion-exchange processes

In view of the aforementioned facts and considerations, Scheidt and Freiling [10] proposed the mechanism shown in Fig. 4 by which ion-exchange processes can proceed between the oxide and halide phases in region A. The figure is self explanatory. In region B the figure should be modified to show the presence of (M+) - BO$_2$(B$_2$O$_3$)$_n$ ion pairs and similar structures which arise from the breakdown of the borate structure and dissociate in the halide phase. The systems we are dealing with have certain basic differences from the familiar aqueous ion-exchange system: there is no neutral phase corresponding to water (or organic solvent); there are no conditions of negligible electrolyte penetration and under most conditions penetration is high; at all compositions,
there is a sensible exchanger solubility, and at some compositions this
solubility is appreciable. In view of these differences, it is worthwhile
clarifying what we mean by "ion exchange" in general before proceeding.

There is no definition which has yet received universal acceptance by
workers in the field. However, the following set of definitions appears to
represent what workers in the field mean in their correspondence:

**Ion-exchange mechanism** A mechanism which produces a heterogeneous,
ionic metathesis.

**Ion-exchange process** A chemical process which proceeds by an ion-
exchange mechanism.

**Ion-exchanger process** A chemical process carried out by an ion ex-
changer (e.g. catalysis, ion exclusion, site sharing, etc., including ion-exchange
processes).

This definition of ion-exchange mechanism is operational and applicable
to any heterogeneous system.

Returning now to Fig. 4, suppose a solute halide NX is introduced into
the salt phase. This can distribute itself between the salt phase and the MX
dissolved in the oxide phase according to the equilibrium

\[ K_s = \frac{(a_{NX})_O}{(a_{NX})_S} \]

where a indicates thermodynamic activity and subscripts O and S indicate
the oxide and salt phases respectively. If this were the only process occurring,
the concentration \( C_{N^+} \) of \( N^+ \) in the oxide phase would be clearly equal to or
less than \( C_{X^-} \) the concentration of \( X^- \) in that phase. However, if ion exchange
occurs there is the additional equilibrium

\[ K_I = \frac{(a_{N^+})_O(a_{M^+})_S}{(a_{N^+})_S(a_{M^+})_O} \]
This equilibrium permits additional $N^+$ to be concentrated in the oxide phase and the possibility that the concentration of $N^+$ will exceed that of $X^-$. Therefore, a sufficient, but not necessary, condition for proving the occurrence of an ion-exchange process is that

$$(C_{N^+})_O > (C_{X^-})_O$$

The possibility of exchange occurring in the salt phase subsequent to dissolution of oxide as $MBO_2$ leads to the same results. If the halide phase consists of pure $NX$, similar considerations lead to the alternative condition

$$(C_{M^+})_S > (C_{BO_2(B_2O_5)^-})_S$$

Scheidt and Freiling tested the presence of these relationships at various points in regions A and B by equilibrating molten phases of composition $Na_2O \cdot xB_2O_3$ with molten KCl at 830°C. Their results are shown in Figs. 5 and 6.

![Graph showing concentrations of potassium and chloride ions in the oxide phase as a function of composition for the system $Na_2O-B_2O_3-KCl$ (830°C).](image)

**Fig. 5.** Concentrations of potassium and chloride ions in the oxide phase as a function of composition for the system $Na_2O-B_2O_3-KCl$ (830°C).

Fig. 5 shows the values of $C_{K^+}$ and $C_{Cl^-}$ in the oxide phase for each run. The abscissa in this figure is $m_B$, the mole fraction of $BO_2$ (regardless of associated cation) that would be present in the oxide phase were no chloride present. This is a convenient measure of position in the miscibility diagram.
for comparing results between systems containing different alkali halides. The higher value of $C_{K^+}$ in every case clearly establishes the operation of cation-exchange processes.

The results of Fig. 6 confirm the above conclusion. This figure presents the complementary data for $C_{Na^+}$ and $C_{BO_2^-}$ in the salt phase. Again the concentration of the foreign cation exceeds that of the foreign anion for every case.

The cation and anion concentration curves meet at the plait point, of course, and should meet again at the value $m_B = 0$.

2.5. Distribution studies

Figs. 7 and 8 show the distributions of various cations as determined by Rowell for the sodium borate-sodium chloride system at 830°C [9]. These are plotted against $M_B$, which is simply half of the $m_B$ described in the
previous section. Fig. 7 shows data for alkali metal and alkaline earth ions, and Fig. 8 shows data for the rare earths. The distributions were obtained using the gamma-emitting radionuclides $^{137}$Cs, $^{85}$Rb, $^{85}$Sr, $^{133}$Ba, $^{147}$Nd,
$^{152-154}$Eu and $^{110m}$Ag to trace small quantities of the corresponding metal chlorides. The graphs are plotted in terms of the distribution coefficient

$$K_d = \frac{(C_{\text{solute}})_0}{(C_{\text{solute}})_S}$$

FIG. 8. Alkaline earth and rare earth distribution coefficients in the system Na$_2$O-B$_2$O$_3$-NaCl ($839^\circ$C).
In interpreting these results, consider first the behaviour in region B. Table I shows Rowell's comparison of field strength (calculated as the ratio of the ionic charge to the square of the ionic radius) with the distribution coefficient at a value for \( M_B \) of 25. The comparison clearly indicates the importance of coulombic forces in determining \( K_d \) at this point. It will be recalled that the \( B\sigma_4O^- \) sites predominate in this region. As \( M_B \) increases beyond 30, the curves all converge to the expected value of unity at the plait point. The behaviour in region \( A (M_B = 5) \) shows that the alkali metal curves

### TABLE I

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius</th>
<th>Field Strength</th>
<th>( K_d ) at ( M_B = 25 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(^+)</td>
<td>1.67Å</td>
<td>0.36</td>
<td>0.275</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>1.48</td>
<td>0.46</td>
<td>0.32</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.98</td>
<td>1.04</td>
<td>0.51</td>
</tr>
<tr>
<td>Ba(^{++})</td>
<td>1.31</td>
<td>1.17</td>
<td>4.0</td>
</tr>
<tr>
<td>Sr(^{++})</td>
<td>1.51</td>
<td>1.51</td>
<td>4.0</td>
</tr>
<tr>
<td>Nd(^{+++})</td>
<td>0.99</td>
<td>3.06</td>
<td>1750</td>
</tr>
<tr>
<td>Eu(^{+++})</td>
<td>0.97</td>
<td>3.19</td>
<td>3400</td>
</tr>
</tbody>
</table>

have reversed their position and the alkaline-earth and rare-earth curves appear to be on the verge of reversing, so that the order of selectivity at \( M_B = 0 \) would be the reverse of that at \( M_B = 25 \). The predominant exchange sites here are probably \( B\sigma_6 \) sites. The shapes of the curves can therefore be qualitatively explained on the following basis, similar to that used by Diamond and Whitney [11] for concentrated electrolyte solutions. The chloride ions are better able to satisfy the field strengths of the positive charges than the \( B\sigma_4 \) sites, but less able than the \( B\sigma_6O^- \) sites. At the extreme of each region, the cation with the higher field strength competes more successfully with the sodium ions for the desirable anion. At intermediate values of \( M_B \), both kinds of sites are present at the equilibrium concentrations, and it appears that lower concentrations of \( B\sigma_6O^- \) sites can attract the rare-earth ions into the borate phase than are needed to attract the alkaline earths. As shown by the work of Adams and Quan [7] there is also the possibility that a cation of high field strength will produce the conversion of a \( B\sigma_4 \) group to a \( B\sigma_2O^- \) group.

The actinide elements \( Am^{3+} \) and \( Cm^{3+} \) have also been measured. They have curves similar to, but slightly lower than, those for rare earths of similar
size. A comparison of these results with those for Dowex-50 in dilute HCl is shown in Table II. The Dowex-50 data is taken from Strelow [12].

Some scattered preliminary data for uranium and plutonium indicate that these actinides have distribution coefficients intermediate between alkaline earths and rare earths.

Fig. 9 compares the distribution curve for Ag\(^+\) with those of Cl\(^-\) and the other 1\(^+\) ions studied. The effect of chloride complexing is evident, and has been determined in other studies [13].

### TABLE II

| Replacement Constants \( K_r = \frac{M^d}{Na^K_d} \) for \( Na_2O-B_2O_3-NaCl \) at 830°C |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( Na_2O \)     | 7.5%            | 16.7%           | 23.0%           | 28.6%           |
| Cs              | 3.75            | 1.3             | 0.66            | 0.42            |
| Rb              | 2.7             | 1.3             | 0.74            | 0.50            |
| Ba              | 0.16            | 0.44            | 2.2             | 4.5             |
| Sr              | 0.16            | 1.0             | 2.6             | 12.7            |
| Ca              | 0.2             | 1.4             | -               | 50              |
| Nd              | 0.3             | 20              | 1800            | 2000            |
| Eu              | 0.35            | 30              | 3200            | 4000            |

| Replacement Constants \( K_r = \frac{M^d}{Na^K_d} \) for (Dowex 50)-HCl at Room Temperature |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( Na_2O \)     | 0.1 N           | 0.2 N           | 0.5 N           | 1.0 N           | 2.0 N           |
| Cs              | 3.50            | 3.50            | 3.67            | 3.47            | 2.89            |
| Rb              | 2.31            | 2.54            | 2.75            | 2.76            | 2.25            |
| Ba              | >200            | 103             | 49.2            | 22.7            | 10.0            |
| Sr              | 90.3            | 37.8            | 18.1            | 10.8            | 4.95            |
| Ca              | 61.6            | 27.9            | 12.6            | 7.57            | 3.39            |
| La              | >2000           | 350             | 207             | 47.4            | 13.3            |
| Ce              | >2000           | 350             | 205             | 47.3            | 13.3            |
| Y               | >2000           | 35              | 122             | 25.8            | 8.2             |

2.6. Kinetics

Only qualitative information on the kinetics of these distributions is available at this time. Preliminary results indicate that diffusion in the borate phase is the rate determining process, and this becomes slower as the acidity of the phase decreases. Equilibrations with \(^{22}\)Na-labelled phases
reached completion in 10 minutes. Some equilibrations with rare earths had to be carried out for almost an hour.

2.7. Conclusion

From what has been said, it is evident that molten ion-exchangers offer a new dimension in ion exchange processing, a dimension which reaches into the high temperature regions required for molten-salt solvents, a dimension characterized by rapid exchange processes, a dimension where control of the exchange capacity, cross-linkage, and functional behaviour of the exchange sites is easily manipulated, a dimension which offers separation factors equal to, and in some cases beyond, those available in aqueous systems. These fundamental studies now need to be extended to investigations more directly concerned with molten-salt reactor applications.

At this time it is convenient to summarize the selectivity series observed here in terms of the more familiar series observed between dilute
aqueous solutions and strongly acidic organic cation exchangers. In the latter case, the effect of ion size gives the series

\[ \text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ \]

and the effect of charge gives the series \[ M^+ < M^{++} < M^{+++} \].

The size effect is reversed by high electrolyte concentrations [11]. If we call the series for dilute aqueous solutions "normal", then the basic borates show a normal charge effect and a reversed size effect, while the acidic borates tend toward a normal size effect and reversed charge effect. Thus, the basic borates behave like strong acid organic cation exchangers in highly concentrated electrolytes where no water is present to hydrate the ions.

3. HIGH-POROSITY GLASSES

Rowell has made glasses of various compositions and tested their suitability as ion-exchangers when contacted with molten salts [15]. Of primary importance in these studies are: (1) the relative melting points of glass and salt; (2) the solubility of the glass in the salt; and (3) ion mobility within the glass.

Glasses were made by fusing intimate mixtures of the desired proportions of powdered dry ingredients. So that these studies served at the same time as a link between molten borate studies in NaCl and zeolite studies in NaN0₃, NaNO₃ was used as a salt and all glasses used contained borate. The first glass used was a sodium borosilicate of composition 10% Na₂O, 75% B₂O₃ and 15% SiO₂. The rate of ²²Na equilibration in the system was followed as an indication of ion mobility. The SiO₂ raised the melting point and reduced the solubility of the glass in NaN0₃, but the rate of equilibration was very slow. A glass of composition 21% Na₂O and 79% B₂O₃ was much faster in approaching equilibrium, but still far from being satisfactory. When the sodium borate glasses were pre-saturated with salt, however, favourable equilibration rates were finally achieved, and equilibrium distributions could be obtained in about 45 min. with 65-100 mesh glass at 500°C. Alkali and alkaline earth phosphate glasses were also tested and found to be too soluble in NaNO₃ to be useful exchangers in this medium. Further studies described here are therefore limited to alkali borate glasses, and specifically with presaturated Na₂O.3B₂O₃. The distribution coefficients of ¹³⁷Cs, ¹³³Ba and ¹⁵²-¹⁵⁴Eu were measured between the 80-115 mesh glass and molten NaN0₃ at 550°C. The results are tabulated in Table III and compared with those for molten Na₂O.3B₂O₃ in contact with NaCl at 830°C. The two systems show identical orders of selectivity for these ions, but the glass-nitrate system shows a much wider range of selectivities than the liquid-chloride systems. This difference may be due partially to the temperature difference between the two systems, partially to the effect of the different anions, and partially to the difference between the relative capacities of salt and exchanger phase in the two cases, as shown by the different distribution coefficients for sodium.
### TABLE III
Comparison of $K_d$ values Between Solid $\text{Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ (NaCl Saturated)
/ Molten NaNO$_3$ and Between Molten Na$_2$O$\cdot$3B$_2$O$_3$ (NaCl Saturated)/
Molten NaCl

<table>
<thead>
<tr>
<th>Solute</th>
<th>Adsorption</th>
<th>Desorption</th>
<th>Equilibrium Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$^+$</td>
<td>.0015</td>
<td>--</td>
<td>0.275</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.84$^a$</td>
<td>0.84$^a$</td>
<td>0.51$^a$</td>
</tr>
<tr>
<td>Ba$^{++}$</td>
<td>1.6</td>
<td>32</td>
<td>1.7</td>
</tr>
<tr>
<td>Sr$^{++}$</td>
<td>122</td>
<td>204</td>
<td>4.0</td>
</tr>
<tr>
<td>Eu$^{+++}$</td>
<td>6150</td>
<td>8800</td>
<td>3400</td>
</tr>
</tbody>
</table>

*a. Calculated*

4. INORGANIC ZEOLITES

4.1. Natural zeolites

Callahan and Kay [16] have studied the ion-exchange characteristics of the zeolitic minerals chabazite, heulandite, analcite, and natrolite, and of a felspathoid mineral sodalite, when in contact with molten NaNO$_3$. Although no plans to use nitrate salts in reactors are known to the author, the results of the previous section show that there is considerable similarity between solute behaviour in nitrates and chlorides. Furthermore, there is always the possibility of using nitrates for subsequent exchanger processing. The solutes employed were $^{22}\text{Na}$, $^{86}\text{Rb}$, $^{137}\text{Cs}$ and $^{133}\text{Ba}$ tracers, and the equilibration temperature chosen was 330°C. The characteristics investigated were the magnitude of the distribution coefficients, the reversibility of the exchange reaction, the time required to attain equilibrium in the exchange reaction, the thermal stability of the solid exchangers, and the compatibility of the solid exchanger with the molten salt.

The thermal dehydration curves for these minerals are shown in Fig. 10 and the rehydration curves are indicated by dots. Curves A, B, C, D, E and F refer to sodalite, analcite, chabazite (Nova Scotia), natrolite, heulandite and chabazite (Oregon), respectively. The Nova Scotia chabazite was used for the distribution studies. These curves illustrate the distinctive property of the zeolites, to lose water continuously over a rather wide range of temperature. These also illustrate the tenacity with which water is held by them. These
curves were used to determine the amount of water held in the channels and cages of the zeolites. This information in turn can be correlated with the porosity of the mineral's crystal structure, which has a direct bearing on both the sieving action and ion-exchange properties of the zeolites. Complete dehydration of zeolites results in the collapse of their mineral structure. When in contact with molten NaNO₃, however, about half the water is driven off by salt invasion.

Table IV shows the formulas of the zeolites studied, the percentage of water in the zeolites at room temperature and before equilibration, and the
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Formula Used for Calculation</th>
<th>Distribution Coefficient for Na+</th>
<th>Equilibration Time (hr)</th>
<th>Degree Hysteresis (%)</th>
<th>Water in Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Network Zeolites</strong></td>
<td></td>
<td>Found</td>
<td>Calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chabazite</td>
<td>(0.751 CaO·0.312 Na₂O·0.152 K₂O)Al₂O₃·6.633 SiO₂·8330 H₂O</td>
<td>0.49</td>
<td>0.23</td>
<td>4</td>
<td>none</td>
</tr>
<tr>
<td>Analcite</td>
<td>Na₂O·Al₂O₃·4SiO₂·2H₂O</td>
<td>0.39</td>
<td>0.39</td>
<td>~8</td>
<td>moderate</td>
</tr>
<tr>
<td>Sodalite</td>
<td>Na₂O·Al₂O₃·2SiO₂·2NaCl</td>
<td>0.13</td>
<td>0.52</td>
<td>&gt;90</td>
<td>strong</td>
</tr>
<tr>
<td><strong>Other Zeolites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heulandite</td>
<td>CaO·Al₂O₃·6SiO₂·5H₂O</td>
<td>0.47</td>
<td>0.28</td>
<td>2</td>
<td>moderate</td>
</tr>
<tr>
<td>Natrolite</td>
<td>Na₂O·Al₂O₃·3SiO₂·2H₂O</td>
<td>0.47</td>
<td>0.45</td>
<td>~24</td>
<td>strong</td>
</tr>
</tbody>
</table>

a. Calculated distribution based on equation $K_{calc} = \frac{\text{exchangeable Na}^+ \text{ ions per gram of zeolite}}{\text{Na}^+ \text{ ions per gram of NaNO}_3}$

b. At room temperature, before equilibration.
results of equilibrating $^{22}$Na between the zeolite and the salt. The table illustrates the strong correlation between the original amount of water present, the speed of equilibration, and the degree of hysteresis (i.e. the difficulty of desorbing ions as indicated by discrepancies in distribution coefficients determined from adsorption and desorption reactions).

Table V shows the distribution coefficients calculated for both the forward and reverse reactions for tracers studied. The hysteresis in each case is indicated by the departure of the ratios from unity. The selectivity series are normal with respect to both size and charge.

### TABLE V

Distribution Coefficients for Natural Zeolites

in Molten NaNO$_3$ at 330°C

<table>
<thead>
<tr>
<th>Cation</th>
<th>Distribution Coefficients</th>
<th>Cation</th>
<th>Distribution Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorption</td>
<td>Desorption</td>
<td>Ratio</td>
</tr>
<tr>
<td>chabazite (10-35 mesh)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$^{22}$</td>
<td>0.488</td>
<td>0.490</td>
<td>0.996</td>
</tr>
<tr>
<td>Rb$^{86}$</td>
<td>16.6</td>
<td>17.5</td>
<td>0.946</td>
</tr>
<tr>
<td>Cs$^{137}$</td>
<td>26.1</td>
<td>36.1$^a$</td>
<td>0.723</td>
</tr>
<tr>
<td>Ba$^{133}$</td>
<td>134</td>
<td>138</td>
<td>0.971</td>
</tr>
<tr>
<td>neulandite (10-35 mesh)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$^{22}$</td>
<td>0.470</td>
<td>0.506</td>
<td>0.929</td>
</tr>
<tr>
<td>Rb$^{86}$</td>
<td>6.52</td>
<td>7.52</td>
<td>0.867</td>
</tr>
<tr>
<td>Cs$^{137}$</td>
<td>8.16</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>Na$^{22}$</td>
<td>0.466</td>
<td>0.554</td>
<td>0.841</td>
</tr>
<tr>
<td>Cs$^{137}$</td>
<td>3.33</td>
<td>10.7</td>
<td>0.311</td>
</tr>
</tbody>
</table>

a. Non-equilibrium values after 96 hours. Apparent distribution coefficient.
b. Not determined.
c. Non-equilibrium value after 24 hours. Apparent distribution coefficient.

Callahan [17] has also studied the effect of the cation on the distribution coefficients of alkali and alkaline earth tracers. For these studies he used chabazite, LiNO$_3$ and KNO$_3$. The results are shown in Table VI. The cation effect is seen to be considerable, not only on the absolute magnitude of the distribution coefficients, but on the relative magnitudes as well. No longer
### TABLE VI

Distribution Coefficients between Chabazite and Molten Nitrates

<table>
<thead>
<tr>
<th>Cation</th>
<th>( K_d ) Adsorption</th>
<th>Equilibration Time (hrs)</th>
<th>( K_d ) Desorption</th>
<th>Equilibration Time (hrs)</th>
<th>Ratio of ( K_d )'s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li NO₃ at 330°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na²²</td>
<td>1.6</td>
<td>18</td>
<td>1.8</td>
<td>4</td>
<td>0.91</td>
</tr>
<tr>
<td>Rb⁸⁶</td>
<td>76</td>
<td>16</td>
<td>72</td>
<td>240</td>
<td>1.06</td>
</tr>
<tr>
<td>Cs¹³⁷</td>
<td>94</td>
<td>19</td>
<td>60</td>
<td>168</td>
<td>1.56</td>
</tr>
<tr>
<td>Ba¹³³</td>
<td>10</td>
<td>168</td>
<td>12</td>
<td>168</td>
<td>0.84</td>
</tr>
<tr>
<td>KNO₃ at 365°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na²²</td>
<td>8.7</td>
<td>24</td>
<td>9.0</td>
<td>24</td>
<td>0.97</td>
</tr>
<tr>
<td>Rb⁸⁶</td>
<td>1.2</td>
<td>4</td>
<td>1.2</td>
<td>24</td>
<td>0.94</td>
</tr>
<tr>
<td>Cs¹³⁷</td>
<td>1.9</td>
<td>4</td>
<td>1.9</td>
<td>24</td>
<td>0.98</td>
</tr>
<tr>
<td>Ba¹³³</td>
<td>1.4</td>
<td>18</td>
<td>1.8</td>
<td>24</td>
<td>0.77</td>
</tr>
</tbody>
</table>

is there an evident "charge effect", but the divalent barium ions have distribution coefficients intermediate between Na⁺ and Rb⁺ in each case, and also between Rb⁺ and Cs⁺ in the case of KNO₃.

4.2. Synthetic zeolites

Although the suitability of synthetic zeolites for ion-exchange studies in molten salts has attracted a number of investigators, and a number of interesting results have been published, no systematic investigation of the selectivity series has appeared.

4.2.1. Nitrate melts. Liquornik and Marcus [18] studied the behaviour of Linde Molecular Sieve 4A in the monovalent nitrates at 320°C. By equilibrating one of these nitrates with the exchanger in the same cationic form they found that NaNO₃ and AgNO₃ formed occlusion compounds. Thus, NaNO₃ and AgNO₃ both entered the zeolite to the extent of 9-10 moles of salt per mole of exchangeable ion in the zeolite, eliminating water in the process. LiNO₃ also gave an occlusion compound but it was too hygroscopic for characterization. KNO₃ and TINO₃ showed no detectable occlusion compound formation.

Exchange studies with AgNO₃ and TINO₃ solutes between the sodium form of the zeolite and NaNO₃ were carried out as a function of solute concentration up to 12 and 18 mole % solute, respectively. Although silver entered to the extent of 20 moles per unit cell, thallium only entered to the extent of 6.
These authors further followed the progress of silver-sodium exchange potentiometrically with a silver electrode. From the behaviour of the selectivity coefficient with composition they concluded that exchange was preceded by dissolution in the occluded salt.

Callahan [19] used $^{110m}$Ag to study the distribution of tracer AgNO$_3$ between NaNO$_3$ and Molecular Sieves Type 4A and 13X. He found distribution coefficients of 15 and 23, respectively. Addition of Cl$^-$, I$^-$ and CN$^-$ in the Type 4A case reduced the distribution coefficient.

4.2.2. Chloride melts. Platek and Marinsky [20] have studied the ion exchange behaviour of trace components between Linde Molecular Sieve Type A and LiCl as a function of LiCl concentration. They found a normal size effect at dilute concentrations, but extrapolation of thermodynamic data to high

| Table VII |
| SUMMARY OF SELECTIVITIES |

<table>
<thead>
<tr>
<th>Exchanger</th>
<th>Co-Phase</th>
<th>Size Effect</th>
<th>Charged Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowex-50</td>
<td>Dilute aq. HCl or Salt</td>
<td>Normal</td>
<td>Normal</td>
<td>[14]</td>
</tr>
<tr>
<td>Type A Molecular</td>
<td>Dilute or Conc. LiCl</td>
<td>Normal</td>
<td>-</td>
<td>[20]</td>
</tr>
<tr>
<td>Type A Molecular</td>
<td>Molten LiCl</td>
<td>Irregular</td>
<td>-</td>
<td>[20]</td>
</tr>
<tr>
<td>Natural Zeolites</td>
<td>Molten NaNO$_3$</td>
<td>Normal</td>
<td>Normal</td>
<td>[17]</td>
</tr>
<tr>
<td>Chabazite</td>
<td>Molten KNO$_3$</td>
<td>Irregular</td>
<td>Irregular</td>
<td>[17]</td>
</tr>
<tr>
<td>B$_2$O$_3$-rich</td>
<td>Molten NaCl</td>
<td>Normal</td>
<td>Reversed</td>
<td>[9]</td>
</tr>
<tr>
<td>Na$_2$O-rich Borate</td>
<td>Molten NaCl</td>
<td>Reversed</td>
<td>Normal</td>
<td>[9]</td>
</tr>
<tr>
<td>Na$_2$O-rich Borate</td>
<td>Molten NaNO$_3$</td>
<td>Reversed</td>
<td>Normal</td>
<td>[21]</td>
</tr>
<tr>
<td>Dowex-50</td>
<td>Conc. HCl</td>
<td>Reversed</td>
<td>Irregular</td>
<td>[11, 22]</td>
</tr>
<tr>
<td>Dowex-50</td>
<td>Conc. HClO$_4$</td>
<td>Reversed</td>
<td>Normal</td>
<td>[11, 22]</td>
</tr>
<tr>
<td>Dowex-50</td>
<td>Conc. LiCl, LiClO$_4$, HNO$_3$</td>
<td>Reversed</td>
<td>-</td>
<td>[11]</td>
</tr>
</tbody>
</table>
temperatures indicated that the order would change to Li < Cs < Na < Rb. The effect was observed in additional equilibrations with LiCl melt at 650°C.

5. SUMMARY AND CONCLUSIONS

By way of summary, the results given in this paper can be presented as shown in Table VII. Here, in addition to our previous designations of normal and reversed, we add "irregular" to indicate that neither pattern is followed. Although these designations are convenient for summarizing, they are limited in application and should not be pushed too far.

As seen from the table, the ion exchangers described here offer a wide variety of properties, some of which appear applicable to processing chloride salts from reactors. These include high thermal and radiation stability and high affinity for rare earths (many of which are fission product poisons) and uranium and plutonium. Before the value of these exchangers can be fully assessed, more data is needed on the actinide elements thorium, protactinium, uranium, neptunium and plutonium, and on fission product poisons (131, 133, 135Xe, 112Cd, 88Kr, 103Rh, 99Tc, 95Mo). Conditions must be sought, perhaps involving complexing agents, where fertile and bred material or where fuel and poison are adsorbed to widely different extents. Loading effects must be accounted for. Additional exchangers must be sought for fluoride melts. Immiscible molten phases that act as solvent extractants should not be overlooked.

REFERENCES

PRACTICAL APPLICATION OF THERMODYNAMICS TO PLUTONIUM PROCESS REACTIONS AT HIGH TEMPERATURE

J.A. LEARY AND L.J. MULLINS
UNIVERSITY OF CALIFORNIA,
LOS ALAMOS SCIENTIFIC LABORATORY,
N. MEX., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

PRACTICAL APPLICATION OF THERMODYNAMICS TO PLUTONIUM PROCESS REACTIONS AT HIGH TEMPERATURE. Several important high temperature reactions for processing plutonium involve equilibria between the metal and a fused salt system. In almost all these processes, the kinetics are rapid, and equilibria are of overwhelming importance. Therefore, the application of appropriate thermodynamic data and estimates are of major importance in selecting the proper reaction system.

Examples of high temperature plutonium processes where thermodynamic considerations are of principal importance are bomb reduction of plutonium halides by an active metal such as calcium, electrorefining of liquid plutonium in fused salt media, and extraction of impurities such as radionuclides from molten plutonium by fused salt media or solid oxide media. The thermodynamic principles involved in these processes, including selection of container materials, are reviewed and compared with experimental results.
constantes y estimaciones termodinámicas apropiadas al proceder a la selección de un determinado sistema de reacción.

Ejemplos de procesos a temperaturas elevadas donde revisten importancia las consideraciones termodinámicas son la reducción de los haluros de plutonio en bomba mediante un metal activo tal como el calcio, la electrorefinación del plutonio líquido en sales fundidas y el uso de estas últimas para extraer del plutonio fundido impurezas tales como radionúcidos o óxidos sólidos. En la memoria se pasa revista a los principios termodinámicos en que se basa estos procesos, incluyendo la selección de materiales para recipientes, y se los compara con los resultados experimentales.

INTRODUCTION

The important high temperature reactions for processing plutonium involve equilibria between the liquid metal and a fused salt system. In almost all of these processes, the kinetics are rapid, and equilibria are of overwhelming importance. The attainment of equilibrium is usually faster by many orders of magnitude in liquid phases than in solid phases. For example the self diffusion coefficient of Pb in solid lead is \(5.5 \times 10^{-10} \text{ cm}^2/\text{sec} \) at 597°K [1]. In liquid lead at 616°K the self diffusion coefficient is \(2.6 \times 10^{-5} \text{ cm}^2/\text{sec} \) [2]. Therefore, the application of appropriate thermodynamic data and estimates are of major importance in selecting the proper reaction system.

Examples of high temperature plutonium processes where thermodynamic considerations are of principal importance are (1) bomb reduction of plutonium halides by an active metal such as calcium, (2) electrorefining of liquid plutonium in fused salt media, and (3) extraction of impurities such as radionuclides from molten plutonium into fused salt media. These three processes represent varying degrees of the equilibrium reaction. Although they are superficially different, they are best understood by considering the individual metal-salt phase heterogeneous equilibria. The reaction of principal importance is represented by the generalized equation

\[\text{PuX} + \text{M} = \text{MX} + \text{Pu}\]  

(1)

where X is either a halogen or oxygen. If the process reaches equilibrium, the standard free energy change for equation (1) at temperature T, can be used to calculate the equilibrium ratio of the activities of reactants and products by the standard manner:

\[-\Delta F^\circ_T = RT \ln K\]  

(2)

where

\[K = \frac{a_{MX}a_{Pu}}{a_{PuX}a_{M}} = \frac{[X_{MX}][X_{Pu}]}{[X_{PuX}][X_{M}]} \frac{\gamma_{MX} \gamma_{Pu}}{\gamma_{PuX} \gamma_{M}}\]  

(3)

or

\[K = K_c K_Y\]

In almost all cases, the activity coefficients, \(\gamma\), are not known and their experimental determination would indeed be a monumental if not impossible task. In spite of this, useful estimates of the concentrations at equilibrium can be made by assuming ideal
or regular solution behavior or by estimating the activity coefficients from the phase diagrams, when available.

Glossary of Symbols and Terms

\( \Delta F^\circ_T \) Gibbs free energy change, standard state conditions for reactants and products, at temperature \( T \)

\( \Delta F_T \) Gibbs free energy change, at temperature \( T \)

\( \Delta H^\circ_T \) Heat of reaction, standard state conditions for reactants and products, at temperature \( T \)

\( a_i \) activity of component \( i \)

\( \gamma_i \) activity coefficient of component \( i \)

\( x_i \) mole fraction of component \( i \)

\( a_i = y_i x_i \)

FUSED SALT EXTRACTION PROCESSES

Plutonium fused salt extraction processes can be represented by the generalized equation

\[
Pu \ X (l) + M (l) = MX (l) + Pu (l)
\]

(5)

(salt phase, \( x_{PuX} \)) (metal phase, \( x_M \)) (salt phase, \( x_{MX} \)) (metal phase, \( x_{Pu} \))

Examples of this type process are the removal of impurities from plutonium metal or plutonium metallic fuels and the removal of plutonium metal from uranium. The liquid salt and metal phases are thoroughly mixed at constant temperature for a period of time that is sufficient to insure the attainment of equilibrium.

The purification of Pu-10 atom % Fe "fissium" fuel by fused salt extraction processes has been reported [3,4]. PuCl₃ dissolved in NaCl and MgCl₂ dissolved in either LiCl–KCl or NaCl–KCl were used to extract rare earth impurities from the metal fuel into the salt phase. The total rare earth concentrations were reduced from 3 wt. % to <0.05 wt. % in the liquid metal. The results were in agreement with qualitative predictions based on standard free energy data. The rare earths concentrated in the salt phase and the metals more noble than plutonium, i.e. Fe, Mo and Ru, concentrated in the metal phase. The removal of Ce by PuCl₃ can be written

\[
PuCl₃ (l) + Ce (l) = CeCl₃ (l) + Pu (l)
\]

(6)

(salt phase, \( x_{PuCl₃} \)) (Pu–Fe, \( x_{Ce} \)) (salt phase, \( x_{CeCl₃} \)) (Pu–Fe, \( x_{Pu} \))
In the case of MgCl₂, the MgCl₂ reacted with the large excess of Pu to form PuCl₃ so that the ratio of Ce to Pu in the purified fuel was still dictated by equation (6). Although Ce was reduced to less than detectable amounts in the Pu-Fe alloy, estimates of $K_c$ can be made. The estimated value is $>1 \times 10^4$. A consideration of the free energy values* given in ref. [5] predicts that the equilibrium constant $K$, for reaction (6) at 973°K should be $5 \times 10^4$.

Recent measurements[5] of $K_c$ for the reaction

$$\text{PuCl}_3 (\ell) + \text{Ce}(\ell) = \text{CeCl}_3 (\ell) + \text{Pu}(\ell) \quad (7)$$

(salt phase, $x_{\text{PuCl}_3}$) (U-Pu, $x_{\text{Ce}}$) (salt phase, $x_{\text{CeCl}_3}$) (U-Pu, $x_{\text{Pu}}$)

at 1423°K resulted in a value of $0.7 \times 10^4$. The calculated value of $K$ is again $5 \times 10^4$.

For the removal of La from a Pu-Fe fissium alloy an equation similar to (6) can be written. The estimated value of $K_c$ at 973°K is $>0.04 \times 10^5$ [6]. The calculated value of $K$ at 973°K is $1.8 \times 10^5$.

In all of the above cases the values of $K_c$ and $K$ are significantly different. However, from the practical viewpoint of predicting process feasibility the calculated values of $K$ afford excellent estimates of $K_c$. In other cases however, the estimates must be used with extreme caution. For example, studies of the assumed equilibrium

$$\text{PuCl}_3 (\ell) + \text{Am}(\ell) = \text{AmCl}_3 (\ell) + \text{Pu}(\ell) \quad (8)$$

(salt phase, $x_{\text{PuCl}_3}$) (Pu, $x_{\text{Am}}$) (salt phase, $x_{\text{AmCl}_3}$) (Pu, $x_{\text{Pu}}$)

yielded a value of $K_c$ at 1000°K of 227 in a 2.10 mole % PuCl₃ solution [7]. The calculated value of $K$ for reaction (8) at this temperature is $2 \times 10^5$. This large difference between $K_c$ and $K$ would occur if either equation (8) did not represent the true equilibrium or if $K_y$ varied over a wide range. Recent experimental data [8] indicate that the reaction actually is

$$\frac{2}{3} \text{PuCl}_3 (\ell) + \text{Am}(\ell) = \text{AmCl}_2 (\ell) + \frac{2}{3} \text{Pu}(\ell) \quad (9)$$

(salt phase, $x_{\text{PuCl}_3}$) (Pu, $x_{\text{Am}}$) (salt phase, $x_{\text{AmCl}_2}$) (Pu, $x_{\text{Pu}}$)

**ELECTROREFINING**

A "near equilibrium" process, the LAMEX electrorefining process [8-15], has been developed for producing high purity Pu metal from impure Pu or alloys of Pu-Fe and Pu-Ga on the multikilogram scale. A schematic drawing of the LAMEX cell is given in Fig. 1. During operation, Pu is oxidized at the anode, enters the molten salt electrolyte

*The free energy values discussed in this text are the standard Gibbs free energy values.
and is reduced to metal at the cathode. The molten product drains continuously into the annular product collection zone. The theory of operation of the cell is discussed in ref. [7].

Table I, [7], presents data derived from many electrorefining runs. The behavior of impurity elements is compared qualitatively with the behavior predicted on the basis of standard free energy of formation data. In every case qualitative agreement of experiment with prediction was obtained. Metals less noble (more electropositive) than Pu concentrated in the salt phase and the more noble metals concentrated in the anode. Unfortunately the data of Table I permit quantitative comparisons for only a few elements since most of the elements are below the limits of detectability. The Am data however, can be compared with the fused salt extraction data reported above. A value of $K_c$ for reaction
TABLE I
BEHAVIOR OF IMPURITY ELEMENTS IN ELECTROREFINING

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta F^\circ$, a</th>
<th>Concentration, p.p.m.</th>
<th>Element Concentrated in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>18</td>
<td>Feed: 750, Product: 10</td>
<td>Anode</td>
</tr>
<tr>
<td>Cu</td>
<td>21</td>
<td>Feed: 100, Product: 2</td>
<td>Anode</td>
</tr>
<tr>
<td>Ta</td>
<td>22</td>
<td>Feed: 5000, Product: 80</td>
<td>Anode</td>
</tr>
<tr>
<td>Fe</td>
<td>27</td>
<td>Feed: 25000, Product: 20</td>
<td>Anode</td>
</tr>
<tr>
<td>Cr</td>
<td>32</td>
<td>Feed: 280, Product: &lt;10</td>
<td>Anode</td>
</tr>
<tr>
<td>Ga</td>
<td>32</td>
<td>Feed: 10000, Product: &lt;25</td>
<td>Anode</td>
</tr>
<tr>
<td>Mn</td>
<td>41</td>
<td>Feed: 70, Product: &lt; 2</td>
<td>Anode</td>
</tr>
<tr>
<td>Al</td>
<td>46</td>
<td>Feed: 2700, Product: &lt; 5</td>
<td>Anode</td>
</tr>
<tr>
<td>U</td>
<td>54</td>
<td>Feed: 275, Product: &lt;20</td>
<td>Anode</td>
</tr>
<tr>
<td>Th</td>
<td>59</td>
<td>Feed: 365, Product: &lt;10</td>
<td>Anode</td>
</tr>
<tr>
<td>Pu</td>
<td>59</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ce</td>
<td>66</td>
<td>Feed: 527, Product: &lt;25</td>
<td>Salt</td>
</tr>
<tr>
<td>Am</td>
<td>67</td>
<td>Feed: 850, Product: 82</td>
<td>Salt</td>
</tr>
</tbody>
</table>

$\Delta F^\circ$ at 1000°K is tabulated. For elements having a multiplicity of oxidation states, the $\Delta F^\circ$ for the most stable form of the chloride is given.

(8) of 190, (±20), was obtained in electrorefining experiments at 1000°K in a 2.10 mole % PuCl$_3$ solution. This value of K$_c$ approaches the value 227 which was obtained at 2.10 mole % PuCl$_3$ in the fused salt extraction described above [7].

The electrorefining of the Pu-Fe fuels irradiated to 0.1% burnup gave K$_c$ values of $1 \times 10^4$ for Ce and $1 \times 10^3$ for Nd at 1000°K. The calculated values of K are $4 \times 10^4$ and $4 \times 10^5$ for Ce and Nd, respectively.

The LAMEX process for electrorefining Pu-Fe and Pu-Ga alloys affords an interesting example of the use of phase diagrams for optimizing the yield of a process and affording a means for control of product purity. To illustrate these points consider the case of electrorefining a Pu-10 atom % Fe alloy. Since only Pu will be dissolved at the anode, the Fe concentration will increase continuously during the electrorefining. From the Pu-Fe phase diagram [16], this increase will result in phase changes in the anode at all temperatures lower than 1809°K. For example, at 1013°K, the anode will be a single phase liquid up to ~25 atom % Fe, liquid plus solid PuFe$_2$ up to 66.7 atom %
Fe and completely solid at 66.7 atom % Fe. As long as the Fe concentration is less than 25 atom %, there should be essentially no significant polarization of a well-stirred anode. At this stage of the electrorefining process the net reaction is

$$\text{Pu (liquid anode)} - \text{Pu (liquid cathode)}$$ (10)

and the free energy change is

$$\Delta F = -RT \ln (a_{\text{Pu}})_{\text{anode}}$$ (11)

Since the initial plutonium anode atom fraction is 0.9, the free energy change is small.

When the Fe concentration reaches 25 a/o, the PuFe solid phase appears. Unless the anode is stirred well, this solid phase will float in the anode surface, thereby producing a polarized anode. However, polarization can be minimized by stirring as long as some liquid phase remains. As the limit of this two phase region is approached, it becomes less possible to maintain a well-stirred anode, and serious anode polarization occurs. When the anode is seriously polarized, the net electrorefining reaction is

$$\text{Pu (solid anode)} - \text{Pu (liquid cathode)}$$ (12)

which corresponds to a potential

$$E = 0.0291 \ln (a_{\text{Pu}})_{\text{solid anode surface}}$$ (13)

Generally the activity of Pu in the polarized anode surface will be considerably less than unity, which results in a measurable e.m.f. for the cell. For example, when $a_{\text{Pu}}$ is $10^{-3}$, E is -0.20 volt.

During the initial stages of electrorefining, while there is a stirred liquid Pu anode, the cell can be operated at high anode current densities that are required for reasonable processing times. However, after the anode solidifies, the same high anode current densities can be maintained only by dissolving Fe at the anode. (The diffusion of Pu in the solid anode is much too slow to meet the high current density requirements.) Therefore, the electrorefining must be terminated before a significant amount of Fe is dissolved anodically, if a pure Pu product is to be achieved. This condition is indicated by a rapid rise in the back e.m.f. of the cell, corresponding to equation (13).

The experimental control of product purity and anode depletion was in general agreement [15], with the theory. Theory predicts serious anode polarization at Fe concentration $\approx$ 66.7 atom % Fe. The experiments gave an average value of 47%. Although this value is smaller than expected, the extremely slow rate of diffusion of plutonium in the anode at the end of a run and the physical appearance of the anode residue show that the anode is actually in a "paste-like" condition at the termination of the electrorefining.

For the case of electrorefining Pu-Ga alloys at 1000°K, the phase diagram [17] predicts anode solidification at 24 atom % Ga. The experiments gave a value of 23 atom % Ga.
LEARY and MULLINS

BOMB REDUCTION PROCESSES

Baker's process for producing Pu metal by the bomb reduction of PuF₄ by Ca [18] is the primary method used by all of the major plutonium laboratories in the United States. A recent literature survey by Conner [19] provides an excellent summary of the refinements which have been made to this process. In the bomb reduction, PuF₄ and Ca are mixed in a refractory lined metal container and heated until the reduction reaction is initiated. To obtain good yields the metal must separate cleanly from the salt. To realize the latter condition both metal and salt phases must be in the liquid state. The attainment of equilibrium in this process is doubtful. Although the temperature attained in the bomb reduction is very high, ~1900°K [20] the components are in the liquid state for only a brief period of time [20]. Nevertheless thermodynamic considerations can be applied to bomb reduction processes and indeed such calculations are useful in estimating both the extent of a proposed reaction and the heat requirements necessary to yield a liquid metal–salt system.

Table I lists some thermodynamic properties of reactions which have been studied by various investigators. The maximum temperature rise was estimated by assuming adiabatic conditions in the reduction process [21].

Table II illustrates several interesting points. Although the free energy change for all of the reactions listed predict favorable production of Pu metal, only reactions (1), (2), (3), (6) and (8) yield sufficient heat to produce metal and molten slag without the application of additional heat. PuF₄ has been reduced successfully to metal by Li [28], Ca [18] and Ba [28]. PuF₃ has reduced successfully to metal by Li [29]. Successful reductions of PuF₃ by Ca required either an I₂ booster [18] or additional external heating [34]. Quantitative reduction of PuCl₃ by Ca required an iodine booster [18, 31]. It has been reported that PuBr₃ and PuI₃ can be reduced by Ca [29], but details of the procedure are not available. Reductions of CaPuF₆ by Li and Ca resulted in high reduction efficiencies but poor separation of metal globules from the slag [29]. Reduction of Cs₂PuCl₆ resulted in metal powders [29]. Attempts to prepare coalesced Pu metal from PuO₂ have been unsuccessful, but small spherical particles of Pu were produced by the heating of PuO₂ with Ca chips for 15 min. at 1273°K [30]. Metal powders have been produced by the reduction of PuO₂ with Ca in a CaCl₂ flux and with Li in a LiCl flux [29]. The results of these studies are in good agreement with the thermodynamic estimates.

The heat required to melt the slag may be decreased by reducing the melting point of the slag. Additional heat may be provided either by external heating or by a booster reaction such as

$$\text{Ca} + \text{I}_2 = \text{Ca} \text{I}_2 \quad (\Delta H^\circ)_{298} = -128 \text{ kcal} \quad (14)$$

The heat loss will obviously be greater in small scale reductions than in large ones.
**TABLE II**

**Bomb Reduction Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta F^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>Max. Temp. Rise</th>
<th>Slag M.P. (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal 1000°C</td>
<td>kcal 298°C</td>
<td>°K</td>
<td>°K</td>
</tr>
<tr>
<td>(1) PuF$_4$ + 4 Li = Pu + 4 LiF</td>
<td>136</td>
<td>158.4</td>
<td>2200</td>
<td>1123</td>
</tr>
<tr>
<td>(2) PuF$_4$ + 2 Ca = Pu + 2 CaF$_2$</td>
<td>148</td>
<td>156.6</td>
<td>2450</td>
<td>1691</td>
</tr>
<tr>
<td>(3) PuF$_4$ + 2 Ba = Pu + 2 BaF$_2$</td>
<td>140</td>
<td>148</td>
<td>2450</td>
<td>1866</td>
</tr>
<tr>
<td>(4) PuF$_3$ + 3/2 Ca = Pu + 3/2 CaF$_2$</td>
<td>56</td>
<td>60.8</td>
<td>1160</td>
<td>1691</td>
</tr>
<tr>
<td>(5) PuF$_3$ + 3 Li = Pu + 3 LiF</td>
<td>47</td>
<td>62</td>
<td>844</td>
<td>1120</td>
</tr>
<tr>
<td>(6) PuCl$_3$ + 3/2 Ca = Pu + 3/2 CaCl$_2$</td>
<td>57</td>
<td>56.3</td>
<td>1100</td>
<td>1055</td>
</tr>
<tr>
<td>(7) PuBr$_3$ + 3/2 Ca = Pu + 3/2 CaBr$_2$</td>
<td>56</td>
<td>62</td>
<td>844</td>
<td>1033</td>
</tr>
<tr>
<td>(8) PuF$_3$ + 3/2 Ca = Pu + 3/2 Ca$_2$</td>
<td>56</td>
<td>60</td>
<td>1250</td>
<td>1013</td>
</tr>
<tr>
<td>(9) CaPuF$_6$ + 4 Li = Pu + 4 LiF + CaF$_2$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1040</td>
</tr>
<tr>
<td>(10) CaPuF$_6$ + 2 Ca = Pu + 3 CaF$_2$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1691</td>
</tr>
<tr>
<td>(11) Cs$_2$PuF$_6$ + 4 Li = Pu + 4 LiF + 2 CsF</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>970</td>
</tr>
<tr>
<td>(12) Cs$_2$PuF$_6$ + 2 Ca = Pu + 2 CaF$_2$ + 2 CsF</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(13) PuO$_2$ + 4 Li = Pu + 2 Li$_2$O</td>
<td>18</td>
<td>39.1</td>
<td>185</td>
<td>2000</td>
</tr>
<tr>
<td>(14) PuO$_2$ + 2 Ca = Pu + 2 CaO</td>
<td>54</td>
<td>57.4</td>
<td>500</td>
<td>2873</td>
</tr>
<tr>
<td>(15) PuO$_2$ + Mg = Pu + 2 MgO</td>
<td>34</td>
<td>41.7</td>
<td>55</td>
<td>3075</td>
</tr>
</tbody>
</table>

(a) Melting Point

**Sources of Data**

Thermodynamic and thermochemical properties of the elements, oxides, chlorides and fluorides [5].

Thermodynamic and thermochemical properties of the bromides and iodides [22]

CaF$_2$ - LiF melting points [23]

CsF - LiF melting points [24].

Heats of transition and heat capacity of Pu [25].

If a booster reaction is used to supply additional heat, the amount of booster used will depend on the scale and geometry of the system. For example, the reduction of PuF$_4$ on the 2 kg scale can be done successfully without a booster [27]. Reductions on the 160 g scale are made with a booster [18].
If equilibrium conditions existed during the bomb reduction of PuF₄ by excess Ca, little or no separation of plutonium from impurities could be expected by virtue of metal salt reactions discussed above. Metals which are more soluble in Ca than in Pu could be expected to concentrate in the Ca metal phase if an excess of Ca is used.

The degree of purification obtained during the bomb reduction of PuF₄ by Ca is a matter of controversy. Separation to some degree of Na, Cu, Ag, B, Sn, Pb, Bi [32] and of Mg, Al, Si, Ni, Fe [33] from Pu has been reported. Other data show no separation for Mg, Al, Ni, Fe [34]. Reduction of PuF₃ by Ca results in little or no separation of Al, Cr and Ni [35]. These conflicting results are probably due to the fact that equilibrium conditions are not achieved in bomb reductions. Kinetic effects are extremely important and a direct comparison of data would require exact duplication of experimental conditions.

**OXIDE DROSSING OF LIQUID PLUTONIUM FUELS**

The remaining processes to be considered are characterized by reactions between a liquid metal phase and a solid phase. Reactions proceed quite slowly and generally the processes do not reach equilibrium. Kinetic considerations in the oxide are most important and indeed much of the development work on these processes has been concerned with studying solid phase kinetics.

Oxide drossing methods have been studied extensively with uranium fuel [36-39]. The method consists of holding the impure molten metal in a refractory oxide crucible for several hours to accomplish selective oxidation of impurities. For the removal of Ce from Pu-rich fuels by MgO at 1700°K the idealized reactions can be written as

\[
2 \text{Pu}(l) + 3 \text{MgO}(s) \rightarrow \text{Pu}_2\text{O}_3(s) + 3 \text{Mg}(v) \quad (15)
\]

\[
2 \text{Ce}(l) + \text{Pu}_2\text{O}_3(s) \rightarrow \text{Ce}_2\text{O}_3(s) + 2 \text{Pu}(l) \quad (16)
\]

Small scale experiments with MgO have shown that temperatures of ~1700°K were required to achieve reasonable rates of removal of Ce and La from liquid Pu-Fe and Pu-Co fuels [41,3]. Similar results were obtained with ZrO₂, Table III [41]. A comparison of ZrO₂ and MgO as reaction crucibles is given in Table IV [41]. ZrO₂ removed La more rapidly from Pu-Fe fissium fuel than did MgO. However, removal of Ce was very slow in both media. Essentially complete removal of Ce was achieved in MgO in 8 hrs, at the expense of high losses (28%) of plutonium to the crucible as shown in Table IV. The behavior of the "noble" elements Fe, Zr, Mo, and Ru in all cases was in agreement with standard free energy estimates.
TABLE III

Effect of Drossing Temperature on Purification of Pu-10 atom % Fe Fissium Alloy by Melting in ZrO$_2$ Crucibles

<table>
<thead>
<tr>
<th>Temp., $^\circ$K</th>
<th>Time, Hr.</th>
<th>$\frac{C}{C_0}$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fe</th>
<th>Zr</th>
<th>Mo</th>
<th>Ru</th>
<th>Ce</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273</td>
<td>4</td>
<td>1.01</td>
<td>1.00</td>
<td>1.04</td>
<td>1.01</td>
<td>0.99</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>1473</td>
<td>4</td>
<td>0.99</td>
<td>0.99</td>
<td>0.96</td>
<td>1.00</td>
<td>0.79</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>1673</td>
<td>4</td>
<td>1.02</td>
<td>0.98</td>
<td>1.09</td>
<td>0.99</td>
<td>0.39</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>C = grams of element per gram of plutonium after reaction.

C<sub>0</sub> = grams of element per gram of plutonium before reaction.

TABLE IV

Effect of Drossing Time at 1673$^\circ$K on Purification of Pu-10 atom % Fe Fissium Alloy and Recovery of Plutonium

<table>
<thead>
<tr>
<th>Time Hr.</th>
<th>Crucible</th>
<th>$\frac{C}{C_0}$</th>
<th>Fe</th>
<th>Zr</th>
<th>Mo</th>
<th>Ru</th>
<th>Ce</th>
<th>La</th>
<th>Pu Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>MgO</td>
<td>0.90</td>
<td>0.93</td>
<td>0.95</td>
<td>1.01</td>
<td>0.57</td>
<td>0.40</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>ZrO$_2$</td>
<td>1.00</td>
<td>0.98</td>
<td>0.95</td>
<td>1.03</td>
<td>0.63</td>
<td>0.16</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ZrO$_2$</td>
<td>1.02</td>
<td>0.98</td>
<td>1.09</td>
<td>0.99</td>
<td>0.39</td>
<td>0.03</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>MgO</td>
<td>1.02</td>
<td>0.98</td>
<td>0.98</td>
<td>1.07</td>
<td>0.40</td>
<td>0.13</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>8, 3</td>
<td>MgO</td>
<td>1.02</td>
<td>0.81</td>
<td>0.85</td>
<td>1.00</td>
<td>&lt;0.006</td>
<td>&lt;0.01</td>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>

REFRACTORY OXIDES AND FLUORIDES AS CONTAINER MATERIALS FOR PLUTONIUM

An examination of standard free energy of formation data for oxides at 1000$^\circ$K suggests the use of MgO, ThO$_2$, and CaO as container materials for molten Pu [5]. The reaction of MgO with Pu in an inert atmosphere, 1 atmosphere pressure at 1000$^\circ$K can be represented as

$$2 \text{Pu}(l) + 3 \text{MgO}(s) \rightarrow \text{Pu}_2O_3(s) + 3 \text{Mg}(l)$$

(17)

It is assumed that Pu$_2O_3(s)$ is immiscible with MgO(s) and the activity of Pu(l) is $\sim$1, the equilibrium activity of Mg in Pu is $6.6 \times 10^{-3}$. From the Pu-Mg phase diagram
[42] and the assumption that Mg behaves ideally in the Mg-rich liquid, the activity coefficient of Mg in Pu-rich liquid is estimated to be ~20. The equilibrium concentration of Mg in Pu would therefore be ~33 parts of Mg per million parts of Pu, wt. basis. The corresponding amount of oxide formed, would be 22 parts of O per million parts Pu. These estimates can be compared with results obtained in the electrorefining process where MgO is contacted for several days with Pu(£). The Mg concentration in the product metal is equal to or less than 5 p.p.m. and the O concentration is ~20 p.p.m.

Similar estimates for CaO and CaF₂ as container materials for Pu show that the equilibrium activity of Ca in Pu for both cases will be ~1 x 10⁻⁴ at 1000°K and 1 atm pressure. Similarly, the estimated equilibrium activity of Th in Pu is ~2 x 10⁻⁷.

REFERENCES


[40] Leary, J. A., LA-2132 (1957).


DENSITIES OF SOME LOW MELTING PLUTONIUM ALLOYS*

R. H. PERKINS, L. A. GEOFFRION AND J. C. BIERY,
UNIVERSITY OF CALIFORNIA,
LOS ALAMOS SCIENTIFIC LABORATORY,
N. MEX., UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

DENSITIES OF SOME LOW MELTING PLUTONIUM ALLOYS. The change in fuel density with temperature is an important parameter in nuclear reactor design. For molten fuels, such as are used in LAMPRE-type reactors, it is also necessary to know the volume change on melting. A volumeter employing NaK as a working fluid was used to obtain these data for various plutonium and cerium base alloys over the range 25–800°C. Cerium and several low-melting binary cerium alloys were studied with this equipment. Cerium, Ce-Co, Ce-Ni, and Ce-Cu alloys all exhibit an increase in density on melting, while a Ce-Mn alloy expands on melting. The melting temperatures of several of these alloys differ from those reported in the literature, and the compositions of several eutectics in these systems are also reported incorrectly. The densities of unstabilized and gallium-stabilized plutonium and Pu-10 at.%Fe were measured and compared over this temperature range. All these materials expand on freezing. At 675°C, molten unstabilized plutonium is approximately 2% more dense than Pu-1 wt.%Ga alloy. Molten Pu-Fe alloy containing 0.2 wt.%Ga at 435°C is 0.3% less dense than unstabilized alloy. This indicates that there is short-range ordering of plutonium atoms by gallium in the liquid state. The materials containing gallium melted over a 20°C temperature range, while the unstabilized materials melted sharply. Pu-Co-Ce alloys containing 3, 5, 6.2 and 8 g Pu/cm³ were investigated. They all melt in the range 425–442°C and expand on freezing. This expansion increases with increasing plutonium content from 1.3% for the 3 g Pu/cm³ alloy to 3% for the 8 g Pu/cm³ material. Manganese additions to this fuel system are being studied in an attempt to reduce this expansion on freezing.

DENSITE DE CERTAINS ALLIAGES AU PLUTONIUM A BAS POINT DE FUSION. La variation de la densité du combustible en fonction de la température est un paramètre important pour l'étude des réacteurs nucléaires. Pour certains combustibles fondu, comme ceux que l'on utilise dans les réacteurs du type LAMPRE, il faut aussi connaître la variation de volume à la fusion. Les auteurs ont utilisé un volumètre dans lequel NaK était le fluide de service pour déterminer ces données pour certains alliages à base de plutonium et de céridum, dans l'intervalle de température compris entre 25 et 800°C. Avec ce dispositif, ils ont étudié le céridum et plusieurs alliages binaires au céridum à bas point de fusion. Le céridum et les alliages Ce-Co, Ce-Ni et Ce-Cu ont accusé une augmentation de la densité à la fusion; en revanche, l'alliague Ce-Mn se dilata à la fusion. Les points de fusion de plusieurs de ces alliages diffèrent des valeurs déjà publiées; de même, les compositions indiquées pour plusieurs mélanges eutectiques sont incorrectes. Les auteurs ont mesuré et comparé, pour l'intervalle de température indiqué ci-dessus, les densités du plutonium et du plutonium contenant 10 atomes pour cent de fer, non stabilisés et stabilisés au gallium. Tous ces alliages se dilatent en se solidifiant. A 675°C, la densité du plutonium fondu non stabilisé est supérieure d'environ 2% à celle du plutonium à 1% en poids de gallium. À 435°C, la densité de l'alliague Pu-Fe fondu, à 0,3% en poids de gallium, est inférieure de 0,3% à celle de l'alliague non stabilisée. Cela indique qu'à l'état liquide le gallium assure un ordre à faible portée des atomes de plutonium. Les alliages contenant du gallium fondent dans un intervalle de température de 20°C, tandis que les alliages non stabilisés fondent brusquement. Les auteurs ont étudié des alliages de Pu-Co-Ce contenant 3, 5, 6.2 et 8 g de Pu/cm³. Tous fondent entre 425 et 442°C et se dilatent en se solidifiant. Cette dilatation augmente, en fonction de la teneur en plutonium, de 1,3% pour un alliage contenant 3 g de Pu/cm³ à 3% pour un alliage contenant 8 g de Pu/cm³. Les auteurs cherchent à réduire cette dilatation en ajoutant du manganèse à ce combustible.

* Work performed under the auspices of the USAEC.
1. Introduction

The Reactor Division of Los Alamos Scientific Laboratory is investigating the use of molten plutonium-containing fuels for fast reactor application. The molten fuel does not suffer from irradiation damage, so higher fuel burnup is feasible.

For the proper design and safe operation of a nuclear reactor, several of the physical properties of the fuel must be known to a high degree of ac-
Accuracy. Two of the most important of these are the density of the fuel at operating temperature, and the change of density with temperature. Since all plutonium alloys that have been studied pass through a solid-liquid transition between room temperature and operating temperature, the change in density on melting must also be known.

The fuel used in LAMPRE (Los Alamos Molten Plutonium Reactor Experiment) was a Pu-2.5 w/o (weight per cent) Fe eutectic alloy with a melting temperature of 411°C. However, limitations imposed on reactor design by this fuel caused consideration of other plutonium-containing alloys for use in future generations of this type of reactor. Several ternary alloys containing plutonium and cerium as two components have satisfactorily low melting points. The Pu-Ce-Co system at the present time appears to be the most acceptable. It exhibits little change in melting temperature with wide variation in plutonium concentration, which allows flexibility in reactor design. Other alloys that have received some consideration contain nickel, copper, and manganese as the third constituent.

These fuel alloys are difficult to handle experimentally since they oxidize readily, react with many solvents, and contain a poisonous fissile material. The densities of these alloys must be known throughout the temperature range 25-800°C and through the solid-liquid transition. The only experimental apparatus that appears suitable for measuring expansion coefficients of these materials under these experimental conditions is a volumeter.

While a volumeter is capable of measuring accurately the volume coefficient of expansion of materials, it cannot be used for absolute density measurements. Therefore, a density determination at a known temperature must be coupled with volumeter measurements to give the desired data. The weight loss technique using immersion in bromobenzene at room temperature proved to be satisfactory.

2. Equipment and Operating Procedure

The volumeter that was used in this investigation is described in detail elsewhere [1,2]. Briefly, it consists of two weld-sealed stainless steel containers of nearly equal volume located in a copper block inside a furnace. One container holds a tantalum crucible and the specimen being measured; the other contains a tantalum crucible and a tantalum specimen used as a control reference material. Stainless steel capillaries of equal length and volume connect each stainless steel container to a glass viewing capillary. A schematic diagram of this apparatus is shown in Fig. 1.
The working fluid that fills the specimen containers, the stainless steel capillaries, and portions of the glass capillaries is NaK (22 w/o Na - 78 w/o K). This alloy melts at -10°C and has a vapor pressure of 860 mm Hg at 800°C [3]. This relatively high vapor pressure at 800°C requires an over-pressure of an inert gas to prevent boiling. The NaK and the fuel alloys that were studied are essentially insoluble in each other.

The room temperature densities of the specimens were determined by weight loss immersion in bromobenzene. All weighings were to ± 0.1 mg and
the densities were accurate to ± 0.002 g/cc. The temperatures at which these measurements were made were known to ± 0.1°C.

Calibrated thermocouples were used for temperature measurements throughout the runs. The measurements made in the volumeter furnace have errors of less than ± 2°C when all errors resulting from thermal stability and thermal asymmetries are considered.

The equations utilized in calculating the sample density are derived and presented in the paper by Knight [1]. The main equation necessary in these calculations is given below as Eq. 1.

\[
C_s = - \left\{ \frac{\Delta V_D}{\Delta T} \left[ 1 - (T - T_G)(C_{M-C}) \right] + (V_{FC} - V_{FS})(C_C) \right. \\
\left. + (V_{KS} - V_{KC}) + (V_{MS} - V_{MC})(C_{M-h}) \right\} / V_S
\] (1)

The terms in this equation are defined as follows:

\( t \) = ambient, equilibrium temperature of the entire apparatus at time of initial data recording, °C.

\( T \) = elevated temperature of container assemblies at time of observation, °C.

\( \Delta T = T - t \), °C.

\( T_G \) = temperature of glass capillaries and contained liquid medium at time of observation, °C.

\( \Delta V_C \) = observed volume displacement, between \( t \) and \( T \), of liquid interface in capillary from control sample assembly, \( \text{cm}^3 \).

\( \Delta V_S \) = observed volume displacement, between \( t \) and \( T \), of liquid interface in capillary from specimen container assembly, \( \text{cm}^3 \).

\( \Delta V_D = \Delta V_C - \Delta V_S \), \( \text{cm}^3 \).

\( V_{FC} \) = volume of steel control container at \( t \), \( \text{cm}^3 \).

\( V_{FS} \) = volume of steel specimen container at \( t \), \( \text{cm}^3 \).

\( V_{KC} \) = volume of tantalum crucible and tantalum sample in control container at \( t \), \( \text{cm}^3 \).

\( V_S \) = volume of specimen at \( t \), \( \text{cm}^3 \).

\( V_{KS} \) = volume of tantalum crucible in specimen container at \( t \), \( \text{cm}^3 \).

\( V_{MC} = V_{FC} - V_{KC} \) = volume of NaK in control container at \( t \), \( \text{cm}^3 \).
\[ V_{MS} = V_{FS} - V_{KS} - V_S \] is the volume of NaK in specimen container at \( t \), cm\(^3\).

\[ C_C = \text{cubic expansion coefficient of stainless steel container upon heating from } t \text{ to } T, \text{ cm}^3/\text{cm}^3/°C. \]

\[ C_K = \text{cubic expansion coefficient of tantalum upon heating from } t \text{ to } T, \text{ cm}^3/\text{cm}^3/°C. \]

\[ C_{M-h} = \text{cubic expansion coefficient of NaK upon heating from } t \text{ to } T, \text{ cm}^3/\text{cm}^3/°C. \]

\[ C_{M-c} = \text{cubic expansion coefficient of NaK upon cooling from } T \text{ to } T_G, \text{ cm}^3/\text{cm}^3/°C. \]

\[ C_S = \text{cubic expansion coefficient of specimen upon heating from } t \text{ to } T, \text{ cm}^3/\text{cm}^3/°C. \]

The above equation with the required supporting equations and input data was processed on a 7094 digital computer. From \( C_S \), the known temperature change, and the original sample density, the density of the sample was calculated from Eq. 2.

\[ \rho_T(\text{specimen}) = \rho_T(\text{specimen})/(1.0 + (T - t) C_S) \] (2)

For many applications, a density coefficient is more useful than the volume coefficient. Therefore, the final density data were processed to produce coefficients which can be used in Eq. 3. Two densities at 0°C were calculated. A solid density for use with the solid phase portion of the curve was calculated by the linear extrapolation shown in Eq. 4.

\[ \rho_0°C = \rho_T + (\rho_T - \rho_{T_1})t/(T_1 - t) \] (4)

In a similar manner, a pseudo liquid density at 0°C was calculated by extrapolating the liquid portion of the density curve back to 0°C with Eq. 5.

\[ \rho_L0°C = \rho_{T_N} + (\rho_{T_N} - \rho_{T_{N+1}})(T_N)/(T_{N+1} - T_N) \] (5)

In several of the experiments, small amounts of gas were evolved when the specimens became molten. This caused variations in height of NaK in the glass capillaries with changes in overpressure of helium above the NaK. The volume
of this evolved gas at a given temperature could readily be determined by varying the pressure of the helium above the NaK between known values and observing the effect of this variation on the height of the NaK in the glass capillaries. The computer program was written so the final data were corrected for these evolved gases.

3. Results and Discussion

The apparatus was standardized and experience was gained in its operation by measuring the densities and coefficients of expansion of (1) nickel, (2) cerium, (3) Ce-Co alloys, (4) Ce-Ni alloys, (5) Ce - 15 w/o Cu alloy, and (6) Ce - 6 w/o Mn alloy. Cerium metal and all the binary cerium alloys that were studied except the Ce-Mn alloy increase in density on melting. The latter expands approximately 1% on becoming molten.

3.1 Plutonium Metal

Several investigators have measured the densities and phase transition temperatures of plutonium metal [1,4,5,6]. Unfortunately, the density of this metal is influenced by small amounts of impurities and by microcracks [6]. Since electrorefined plutonium containing less than 300 ppm impurities is now available, it appeared desirable to measure the density and coefficients of expansion of this material using the volumeter technique. The impurities detected in the plutonium that was used in this investigation are listed in Table I.

<table>
<thead>
<tr>
<th>Analysis of Plutonium Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>Pu</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Am</td>
</tr>
<tr>
<td>Si</td>
</tr>
</tbody>
</table>

The density data for this material are plotted in Fig. 2. Experimental points were obtained on both heating and cooling. In most respects these data agree with the information obtained by other investigators [1,4,5,6]. The coefficients of expansion of all phases and the densities of the delta, delta
prime, epsilon, and liquid phases are in excellent agreement with the best information that is available in the literature. Transition temperatures between the different phases also agree closely. However, the densities of the alpha, beta, and gamma phases that were obtained in this study are somewhat less than the values obtained by other investigators, apparently due to microcracks in the specimen [6].

![Graph showing densities of unstabilized and stabilized (1 w/o Ga) plutonium as functions of temperature.](image)

**FIG. 2.** Densities of unstabilized and stabilized (1 w/o Ga) plutonium as functions of temperature.

The addition of gallium to plutonium metal stabilizes the delta phase at room temperature [7]. A specimen of Pu - 1 w/o Ga alloy was studied in the volumeter. The data are plotted in Fig. 2.
At room temperature the specimen was almost completely delta plutonium, though a very small fraction existed as the alpha phase. As the temperature was raised this small amount of alpha was transformed successively to beta, gamma, and delta plutonium. At 325°C, a temperature at which unstabilized plutonium is in the delta phase, the densities of the unstabilized and stabilized materials are identical. However, the coefficients of expansion of the two materials are considerably different. While the coefficients of expansion of both unstabilized and stabilized are negative, the former exhibits a much larger (negative) coefficient.

The addition of gallium suppresses the transformation to the delta prime phase and makes the transformation to the epsilon phase sluggish and incomplete. While the delta prime - epsilon transition temperature is 480°C, a change in expansion coefficient of the stabilized plutonium did not become noticeable until a temperature of 500°C was reached. Between 500 and 585°C, the stabilized material exhibits a rather large negative coefficient of expansion. (The volume coefficient of expansion in this region is approximately $-2.1 \times 10^{-4}$, as compared to $-5.0 \times 10^{-5}$ for unstabilized delta plutonium.)

In this temperature range, both delta and epsilon phases are stable. As the temperature is raised, more of the plutonium is converted to the epsilon phase, until at 585°C delta plutonium is not stable. Between 585 and 640°C, the epsilon Pu - 1 w/o Ga alloy exhibits a positive coefficient of expansion, though this expansion coefficient is somewhat less than that of unstabilized plutonium. The density of the stabilized material in this temperature range is also less than that of pure plutonium. This density difference is not due to the presence of $\text{Pu}_3\text{Ga}$, since the solubility of gallium in epsilon plutonium is 20%. However, the structure of the solid is apparently influenced by the gallium addition.

The Pu - 1 w/o Ga alloy begins to melt at 640 ± 5°C, but the melting is not complete until a temperature of 665°C is reached. The density of the liquid at this temperature is 2% less than that of pure plutonium. Apparently the addition of gallium to plutonium not only produces an alloy that melts over a 25°C temperature range, but it also influences the structure of the liquid. This density difference between stabilized and unstabilized material becomes smaller as the temperature increases.

A small amount of gas came out of solution in the sample when it became molten. The height of NaK in the glass capillary connected to the sample
container became dependent on the pressure of helium in the gas space above it. Compensations for this evolved gas were introduced into the calculations, and data obtained in the liquid state were satisfactory. However, during cooling some of this evolved gas was trapped when the sample solidified. This entrapment caused the data points obtained on cooling to fall below those that were obtained on heating.

3.2 Pu-Fe

The fuel for LAMPRE was Pu - 2.5 w/o Fe alloy (10 a/o [atomic percent] Fe) stabilized by the addition of 0.2 w/o Ga. The gallium was added to prevent damage to the tantalum container capsules by fuel expansion due to phase transitions during heating and cooling. In the solid state, this alloy is present principally as the intermetallic compound Pu$_6$Fe. Therefore, only 0.2 w/o gallium is required to stabilize the 30 a/o that is present as plutonium. Specimens of both stabilized and unstabilized Pu-Fe alloys were prepared for study in the volumeter. Analyses of these materials are shown in Table II.

### TABLE II

Analyses of Stabilized and Unstabilized Pu-Fe Alloys

<table>
<thead>
<tr>
<th>Element</th>
<th>Per Cent of Element</th>
<th>Unstabilized Alloy</th>
<th>Stabilized Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu</td>
<td>97.55 ± 1</td>
<td>97.5 ± 1</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>2.38 ± 0.1</td>
<td>2.38 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>-</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>0.0288</td>
<td>0.0011</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.0020</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 0.010</td>
<td>&lt; 0.010</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>&lt; 0.010</td>
<td>&lt; 0.012</td>
<td></td>
</tr>
</tbody>
</table>

The results of the volumeter runs on these materials are shown in Fig. 3. The curve obtained for the unstabilized alloy clearly shows the various phase transformations that occur in the solid state. This is a eutectic alloy, and it melts sharply at 411°C. The data obtained during the cooling portion of the cycle agree with those obtained on heating except in the regions where gamma and beta are the stable plutonium phases. Apparently the cooling rate was too rapid for the phase transitions to occur before the measurements were taken.
FIG. 3. Effects of temperature on the densities of stabilized (0.2 w/o Ga) and unstabilized Pu - 2.55 w/o Fe alloys.

The fuel containing gallium stabilizer does not exhibit phase transitions in the solid state. The densities of the stabilized and unstabilized alloys are identical at 400°C. This stabilized alloy begins melting at 411°C, but it does not melt sharply. The alloy is not completely molten until a temperature of 432°C is reached. In addition, the density of the molten stabilized fuel at 435°C is 0.7% less than that of the stabilized material. Again the effect of gallium on density of plutonium appears in the liquid state as well as in the solid state. This difference in density between the stabilized and unstabilized liquid alloys becomes less as the temperature is raised (apparently due to destruction of the ordering effect attributed to the gallium).
The linear portions of the curves - the regions where the alloys are liquid, and the region between 25 and 325°C for the stabilized alloy - can be expressed mathematically in simple terms.

Unstabilized alloy:

\[ 410°C < T < 800°C \quad \rho_L = 16.94 - 1.64 \times 10^{-3} T \]

Stabilized alloy:

\[ 25°C < T < 325°C \quad \rho_S = 16.72 - 1.69 \times 10^{-3} T \]
\[ 435°C < T < 800°C \quad \rho_L = 16.77 - 1.42 \times 10^{-3} T \]

3.3 Pu-Co-Ce

The fuel for the first core of the FRCTF (Fast Reactor Core Test Facility) will be a Pu-Co-Ce alloy containing 6.2-8.0 g Pu/cc. If a large power reactor based on this fuel system is built, it must utilize a fuel of lower plutonium concentration - perhaps as low as 3.0 g Pu/cc. To obtain a complete picture of the densities of potential fuels in this system, volumeter samples of low-melting alloys containing nominally 3.0, 5.0, 6.2, and 8.0 g Pu/cc were prepared. Alloys containing higher concentrations were not studied since they are apparently too corrosive for the container materials that are presently being considered. Analyses of these alloys are shown in Table III.

The density data obtained on the alloy containing nominally 3.0 g Pu/cc are plotted in Fig. 4. There are no phase transitions in the solid state, and the experimental points fall on a straight line. Sufficient cerium is present to stabilize the plutonium in the delta phase. The alloy melts over a very narrow temperature range at 425 ± 2°C. There is a density increase of 1.3% on melting. A straight line also fits the data points in the molten region. The density of this alloy at a given temperature can be calculated from the following equations:

\[ 25°C < T < 425°C \quad \rho_S = 9.080 - 6.80 \times 10^{-4} T \]
\[ 430°C < T < 800°C \quad \rho_L = 9.221 - 7.43 \times 10^{-4} T \]

The specimen evolved a small amount of gas when it melted. While the sample was molten, the amount of gas could be calculated and compensations were made for it. However, when the sample was solidified, it trapped some of this gas, and the density readings were erroneously low. Additional lowering of the temperature cracked the sample in a number of places. These cracks contacted some of the gas bubbles, and the NaK filled these voids. At 25°C, the density agreed with that originally measured at this temperature.
Volumeter runs were made on two Pu-Co-Ce samples containing nominally 5.0 g Pu/cc. Although the two samples came from the same fuel batch, their densities at 25°C differed by 1.3%. The density curves for these two specimens are plotted in Fig. 5.

In the solid state, the two specimens exhibited the same coefficients of expansion. Although the two curves are displaced from one another, they are parallel. The data obtained with solid samples can best be fit with a slightly curved, rather than a straight, line. Both specimens began melting at 438 ± 2°C. However, the less dense sample did not become completely molten until a temperature of 500°C was reached, while the other specimen was molten at 465°C. The slopes of the two curves in the liquidus region are somewhat different. The more dense specimen increased in density by 1.8% on melting, while the less dense sample decreased in volume by 1.0%.

Linear expressions that closely approximate the solid and liquid regions for the more dense alloy are as follows:

\[
\begin{align*}
25°C < T < 435°C & \quad \rho_S = 10.40 - 7.80 \times 10^{-4} T \\
465°C < T < 800°C & \quad \rho_L = 10.68 - 9.65 \times 10^{-4} T
\end{align*}
\]
The two samples of nominally 6.2 g Pu/cc Pu-Co-Ce alloy behaved almost identically in the volumeter runs. At 25°C, their densities differed by only 0.12%, and they were essentially identical over the entire temperature range. The samples melted sharply at 440 ± 2°C, and the alloy exhibited a 2.2% increase in density on melting. A plot of the data for these two tests is shown as Fig. 6.

While the density curve in the solid region is not linear below 100°C, the portion between 150 and 435°C can be approximated by a linear expression. The region between 450 and 800°C also is linear. These portions of the curve for the more dense sample fit the following equations.

\[
\begin{align*}
150^\circ C &< T < 435^\circ C & \rho_S &= 10.944 - 8.37 \times 10^{-4} T \\
450^\circ C &< T < 800^\circ C & \rho_L &= 11.215 - 9.27 \times 10^{-4} T
\end{align*}
\]
Again gas bubbles were entrapped by the samples on freezing and the density data obtained on cooling in the solid state were low.

Volumeter runs were also made on two samples of a Pu-Co-Ce alloy containing approximately 8.0 g Pu/cc. This information is plotted in Fig. 7. The densities of the two samples differed by 0.66% at 25°C, and the specimens exhibited very similar expansion characteristics throughout the runs. They both began melting at 415 ± 3°C, but they did not become completely molten until a temperature of 445 ± 3°C was reached. Although both samples evolved gas on melting, apparently only a small fraction of this was trapped in the samples when they solidified. Therefore, the heating and cooling data are not significantly different.
Equations that fit the linear portions of the density curve for the most dense sample are as follows:

\[
200°C < T < 410°C \quad \rho_S = 11.75 - 7.85 \times 10^{-3} \, T
\]
\[
445°C < T < 800°C \quad \rho_L = 12.164 - 8.78 \times 10^{-4} \, T
\]

3.4 Mn Additions to Pu-Co-Ce

Plutonium and the plutonium-containing alloys that were studied all expand on freezing. In the Pu-Co-Ce system, there is an increase in this expansion with increasing plutonium concentration. This expansion on freezing is a potential source of trouble in a nuclear reactor. While it is intended that the fuel be molten at all times in an operating system, some unforeseen loss
of power could result in freezing of the fuel in the reactor core. Under certain freezing conditions the container capsules might be bulged or ruptured. While this problem may be eliminated by controlling the freezing conditions or increasing the strength of the container material, it is more desirable to modify the fuel system to eliminate or reduce the expansion on freezing.

As was previously stated, the Ce-Mn alloy is the only binary cerium-containing alloy of those investigated that becomes more dense (by approximately 1%) on freezing. Alloys in the Pu-Mn-Ce system with plutonium concentrations less than 8 g/cc all melt at temperatures in excess of 600°C [8], so they are not suitable for use in a molten fuel system. An alternate ap-
The approach is the addition of Mn to Pu-Co-Ce fuels to reduce their expansion on freezing.

Specimens of alloys containing 6.5 and 8.0 g Pu/cc with Mn additions were prepared and studied with the volumeter. The results of this investigation are summarized in Table IV.

**TABLE IV**

<table>
<thead>
<tr>
<th>Nominal g Pu/cc</th>
<th>Wt.% Pu</th>
<th>Wt.% Ce</th>
<th>Wt.% Mn</th>
<th>Melting Temp. (°C)</th>
<th>% Expansion on Freezing</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>60.8</td>
<td>30.3</td>
<td>0</td>
<td>440-442</td>
<td>2.3</td>
</tr>
<tr>
<td>6.5</td>
<td>60.2</td>
<td>26.3</td>
<td>3.0</td>
<td>432-435</td>
<td>2.0</td>
</tr>
<tr>
<td>6.5</td>
<td>59.1</td>
<td>22.2</td>
<td>5.5</td>
<td>440-442</td>
<td>1.5</td>
</tr>
<tr>
<td>6.5</td>
<td>58.7</td>
<td>19.2</td>
<td>9.0</td>
<td>440-442</td>
<td>1.0</td>
</tr>
<tr>
<td>8.0</td>
<td>68.1</td>
<td>23.9</td>
<td>0</td>
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</tr>
<tr>
<td>8.0</td>
<td>67.1</td>
<td>15.2</td>
<td>7.5</td>
<td>420-435</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The alloy containing 3.0 w/o Mn became completely molten in the narrow range 432-435°C. The alloys with higher manganese contents, however, did not melt completely until higher temperatures were reached. A radiograph of the capsule containing the 9.0 w/o Mn alloy at the conclusion of the volumeter study revealed that it had not become completely molten during the experiment. In all cases, however, the expansion on freezing occurred in a narrow temperature range just above the temperature where the sample began to melt.

Manganese additions reduce the expansion on freezing of Pu-Co-Ce alloys, but do not entirely eliminate it. A limited amount of differential thermal analysis studies indicates that larger additions of manganese to fuels significantly raises their melting temperatures [8]. Because of the relatively high temperatures at which these quaternary alloys become completely molten, they are not suitable fuels for nuclear reactors. Therefore, no additional studies are planned on this system.

4. Summary and Conclusions

Densities of unstabilized and stabilized (1 w/o Ga) plutonium were measured over the temperature range 25°-800°C. Gallium not only stabilizes the delta phase of plutonium in the solid state, but also influences its melting temperature and the density of the liquid metal. The Pu - 2.5 w/o Fe
and the Pu - 2.5 w/o Fe - 0.2 w/o Ga alloys were also studied with the volu-
meter. The unstabilized alloy melts at 411 ± 2°C with a 1.5% decrease in
volume. Gallium addition suppresses phase transitions in the solid state and
affects melting temperature and density of the molten alloy.

Pu-Co-Ce alloys containing 3, 5, 6.2, and 8 g Pu/cc were studied with the
volumeter. These alloys all melt in the range 425 -442°C, and they become more
dense on melting. The change in density on melting increases with increasing
plutonium content from 1.3% for the 3 g Pu/cc alloy to 3% for the 8 g/cc
material. The addition of manganese to 6.2 and 8 g/cc alloys significantly re-
duced this expansion on freezing. However, manganese additions of 5.5 w/o and
higher adversely affected the melting temperatures of these fuels.

5. References

1. Knight, F. W., in Plutonium 1960 (Grison, E., Lord, W. B. H., and
Trans. Met. Soc. AIME.
(1955) 37-38.
5. Coffinberry, A. S. and Waldron, M. B., The Physical Metallurgy of
Plutonium, Progr. in Nuclear Energy, 1, Series V, Pergamon Press,
6. Nelson, R. D., Becker, C. R., Bierlein, T. K., and Bowman, F. E.,
12 (1964) 226-236.
8. Thamer, B. J., Los Alamos Scientific Laboratory, Private Communication.
CALCUL THERMODYNAMIQUE DU COEFFICIENT DE DISTRIBUTION ENTRE PHASES LIQUIDE ET SOLIDE D'UN ELEMENT EN PRESENCE D'AUTRES CONSTITUANTS EN SOLUTION DILUEE DANS UN METAL:
APPLICATION A LA PURIFICATION DU BERYLLIUM

P. DESRE
ECOLE NATIONALE SUPERIEURE D'ELECTROCHIMIE ET D'ELECTROMETALLURGIE,
B. SCHAUB
CENTRE D'ETUDES NUCLEAIRES DE GRENOBLE
ET
E. BONNIER
ECOLE NATIONALE SUPERIEURE D'ELECTROCHIMIE ET D'ELECTROMETALLURGIE,
GRENOBLE, FRANCE

Abstract — Résumé — Аннотация — Resumen

THERMODYNAMIC CALCULATION OF THE DISTRIBUTION COEFFICIENT BETWEEN THE LIQUID AND SOLID PHASES OF AN ELEMENT IN DILUTE SOLUTION IN A METAL: APPLICATION TO THE PURIFICATION OF BERYLLIUM. The authors calculate the distribution coefficient $I_j$ between the liquid and solid phases of an element $i$ in the presence of other elements $j$ in a solvent $M$ ($I_j = x'_i / x_i$, where $x'_i$ and $x_i$ are the atomic fractions of $i$ in the solid and liquid phases respectively) from the thermodynamic properties of binary systems of the type $(i, M)$, $(j, M)$ and $(i, j)$.

They show that the interaction of all the elements present may, under certain conditions, strongly affect the value of the coefficient $I_j$.

This effect is pronounced if the following condition is fulfilled:

$$\gamma_{i(M)} > \gamma_{j(M)} > \gamma_{ij}$$

where $\gamma_{i(M)}$, $\gamma_{j(M)}$, and $\gamma_{ij}$ are the limiting activity coefficients of the constituents $i$ and $j$ in the $(i, M)$, $(j, M)$ and $(i, j)$ liquid state systems.

It is a simple matter to deduce from this condition an application to the purification of metals by the zone-melting method: the condition enables one to choose an element $j$ which is added deliberately to a metal in order to facilitate the elimination of an element $i$ (subsequent elimination of the element $j$ being also, of course, a simple matter).

For example, the authors were able to confirm that the addition of aluminium to beryllium enables one to improve the elimination of iron during the purification of the beryllium by the zone-melting technique, the aluminium acting as a carrier.

CALCUL THERMODYNAMIQUE DU COEFFICIENT DE DISTRIBUTION, ENTRE PHASES LIQUIDE ET SOLIDE, D'UN ELEMENT EN PRESENCE D'AUTRES CONSTITUANTS EN SOLUTION DILUEE DANS UN METAL: APPLICATION A LA PURIFICATION DU BERYLLIUM. Les auteurs calculent le coefficient de distribution $I_j$ entre phases liquide et solide d'un élément $i$ en présence d'autres éléments $j$ dans un solvant $M$ ($I_j = x'_i / x_i$, $x'_i$ et $x_i$ représentant respectivement les fractions atomiques de $i$ dans les phases solide et liquide), à partir des propriétés thermodynamiques des systèmes binaires de type: $(i, M)$, $(j, M)$, $(i, j)$.

On montre que les interactions de tous les éléments en présence peuvent dans certaines conditions influer fortement sur la valeur du coefficient $I_j$. 

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Cette influence sera marquée si la condition suivante est vérifiée:

\[ \gamma_i^{\infty} \cdot \gamma_j^{\infty} > \gamma_{ij} \]

\( \gamma_i^{\infty} \), \( \gamma_j^{\infty} \) et \( \gamma_{ij} \) sont les coefficients d'activité limite des constituants i et j dans les systèmes à l'état liquide: (i, M); (j, M) et (i, j).

Il est aisé d'en déduire une application à la purification des métaux, notamment par la méthode dite de la zone fondu. En effet, la condition précédente permet de choisir un élément j à ajouter volontairement à un métal pour faciliter l'élimination d'un élément i, étant bien entendu qu'il est facile ensuite d'éliminer l'élément j.

Ainsi les auteurs ont vérifié que l'addition d'aluminium au béryllium permettait d'améliorer l'élimination du fer au cours de la purification du béryllium par la technique de la zone fondu, l'aluminium jouant alors le rôle d'entraîneur.

Pour la purification des métaux, notamment par la méthode dite de la zone fondu, il est aisé d'en déduire une application. En effet, la condition précédente permet de choisir un élément j à ajouter volontairement à un métal pour faciliter l'élimination d'un élément i, étant bien entendu qu'il est facile ensuite d'éliminer l'élément j.

Ainsi les auteurs ont vérifié que l'addition d'aluminium au béryllium permettait d'améliorer l'élimination du fer au cours de la purification du béryllium par la technique de la zone fondu, l'aluminium jouant alors le rôle d'entraîneur.
De esta forma, los autores han comprobado que la adición de aluminio al berilio facilita la eliminación del hierro en el proceso de purificación del berilio por la técnica de la zona fundida; en ese caso, el aluminio desempeña el papel de portador.

Le coefficient de distribution $\Gamma_i$ entre phases liquide et solide d'un élément $i$ en présence de $n$ éléments $j$ est défini par le rapport de la fraction atomique du constituant $i$ dans la phase solide $x_i^s$ à la fraction atomique de $i$ dans la phase liquide $x_i^l$:

$$\Gamma_i = \frac{x_i^l}{x_i^s}.$$  

Les coefficients d'activité limites des constituants dans le solvant $M$ ainsi qu'une méthode d'estimation des paramètres d'interaction de Wagner sont utilisés pour le calcul du coefficient de distribution $\Gamma_i$.

Nous traiterons d'abord le calcul du coefficient de distribution d'un constituant $i$ considéré comme unique dans le solvant $M$.

L'écriture thermodynamique de l'équilibre entre les phases liquide et solide conduit à la relation

$$\ln \Gamma_i = \ln \frac{\gamma_i^l}{\gamma_i^s} - \left( \frac{L_{f,i}}{RT} - \frac{T_{f,i}}{R} \right) + \frac{\Delta C_{p,i}}{R} \ln \frac{T}{T_{f,i}}.$$  

$T$ : température à laquelle a lieu l'équilibre.

$\gamma_i^l$ : coefficient d'activité de l'élément $i$ dans $M$ liquide à la température $T$ (référence liquide).

$\gamma_i^s$ : coefficient d'activité de l'élément $i$ dans $M$ solide à la température $T$ (référence solide).

$L_{f,i}$ : chaleur de fusion de l'élément $i$.

$T_{f,i}$ : température de fusion de l'élément $i$.

$\Delta C_{p,i}$ : différence entre les chaleurs spécifiques de $i$ liquide et de $i$ solide.

La concentration de l'élément $i$ dans le solvant $M$ étant faible, on peut développer les fonctions $\ln \gamma_i$ et $\ln \gamma_i'$ en série de Taylor au voisinage de $x_i = 0$ et de $T = T_{f,M}$. En se limitant au premier ordre, on obtient les équations suivantes:

$$\ln \gamma_i = \ln \gamma_i^\infty + x_i \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right) + \frac{T_{f,M} - T}{RT^2} \Delta H_i^\infty,$$

$$\ln \gamma_i' = \ln \gamma_i'^\infty + x_i' \left( \frac{\partial \ln \gamma_i'}{\partial x_i'} \right) + \frac{T_{f,M} - T}{RT^2} \Delta H_i'^\infty.$$  

$\gamma_i^\infty$ et $\gamma_i'^\infty$ sont respectivement les coefficients d'activité limites du constituant $i$ dans la phase liquide et dans la phase solide.

$\Delta H_i^\infty$ et $\Delta H_i'^\infty$ sont respectivement les enthalpies partielles limites du constituant $i$ dans la phase liquide et dans la phase solide.
En combinant les relations (1), (2) et (3), il vient

\[
\ln \gamma_i = \ln \frac{\gamma_i^\infty}{\gamma_i^0} + x_i \left[ \frac{\partial \ln \gamma_i}{\partial x_i} - \frac{\partial \ln \gamma_i^0}{\partial x_i} \right] + \frac{T_{f,M} - T}{RT^2} (\Delta H_i^\infty - \Delta H_i^0) \\
- \left[ L_{f,i} \frac{T - T_{f,i}}{RTT_{f,i}} + \frac{\Delta C_{P,i}}{RT} (T_{f,i} - T) + \frac{\Delta C_{P,i}}{R} \ln \frac{T}{T_{f,i}} \right]
\]

(4)

Cette équation permet de calculer le coefficient de distribution de l'élément i à partir des propriétés thermodynamiques des phases liquide et solide.

On définit le coefficient de distribution limite \( \Gamma_i^0 \) obtenu pour \( x_i = 0 \) et \( T = T_{f,M} \) à partir de l'équation (4):

\[
\ln \Gamma_i^0 = \ln \frac{\gamma_i^\infty}{\gamma_i^0} - \left[ L_{f,i} \frac{T_{f,M} - T_{f,i}}{RTT_{f,i}} + \frac{\Delta C_{P,i}}{RT} (T_{f,i} - T_{f,M}) + \frac{\Delta C_{P,i}}{R} \ln \frac{T}{T_{f,i}} \right]
\]

(5)

En général, on peut négliger dans l'équation (5) la somme des deux derniers termes de l'expression entre crochets.

D'autre part, un développement limité de \( x_i \) et \( x_i' \) au voisinage de \( T = T_{f,M} \) montre que

\[
\lim_{T \to T_{f,M}} \frac{x_i}{x_i'} = \lim_{T \to T_{f,M}} \frac{\text{Pente du liquidus}}{\text{Pente du solidus}} = \Gamma_i^0
\]

Le rapport des pentes du liquidus et du solidus pour \( T = T_{f,M} \) est souvent utilisé pour déterminer le coefficient de distribution thermodynamique d'un élément i partagé entre les phases liquide et solide d'un solvant. Notons que cette méthode est d'une part imprecise et d'autre part inutilisable lorsque le constituant i est en présence de n éléments en solution diluée.

Nous proposons une méthode de calcul du coefficient de distribution de i en présence de n éléments j dans un solvant M à partir des propriétés thermodynamiques des phases liquide et solide.

Lorsque l'élément i est en présence de n éléments j, la relation (1) reste valable puisqu'elle traduit simplement l'identité des potentiels chimiques du constituant i dans les phases en équilibre. Par contre les équations (2) et (3) deviennent

\[
\ln \gamma_i = \ln \gamma_i^\infty + x_i \left[ \frac{\partial \ln \gamma_i}{\partial x_i} \right] + \sum_{j=1}^{j=n} x_j \left[ \frac{\partial \ln \gamma_i}{\partial x_j} \right] + \frac{T_{f,M} - T}{RT^2} \Delta H_i^\infty
\]

(6)

\[
\ln \gamma_i' = \ln \gamma_i^\infty + x_i' \left[ \frac{\partial \ln \gamma_i'}{\partial x_i'} \right] + \sum_{j=1}^{j=n} x_j' \left[ \frac{\partial \ln \gamma_i'}{\partial x_j'} \right] + \frac{T_{f,M} - T}{RT^2} \Delta H_i^\infty
\]

(7)
Les dérivées partielles

\[ \frac{\partial \ln \gamma_i}{\partial x_i}, \frac{\partial \ln \gamma_i'}{\partial x_i'}, \frac{\partial \ln \gamma_j}{\partial x_j}, \frac{\partial \ln \gamma_j'}{\partial x_j'} \]

sont les coefficients d'interaction de Wagner, que nous noterons respectivement

\[ \epsilon_i^i, \epsilon_i^{i'i'}, \epsilon_j^j, \epsilon_j^{j'j''} \]

En combinant les équations (1), (5), (6) et (7), il vient

\[ \ln \Gamma_i = \ln \Gamma_i^\infty + \frac{T_{f,M} - T}{RT^2} (\Delta H_i^\infty - \Delta H_i^{j'j''}) + x_i (\epsilon_i^i - \Gamma_i \epsilon_i^{i'i'}) + \sum_{j=1}^{j=n} x_j (\epsilon_j^j - \Gamma_j \epsilon_j^{j'j''}) \quad (8) \]

Les trois premiers termes du deuxième membre de l'équation (8) caractérisent le comportement thermodynamique du constituant \( i \) dans le système binaire \( (i, M) \). La somme de ces trois termes sera désignée par la fonction \( \Phi_i \):

\[ \Phi_i = \ln \Gamma_i^\infty + \frac{T_{f,M} - T}{RT^2} (\Delta H_i^\infty - \Delta H_i^{j'j''}) + x_i (\epsilon_i^i - \Gamma_i \epsilon_i^{i'i'}) \]

D'où

\[ \ln \Gamma_i = \Phi_i + \sum_{j=1}^{j=n} x_j (\epsilon_j^j - \Gamma_j \epsilon_j^{j'j''}) \quad (9) \]

Le système formé par les \( n+1 \) équations de type (9) permettrait de calculer les \( n+1 \) coefficients de distribution \( \Gamma_i \) dans le solvant \( M \). La résolution pourrait être effectuée à l'aide d'une calculatrice électronique en utilisant la méthode itérative. Les valeurs approchées des coefficients de distribution seraient données par les coefficients de partage limites \( \Gamma_i^\infty \).

Nous nous bornerons à étudier l'influence des éléments \( j \) sur le coefficient de distribution de l'élément \( i \) caractérisée par la fonction \( \xi \):

\[ \xi = \sum_{j=1}^{j=n} x_j (\epsilon_j^j - \Gamma_j \epsilon_j^{j'j''}) \]

L'évaluation de la fonction \( \xi \) est basée sur la connaissance des paramètres d'interaction \( \epsilon_j^j \) et \( \epsilon_j^{j'j''} \) dont nous proposons une méthode d'estimation.

Afin de calculer les paramètres d'interaction de Wagner, nous avons choisi comme représentation analytique de l'enthalpie libre d'excès de mélange...
des solutions liquide et solide une expression de la forme

\[ \Delta G^{xs} = \sum_{i=1}^{i=n+1} f_i(x_i) x_i (1 - \sum_{i=1}^{i=n+1} x_i) + \frac{1}{2} \sum_{i=1}^{i=n+1} h_{ij} (1 - \delta_{ij}) x_i x_j \]  

(10)

avec

\[ \delta_{ij} = 1 \quad i=j \]

\[ \delta_{ij} = 0 \quad i \neq j \]

dans laquelle, à la température T, \( f_i(x_i) \) sont des fonctions continues de \( x_i \); \( h_{ij} \) sont des paramètres ajustables caractéristiques des systèmes binaires \((i, j)\).

Le calcul de \( \Delta G^{xs}_p \) et \( \frac{\partial \Delta G^{xs}_p}{\partial x_k} \) montre que:

\[
\lim \Delta G^{xs}_p = \lim f_p(x_p) = RT \ln \gamma^\infty_p(M)
\]

\[
tous les \( x_i \to 0 \quad x_p \to 0 \)
\]

\[
\lim \frac{\partial \Delta G^{xs}_p}{\partial x_k} = h_p - \lim f_p(x_p) - \lim f_k(x_k)
\]

\[
tous les \( x_i \to 0 \quad x_p \to 0 \quad x_k \to 0 \)
\]

soit:

\[
\epsilon^k_p = \frac{h_p}{RT} - \ln \gamma^\infty_p(M) - \ln \gamma^\infty_k(M)
\]  

(11)

Cette dernière équation permet de calculer les paramètres \( \epsilon^i_j \) à partir des données concernant les binaires \((i, M); (j, M)\) et \((i, j)\). \( h_{ij} \) est un paramètre ajustable caractéristique du binaire \( ij \); suivant les concentrations relatives de \( i \) et de \( j \), on prendra

\[ h_{ij} = RT \ln \gamma^\infty_{ij} \]

ou

\[ h_{ij} = RT \ln \gamma^\infty_{ji} \]

Afin de simplifier l'écriture, nous noterons

\[ h_{ij} = RT \ln \gamma^\infty_{ij} \]

En conséquence, l'estimation des coefficients \( \epsilon^i_j \) et \( \epsilon^j_i \) sera effectuée à l'aide des équations suivantes:
La fonction $\xi$ a pour expression

$$
\xi = \sum_{j=1}^{j=n} x_j \left[ (1 - \Gamma_j) \ln \frac{\gamma_{ij}^0}{\gamma_j^0 \gamma_i^0} + \Gamma_j \ln \frac{\Gamma_{ij}^0}{\Gamma_i^0 \Gamma_j^0} \right]
+ \sum_{j=1}^{j=n} \Gamma_j \left[ \frac{T_{f,j} - T_{i,j}}{RT_{f,j} T_{f,i}} - \frac{T_{f,M} - T_{i,j}}{RT_{f,M} T_{f,i}} - \frac{T_{f,j} - T_{i,j}}{RT_{f,j} T_{f,i}} \right]
$$

Cette dernière équation permet d'évaluer l'influence des constituants $j$ sur le coefficient de distribution de l'élément $i$ à partir des propriétés thermodynamiques des binaires. En particulier on remarque que, si les coefficients de distribution $\Gamma_j$ sont suffisamment petits, la fonction $\xi$ sera d'autant plus négative que $\gamma_{ij}^0$ est plus petit devant le produit $\gamma_j^0 \gamma_i^0$.

Nous avons appliqué la méthode précédente au calcul de la variation du coefficient de distribution d'un élément $A$ en solution dans un solvant $M$ en fonction de l'ajout d'un autre élément $B$.

Dans le cas particulier de la technique de purification par fusion de zone, l'expression de $\xi$ permet de choisir l'élément $B$ à introduire volontairement dans le métal à purifier pour faciliter l'élimination de $A$.

L'élimination de $A$ sera facilitée si $\Gamma_B$ diminue du fait de la présence de $B$, c'est-à-dire si la valeur de $\xi$ est négative. Comme en outre $B$ sera choisi de telle manière que sa propre élimination par fusion de zone soit facile ($\Gamma_B$ de l'ordre de 0,01), $\xi$ sera négative si

$$
\gamma_{A(M)}^0 \gamma_{B(M)}^0 > \gamma_{A(B)}^0
$$

Dans ce cas $\gamma_{A,B}^0 = \gamma_{A(B)}^0$ puisque la concentration en élément $B$ est nettement supérieure à celle de $A$.

La condition (15) sera en particulier vérifiée par un choix de $B$ tel qu'il forme de nombreux composés définis avec $A$ (interactions $(A, B)$ fortes) et qu'il présente avec $M$ un diagramme d'équilibre de phases à eutectique simple (interactions $(B, M)$ faibles) avec une très faible solubilité solide de $B$ dans $M$ ($\Gamma_B$ petit).

Le calcul précédent a permis de déterminer que la présence d'aluminium dans le béryllium diminue sensiblement le coefficient de distribution du fer dans ce solvant. En effet, si l'on prend comme valeur à 1300°C

$$
\gamma_{Al(Be)}^0 = 8,5 \ [1], \quad \gamma_{Fe(Be)}^0 = 0,01 \ [2], \quad \gamma_{Fe(Al)}^0 = 0,1 \ [3],
$$

la relation 15 est vérifiée; ce qui doit diminuer sensiblement le coefficient
de distribution du fer dans le béryllium exempt d'aluminium, lequel est voisin de l'unité et de ce fait défavorable à une purification complète du béryllium par la technique de la zone fondue. Il est donc intéressant «d'entraîner» le fer par un ajout d'aluminium.

Des essais ont montré qu'à la vitesse de 40 min/h en fusion de zone flottante le coefficient de distribution effectif du fer dans le béryllium est de 0,9 ± 0,05. L'addition de 3% en poids d'aluminium à la zone fondue de béryllium fait passer ce coefficient à la valeur 0,75 ± 0,05. Ce gain est appréciable, car il faut noter que l'efficacité de la purification par fusion de zone est une fonction exponentielle des coefficients de distribution.

En conclusion, nous avons théoriquement et pratiquement montré que les interactions d'éléments en solution diluée dans un solvant pouvaient être utilisées à une meilleure purification par la technique de la zone fondue. De même on peut éventuellement montrer que l'existence ou l'ajout de certains éléments, au cours de la technique de purification d'un métal par distillation, peut en améliorer l'efficacité en diminuant notablement la tension de vapeur d'une impureté notoire. La méthode précédente permet même de calculer les variations de tension de vapeur qui s'en suivent.

D'une manière générale, la mise en équation précédente autorise le calcul des coefficients de distribution de n + 1 éléments partagés entre les phases solides et liquides d'un solvant.

REFERENCES

THE ACTIVITY OF URANIUM IN DILUTE SOLUTION IN LIQUID BISMUTH

L.C. TIEN, K.J. GUION AND R.D. PEHLKE,
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.,
UNITED STATES OF AMERICA

Abstract — Résumé — Аннотация — Resumen

THE ACTIVITY OF URANIUM IN DILUTE SOLUTION IN LIQUID BISMUTH. The activity of uranium has been measured in dilute solution in liquid bismuth. The study employed a galvanic cell with a liquid chloride electrolyte in the temperature range 400 - 600°C. The cell was

| Pure solid uranium | U^{+++} (in fused KCl + LiCl electrolyte) | Uranium (in bismuth alloy) |

The activity of uranium has been shown to follow Henry's Law, and the activity coefficient in this range is given by the expression:

\[
\log_{10} \gamma_U = \frac{-3700}{T(K)} + 0.4
\]

The activity of uranium in UBi₂ has been measured over this temperature range, and previous measurements of the solubility of uranium in liquid bismuth have been corroborated. Coulometric titration was used to determine the ionic valence in the electrolyte, and the concentration of uranium in the liquid bismuth alloys was determined by chemical sampling of the electrodes.

ACTIVITE DE L'URANIUM DILUE DANS LE BISMUTH LIQUE. Les auteurs ont mesuré l'activité de l'uranium en solution diluée dans le bismuth liquide. Au cours de leurs travaux, ils ont utilisé une cellule galvanique à électrolyte de chlorure liquide dans l'intervalle de température compris entre 400 et 600°C. La cellule était composée comme suit:

| Uranium solide pur | U^{+++} (dans l'électrolyte de KCl + LiCl fondu) | U (dans un alliage au bismuth) |

Les auteurs montrent que l'activité de l'uranium suit la loi d'Henry et que le coefficient d'activité pour cet intervalle est donné par l'expression

\[
\log_{10} \gamma_U = \frac{-3700}{T(K)} + 0.4
\]

Ils ont mesuré l'activité de l'uranium dans UBi₂ pour cet intervalle de température; leur résultats ont confirmé les mesures antérieures de la solubilité de l'uranium dans le bismuth liquide. Ils ont déterminé la valence ionique de l'électrolyte par titrage coulombométrique, et la concentration de l'uranium dans les alliages de bismuth liquides au moyen d'échantillons chimiques prélevés sur les électrodes.

АКТИВНОСТЬ УРАНА В РАЗБАВЛЕННОМ РАСТВОРЕ В ЖИДКОМ ВИСМУТЕ. Активность урана измеряли в разбавленном растворе в жидким висмуте. Для исследований использовали гальванический элемент с жидким хлоридом в качестве электролита в температурном интервале 400 - 600°C. Устройство элемента:

| Чистый твердый уран | U^{+++} (В электролите из расплавленного KCl + LiCl) | U (В сплаве с висмутом). |
Показано, что активность урана подчиняется закону Генри и коэффициент активности в этом интервале определяется выражением

\[
\log_{10} \gamma_u^0 = -\left[\frac{3700}{T(°K)}\right] + 0.4.
\]

Активность урана в UB\textsubscript{2} измерена в этом температурном интервале, и подтверждены результаты предыдущих измерений растворимости урана в жидком висмуте. Для определения ионной валентности в электролите применялось кулометрическое титрование. Концентрация урана в жидких сплавах висмута определялась путем химического опробования электродов.

**INTRODUCTION**

The uranium-bismuth system has been the focus of many research efforts because of its potential applications in nuclear technology. Bismuth possesses several essential qualities for a liquid reactor fuel in that it has a low melting point and a low thermal neutron cross-section property.

Previous studies of the activity of uranium in bismuth have utilized direct galvanic cell measurements [1, 2] or have obtained the uranium activity indirectly from vapour pressure measurements of the bismuth activity followed by a Gibbs-Duhem integration [3, 4].

By an effusion method, Gross, Levi and Lewin [3] measured the vapour pressure of bismuth over uranium-bismuth alloys. The amount of the condensed bismuth vapour was estimated gravimetrically as the phosphate BiPO\textsubscript{4}. However, since bismuth vapour has two species, Bi and Bi\textsubscript{2}, the derivation of bismuth pressure from the effusion rate requires that the equilibrium between monatomic and diatomic bismuth vapour be taken into account.

An optical absorption technique [5] has been employed for independent determination of the concentration of each vapour species. With this technique, Rice, Balzhiser and Ragoné [4] determined the activity of bismuth over the various regions of the uranium-bismuth diagram, and then calculated the activity of uranium using the Gibbs-Duhem relationship.
Egan and Wiswall [1, 2] utilized a galvanic cell of the type

$$\text{U(s)} \mid \text{KCl+LiCl eutectic} \mid \text{U (In Bismuth Alloy)} \\text{UCl}_3(5\%)$$

One electrode of their galvanic cell was a liquid alloy of variable composition, which was contained in a molybdenum cup dipped beneath the surface of the fused-salt electrolyte. The other electrode was solid uranium mounted on a molybdenum contact. They stated that in the dilute uranium region, reproducible results were hard to achieve, and therefore reported uranium activity coefficients at only two temperatures.

The reversibility of a solid uranium electrode with respect to the reaction

$$\text{U(s)} = \text{U}^{3+} + 3\text{e}$$

has been shown by Inman, Hills, Young and Bockris [6]. Gruen and Osteryoung [7] have shown that uranium metal does not react with the anhydrous eutectic salt mixture.

In studies of the uranium-cadmium system, Johnson and Feder [8] used a uranium wire for the standard electrode, thus avoiding a molybdenum contact or junction. Their cell EMF's were each corrected by the appropriate thermal EMF, which was determined with thermocouples constructed from the uranium electrode and the lead for the alloy electrode. This technique was employed here.

The present investigation was undertaken on the uranium-bismuth system to extend the results of Wiswall and Egan [1, 2]. The cell design was similar to theirs and that used by Johnson and Feder [8] on the uranium-cadmium system. The cell EMF was measured over the range 400-600°C, and the logarithm of the activity coefficient of uranium in the alloy was calculated by the relation

$$\log_{10}\gamma_U = \frac{-nFE}{2.303RT} - \log_{10} X_U$$

where $\gamma_U$ is the activity coefficient of uranium, $n$ the valence of uranium ion in the electrolyte, $F$ – Faraday's constant, $E$ the cell EMF, $R$ the gas constant, $T$ the absolute temperature and $X_U$ the mole fraction of uranium in bismuth.

The phase diagram of the uranium-bismuth system has been reported by Teitel [9]. In the dilute uranium region, the solid phase that can be present is the compound $\text{UBi}_2$. The bound form of uranium results in a low value of the activity coefficient of uranium in bismuth, of the order of $10^{-5}$ to $10^{-4}$ for the present investigation.

By the spectrophotometric method, Balzhiser and Ragone [10] determined that the solubility of uranium in bismuth in the range 400-800°C is given by the expression

$$\log_{10} X_U = -\frac{2.690}{T} + 1.215$$
According to the above equation, in the temperature range of this investigation the uranium-bismuth solutions are dilute, containing generally less than one mole percent of uranium.

EXPERIMENTAL PROCEDURE AND OBSERVATIONS

The cell assembly used in this investigation is shown schematically in Fig. 1. The cell was held in a recrystallized alumina crucible placed inside a Vycor tube. The Vycor tube was closed by a metal head sealed with an O-ring, and five 9 mm Vycor tubes were sealed into the head with O-rings.

Three of the tubes contained (1) the chromel-alumel thermocouple; (2) the uranium electrode, which was immersed in the electrolyte and (3) the tungsten lead wire, which was immersed in the uranium-bismuth alloy electrode. The fourth tube was used for adding uranium to change the alloy composition, and the fifth tube, which was perforated, was used for the storage of uranium above the melt to act as a "getter" for the cell atmosphere. Also, small pieces of uranium were placed underneath the cell for the same purpose.

The cell assembly was placed in a chromel-wound resistance furnace which was regulated by an auto-transformer and Foxboro controller, which generally held the cell temperature within ±1.5°C over a period of several hours. The cell was protected by an argon atmosphere which had been dried and deoxidized by passing over Dryrite, heated copper and titanium.

The electrolyte, weighing 80 grams, was the eutectic mixture of potassium and lithium chlorides plus 5-7 wt.% uranium trichloride. The alkali metal salts were of Baker Chemical Company reagent grade, and the uranium salt was supplied by the Rocky Mountain Research Company and K and K Laboratories, Inc. To dry them, these salts were heated separately under vacuum, to 400°C for the alkali metal salts, and to 150°C for the uranium salt.

The high purity bismuth was supplied by the American Smelting and Refining Company. The uranium charged to the cell was in the form of chips, which were machined from slugs of Mallinckrodt's reagent grade uranium and then electrolytically cleaned. The uranium electrode, 0.063 in. in diameter, was obtained in high purity form from A.D. Mackay, Inc.

Before starting a run, a tungsten wire was fused into about 290 grams of bismuth in an alumina cell crucible under the protection of an argon atmosphere. The dried and then-mixed chloride salts were charged to the crucible cold, and after evacuating, flushing and filling the cell assembly with purified argon, the cell temperature was raised to approximately 500°C.

During the run, the cell assembly was opened several times momentarily for putting in or taking out the uranium electrode, renewing the uranium carried by the perforated tube and sampling. No significant effect from these operations was observed on the stability of the cell EMF.

The cell EMF usually took one or two days to become stabilized and then for several days remained stable or else drifted slowly. When the temperature was varied, the short time EMF-temperature slope was usually
FIG. 1. Experimental cell.
steeper than the long time (several hours) slope, thus indicating that long times were required to establish an equilibrium condition.

The alloy electrode of a number of the cells was sampled for spectrophotometric analysis [10] of the uranium content. The quantity of uranium found on analysis was always lower than that expected from calculations based on the amount of uranium charged. This was presumed to be due to oxidation of part of the uranium in the alloy. The uranium electrode wire was also subjected to attack. Its tip, which was immersed in the electrolyte, became thin, and the part of the wire immediately outside the electrolyte was covered with a dark brown or black mass. Despite this, such a uranium electrode showed practically the same EMF reading as a newly cleaned uranium electrode. In addition, chemically or mechanically cleaned uranium electrodes showed practically the same EMF readings.

The uranium-tungsten thermocouple effect was small and essentially linear, ranging from 0.65 to 3.55 mV for a cold junction at 0°C with the hot junction at 100°C and 500°C, respectively. While the polarity of uranium was positive for the uranium-tungsten thermocouple, that of the uranium electrode was negative, and, therefore, a positive correction on the cell EMF was made for the uranium-tungsten thermocouple effect.

RESULTS AND DISCUSSION

The experimental results of the present investigation include EMF measurements of the uranium activity in liquid bismuth in twelve unsaturated solutions. Immediately following stable EMF measurements on these cells, the liquid alloy electrodes were sampled for spectrophotometric analysis [10]. The results also include EMF measurements of the uranium activity in liquid bismuth electrodes containing a sufficient amount of uranium to saturate the liquid with UB₁₂. Analyses were made on four of these nineteen electrodes. The logarithm of the activity coefficient of uranium was calculated using Eq. (1) in the form

$$\log_{10} \gamma_U = -15.12 \frac{E}{T} - \log_{10} X_U$$

(3)

for a uranium ion valence of 3 in the electrolyte and for E in millivolts.

The experimental data and calculated results are summarized in Tables I and II for alloy electrodes of bismuth unsaturated and saturated with uranium, respectively.

The data of Table I are plotted as $\log_{10} \gamma_U$ versus reciprocal temperature in Fig. 2. The points of Fig. 2 lie along a least-squares line given by the expression

$$\log_{10} \gamma_U = -\frac{3870 \pm 320}{T} + (0.64 \pm 0.12)$$

(4)

where the uncertainties are the standard deviations of the slope and the intercept.
TABLE I
Data and Calculated Results, Unsaturated Uranium-Bismuth Cells

<table>
<thead>
<tr>
<th>Data</th>
<th>Temperature (°C)</th>
<th>Analysed (U mole %)</th>
<th>Emf (mV)</th>
<th>(1000/T(°K))</th>
<th>log₁₀γ_U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>436.5</td>
<td>0.10</td>
<td>364.5</td>
<td>1.409</td>
<td>-4.768</td>
</tr>
<tr>
<td>3-12</td>
<td>571.6</td>
<td>0.21</td>
<td>360.1</td>
<td>1.184</td>
<td>-3.776</td>
</tr>
<tr>
<td>4-1</td>
<td>578.3</td>
<td>0.013</td>
<td>438.3</td>
<td>1.175</td>
<td>-3.915</td>
</tr>
<tr>
<td>4-2</td>
<td>414.3</td>
<td>0.013</td>
<td>399.4</td>
<td>1.455</td>
<td>-4.907</td>
</tr>
<tr>
<td>4-4</td>
<td>437.8</td>
<td>0.054</td>
<td>381.2</td>
<td>1.407</td>
<td>-4.842</td>
</tr>
<tr>
<td>4-5</td>
<td>585.8</td>
<td>0.054</td>
<td>414.3</td>
<td>1.165</td>
<td>-4.025</td>
</tr>
<tr>
<td>6-1</td>
<td>414.3</td>
<td>0.17</td>
<td>358.1</td>
<td>1.455</td>
<td>-5.109</td>
</tr>
<tr>
<td>6-3</td>
<td>461.5</td>
<td>0.29</td>
<td>344.6</td>
<td>1.361</td>
<td>-4.557</td>
</tr>
<tr>
<td>6-4</td>
<td>520.0</td>
<td>0.62</td>
<td>332.9</td>
<td>1.261</td>
<td>-4.141</td>
</tr>
<tr>
<td>12-5</td>
<td>559.0</td>
<td>0.28</td>
<td>358.6</td>
<td>1.201</td>
<td>-3.965</td>
</tr>
<tr>
<td>12-7</td>
<td>497.8</td>
<td>0.46</td>
<td>351.8</td>
<td>1.283</td>
<td>-4.565</td>
</tr>
<tr>
<td>13-1</td>
<td>561.0</td>
<td>0.48</td>
<td>349.1</td>
<td>1.199</td>
<td>-4.012</td>
</tr>
</tbody>
</table>

The data of Table II for alloy electrodes of bismuth saturated with uranium are plotted as log₁₀γ_U versus reciprocal temperature in Fig. 3. The activity coefficient was usually calculated from the solubility of uranium in liquid bismuth as determined by Balzhiser and Ragone [10]. However, four of the points shown in Fig. 3 are based on the mole fractions determined by spectrophotometric analysis of the sample from the alloy electrode. These results are consistent within experimental error with the remainder of the data, indicating that all these electrodes were indeed saturated. The least-squares line for the points of Fig. 3 (except the four triangles) is given by the expression

\[ \log_{10} \gamma_U = -\frac{3560 \pm 180}{T} + (0.19 \pm 0.07) \] (5)

The points of Fig. 2, which represent a range of compositions in the unsaturated solution region, and the points of Fig. 3, which represent the composition of the saturated solution, can be represented by one linear relationship as suggested by the approximate statistical identity of Eqs.(4) and (5). This demonstrates the validity of Henry's law in the dilute uranium-bismuth solution up to saturation with U Bi₂.

The validity of Henry's law is also shown directly in Fig. 4, where the activity of uranium in the dilute bismuth solution is plotted against composition for temperatures at 436°C and 561°C. The points for each of the two
<table>
<thead>
<tr>
<th>Data</th>
<th>Temperature (°C)</th>
<th>Correlated (U mole %)</th>
<th>Analysed (U mole %)</th>
<th>Emf (mV)</th>
<th>(1000/T(°K))</th>
<th>$\log_{10}^7 U$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-9</td>
<td>555.2</td>
<td>0.924</td>
<td>0.98</td>
<td>339.9</td>
<td>1.208</td>
<td>$-4.172$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($-4.197$)</td>
</tr>
<tr>
<td>13-3</td>
<td>1564.2</td>
<td>1.01</td>
<td>0.98</td>
<td>336.1</td>
<td>1.194</td>
<td>$-4.075$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($-4.062$)</td>
</tr>
<tr>
<td>13-4</td>
<td>501.5</td>
<td>0.552</td>
<td>0.58</td>
<td>345.4</td>
<td>1.291</td>
<td>$-4.486$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($-4.507$)</td>
</tr>
<tr>
<td>13-5</td>
<td>434.0</td>
<td>0.258</td>
<td>0.21</td>
<td>350.2</td>
<td>1.414</td>
<td>$-4.902$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($-4.813$)</td>
</tr>
<tr>
<td>18-1</td>
<td>458.0</td>
<td>0.345</td>
<td></td>
<td>347.8</td>
<td>1.368</td>
<td>$-4.730$</td>
</tr>
<tr>
<td>19-1</td>
<td>461.5</td>
<td>0.358</td>
<td></td>
<td>350.8</td>
<td>1.361</td>
<td>$-4.776$</td>
</tr>
<tr>
<td>20-1</td>
<td>507.5</td>
<td>0.587</td>
<td></td>
<td>333.6</td>
<td>1.281</td>
<td>$-4.231$</td>
</tr>
<tr>
<td>20-2</td>
<td>466.2</td>
<td>0.376</td>
<td></td>
<td>339.4</td>
<td>1.353</td>
<td>$-4.519$</td>
</tr>
<tr>
<td>20-3</td>
<td>414.3</td>
<td>0.200</td>
<td></td>
<td>347.3</td>
<td>1.455</td>
<td>$-4.942$</td>
</tr>
<tr>
<td>20-5</td>
<td>422.2</td>
<td>0.222</td>
<td></td>
<td>349.6</td>
<td>1.438</td>
<td>$-4.951$</td>
</tr>
<tr>
<td>20-6</td>
<td>484.6</td>
<td>0.462</td>
<td></td>
<td>344.2</td>
<td>1.320</td>
<td>$-4.534$</td>
</tr>
<tr>
<td>20-7</td>
<td>548.3</td>
<td>0.871</td>
<td></td>
<td>337.0</td>
<td>1.217</td>
<td>$-4.145$</td>
</tr>
<tr>
<td>20-8</td>
<td>548.3</td>
<td>0.871</td>
<td></td>
<td>335.5</td>
<td>1.217</td>
<td>$-4.117$</td>
</tr>
<tr>
<td>20-9</td>
<td>486.5</td>
<td>0.472</td>
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<td>342.6</td>
<td>1.316</td>
<td>$-4.495$</td>
</tr>
<tr>
<td>20-10</td>
<td>429.8</td>
<td>0.244</td>
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<td>348.6</td>
<td>1.423</td>
<td>$-4.888$</td>
</tr>
<tr>
<td>20-11</td>
<td>553.8</td>
<td>0.916</td>
<td></td>
<td>334.2</td>
<td>1.209</td>
<td>$-4.074$</td>
</tr>
<tr>
<td>20-12</td>
<td>519.0</td>
<td>0.659</td>
<td></td>
<td>337.1</td>
<td>1.262</td>
<td>$-4.256$</td>
</tr>
<tr>
<td>20-13</td>
<td>480.8</td>
<td>0.452</td>
<td></td>
<td>341.9</td>
<td>1.323</td>
<td>$-4.514$</td>
</tr>
<tr>
<td>20-14</td>
<td>419.3</td>
<td>0.214</td>
<td></td>
<td>348.6</td>
<td>1.444</td>
<td>$-4.945$</td>
</tr>
</tbody>
</table>

Notes: 1. The correlated U mole % is based on the formula by Balzhiser and Ragone [10] for U in Bi solubility.
2. The $\log_{10}^7 U$ values are calculated based on the correlated U mole % except that those in parentheses are calculated based on the analysed U mole %.

Temperatures are shown to lie along a line through the origin within a small scatter, due both to experimental error in chemical analysis and slight temperature deviations for measurements on different cells. The data of Wiswall and Egan [2] at 700°C also show this result.
Combining the points of Figs. 2 and 3, the most reliable experimental determination of the logarithm of the activity coefficient of uranium in liquid bismuth is given by the expression

$$\log_{10} \gamma_U^0 = -\frac{3740 \pm 170}{T} + (0.44 \pm 0.09)$$  \hspace{1cm} (6)$$

where the superscript 0 refers to infinite dilution, because Henry's law is obeyed. Using Eqs. (2) and (6), the activity of uranium in liquid bismuth solution saturated with $\text{UBi}_2$ is given by the expression

$$\log_{10} a_U = -\frac{6430 \pm 170}{T} + (1.66 \pm 0.09)$$  \hspace{1cm} (7)$$
The standard free energy of formation of UBi₂ according to the reaction

\[ \text{U(s)} + 2\text{Bi(l)} = \text{UBi}_2(s) \]

is given by the expression (derived from Eq. (7) and

\[
\Delta F^0 = -RT \ln \left( \frac{a_{\text{UBi}_2}}{a_U a_{\text{Bi}}^2} \right)
\]

where \( a_{\text{UBi}_2} = 1 \) and \( a_{\text{Bi}} = 1 \)

\[
\Delta F^0 = -(29 400 \pm 800) + (7.60 \pm 0.42) \text{T cal/g-mole}
\]
The results of the present investigation are compared with previous EMF measurements [1, 2] and vapour pressure measurements [3, 4] in Fig. 5, for the uranium-dilute region. The dashed lines encompass the 95% confidence band [11] of the data of this investigation. While the latest data (700°C) of Wiswall and Egan [2] is in excellent agreement with this investigation, other data lie reasonably close but outside the 95% confidence band. A possible explanation of these discrepancies is that the valence of the uranium transport ion in the electrolyte is not 3, as used in Eq. (3). Coulometric transference experiments were carried out to evaluate this possibility.

VALENCE OF THE URANIUM ION

The "uranium trichloride" used was analysed chemically and found in one batch to contain less than the stoichiometric amount of chlorine, and
in the second case more than the stoichiometric amount of chlorine. Nevertheless, the cell EMF's in cells charged with these varying uranium-chloride compounds were in good agreement.

Coulometric titrations were performed between two uranium electrodes immersed in the electrolyte. The valence of the uranium ion in the electrolyte was determined by weight loss, which involved weighing a unit length of wire after electrolytic transfer. The results are presented in Table III.

At higher current densities, a slightly higher valence in the electrolyte was indicated. This could be explained on the basis of a possible lower current efficiency. It should be noted that in these runs the uranium salts charged had differing uranium valences as indicated by the uranium/chlorine ratios in them. However, this did not seem to affect the transfer of uranium between the solid wire electrodes. Therefore, one can conclude that the valence of the uranium ion in the electrolyte was three and can rule out devi-
TABLE III

Results of Coulometric Titration Experiments

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>Current (mA)</th>
<th>Approx. Current Densities (mA/cm²)</th>
<th>Duration (Hours)</th>
<th>Uranium Loss (mg)</th>
<th>Calculated Valence of Uranium ion (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>458</td>
<td>20</td>
<td>50,150</td>
<td>3.83</td>
<td>195</td>
<td>3.5</td>
</tr>
<tr>
<td>19</td>
<td>462</td>
<td>5</td>
<td>10,15</td>
<td>11.4</td>
<td>170</td>
<td>3.04</td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td></td>
<td>25,50</td>
<td>6.0</td>
<td>196</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td></td>
<td>40,100</td>
<td>5.0</td>
<td>206</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td></td>
<td>35,50</td>
<td>3.0</td>
<td>170</td>
<td>3.3</td>
</tr>
<tr>
<td>20</td>
<td>450</td>
<td>5</td>
<td>10,20</td>
<td>12.0</td>
<td>187</td>
<td>2.9</td>
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<tr>
<td></td>
<td>10.1</td>
<td></td>
<td>15,25</td>
<td>6.0</td>
<td>194</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Ations from this value as a possible explanation of the discrepancy between the present direct galvanic cell results and previous results derived from vapour pressure measurements in bismuth [3, 4].

SUMMARY

1. The activity of uranium in dilute bismuth follows Henry's law up to saturation with UBi₂, in the range 400-600°C.

2. The logarithm of the activity coefficient of uranium in dilute solution in liquid bismuth is given by the expression

   \[ \log_{10} \gamma_U^0 = \frac{-3700}{T(°K)} + 0.4 \]

3. The standard free energy of formation of UBi₂ according to the equation

   \[ U(s) + 2Bi(l) = UBi₂(s) \]

is given by the expression

   \[ \Delta F^0 = -29400 + 7.6 \ T(°K) \ \text{cal/g-mole} \]

4. Coulometric titration has shown that the valence of uranium is 3 when added to a eutectic mixture of lithium and potassium chlorides as uranium trichloride (UCl₃).
5. The solubility of uranium in liquid bismuth has been checked and the results reported by Balzhiser and Ragone [10] corroborated.

REFERENCES

Discussion to Session 4

THERMODYNAMICS OF THE LIQUID STATE

Discussion Leader: E. BONNIER
FRANCE

Paper SM-66/89 (O. J. Kleppa)

M. DIAZ-PEÑA (Chairman): It appears that some of the current theories on the liquid state have been applied to the study of fused salts. It also appears that some fused salts behave in accordance with the corresponding states theory, as has been shown by Reiss. I should like to know if there has been any attempt to apply the average potential theory developed by Prigogine and co-workers to fused salts, in view of the fact that this theory is basically an amplification of the corresponding states theory.

O.J. KLEPPA: It is, I think, fair to say that all the successful theories, both for pure fused salts and for mixtures of fused salts, have the character of corresponding states theories. In some cases they have modified or changed the symbols, but basically they are corresponding states theories; this certainly applies to all the theoretical work that has resulted from the introduction of the model ionic melt of Reiss and co-workers. There has been, to my knowledge, no similar general effort to apply other theoretical approaches which may be considered to be related to the theory of corresponding states; such theories, however, may be forthcoming.

D. I. MARCHIDAN: The specialized literature indicates several methods for the theoretical determination of the heat of mixing in binary systems of fused salts. Unfortunately, each of these can only be used for a limited range of mixtures; none is of general use. This is also a problem with regard to thermodynamic properties, for which there is as yet no single method of interpretation. An even less comforting fact is that sometimes disagreement exists between two experimentally determined values.

All the current theories are based on the lattice parameters of individual salts, and generally derive from Wasastjerna's relationship. Thus the relationships developed by Murgulescu and Steinberg are applicable to systems forming mixed crystals. According to these authors only the potential interaction energy varies; it therefore follows that in the parabolic equation

$$\Delta H^M = B x_1 x_2$$

the constant B represents the interaction potential. You have developed another system, giving for groups of systems of salts semi-empirical relationships which are not always applicable. According to Lumsden's
system of calculation, which takes into account only the polarization energy and the van der Waals forces, only four systems among those with a common anion can have positive heats of mixing; these are the systems containing fluorine.

In our laboratories, Mme Vîlcu has used Eyring's significant structures theory to study the heats of mixing of the binary system KBr + KCl, which we had already studied experimentally. The values she gives are very close to our experimental figures (±5 cal/mole).

O.J. KLEPPA: I believe it is fair to say that no final solution has yet been reached in the theory of fused salt mixtures, even for such simple mixtures as the ones I discussed in my oral presentation. However, it is a common feature of virtually all theories relating to mixtures of fused salts that the leading term will have the form of the Wasastjerna relation or the Tobolsky relation or the Kleppa relation or the Reiss relation; in other words, it will depend on the square of the difference in interionic distance between the ions in the two components. Such a result is inherent in the corresponding states character of all these theories, and I am prepared to let the future decide which theoretical approach is the most satisfactory.

I would only add that the application of the Wasastjerna theory to fused salts mixtures is undoubtedly unrealistic. It is clear that the same theoretical approach must be capable of explaining a wide range of fused salt solutions within the scheme given in my paper. To single out for special consideration those systems which form solid solutions can never advance our general understanding of fused salt mixtures.

R. VÎLCU: Your paper refers only to binary mixtures of fused salts with a common anion.

The equation of Hersh and Kleppa for the relationship between the heat of mixing and the composition (Eq. (9) in your paper) would seem to be approximate, since it does not take into account the deviations of this relationship from the equation for a perfect parabola. Such a deviation can be shown for the systems studied (alkaline halogenides and nitrates) either by using experimental data or by calculating the heats of mixing for differing compositions of the mixture.

As Dr. Marchidan has indicated, we have studied the system KCl + KBr using the statistical method. The statistical elements were calculated according to the significant structures theory of Eyring and co-workers. The motive for these calculations was the differences observed between the experimental figures obtained by various authors for the heats of mixing of the system K(Cl-Br). In some cases there are differences of 200% between your results and those of Toguri, Murgulescu and Marchidan.

The results of our calculations, which have just appeared in the Revue Roumaine de Chimie, show that, for the system KCl + KBr in the fused state, there is perfect agreement between the heats of mixing calculated in this way and the experimental data of Murgulescu and Marchidan. For example, for an equimolar composition of KBr and KCl at 810°C, we agreed with the experimental value of about 50 cal/mole, whereas your results give 15 cal/mole. For other compositions the agreement between theory and the experiments of Murgulescu and Marchidan is maintained, with minor variations (±5 cal/mole).
O. J. KLEPPA: You have, I think, made two main points. One is the fact that in my oral presentation I paid no attention to energetic asymmetry, i.e. to the fact that the heats of mixing do not obey the equation for a perfect parabola. This is, of course, perfectly well known, both from our earlier and our recent work. Anyone who is interested will be able to find the detailed information in our recent paper in the Journal of Chemical Physics 42 (1965) 1309. However, it must be recognized that, if we are dealing with first-order effects, the leading term in any solution theory will give rise to a symmetrical expression for the enthalpy of mixing. It is the higher terms in the theory which give rise to asymmetries. This has also been discussed in our more detailed paper as well as elsewhere in the literature.

The second point is that of experimental discrepancies. I have noted with interest that there is in some cases excellent agreement between the results obtained in the Roumanian laboratory and in our own, while in other cases there is a substantial discrepancy. I cannot, at the present time, discuss this problem in detail, although I feel that the enthalpies of mixing are susceptible to errors due to impurities and errors in measurement. However, I do believe that the data that I have presented for the case of the reciprocal mixtures indicated a very high degree of internal experimental consistency in our own data. You will remember that I determined the ternary excess enthalpy by three independent, or nearly independent, methods and found results which were in extremely good agreement. This could hardly have occurred unless the experiments were basically sound. Once again I am with confidence awaiting future developments and I have no doubt that our experimental results are good, although they can undoubtedly be improved in some cases.

O. KUBASCHEWSKI: Dr. Kleppa has described sensible models for estimation of the heats of mixing in molten salt systems. The enthalpies represent, of course, only half the story. The time has now come for someone to assess the thermodynamic properties of salt mixtures and so render a service similar to the one Hultgren, Kelley and their colleagues have rendered for alloy systems. In a paper to be presented later at this symposium\(^1\) I shall show a plot of maximum (or minimum) excess entropies versus heats of mixing. This seems to dispose of the regular solution model but indicates a direct relationship between the two functions. Is there any indication that a similar relationship may apply to ionic mixtures?

O. J. KLEPPA: Clearly, as I pointed out in my oral presentation, information on the excess entropy in fused salt mixtures should be obtained, and no doubt it will be as time passes. At present the information available on excess entropies is rather restricted. We have made, in our papers, some comparison between our enthalpy data and free energy data which have been derived by EMF techniques, notably for the systems involving silver halides. The Norwegian group, Fyrland and co-workers, have made similar comparisons between our enthalpy data and their own free energy data which have been derived by exchange equilibrium measurements. All this information is available in the literature, but it is scattered, somewhat unsystematic,

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\(^1\) These Proceedings, Vol. 2, paper SM-66/92.
and does not, at the present time, give a very clear picture. It can be said that in a fused system, for which the information appears to be reliable, the excess entropies are small, and in some cases they appear to be small and negative, but I would not wish to say anything more.

Paper SM-66/60 (C. F. Baes, Jr.)

A. BÜCHLER: Dr. Baes was kind enough to send us a copy of his and Mr. Mathews' report on the LiF-BeF$_2$ system (A. L. Mathews and C. F. Baes, Jr., ORNL-TM-1129 (1965)). The diagram shows a part of his plot of the BeF$_2$ activity coefficient as a function of concentration and temperature, together with three points taken from our own (mass spectrometric) work. Our points correspond to the LiF-BeF$_2$ melt saturated with LiF. The agreement between the two sets of data, which were obtained by entirely different methods, is very satisfactory. We find it particularly gratifying that the mass-spectrometric data complement the data of Mathews and Baes at very low BeF$_2$ activities, just at the point where the experiments of these authors reach their limit.
C. F. BAES, Jr.: Thank you for your additional information; I also feel that the agreement is satisfactory. We, of course, were concerned by the presence of oxide in our solution.

A. BÜCHLER: Although we tried to keep our solution as dry as possible, I would not guarantee, in view of the fact that we were using water vapour, that there was no oxide present.

C. F. BAES, Jr.: We are at present making EMF measurements of the system, using the cell described just before Eq. (6) in our paper, in order to verify the activity measurements in the absence of oxide.

Paper SM-66/86 (E. C. Freiling)

There was no discussion of this paper.

Paper SM-66/69 (J. A. Leary and L. J. Mullins)

J. WURM: I have two questions about Table I of your paper. Firstly, it shows the behaviour of a few impurity elements during the electro-refining of plutonium in liquid electrodes, and I would be interested to know if you have more data on the behaviour of, for example, noble metals. Secondly, the table also shows a very good separation factor for uranium and plutonium (276 ppm and <20 ppm). If this separation factor could be maintained up to higher concentrations of uranium and plutonium, electro-refining could be a very good processing method for plutonium fast-breeder blanket fuels. Could you comment on this possibility?

L. J. MULLINS: The removal of all the noble metals was extremely good. I believe that the plutonium-uranium separation factor could be maintained at higher concentrations of uranium provided the electro-refining cell is operated under conditions of negligible electrode polarization. A necessary requirement would therefore be a liquid anode. The use of a low-melting metal as an anode solvent is a distinct possibility for processing fuels with a high melting point. We have done some work using liquid bismuth as a solvent for PuFe$_2$ in electro-refining.

G. CAMOZZO: The plutonium electro-refining technique described in your paper uses chlorides. Has it also been used with plutonium fluorides, and if so what were the results?

L. J. MULLINS: Both PuF$_3$ and PuF$_4$ can be used in the equimolar NaCl-KCl solvent. In the case of PuF$_4$, PuF$_4$ is reduced to PuF$_3$ by molten plutonium. The fluoride salts are in most respects satisfactory substitutes for PuCl$_3$; however, the following points should be mentioned. The Pu-Am separation is poorer and alumina cannot be substituted for magnesia in the case of fluorides. In an all-chloride system the use of alumina ceramics introduces about 50 ppm of aluminium into the plutonium product. In mixed chloride-fluoride salts the aluminium concentration in the product metal is several hundred parts per million.

J. WURM: I should like to add a further comment. In our work on electro-refining we have developed a new refractory material specially
designed for electro-refining molten salts and liquid electrodes. It is a compound of beryllium oxide and lanthanum oxide, and since it has a melting point of about 1450°C a very good sintered material can be obtained. The inertia compared to molten uranium is excellent; results have shown that, when uranium is melted with this compound for a few hours under vacuum, it is contaminated with only a few parts per million of beryllium and lanthanum.

A paper on this new material will be presented at the Nuclear and Engineering Ceramics Conference to be held at Harwell in the United Kingdom from 25 to 27 October 1965.

Paper SM-66/73 (R. H. Perkins et al.)

L. E. J. ROBERTS: What are the most suitable container materials for use with molten plutonium alloys?

R. H. PERKINS: The best container material found to date is a Ta-5W alloy with a 2-5 µm layer of carbide on the inner surface.

Paper SM-66/56 (P. Desré et al.)

E. BONNIER (Discussion Leader): I should merely like to add that the calculation method developed by Dr. Desré and co-workers can also be applied without great difficulty to the equilibria between liquid or solid and gaseous phases.


There was no discussion of this paper.

General Discussion

E. BONNIER (Discussion Leader): Perhaps we should concentrate our general discussion on the methods of thermodynamic study available in the fields of fused salts on the one hand and alloys on the other.

C. F. BAES, Jr.: When one is concerned with the chemical problems encountered in a reactor development programme, the system at hand is often so complicated that the thermodynamic data in the literature are insufficient to answer questions of chemical compatibility or stability. Hence, the chemist often resorts to direct experiment to answer his questions. We have found the method of heterogeneous equilibrium the most useful. If such experiments are done with sufficient care and control, not only can one answer the chemical questions that arise, but one can also increase the thermodynamic knowledge of the system, and of related systems. I agree, of course, that more than one method should be used to establish such thermodynamic information, and this undoubtedly will be done as time goes on. The basic difficulty, however, is that established methods for dealing with these high-temperature systems are limited. Often there is
only one suitable method at hand - if any at all - and others must be developed as they are needed and as time permits.

J. DROWART: In my view, it should in many cases be possible to perform combined EMF-vapour pressure measurements in which thermodynamic data are obtained simultaneously but independently by the two methods in the same experiment. In several instances this would probably eliminate the discrepancies or give one a better insight into the reasons for the differences in results, if such remain.

A. BÜCHLER: The question of standard states for fused salts has come up. In our work we measure activities fairly directly by means of (in the case of $\text{BeF}_2$ in $\text{LiF-BeF}_2$, for example) a direct comparison between the partial pressure of $\text{BeF}_2$ over the melt and its vapour pressure over pure liquid or solid. On the other hand, in a number of papers on molten cryolite we find activities expressed in terms of such components as $\text{NaAlF}_4$ (which, it happens, does exist in the vapour) and $\text{Na}_3\text{AlF}_6$ (which does not). I wonder if such a formulation of the activities in fused salts is still considered useful by the fused salt experts present here.

O.J. KLEPPA: I must confess that I have never personally looked at anything as complicated as molten cryolite, although it undoubtedly deserves attention in the future. I would, however, like to say that there have been a number of approximate treatments of fused-salt problems in the past which have been based on more or less realistic models regarding the species present in the melt. I believe the most realistic calculations in this field have been due to the Norwegian school of Flood, Førland, Grjøtheim, etc. However, I feel that one should accept these early calculations for what they are: approximate calculations aimed at a limited objective without really unravelling the basic problems involved. We shall have to await future developments.

C.B. ALCOCK: The reason why molecular species were introduced into the calculation of activities in fused salt melts is largely a matter of history. It was done under the misapprehension that, by a proper choice of molecular components, activity coefficients could all be made equal to unity. This approach is largely discredited nowadays, and, in fact, there is a lot to be said for basing calculations on the activities of the elements.

E.A. AITKEN: Would Dr. Kleppa please make a few comments regarding the applicability of fused salt concepts to solid solution oxides, in particular mixed uranium oxides? I should especially welcome information on the role of size parameters and the effect of different cation valencies.

O.J. KLEPPA: The size parameter we use was developed originally by Tobolsky for the case of solid solutions; it reflects the applicability of the corresponding states approach. Once again the Norwegians, and in particular, I think, Flood, have made calculations which offer prospects of understanding complex mixed oxide systems in terms of simpler concepts. For some time the Norwegian school of fused salt chemistry used the concept of vacancies in the liquid state, but this is clearly wrong.

In a solid lattice, on the other hand, the vacancy clearly has a very real existence and value in statistical calculations, and can serve as a basis for significant theoretical developments.
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Session 9  G. WADDINGTON

DISCUSSION LEADERS

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Session 2  C. WAGNER
Session 3  C.B. ALCOCK
Session 4  E. BONNIER
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