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THERMOCHEMICAL DATA FOR REACTOR MATERIALS AND FISSION PRODUCTS: THE ECN DATABASE

E.H.P. CORDFUNKE
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Thermochemical data for reactor materials and fission products: the ECN database

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Abstract

The activities of the authors regarding the compilation of a database of thermochemical properties for reactor materials and fission products is reviewed. The evaluation procedures and techniques are outlined and examples are given. In addition, examples of the use of thermochemical data for the application in the field of Nuclear Technology are given.

1 Introduction

In his Preface to the book "Thermochemical Data for Reactor Materials and Fission Products" [90Cor] Professor O. Kubaschewski wrote: "For someone who has spent 50 years of his life to produce and assess thermochemical and other physico-chemical data for practical application, it is a pleasure to introduce the present volume". And he continued, after having emphasized the need for and the importance of critical assessments "... the arrival of the computer has been a godsend. With this, it is now possible to combine the results of various experimental methods and, where these are missing, the estimations (a new art) to a consistent set of thermochemical tables, and, what is more, to keep these up-to-date."

Of the present authors, being the editors of the book mentioned, the first one has co-operated for more than 25 years with Professor Kubaschewski. The basic principles of experimental thermochemistry and the approach to the solution of practical problems he learnt in discussions with him, has been of lasting value. Some of these principles will be described in this paper to illustrate the efforts involved in the development of a consistent database of thermochemical properties required in Nuclear Technology.

2 Procedure and evaluation techniques

Figure 1 shows a diagram of the computer codes developed at ECN for the evaluation procedure of thermodynamic properties of inorganic compounds. In short, the procedure

is as follows. After all literature data have been collected, the heat capacity of the condensed and gaseous states of the species in a specific system are established first; in many, but by far not all cases, values for the entropy can be derived. Next the chemical equilibrium studies and enthalpy of formation studies are recalculated to obtain the enthalpies of formation at 298.15 K. The recommended values are stored in the database together with crystal structure data and an explanatory text. The evaluation techniques are further outlined below.

2.1 Heat capacity and enthalpy increment

The treatment of the heat capacity of condensed phases falls into two regions, the low-temperature range (0 to 300 K), which is mostly studied by adiabatic calorimetry, and the high-temperature region (≥ 298.15 K) which is in most cases studied indirectly by enthalpy increment measurements.

The data are processed by the programme ENTHAL, which employs a polynomial fitting procedure. The standard entropy at 298.15 K is obtained by integration of the low-temperature results. The high-temperature data are generally represented by the polynomial equation of the form:

$$\{H^\circ(T) - H^\circ(298.15 \text{ K})\} = a(T/K) - b(T/K)^2 - c(T/K)^{-1} + d \quad (1)$$

as suggested by Maier and Kelley [32Mai]. If the value of C_p at 298.15 K is known from low-temperature measurements, equation (1) is constrained to $C_p(T) = C_p(298.15 \text{ K})$ for $T = 298.15 \text{ K}$. In practice equation (1) will not describe the enthalpy increment adequately for each substance over the whole temperature range. Near phase transitions or over wide temperature regions the curvature can be considerably strong, and higher polynomial terms (up to T^5) have to be included then. In that case, extrapolation beyond the range of the experiments may give serious deviations from the real values depending on the curvature of the polynomial used.

To judge whether the C_p values from the low-temperature adiabatic measurements show continuity with the high-temperature measurements, the function

$$\frac{\{H^\circ(T) - H^\circ(298.15 \text{ K})\}}{T - 298.15 \text{ K}} \quad (2)$$

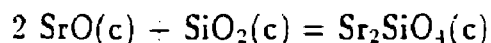
is used. At 298.15 K it has a value which is identical to the true heat capacity, as obtained from adiabatic low-temperature heat-capacity measurements. This function, representing the reduced enthalpy increment or mean heat capacity, is sensitive enough to show deviations from smooth continuity within the precision attained by the measuring techniques and is an accurate means of comparing heat capacity data from different sources.

For gases the thermal functions are normally obtained from molecular parameters and spectroscopic data via statistical mechanical calculations. The programme MOTHER (MOlecular THERmodynamics) has been developed for this purpose. It requires data for

various molecular parameters to calculate the translational, vibrational, rotational and electronic contribution to the thermal functions. Examples of input data are given in Table 1. In most cases a harmonic-oscillator/rigid-rotor approach is used, but detailed anharmonicity corrections can be applied for specific cases.

2.2 The enthalpy of formation

Enthalpies of formation can often be obtained directly either by combustion calorimetry or by enthalpy-of-solution calorimetry. Only when the full details of the measurements are given in the original paper, it is possible to recalculate the thermodynamic cycles. This is in most cases necessary, let alone the fact that the auxiliary values have been changed since the date of publication of the original paper. A case in point is the enthalpy of formation of Sr_2SiO_4 which has been derived by Barany et al. [57Bar] from the enthalpy of solution in $\text{HF}(\text{aq})$, according to the cycle given in Table 2. From the enthalpy of the reaction:



they derived $\Delta_f H^\circ(298.15 \text{ K}) = -2269.8 \text{ kJ}\cdot\text{mol}^{-1}$. However, because of a change in the values for the enthalpies of formation of $\text{SrO}(\text{c})$ [90Cor] and $\text{SiO}_2(\text{c})$ [89Cox] the recalculated value of the enthalpy of formation of $\text{Sr}_2\text{SiO}_4(\text{c})$ becomes $\Delta_f H^\circ(298.15 \text{ K}) = -(2304.4 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$.

2.3 Chemical equilibria

Data for many chemical reactions are obtained from measurements of equilibrium constants at temperatures which are in many cases well above the standard reference temperature of 298.15 K. Such measurements supply data for the Gibbs Energy of the reaction which can be used in the evaluation of the enthalpy of formation of one (or more) of the species involved. In order to facilitate comparison of different studies which generally cover different temperature ranges, it is common practice to express the derived information as the enthalpy of reaction at 298.15 K. The calculational methods used to this purpose are called the second- and third-law methods and are outlined below.

The equilibrium constant of a chemical reaction is given by:

$$\Delta_r G^\circ(T) = -RT \ln K_p = \Delta_r H^\circ(T) - T \Delta_r S^\circ(T) \quad (3)$$

where $\Delta_r G^\circ(T)$ is the standard Gibbs Energy of reaction at temperature T , R is the gas constant, and K_p the equilibrium constant. Differentiation of equation (3) leads to:

$$\frac{\Delta_r H^\circ(T)}{R} = \frac{d \ln K_p}{d(1/T)} \quad (4)$$

in which $\Delta_r H^\circ(T)$ is the standard enthalpy of the reaction. Equation (4) shows that the relationship between $\ln K_p$ and $1/T$ is a straight line, of which the slope equals $\Delta_r H^\circ(T)/R$. This value of the enthalpy of reaction is generally referred to as the second-law enthalpy, which is thus obtained from a linear regression of a set of data points for the equilibrium constant. In addition, the intercept of the linear equation corresponds to the entropy of reaction, $\Delta_r S^\circ(T)/R$.

The third-law method involves the calculation of the enthalpy of reaction from each individual data point, by making use of the Gibbs Energy function:

$$\Phi^\circ(T) = -\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T \quad (5)$$

Rewriting equation (5) for a change in a chemical reaction and substitution of equation (3), gives:

$$\Delta_r H^\circ(298.15 \text{ K}) = -RT \ln K_p - T \Delta_r \Phi^\circ(T) \quad (6)$$

The third-law method thus relies on an accurate knowledge of the heat capacity and the absolute entropy of the products and reactants of a chemical equilibrium, and thus gives principally more precise results than the second-law method which is particularly useful when entropy data are lacking.

This analysis is performed by the THIRDLAW programme. An output example is given in Table 3. It can be seen that a second-/third-law agreement can be easily checked, and also the agreement between the second-law entropy and the value calculated statistically from the selected molecular parameters. For the example shown, the vapour pressure measurements of ZrI_4 by Cubicciotti et al. [78Cub], the second-law and third-law enthalpies as well as the second-law and statistically calculated entropies agree excellently.

The enthalpies of reaction thus obtained, are combined with auxiliary data in the programme CYCLE to obtain a reaction scheme for the derivation of the enthalpy of formation. Similarly, reaction schemes for the recalculation of enthalpy-of-solution measurements is performed with CYCLE. All input files for either THIRDLAW or CYCLE are being stored on disk.

2.4 Consistency

An important aspect of any thermodynamic database is its internal consistency. Since especially the formation quantities of many substances are interrelated, all recommended quantities should be mutually consistent. This holds for all thermochemical data including the thermal functions [90Gur]. This consistency is achieved by recalculation, when possible, of all thermochemical cycles using the internationally accepted CODATA Key values [89Cox] and auxiliary data from the present database. To minimize errors, the computer codes THIRDLAW, CYCLE and TBASE all use the same input files for the thermochemical properties, fundamental constants and atomic masses of the elements.

3 The ruthenium oxides

The Ru-O system was thoroughly treated in the databook [90Cor], where all information up to medio 1989 was considered. However, since that time already six relevant papers have published which contain information that replaces some of the estimates made in the 1989 evaluation. We here present an updated version of this assessment, which demonstrates the procedures outlined above and illustrates that databases are continuously changing as a result of new experimental studies.

3.1 Ruthenium dioxide, RuO₂(s)

The enthalpy of formation of RuO₂(s) has been derived from equilibrium measurements, both dissociation pressure measurements and emf measurements, in an assessment by Rard [85Rar]. In the absence of an experimental entropy value at 298.15 K, he used a modified second-law treatment. As usual, much scatter in the 298.15 values was thus obtained, the values of $\Delta_f H^\circ(298.15 \text{ K})$ ranging from -300 to $-320 \text{ kJ}\cdot\text{mol}^{-1}$. Much of the scatter disappeared, however, after an entropy value became available [89Cor], and a third-law treatment of the experimental equilibrium measurements was possible (Table 4). The recommended value $-(314.2 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$ differs considerably from a combustion-calorimetric value ($-305.4 \text{ kJ}\cdot\text{mol}^{-1}$). This appears to be the case in many assessments, and is often caused by incomplete combustions resulting in values which are too high.

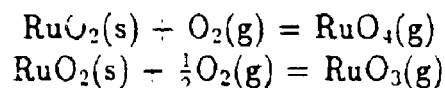
The emf measurements published by Mallika and Shreedharan [90Mal] after completion of our assessment, do not change our recommended value.

3.2 RuO₄(g) and RuO₃(g)

The main volatile ruthenium oxide species up to 2000 K are RuO₃(g) and RuO₄(g). At higher temperatures indications for the presence of RuO₂(g), and even RuO(g), in the vapour have been obtained [68Nor]. Although the volatility of these species has been studied by various authors and under various experimental conditions, quantitative thermochemical information is scarce.

In our 1989 assessment, only molecular data for the RuO₄ species were available. The tetrahedral symmetry being determined by Schäfer and Seip [67Sch], the fundamental frequencies were determined in a number of spectroscopic studies and confirmed by subsequent studies (Table 5). From these data the molecular parameters of RuO₃ could be estimated. Immediately thereafter, Kay et al. [89Kay] studied this molecule by matrix isolation IR spectroscopy, and concluded that RuO₃ is trigonal planar in contrast to the estimated pyramidal geometry assumed before. They reported experimental data for the the Ru-O asymmetric stretching frequency and the symmetric stretch was calculated, both being somewhat higher than our estimates. Hameka et al. [91HAM] performed ab-initio calculations for the molecule which confirmed the planar geometry and showed the internuclear distance to be close to that calculated for RuO₄. Further adjustment of the RuO₃ data had to be made for the degeneracy of the ground state: 3 instead of 1.

In order to maintain the consistency between the spectroscopic and thermodynamic data, a recalculation of the equilibrium studies as have been assessed before [90Cor], is now necessary. The literature data for the following equilibria have been reanalysed:



and the results are summarized in Table 6, from which can be seen that the various studies are in reasonable agreement.

The calculation of the standard entropy of RuO_3 based on these new spectroscopic data is not considerably different from the existing one: $S^\circ(298.15 \text{ K}) = 281.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, compared to $S^\circ(298.15 \text{ K}) = 281.9 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ given in [90Cor]. Similarly, the new value of the enthalpy of formation, $\Delta_f H^\circ(298.15 \text{ K}) = -(64.1 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$, is in reasonable agreement with the value $-(62.5 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$ given in [90Cor]. However, the agreement is rather fortuitous since the higher electronic contribution ($R \ln(3)$) compensates the much lower rotational and vibrational contribution to the thermal functions.

4 The enthalpy of formation of $\text{Sr}_2\text{SiO}_4(\text{s})$

At several occasions Kubaschewski has emphasized that the compilation of the thermochemical properties of substances has become a new field of science, requiring from its contributors "an intimate knowledge of the relevant experimental methods, a complete command of the underlying thermodynamic principles, and a long experience of what the resulting values are likely to be" [66Kub]. Even then pitfalls are sometimes difficult to avoid. A case in point is the assessment of the enthalpies of formation of the strontium and barium silicates. The published values may differ as much as $70 \text{ kJ}\cdot\text{mol}^{-1}$. The enthalpy of formation of $\text{Sr}_2\text{SiO}_4(\text{s})$, for instance, has been measured by enthalpy-of-solution calorimetry by Nacken [30Nac], and Barany et al. [57Bar], the results being grossly discordant. A third-law treatment of the emf measurements by Rog et al. [74Rog] seemed to support the results of Nacken, and a value based on these measurements, was initially selected by us. However, shortly thereafter, new calorimetric measurements by Huntelaar et al. [92Hun] under well-defined conditions changed the picture totally as is shown in Table 7.

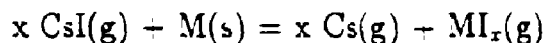
5 Applications

Because of another well-known statement by Kubaschewski: "Thermodynamics has to go into business otherwise it is doomed" [88Cor1], we will give here two examples of applications of assessed thermochemical data to practical problems in the nuclear field.

5.1 The chemical state of iodine in the primary system of a LWR

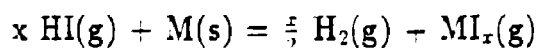
The importance of interactions between the fission product vapours and aerosols generated from the Ag-In-Cd control rod in determining the magnitude of the release to the containment, has been pointed out by Bowsher [87Bow]: the surface area of aerosols generated from bulk reactor materials is estimated to be two to three orders of magnitude greater than the surface area of the reactor coolant system. The analysis of the control-rod materials in the TMI reactor building indicated widely varying ratios of these elements from their initial ratios (80% Ag, 15% In, and 5% Cd), larger fractions of Cd being volatilized and transported than for Ag or In. All three components of the control-rod alloy form stable iodides, and their formation can have considerably different effects on the release of iodine: silver iodide has a negligible solubility in water of pool of the sump whereas that of CsI or CdI₂ is high. As a consequence, the formation of AgI may act as a sink for the biohazardous iodine.

We have performed thermochemical calculations in the multicomponent/multiphase system Cs-I-Te-Ag-In-Cd-O-H using the data from the present assessments in the CHEM-SAGE programme, assuming that iodine is present as either CsI(g) or HI(g) [93Cor]. Thus, for the equilibrium:



the calculations show that CsI is rather stable up to about 1000 K (Fig. 2). Above this temperature the fraction decreases to a constant value of about 10^{-3} , InI being the predominant vapour species. At temperatures above 1500 K the fractions of HI, AgI and CdI further increase. The formation of Cs₂CdI₄ as suggested by Beard et al. [88Bea], is thermodynamically not favoured.

A similar calculation for the reactions of the control-rod materials with HI(g):



shows that the speciation is quite different below 1000 K where the formation of CdI₂(g) predominates. Above this temperature its stability rapidly decreases in favour of InI(g), and the same equilibrium speciation is approached as for the CsI case. These calculations show that in the case of interaction of iodine vapours/aerosols with the (Ag,In,Cd) control-rod alloy, the speciation of iodine is highly different below 1000 K if iodine is transported as CsI or as HI in the steam/hydrogen gas flow from the core region into the primary system.

5.2 Calculation of phase diagrams

The calculation of phase diagrams (or better: equilibrium diagrams) was made possible by the considerable growth in the assessed thermochemical data after the second world war. This was especially the case in metallurgical systems. In many ceramic systems,

however, essential thermochemical information is still lacking. A case in point is the Ba-U-O system, which is of interest in Nuclear Technology since barium is formed in relatively large amounts in irradiated fuel. In order to consider the formation of perovskite-type BaUO_3 , possibly in solid solution with BaZrO_3 , its thermochemical stability under the conditions in the UO_2 fuel must be known.

In the Ba-U-O system six compounds have been identified: BaU_2O_7 , $\text{Ba}_2\text{U}_3\text{O}_{11}$, BaUO_4 , Ba_3UO_6 , BaUO_3 , and $\text{Ba}_2\text{U}_2\text{O}_7$. Of the thermochemical quantities of these ternary compounds only the enthalpies of formation have been measured. Heat capacity data are only available for BaUO_4 [90Cor], and, as a consequence, the entropies of all other phases had to be estimated. For the hexavalent barium uranates the contributions of BaO and UO_3 have been taken additive with $\Delta S^\circ = 0$ at 298.15 K. For the uranates with a lower uranium valency we have taken $12.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for the contribution of $\frac{1}{2} \text{ O}_2$ in the entropy difference between a hexavalent and a pentavalent uranium.

In the absence of high-temperature heat capacity data, the Gibbs energies of the various phases have subsequently been calculated with the relationship [66Alc]:

$$\Delta_f G^\circ(T) = \Delta_f H^\circ(298.15 \text{ K}) - T \Delta_f S^\circ(298.15 \text{ K}) \quad (7)$$

During the calculations it appeared necessary to adjust the entropies of some of the phases slightly in order to get the proper sequences of the various phases (Table 8), thus providing a reliable check on the estimations.

The phase diagram of the Ba-U-O system at 1000 K, as calculated with the PREAREA programme, is shown in Figure 3 indicating that at the low oxygen potentials in UO_2 fuel the formation of only BaUO_3 or Ba_3UO_6 can be expected.

6 Future developments

The availability of reliable thermodynamic data is of prime importance for the risk-assessment of accident conditions in nuclear reactors. The ECN database, which is specially prepared for this purpose, contains carefully evaluated data for most of the relevant chemical species. Compared to the version issued in 1990, the available data set has grown considerably. It is extended with many elements and species which are of interest to the modelling of the interactions in the primary coolant system and core-concrete interactions.

However, the nuclear field is broad and other areas like actinide technology, the design of ceramic blankets for fusion reactors or the design of corrosion-resistant materials, can also benefit from the application of thermodynamic calculations. The ECN database is therefore being extended to these areas also. It is planned to produce a new compilation "Thermochemical Data for Inorganic and Nuclear Materials". Figure 4 shows the elements which we expect to include in this work.

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Table 1: The molecular parameters used for the calculation of the thermal functions of $\text{RuO}_4(\text{g})$ and $\text{RuO}_3(\text{g})$

	RuO_4	$\text{RuO}_3(\text{g})$
symmetry group	T_d	D_{3h}
symmetry number	12	6
$r(\text{Ru-O})/\text{nm}$	0.1706 ± 0.0003	0.171 ± 0.002
vibrational frequencies (degeneracy)/ cm^{-1}	885.3, 319.0(2), 921.0(3), 336.0(3)	950, 390, 893(2), 350(2)
moment of inertia $I_A I_B I_C / \text{g}\cdot\text{cm}^{-2}$	$8.756 \cdot 10^{-114}$	$2.89 \cdot 10^{-114}$
electronic energy levels (degeneracy)/ cm^{-1}	0(1)	0(3)

Table 2: The standard enthalpy of formation of $\text{Sr}_2\text{SiO}_4(\text{s})$, calculated after Barany et al. [57Bar]

1.	$\text{SiO}_2(\text{c}) + 6\text{HF}(\text{aq}) = [\text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}](\text{aq})$	-139.29 ± 0.33
2.	$2\text{SrO}(\text{c}) + 4\text{HF}(\text{aq}) = [2\text{SrF}_2 + 2\text{H}_2\text{O}](\text{aq})$	-548.40 ± 0.42
3.	$\text{Sr}_2\text{SiO}_4(\text{c}) + 10\text{HF}(\text{aq}) = [2\text{SrF}_2 + \text{H}_2\text{SiF}_6 + 4\text{H}_2\text{O}](\text{aq})$	-478.31 ± 0.84
4.	$2\text{SrO}(\text{c}) + \text{SiO}_2(\text{c}) = \text{Sr}_2\text{SiO}_4$	-209.38 ± 1.00

Table 3: A typical output of the THIRDLAW programme

Cubicciotti et al. (1978)		
J. Electrochem. Soc. 125:972		
ZrI ₄ vapour pressure - cell A		
T/K	p/atm	$\Delta H^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$
451.900	0.61500E-05	133.05
458.800	0.10400E-04	133.02
462.600	0.13400E-04	133.12
464.100	0.15100E-04	133.08
470.200	0.23600E-04	133.03
470.900	0.25000E-04	133.00
472.900	0.27800E-04	133.13
475.900	0.34800E-04	133.06
477.300	0.38900E-04	133.00
	mean =	133.05 \pm 0.03
THE SECOND-LAW VALUES:		
At T = 464.6 K:	$\Delta H^\circ = 129.67 \text{ kJ}\cdot\text{mol}^{-1}$	
	$\Delta S^\circ = 187.14 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
At T = 298.15 K:	$\Delta H^\circ = 133.30 \pm 0.33 \text{ kJ}\cdot\text{mol}^{-1}$	
	$\Delta S^\circ = 196.79 \pm 0.71 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
CALCULATED FROM TBASE:		
At T = 464.6 K:	$\Delta S^\circ = 186.62 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
At T = 298.15 K:	$\Delta S^\circ = 196.26 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	

Table 4: The enthalpy of formation of RuO₂(s) at 298.15 K

authors	ref	method*	T/K	$\Delta_f H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	
				2nd-law	3rd-law
Remy and Köhn	[24Rem]	D	1203	-219.7	
Shchucharev and Ryabov	[60Shc]	C	298.15		-305.4
Schäfer et al.	[63Sch1]	D	1377-1451	-259.4 ± 2.0	-314.6 ± 1.7
Bell and Tagami	[63Bel]	D	1380-1776	-304.2 ± 2.0	-310.0 ± 1.2
Kleykamp	[69Kle]	E	780-1040	-344.7 ± 3.0	-316.5 ± 4.5
Pizzini and Rossi	[71Piz]	E	1170-1523	-319.3 ± 3.0	-312.5 ± 1.5
Chatterji and Vest	[71Cha]	E	873-1273	-315.4 ± 1.1	-317.2 ± 0.4
Tagirov et al.	[75Tag]	M	1000-1200	-302.6 ± 6.3	-317.8 ± 1.5
Cordfunke and Konings	[88Cor2]	E	962-1070	-313.2 ± 3.0	-314.15 ± 0.02
Mallika and Shreedharan	[90Mal]	E	1005-1106	-327.8 ± 3.4	-313.7 ± 0.8
			selected value:		-314.2 ± 0.5

Table 5: The vibrational frequencies of RuO₄(g), in cm⁻¹

authors	ref	method/state	ν_1	ν_2	ν_3	ν_4
Dodd	[59Dod]	IR/gas			920	
Levin and Abramowitch	[69Lev]	IR/gas			919.7	329.0
McDowell et al.	[72McD]	IR-R/gas	885.3	319	921.0	336.0
Königer and Müller	[77Kön]	IR/gas			919.5	
Green et al.	[89Gre]	IR/matrix			916.9 ^a	
Snels et al.	[91Sne]	IR/gas			921.7 ^a	

^a ¹⁰⁴Ru¹⁶O₄Table 6: The enthalpy of formation of RuO₃(g) at 298.15 K

authors	ref	T/K	method ^a	$\Delta_f H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	
				1989-value	1993-value
Alcock and Hooper	[60Alc]	1473-1673	T	-63.2 ± 0.8	-64.7 ± 0.5
Schäfer et al.	[63Sch2]	1033-1477	T	-60.3	-61.7
Bell and Tagami	[63Bel]	1076-1776	T	-64.8 ± 0.8	-66.0 ± 0.7
selected value:				-62.5 ± 2.5	-64.1 ± 2.5

^a T = transportation methodTable 7: The enthalpy of formation of Sr₂SiO₄(s) at 298.15 K.

authors	ref	method ^a	$\Delta_f H^\circ/\text{kJ}\cdot\text{mol}^{-1}$
Nacken	[30Nac]	S	-2223.6 ± 5.1
Barany et al.	[57Bar]	S	-2304.4 ± 2.5
Rog et al.	[74Rog]	E	-2230.1 ± 6.1
Huntelaar et al.	[92Hun]	S	-2305.7 ± 2.2
selected values:			-2305.7 ± 2.5

^a S = solution calorimetry, E = electromotive force measurements

Table 8: Thermochemical properties of barium uranates at 298.15 K; estimated values in brackets

compound	$\Delta_f H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$S^\circ(298.15\text{ K})/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
BaU ₂ O ₇	-3234.8 ± 3.4	[260 ± 5]
Ba ₂ U ₃ O ₁₁	[-5250 ± 25]	[405 ± 5]
BaUO ₄	-1992.2 ± 2.1	153.97
Ba ₃ UO ₆	-3213.5 ± 5.6	[298]
BaUO _{3+r}	-1725 ± 10	[142]
Ba ₂ U ₂ O ₇	-3739.8 ± 4.1	[296]

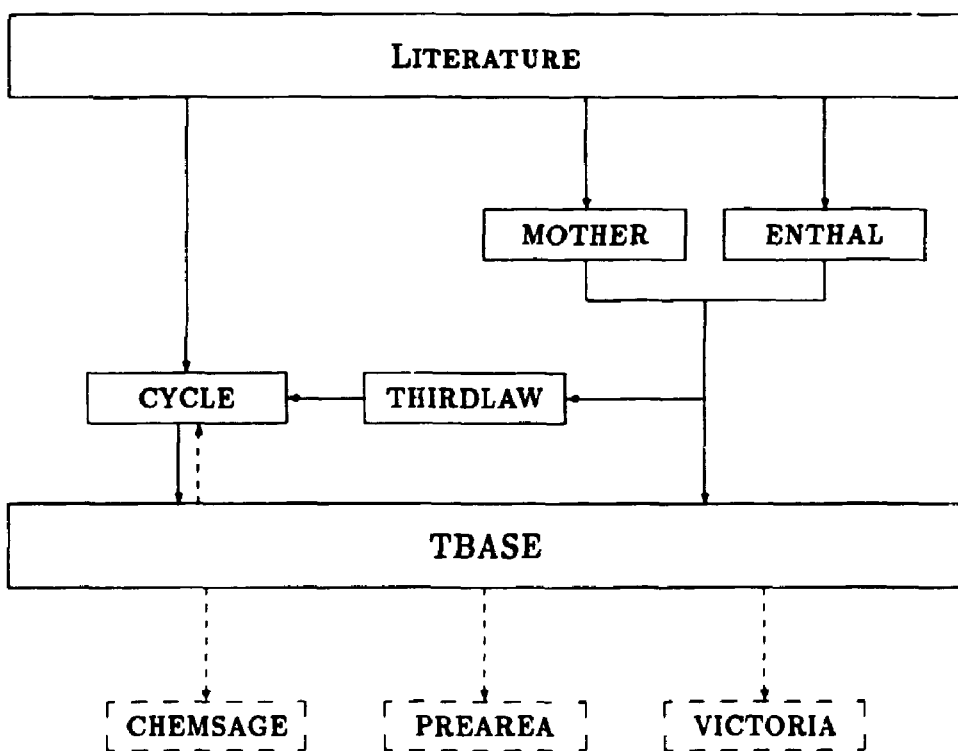


Figure 1: Flow diagram of the ECN computer programmes used in the assessment of thermochemical properties

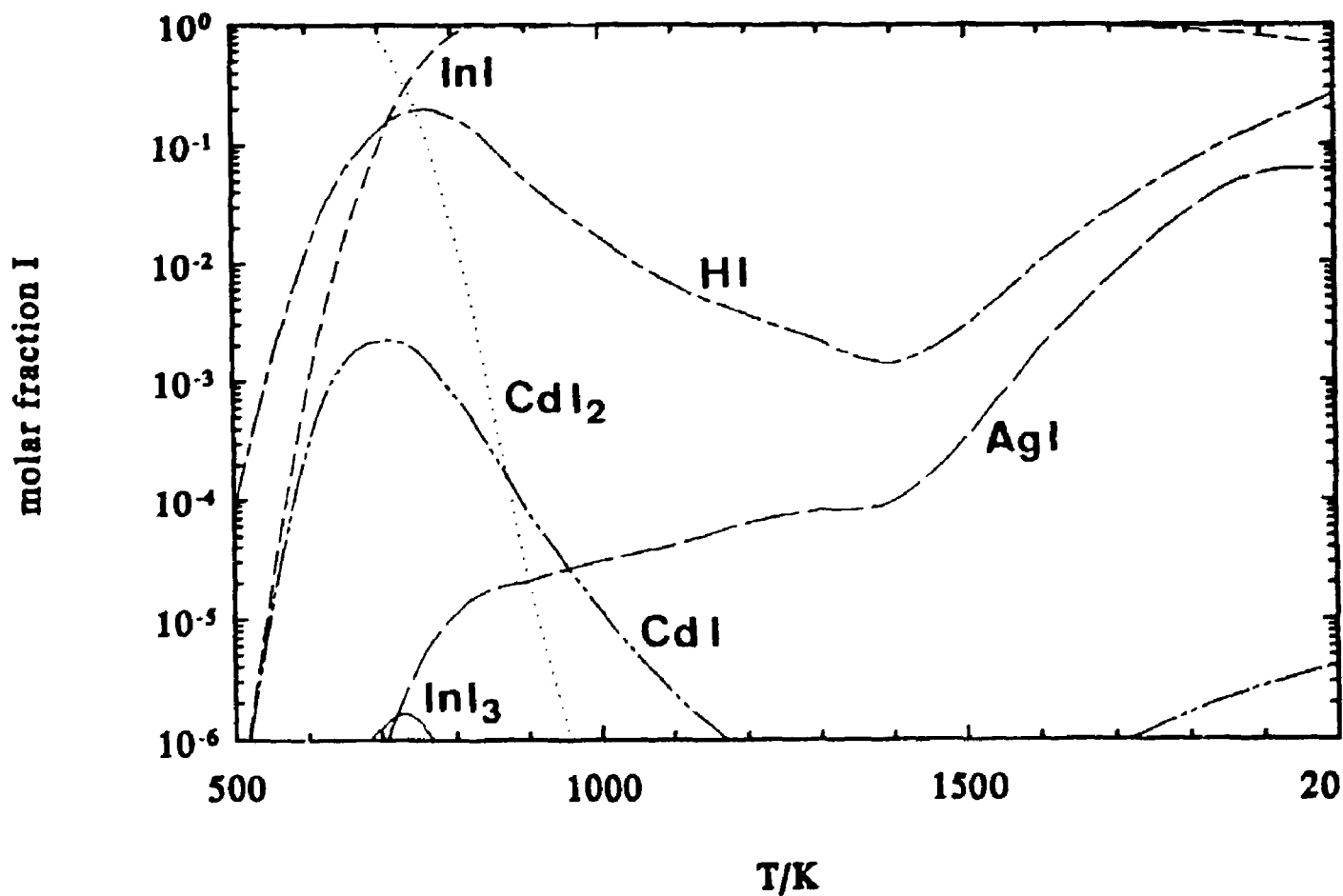
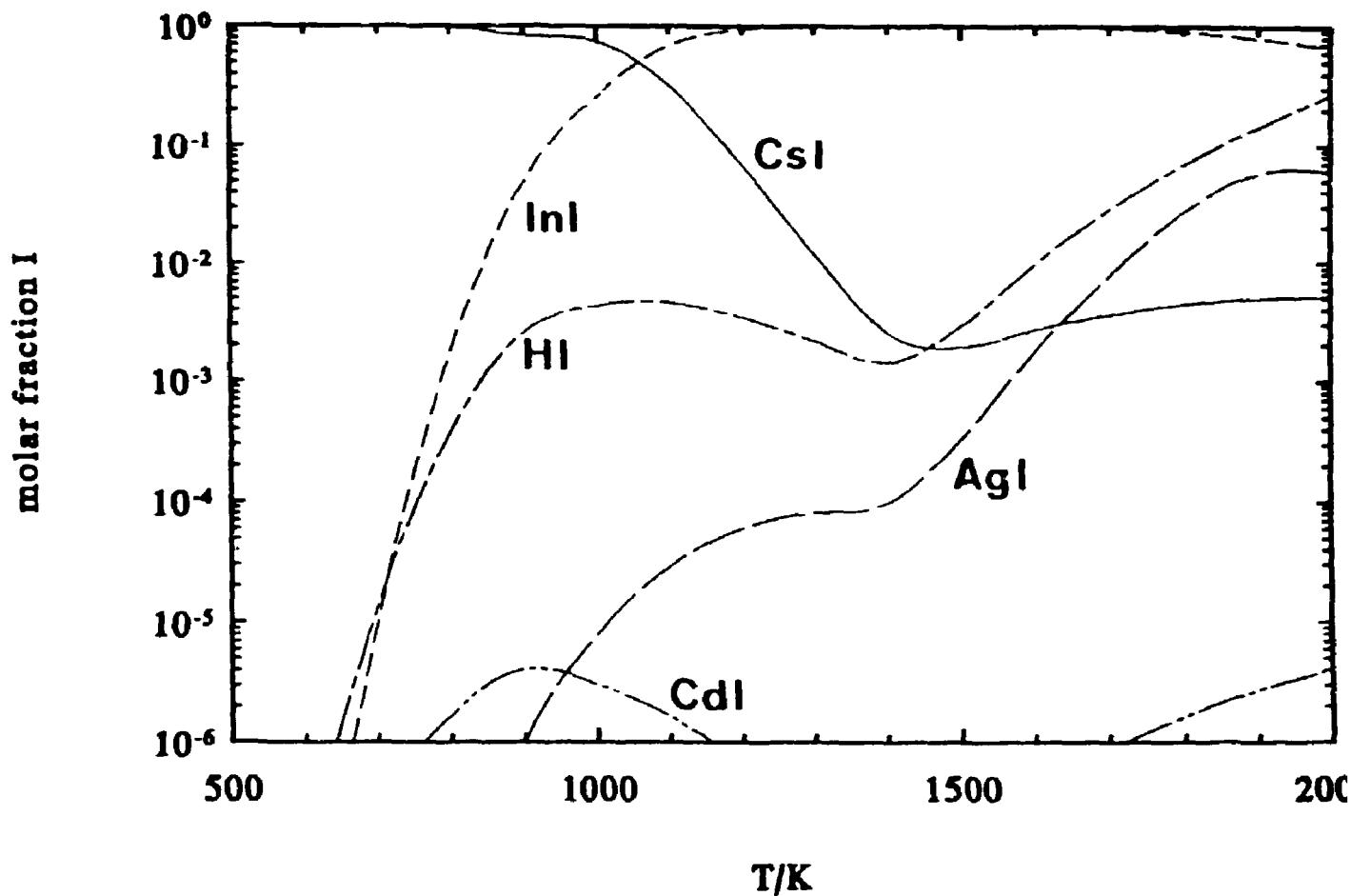


Figure 2: The chemical speciation in the Cs-I-Te-Ag-In-Cd-O-H system as a function of the temperature; $p = 100$ bar, $n(\text{H}_2)/n(\text{H}_2\text{O}) = 1$, $n(\text{I})/n(\text{H}_2\text{O} + \text{H}_2) = 10^{-6}$. Top, reactions with CsI(g) ; bottom reactions with HI

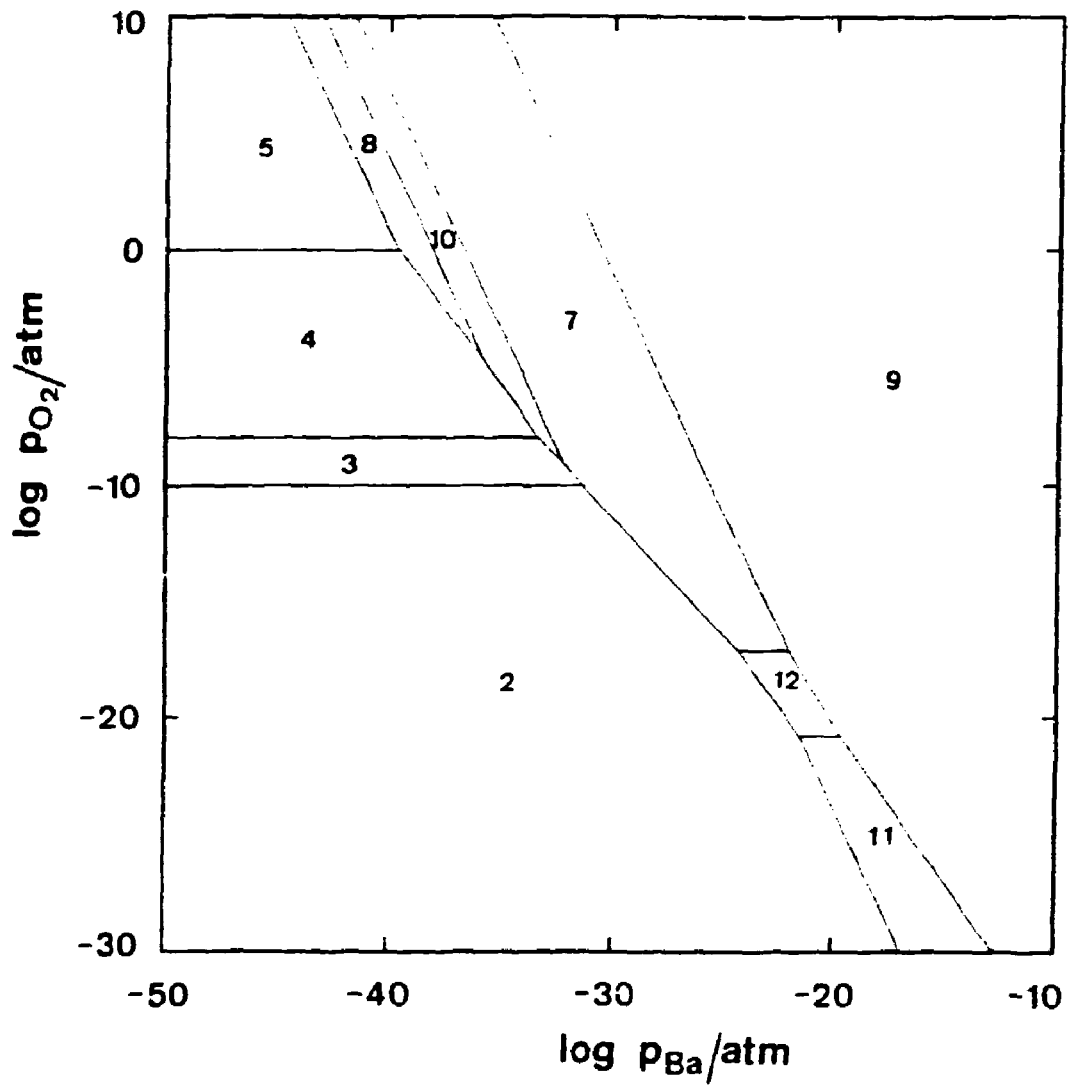


Figure 3: A section of the predominance area diagram of the Ba-U-O system at 1000 K; pressures in atmospheres. 1 = U, 2 = UO_2 , 3 = U_4O_9 , 4 = U_3O_8 , 5 = UO_3 , 6 = BaO , 7 = BaUO_4 , 8 = BaU_2O_7 , 9 = Ba_3UO_6 , 10 = $\text{Ba}_2\text{U}_3\text{O}_{11}$, 11 = BaUO_3 , 12 = $\text{Ba}_2\text{U}_2\text{O}_7$,

