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BLANKET MATERIALS FOR FUSION REACTORS: COMPARISONS OF THERMOCHEMICAL PERFORMANCE

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Thermodynamic calculations have been made to predict the thermochemical performance of the fusion reactor breeder materials, Li_2O , LiAlO_2 , and Li_4SiO_4 in the temperature range 900-1300 K and in the oxygen activity range 10^{-25} to 10^{-5} . Except for a portion of these ranges, the performance of LiAlO_2 is predicted to be better than that of Li_2O and Li_4SiO_4 . The protium purge technique for enhancing tritium release is explored for the Li_2O system; it appears advantageous at higher temperatures but should be used cautiously at lower temperatures. Oxygen activity is an important variable in these systems and must be considered in executing and interpreting measurements on rates of tritium release, the form of released tritium, diffusion of tritiated species and their identities, retention of tritium in the condensed phase, and solubility of hydrogen isotope gases.

1. INTRODUCTION

The recovery of tritium from a lithium-containing ceramic breeder blanket is an area of research crucial in the development of fusion power. This paper is concerned with tritium recovery from ceramic/oxidic breeders only and not metal/alloy breeders. Of the candidate oxidic breeders, Li_2O and LiAlO_2 have received the greatest attention; Li_4SiO_4 and Li_2ZrO_6 are also under consideration. At the present time, suitable thermodynamic data for the oxidic breeders are available in the form of free energies of formation for most of the condensed phases and for the gaseous species. These data permit ideal solution calculations to be performed for all species except LiOH in Li_2O . Recent studies on the solubility of LiOH in Li_2O ¹ have given experimental data for the activity coefficient of LiOH in the solid phase. A supportive study by Norman and Hightower² also shows the existence of significant non-ideality.

in this system. In the case of Li_2O , therefore, extensive calculations based on a non-ideal solution of LiOH in Li_2O are possible and have been reported.³

In this paper, comparisons are made of the results from a series of ideal solution calculations for all species of Li_2O (except LiOH in Li_2O), LiAlO_2 , and Li_4SiO_4 . The SOLGASMIX code^{4,5} was used for calculating the equilibria of multielement-multispecies gas and condensed phases, based on the minimization of system free energy. In these calculations, the ceramic breeder systems are treated on an equal volume basis and are normalized on this to 1 mol Li_2O . The gas phase is taken to be 15 vol% and to contain inert gas at one atmosphere pressure for the system. It is assumed that 10^{-4} g atoms lithium has been transmuted to 10^{-4} g atoms tritium. The oxygen content of the system is established by the requirements of various oxygen activities. Oxygen activity is an important variable in understanding the behavior of ceramic breeder systems.

We start with a brief summary of our work on the Li_2O system. To avoid overly complicating the comparisons, we will first discuss tritium-only systems, that is, free of protium, but at the end of the paper we will go into the question of protium purging for the Li_2O system.

Thermodynamically Controlled Relationships in Oxidic Breeders

1.1. Li_2O Considerations:

The gaseous species considered in the calculations for Li_2O are H_2 , HT , H_2O , HTO , T_2 , T_2O , O_2 , LiOH , $(\text{LiOH})_2$, LiOT , $(\text{LiOT})_2$, Li_2O , Li , LiH , LiT . Figure 1 relates to a basic issue in breeder blanket chemistry, the amounts of T_2 and T_2O that can be swept out of the blanket. The temperatures of 900 and 1300 K cover the range in which activity coefficient data are available for the Li_2O system. For a sweep gas containing 10 ppm oxygen one would have an oxygen activity of 10^{-5} . If stainless steel container material were used in the

Fig. 1. Partial pressures for gaseous species T_2 and T_2O as a function of temperature and oxygen activity.

blanket, the value would be lower than 10^{-25} , perhaps as low as 10^{-32} . This figure shows that for a given temperature there is a critical oxygen activity above which the dominant species will be T_2O ; below this temperature the dominant form will be T_2 . As temperature rises, the importance of T_2O diminishes because of the dissociative equilibrium involving T_2O . The breaks in the curves at low oxygen activity relate to the effect of the growing importance of elemental lithium and lithium tritide.

Figure 2 shows that, for a fixed tritium inventory, the concentration of tritoxide in Li_2O is only slightly dependent on temperature if the oxygen activity is high ($\sim 10^{-5}$). For low oxygen activity ($\sim 10^{-25}$), the situation is markedly different, with the concentration of tritoxide dropping drastically as the temperature is increased. The changes can be understood in terms of another species that is strongly dependent on the redox environment, namely tritide, the analog of hydride. This strongly reducing species is unstable at high oxygen activity, as shown by its low concentration (indicated by the curve at the bottom of the figure). However, at low oxygen activity, this species is more stable and its concentration is seen to rise sharply as the temperature rises. At the highest temperature, its magnitude becomes comparable to the concentration of tritoxide, so that both of these species must be considered as contributors, under these conditions, to the system's tritium inventory. In a subsequent figure, the role of tritide will be seen to also influence the concentration of the gaseous species T_2 and T_2O at low oxygen activities.

One of the concerns in fusion reactor breeder design is identification of the conditions under which gaseous lithium-containing species could be transported to cooler zones. Such redistribution has the potential to constrict or plug purge gas channels. The species most likely to be transported are $LiOT(g)$ and $Li(g)$. Figure 3 shows their activity over Li_2O . Below about

Fig. 2. Partial pressures for tritoxide and tritide species as function temperature and oxygen activity (fixed tritium inventory).

Fig. 3. Partial pressures of gaseous lithium containing species as a function of temperature and oxygen activity.

1100 K, LiOT is the more important species for either high or low oxygen activity, especially at lower temperatures. For the temperature range investigated, the Li vapor pressure is not significant at high oxygen activity. However, for temperatures above 1200 K and low oxygen activity, Li(g) becomes very significant. For a blanket designer, the conditions which might lead to unacceptable lithium transport would involve the flow rate of the sweep gas, the volume of the channels, the potential condensation sites, and the thermodynamic state.

1.2. Li_2O - LiAlO_2 - Li_4SiO_4 Comparisons:

We have greater confidence in the results for the Li_2O calculations because experimentally measured activity coefficients were used; results from calculations on LiAlO_2 and Li_4SiO_4 are based on ideal solutions that allow comparisons of these materials to be made on the basis of best-available data. Such comparisons are useful for the technological purposes of the fusion reactor.

For the LiAlO_2 calculations, the gaseous species considered are T_2 , T_2O , O_2 , LiOT , $(\text{LiOT})_2$, Li_2O , LiO , Al , AlOT , and AlO_2T . Two condensed phases must be considered in this system, the major phase, LiAlO_2 , and the minor phase, LiAl_5O_8 . The latter phase results from the loss of lithium due to neutron-induced transmutation into tritium and helium. The actual amount of this phase produced is small, of course, because we consider the effects of only 100 appm burnup of the lithium. LiOT was taken to be a solute in both of these phases. Elemental lithium and lithium tritide were taken as additional solutes in the LiAlO_2 phase.

For the Li_4SiO_4 calculations, the gaseous species considered were the same as for Li_2O , except for the addition of SiO(g) and $\text{SiO}_2\text{(g)}$. The condensed phases considered for this system were Li_4SiO_4 and Li_2SiO_3 . The SOLGASMIX

calculations also considered the possibility that a phase of LiOT would form, but the result of this calculation was that such a phase would not form under the given conditions. The solutes LiOT , LiT , and Li were considered to be present in both of the condensed silicate phases.

In the following figures, we present a graphic comparison of results from the calculations for the same variables that were just discussed for Li_2O alone.

We begin the comparison by looking at the gaseous species that are of concern in tritium recovery, T_2 and T_2O . In Figs. 4 and 5, we select the two temperatures from the ends of the range under consideration, 900 and 1300 K, and plot the molar quantities of these gaseous species as a function of oxygen activity in order to emphasize the importance of this variable. We see that both the T_2 and the T_2O quantities are greater over LiAlO_2 than over Li_2O or Li_4SiO_4 at 900 K and all oxygen activities. At 1300 K, the same relationship among the breeders holds over the oxygen activity range of 10^{-5} to 10^{-20} . These gaseous components are stronger over Li_4SiO_4 than over Li_2O , but LiAlO_2 still shows the greatest ability to release them.

The $\text{T}_2\text{O}/\text{T}_2$ ratio is of interest to designers because whether the gas is mostly T_2O or T_2 will be very important for tritium containment and processing. We note that this ratio also specifies the oxygen activity and is established by the $\text{O}_2/\text{T}_2/\text{T}_2\text{O}$ equilibrium. At a given temperature, there is a critical oxygen activity above which T_2O is the dominant form. This ranges from about $10^{-23.5}$ at 900 K to about 10^{-14} at 1300 K. These ratios are independent of the breeder material. For any oxidic breeder, therefore, if it is desired to run the blanket so as to produce predominantly T_2O , the oxygen activity would have to be in excess of $10^{-23.5}$ at 900 K and in excess of 10^{-14} at 1300 K.

Fig. 4. Partial pressures for gaseous tritium species over Li_2O , $LiAlO_2$, and Li_4SiO_4 as a function of oxygen activity at 900 K.

Fig. 5. Partial pressures for gaseous tritium species over Li_2O , $LiAlO_2$, and Li_4SiO_4 as a function of oxygen activity at 1300 K.

The sharp downturn in several of the curves at oxygen activities below 10^{-20} deserves comment. Under the reducing conditions represented by these low oxygen activities, LiT becomes a more important species, as was mentioned earlier in connection with Fig. 2. This finding can be related to the increased activity of elemental lithium at high temperature and low oxygen activity. This lithium activity provides a driving force for conversion of tritium to tritide and for the corresponding diminution of tritium as T_2 and T_2O .

Figure 6 illustrates the importance of tritoxide concentration in the condensed phase. At 900 K, the concentration in Li_2O and in Li_4SiO_4 is not very sensitive to oxygen activity. Moreover, in $LiAlO_2$, a significant decline in the concentration begins at oxygen activities less than 10^{-20} . Across the oxygen activity range, the tritoxide concentration is lowest in $LiAlO_2$ at 900 K. Quite different behavior appears at 1300 K. At oxygen activities below 10^{-15} , the concentration drops for Li_2O and $LiAlO_2$; for Li_4SiO_4 , it does not show a decrease until the oxygen activity drops below 10^{-20} . For oxygen activities between 10^{-15} and about 10^{-23} , the concentration in Li_2O is greater than in $LiAlO_2$. At lower oxygen activities, the concentration is greater in $LiAlO_2$. Of the three breeders, the tritoxide concentration is least favorable overall for Li_4SiO_4 .

Next, we compare the breeders with respect to vapor phase transport of lithium-containing species. Again, the species involved are $LiOT(g)$ and $Li(g)$. In Fig. 7, the activities of $LiOT(g)$ are shown as a function of oxygen activity. At 900 K, there is only a slight dependence of $LiOT$ vapor pressure on oxygen activity, and the absolute values of the $LiOT$ vapor pressure are especially small for $LiAlO_2$ --about 3.5 orders of magnitude less than for Li_2O . With respect to $LiOT$ vapor pressure Li_4SiO_4 is nearly as good as $LiAlO_2$. At 1300 K,

Fig. 6. Tritoxide concentration in the Li_2O , LiAlO_2 , and Li_4SiO_4 condensed phase as a function temperature and oxygen activity.

Log (LiOT Vapor Pressure, Atm.)

Fig. 7. Tritoxide vapor pressure over Li_2O , LiAlO_2 , and Li_4SiO_4 as a function of temperature and oxygen activity.

the LiOT vapor concentration over LiAlO_2 is still nearly two orders of magnitude less than over Li_2O at oxygen activities below about 10^{-20} . The two curves approach each other at lower oxygen activities. At the lowest oxygen activity shown, Li_4SiO_4 shows the least desirable behavior; at higher oxygen activities, Li_2O is the poorest performer.

As shown in Fig. 8, elemental lithium vapor, at 1300 K, is a prominent gaseous component over both Li_2O and Li_4SiO_4 at low oxygen activity, exceeding the activity of LiOT(g) (compare with Fig. 7). In general, the lithium vapor pressure over Li_2O at 1300 K is essentially the same as that over Li_4SiO_4 and is nearly three orders of magnitude greater than that over LiAlO_2 . At low oxygen activity and high temperature, therefore, LiAlO_2 should be significantly freer of potential problems from lithium vapor transport.

Summarizing these comparisons, we see that LiAlO_2 offers thermochemical advantages over Li_2O and Li_4SiO_4 in a number of respects:

1. Under given conditions, both the T_2 and T_2O concentrations in the gas phase are greater for LiAlO_2 than for Li_2O or Li_4SiO_4 .
2. The amount of LiOT in solid solution is less for LiAlO_2 than for the other two breeders at low temperature and all oxygen activities studied and also at high temperature and intermediate oxygen activities; this advantage goes to Li_2O at low oxygen activity and high temperature.
3. The amount of lithium-containing species in the vapor is less for LiAlO_2 than for the other two breeders at all temperatures and oxygen activities.

We re-emphasize that these comparisons are based on ideal solution calculations for LiAlO_2 and Li_4SiO_4 . In the case of Li_2O , the measured non-ideality improved the predicted performance over that predicted on an ideal basis. The

Fig. 8. Lithium vapor pressure as a function of oxygen activity for Li_2O , LiAlO_2 , and Li_4SiO_4 .

direction of the change that might result for non-ideality of the other systems is not known. Of course, the ultimate choice of a breeder involves many considerations in addition to the thermochemical ones.

1.3. Protium Purge

As a final example of insights that come from these calculations, we wish to explore the implications of the protium-purge technique. With protium purging, the release of tritium is enhanced by deliberately introducing protium as a reagent in the form of H_2 and H_2O in the gas phase, which exchanges with tritium-containing species on and in the condensed phase. The exchange products, HT and HTO, are the species responsible for carrying off the tritium. The exchange process, of course, has a thermodynamic requirement which can be treated with the SOLGASMIX calculations. The free energies of formation of the gaseous species HT, T_2O , and HTO were included in the list of species the program considered. In the condensed phases, the free energies of formation of the tritiated species were taken as equal to those of the corresponding protonic species, e.g., $LiOT = LiOH$ and $LiT = LiH$.

In the execution of protium purging, the proper $H_2O:H_2$ ratio must be selected to provide the oxygen activity that results in the lowest residual concentration of tritium species in the condensed phase and the desired dominant form of gaseous species (HTO). Thus, the introduction of a given amount of protium would require consideration of a balance between H_2O and H_2 . However, for the purpose of illustrating the effects of oxygen activity, temperature, and concentration, two figures are presented for the Li_2O system in which the protium-tritium relationship is presented simply as a H:T ratio with values of 100, 10, 1, and 0. The 0 case (the absence of any protium-purge effects) provides a baseline for comparison. Each figure pertains to a fixed oxygen activity, one for 10^{-10} and one for 10^{-20} .

The ordinate in Fig. 9 is for the total gram atoms of tritium in the gas phase for the released forms, T_2 , HT, T_2O , and HTO. At high temperature, increasing amounts of protium result in enhanced release of tritium to the gas phase. However, this trend is not followed at 1000 K where a gain in tritium liberation is experienced as the H:T ratio is increased to 10:1, but much poorer tritium release follows from the H:T ratio at 100:1. It is evident that introduction of excessive protium can be counterproductive. The reason for the apparently contrary behavior of the 100:1 curve lies in the balance of the various quantities that are required by the equilibrium and mass balance conditions treated by SOLGASMIX. At 10^{-10} oxygen activity, the dominant gaseous forms are the aqueous ones, H_2O , HTO, and T_2O . With so much protium in the system at the 100:1 ratio, the activity of $H_2O(g)$ is relatively high, which means that the concentration of LiOH as a solute in the Li_2O is high. The result is that a sizable exchange sink is available to retain tritium in the condensed phase. The effect is dramatic for the 100:1 curve but is also shown by the break in the 10:1 curve. At lower temperatures, the solute approaches closer to saturation. At 900 K, indeed, two condensed phases are present, Li_2O and LiOH, for the H:T ratios of 10:1 and 100:1.

For an oxygen activity of 10^{-20} , the consequences of protium purging are shown in Fig. 10. At this oxygen activity the dominant gaseous species are the reduced ones, H_2 , HT, and T_2 . At the high temperature end, compared to the case of Fig. 9, protium purging is beneficial in enhancing tritium release. For the same reasons given in the previous case, the 100:1 curve reflects markedly different behavior from the others. In the higher temperature range (>1000 K), the quantity of tritium in the gas phase is two to three orders of magnitude greater for the oxygen activity of 10^{-20} (Fig. 10) than for 10^{-10} (Fig. 9). On thermodynamic grounds, protium purging appears to offer signifi-

Fig. 9. Gaseous tritium concentration as a function of temperature and fixed oxygen activity of 10^{-10} and H:T ratios of 100:1, 10:1, and 1:1.

Fig. 10. Gaseous tritium concentration as a function of temperature and fixed oxygen activity of 10^{-20} and H:T ratios of 100:1, 10:1, and 1:1.

cantly enhanced tritium release at higher operating temperatures, but should be used cautiously at lower temperatures.

2. IMPLICATIONS FOR OTHER ISSUES AND STUDIES

The importance of oxygen activity in the thermodynamics of the oxidic breeders has consequences for many measurements on these materials, particularly at lower values of oxygen activity (below about 10^{-15}). Such measurements include rates of tritium release, the form of released tritium (HT or HTO), retention of tritium in the condensed phase, diffusion of tritiated species, and solubility of various gaseous reagents (like D_2 or T_2) in the condensed phase. The chemical form of the participating species is influenced by thermodynamics and the experimental conditions bear on the thermodynamics. For example, the amount of oxygen present as adsorbed impurities on the walls of the apparatus becomes significant because of the small quantities that are involved in the equilibrium thermodynamic state. This importance extends, of course, to irradiation experiments as well as to laboratory measurements. In an irradiation experiment, it is not always easy to control or even to measure the oxygen activity as a unique quantity for the whole system as local variations determine the gas phase composition; for all experiments, attention to the gas phase composition, the apparatus walls, and the container material seems a necessary requirement for consistent data. Our measurements¹ on the solubility of LiOH in Li_2O were performed before the need for such close attention to the oxygen activity became apparent. Fortunately, those particular measurements were made at relatively high oxygen activities, above about 10^{-15} , where the solubility is not strongly dependent on oxygen activity.

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