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**STUDIES OF SURFACE ADSORPTION ON  $\text{LiAlO}_2$**

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**Abstract**

Computational and experimental approaches are being taken to understanding surface adsorption/desorption effects on tritium inventory and release. The computational survey integrates a thermodynamic treatment of surface adsorption and bulk phase effects such as solubility and gas phase composition. The system  $\text{T}_2\text{O}:\text{T}_2:\text{LiAlO}_2$  was examined. The calculations indicate that surface adsorption can be expected to contribute most to tritium inventory under the conditions of lower temperatures and higher oxygen activities. Higher temperature and lower oxygen activity favor lower surface inventory. In the experimental work, a high temperature gas chromatograph was constructed in order to measure the  $\text{H}_2\text{O}:\text{H}_2$  surface adsorption isotherms and the solubility of hydroxide in  $\text{LiAlO}_2$ . Preliminary data indicate that at 478K approximately 15% of the surface is covered for a partial pressure of  $\text{H}_2\text{O}$  of approximately 52 Pa. Calculated values can be obtained that are in reasonable agreement with this.

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## STUDIES OF SURFACE ADSORPTION ON $\text{LiAlO}_2$

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### Introduction

Lithium-containing ceramics are being considered as tritium breeding blankets for fusion reactors. Evaluation of the technological viability of a reactor system depends, in part, on assessments of the tritium inventory in various parts of the reactor, including the blanket. At thermodynamic equilibrium, tritium inventory in a ceramic breeder blanket will be composed of a portion due to dissolved tritium (tritoxide and, under some conditions, tritide) and a portion due to adsorbed tritium ( $\text{HTO}$ ,  $\text{T}_2\text{O}$ ,  $\text{HT}$  and  $\text{T}_2$ ) on the breeder surfaces. Contributions from both portions must be assessed because their relative contributions to inventory will differ depending on conditions. Both calculational and experimental approaches to the problem are being used for  $\text{LiAlO}_2$ .

### Calculational Survey

Various aspects of the solubility question for  $\text{Li}_2\text{O}$ ,  $\text{LiAlO}_2$ , and  $\text{Li}_4\text{SiO}_4$  were discussed on a calculational basis in earlier papers. [1] Those calculations yielded a predicted ranking of expected thermochemical performance. For the calculational approach to an integrated treatment of both the surface adsorption and solubility issues for  $\text{LiAlO}_2$ , an innovation in the use the SOLGASMIX code has been made to include surface effects. To do this, a hypothetical element, "Ad", is introduced to form a hypothetical surface phase, " $\text{Ad}_2\text{O}$ ", to allow the program to distinguish between surface processes and bulk solubility processes. This surface phase is taken to be identical in its free energy of formation to  $\text{LiAlO}_2$ . The reaction products formed on the surface by the adsorption of  $\text{H}_2\text{O}$  or  $\text{T}_2\text{O}$  or  $\text{HTO}$  are taken to be " $\text{AdOH}$ " and " $\text{AdOT}$ ". The calculations treat the  $\text{AdOH}$  and  $\text{AdOT}$  as forming an ideal solution in the surface phase.

The amount of Ad in the input to the code determines the amount of surface being considered in the calculations. This amount rests on the assumption that there are  $10^{15}$  adsorption sites per  $\text{cm}^2$ . This is an approximation based on observations by DeBoer et al [2] of the water monolayer capacity on alumina corresponding to  $1.1 \times 10^{15}$  sites/ $\text{cm}^2$ . Also, Morimoto et al [3] indicate that the crystallographic surface density of Al atoms on  $\alpha$ -alumina is  $1.02 \times 10^{15}$ / $\text{cm}^2$ . A possible maximum value for sites might be set by the fact that there are  $1.7 \times 10^{15}$  oxide ions in a close-packed sheet [4]

but it is not necessarily true that all crystal faces on the  $\text{LiAlO}_2$  sample would present close-packed sites.

The system treated in the calculations contains 0.001 mole  $\text{LiAlO}_2$  with an assumed surface area of  $1 \text{ m}^2/\text{gm}$ , 15 vol.% void space, and  $10^{-4}$  g.at. tritium. In respect to total quantities of elements, this is the same system that was considered in the earlier calculations [1] and it therefore allows comparisons to be made directly with the earlier results. Three temperatures were selected to cover the range of interest, 700K, 1000K, and 1300K. The oxygen activity range covered in the calculations,  $10^{-25}$  to  $10^{-5}$ , brackets the oxygen activity at which the oxidized and reduced forms of tritium in the gas phase are equal.

By analogy with data for the energetics of adsorption in the alumina-water system published by Fubini et al [5], a value for the enthalpy of adsorption of water equal to  $-25 \text{ kcal/mole}$  was assumed together with a value of  $-30 \text{ cal/mole-K}$  for the entropy of adsorption. These values allowed the free energies of formation of the AdOH and AdOT species to be calculated.

For simplicity, the calculations presented here are for protium-free conditions. Protium-purge effects, therefore, are not addressed, though the introduction of  $\text{H}_2$  in real systems has a thermodynamic (and kinetic) impact. Surface adsorption of the reduced form,  $\text{T}_2$ , is not included because available evidence indicates that adsorption of  $\text{T}_2$  (or  $\text{H}_2$ ) at the high temperatures of interest would be minor compared to adsorption of  $\text{T}_2\text{O}$  (or  $\text{H}_2\text{O}$ ). The data from Cirillo et al [6] for the adsorption of  $\text{H}_2$  on alumina show that the fractional surface coverage at 120K is on the order of 0.001 for  $\text{H}_2$  pressures from 10 to 100 Torr. Because surface adsorption decreases as temperature rises, it is reasonable to expect an insignificant contribution from  $\text{T}_2$  adsorption at temperatures of 700K and above and for lower partial pressures of  $\text{T}_2$ .

Figures 1 through 3 summarize findings from the calculations. They suggest that the degree of surface adsorption at 700K is essentially independent of oxygen activity in the range of  $10^{-25}$  to  $10^{-5}$ . Under these conditions, the magnitude of adsorption is substantial and accounts for 89% of the tritium in the system; 13.5% of the surface holds adsorbed material. Only 1% of the tritium in the system is in the gas phase and 10% is in solution in the  $\text{LiAlO}_2$  as tritoxide. Dependence on oxygen activity becomes more significant at higher temperatures and becomes noticeable at 1000K for oxygen activities below  $10^{-20}$ . There is substantial dependence on oxygen activity at 1300K for oxygen activities lower than  $10^{-15}$ . In the plateau region of the 1300K curve in Figure 1, where there is still independence of oxygen activity, only about 2% of the tritium is adsorbed on the surface, but 94% is in solution as tritoxide.

From a thermodynamic perspective, the most favorable condition for tritium release is at high temperature and low oxygen activity; the reduced form of tritium would be favored. The low oxygen activity extremity of the 1300K curve in Figure 1 represents 0.04% of the tritium in the system as adsorbed on the surface. Under these conditions, 94% of the tritium is in the gas (as  $T_2$ ) and 6% is in solid solution as tritoxide.

Figure 2 shows that the relative amounts of tritium adsorbed on the surface and of tritium in solid solution remain essentially constant over the oxygen activity range for 700K and 1000K, though the absolute quantities differ. This constancy holds also for 1300K except for low oxygen activity. Under these conditions, the departure from constancy arises from the growing importance of tritide,  $T^-$ , as a solute species in the  $LiAlO_2$ .

Under low oxygen activity the growing importance of the reduced species,  $T_2$ , in the gas phase is reflected in Figure 3. This species is more poorly adsorbed than  $T_2O$  with the combined effect of less tritium being on the surface and more in the gas phase.

The calculations predict that surface adsorption can be expected to make its greatest impact on inventory under conditions of combined lower temperatures and higher oxygen activities. It is noteworthy that nominally pure helium sweep gas which might contain 1 ppm of oxygen would provide an oxygen activity of  $10^{-6}$ , a high oxygen activity in the context of ceramic breeders. Higher temperature and lower oxygen activity favor lower surface inventory. This outcome provides a thermodynamic rationale for the reports of enhanced tritium recovery, ascribed to "surface effects", when elemental hydrogen, which provides reduced oxygen activity, is in the sweep gas (the protium purge technique). The effect is not only a kinetic one.

### Experimental Aspects

The foregoing discussion of a calculational analysis of a system was useful for predicting trends in relationships among a number of variables that are important to the performance of a breeder. The procedure necessarily assumed values for certain variables which are plausible but for which firm data are lacking. Experimental work was undertaken to provide measured values for some of those variables. For the experimental work, a high temperature gas chromatograph was constructed to measure surface adsorption/desorption isotherms for  $H_2O$  and/or  $H_2$  on  $LiAlO_2$  by the frontal analysis method of gas chromatography [7]. The collected isotherms will yield experimental values for the heats and entropies of adsorption. Solubility data will also become available.

The sample and reference columns of the gas chromatograph are identical spiral columns with packings of 99.9% pure  $\gamma$ - $LiAlO_2$  particles supplied by Cerac in the 150 to 300 $\mu$ m range and with

a surface area of  $0.16 \text{ m}^2/\text{gm}$ . The major impurities are Na (0.05%), Fe (0.03%), Ca (0.01%), Mg (0.005%), and Cu (0.002%). Temperature control at the 773K level is such as to provide axial uniformity within 0.9K. Temperatures up to about 1073K will be accessible.

Mass flow controllers provide control for pure helium, a mixture of 515 vppm  $\text{H}_2\text{O}$  in helium, a mixture of 990 vppm  $\text{H}_2$  in helium and a mixture of 1000 vppm  $\text{D}_2$  in helium. Mixtures of desired diluted concentrations of these gases can be prepared by varying individual mass flow rates. Nitrogen is provided for the BET surface area measurements. Deuterium is provided on the system for assessment of the isotope effect involved in the comparative effectiveness of deuterium and protium as agents for purging and for oxygen activity adjustment. Oxygen activity will be controlled by controlling the partial pressure ratio of  $\text{H}_2\text{O}:\text{H}_2$ . This control will be of particular interest and importance in the low oxygen activity range where there is a dominance of the "reduced" form,  $\text{H}_2$ , over the "oxidized" form,  $\text{H}_2\text{O}$ , and where the calculations predict the greatest effect on adsorption.

A moisture analyzer and a thermal conductivity detector supplement each other in identifying the breakthrough points. The thermal conductivity detector, with a response time of 0.5 sec, is connected close to the outlet from the sample column and is operated at a temperature of  $473.0 \pm 0.1\text{K}$ . Steady state levels of  $\text{H}_2\text{O}$  vapor concentration in the effluent from the sample column are measured amperometrically with a Beckman moisture analyzer. Flow rates are determined either by the mass flow controllers or by a soap film flowmeter. Detection of breakthrough times is based on either the thermal conductivity detector or the moisture analyzer depending on conditions. The thermal conductivity detector provides a faster response than does the moisture analyzer, but the sensitivity of the moisture analyzer (less than 1 vppm) is better than that of the thermal conductivity detector at low concentrations of  $\text{H}_2\text{O}$ . For long breakthrough times, the error from slow response of the moisture analyzer is minimized.

Exploratory measurements have been made at 771K and at 478K with a gas of 515 vppm  $\text{H}_2\text{O}$  in 99.9999% pure helium. For the sake of ease of early measurements, advantage was taken of the calculated predicted insensitivity to oxygen activity in the low temperature region and at high oxygen activities. In the absence of added protium, and with the likely oxygen impurity level in the "pure" helium, this condition is likely to be satisfied at a temperature of  $500^\circ\text{C}$  and below. The oxygen activity is not being specified because it should be immaterial for the present experiments.

At 771K, it became apparent that the rate of the hydrolytic reaction to absorb water vapor and to form a solid solution of hydroxide is more rapid than was at first expected. When a step function change in gas composition from pure helium to the helium-water mixture was introduced, a quickly

appearing breakthrough denoting a small degree of adsorption was recorded initially, but the absorption-dissolution process was established soon and was fast enough to essentially dehydrate the helium-water stream, as judged from the response of the thermal conductivity detector. After the solubility requirement of the  $\text{LiAlO}_2$  for hydroxide was satisfied, the detector showed that the effluent gas from the column was again carrying water at the input level. A changeover to pure helium then resulted in an initial continuation of the water signal at the high level followed by a decline and an asymptotic approach to the baseline for pure helium. The process was reversible.

To distinguish more clearly between adsorption and absorption-dissolution, measurements at a significantly lower temperature, 487K, were made. This change would increase the degree of adsorption and decrease the degree of solubility and the rate of dissolution. The adsorption recorded at this temperature corresponded to formation of approximately 0.15 monolayer at a partial pressure of water vapor of approximately 52 Pa. To establish whether solubility increases as temperature rises, measurements were made at a constant partial pressure of water (515 ppm) while the temperature was raised to 773K. Absorption of water was observed. This is a qualitative indication that dissolution of hydroxide in  $\text{LiAlO}_2$  is endothermic, as is true for most condensed phase solubility relationships, and as was also observed for the  $\text{Li}_2\text{O}$  system [8].

Some calculations were made with the SOLGASMIX code with input corresponding to conditions in the adsorption experiments. By making the free energy of formation of  $\text{AdOH}$  3 kcal more positive than the values assumed in the survey calculations discussed in the Computational Aspects section of this paper, a fractional monolayer coverage of 0.11 was calculated. This compares favorably with the preliminary experimental estimate of 0.15 mentioned above.

### Conclusions

The calculational approach has described broadly the thermochemical conditions that result in low surface inventory of tritium, namely, high temperature and low oxygen activity. Surface inventory extensive enough to dominate over that due to solubility will result at low temperatures and high oxygen activities. Preliminary experimental data for fractional surface coverage and values calculated for the experimental conditions agree reasonably well if the assumed values for energetics of adsorption used in the survey calculations are modified only moderately. However, further experimental data are needed to establish these surface thermodynamic values and the activity coefficients for solutions of hydroxide in  $\text{LiAlO}_2$ .

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### Figure Captions

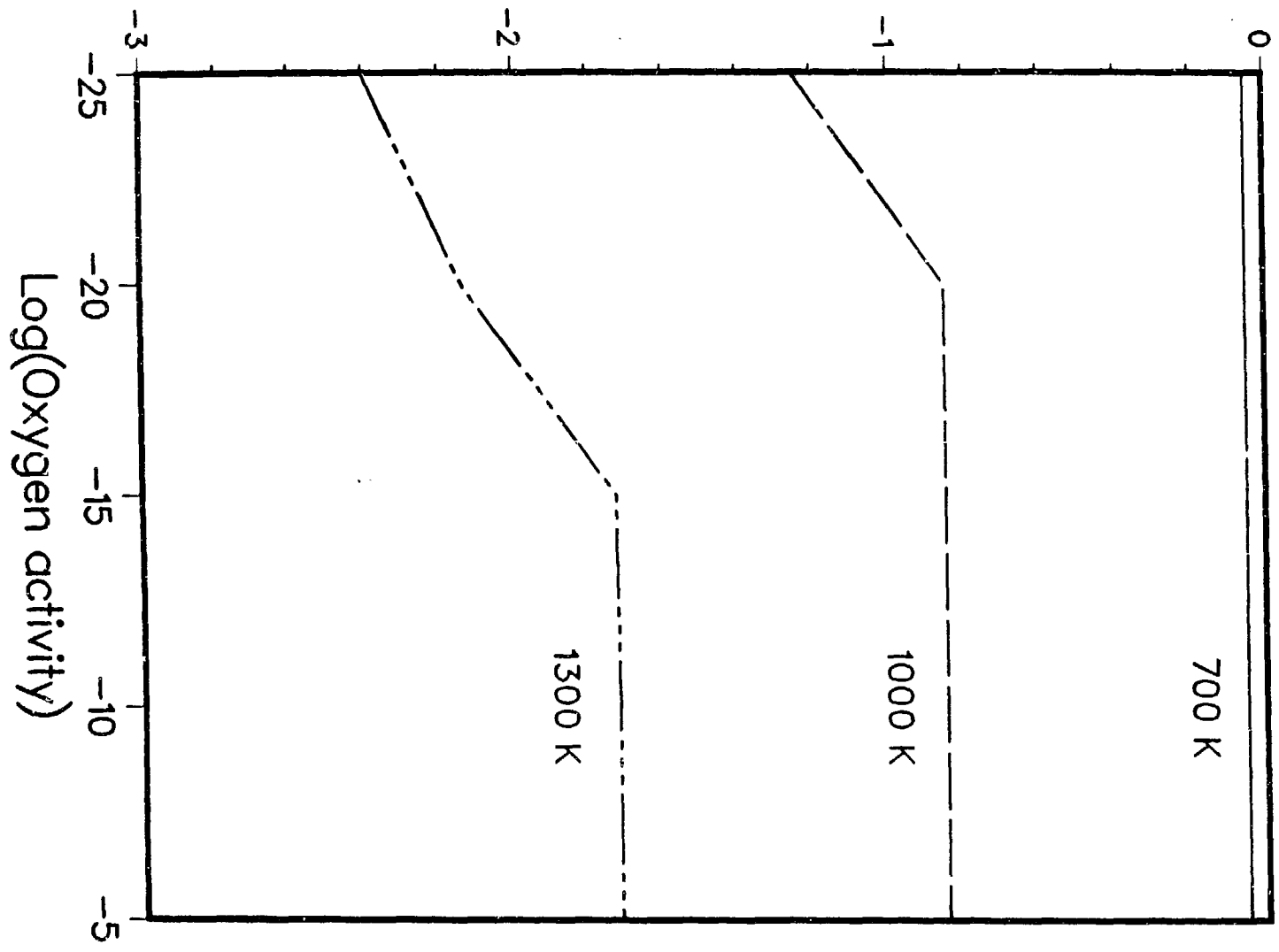
Figure 1. Dependence on oxygen activity and temperature of the fraction of total system tritium adsorbed on the surface.

Figure 2. Relationship between amount of tritium adsorbed on surface and amount of tritium dissolved as tritoxide (and tritide at low oxygen activity and high temperature) in  $\text{LiAlO}_2$ .

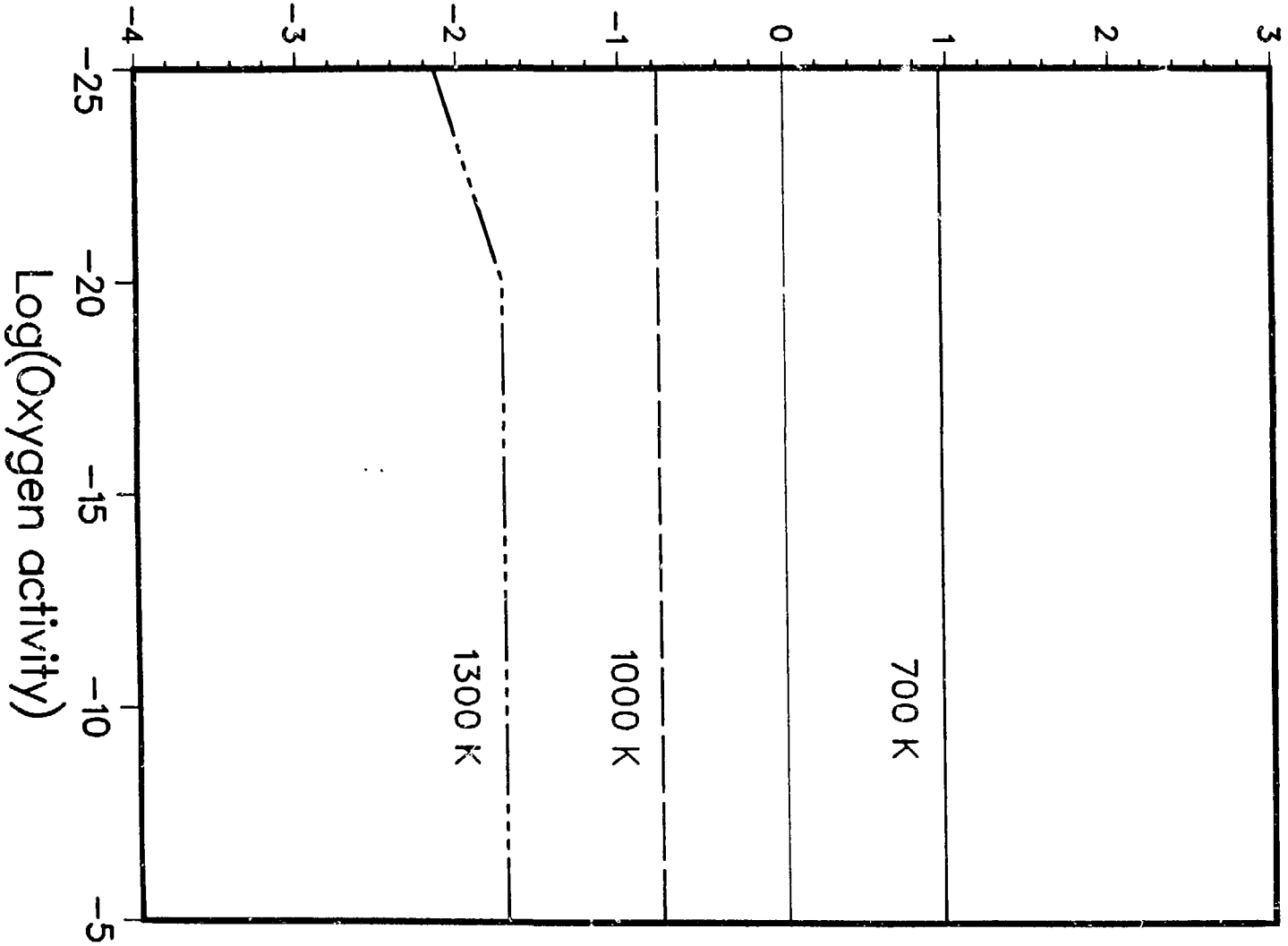
Figure 3. Relationship between amount of tritium adsorbed on surface and amount of tritium in the gas phase (sum of  $\text{T}_2$  and  $\text{T}_2\text{O}$ ).



Log(Fraction of system's tritium adsorbed on surface)



Log(Ratio, Fraction T on surface : Fraction T in solution)



Log(Ratio, Fraction T on surface : Fraction T in gas)

