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Leo Brewer

June 1957

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Leo Brewer

Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

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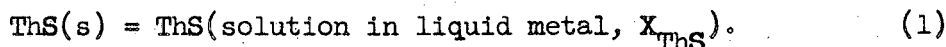
ABSTRACT

The thermodynamic quantities necessary for the calculation of the ThS-Ti and Th-U phase diagrams are estimated and the phase diagrams calculated.

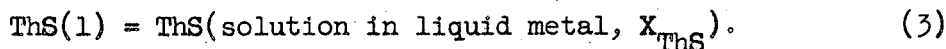
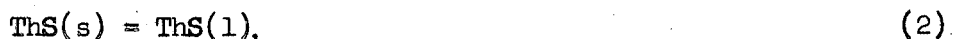
It is of interest to determine if it is possible to calculate the phase diagrams of systems consisting of metals and refractory ceramic materials. In carrying out these calculations, two simplifying assumptions will be made. It will be assumed that the ΔC_p of fusion can be neglected and that the entropy of mixing of liquid ThS and liquid metals is ideal. The first assumption will not introduce any serious error. The error introduced by the second assumption is unknown, as no pertinent data exist for systems of the type being considered here. However, the error introduced should not affect the order of magnitude of the calculations.

Unfortunately, the heats of fusion are unknown for all of the substances under consideration. To estimate these quantities, the entropy of fusion will be taken as 2 e.u. per gram atom. As the melting point of uranium is 1406°K, the heat of fusion will be taken as 2800 calories per gram atom. The melting point of Ti is 1933°K, and its heat of fusion will be taken as 3900 calories per gram atom. The melting point of ThS is estimated to be around 2800°K, yielding a heat of fusion of 11,200 calories per mole.

If X_{ThS} is the equilibrium molefraction of ThS in the liquid metal saturated by solid ThS, then $\Delta \bar{F} = 0$ for the following reaction:

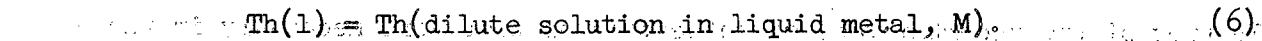
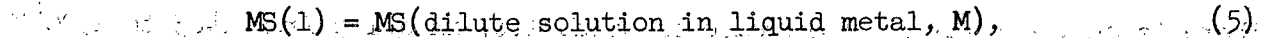
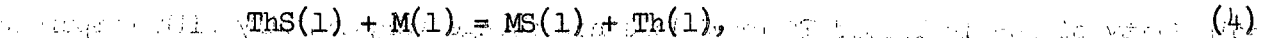


This change in state is profitably considered in two steps,



For reaction (2), $\Delta F^0 = 11,200 - 4 T$ calories on the basis of the above assumptions. To evaluate the free-energy change for reaction (3), we find it useful to consider the following reactions that add up to the reaction

corresponding to reaction (3) if the solubility of ThS is not large:



By comparison of the stabilities of TiO, UO, and ThO and of other compounds of Ti, U, and Th,¹ one can estimate $\Delta\bar{H}^\circ$ values for reaction (4). From the phase diagrams for the Th-Ti and Th-U systems,² one can estimate $\Delta\bar{H}$ values for reaction (6). Finally, one must estimate the $\Delta\bar{H}$ value for reaction (5). The combination of these values yields around $\Delta\bar{H} = 35,000$ calories for reaction (3) for either the U or Ti systems, with an uncertainty of at least 5 kilocal. For the $\Delta\bar{S}$ of reaction (3), we obtain $\Delta\bar{S} = -R \ln X_{\text{ThS}}^2$ on the basis of ideal entropy of mixing and the assumption that ThS molecules would not exist as such in the metal melt. The Th and S atoms or ions would surely be free in this solution. Thus for reaction (3), we obtain $\Delta\bar{F} = 35,000 + RT \ln X_{\text{ThS}}^2$. By combination of the free-energy equations for reactions (2) and (3), we obtain for reaction (1), $\Delta\bar{F} = 11,200 - 4T + 35,000 + RT \ln X_{\text{ThS}}^2 = 0$, where X_{ThS} is the equilibrium solubility of ThS in uranium or titanium liquid. This equation would be valid only if X_{ThS} were small. For larger values of the solubility, one would have to take into account deviations from Henry's Law. The equation can be condensed to obtain $\ln X_{\text{ThS}} = 2/R - 23,100/RT$. At 2500°K, $X_{\text{ThS}} = 3 \times 10^{-2}$. At 2000°K, $X_{\text{ThS}} = 8 \times 10^{-3}$. At the eutectic between Ti and ThS at 1930°K, the solubility of ThS in Ti is calculated to be a mole fraction of 6×10^{-3} . At the eutectic between U and ThS at 1405°K, the solubility of ThS is calculated to be 8×10^{-4} for X_{ThS} . This corresponds to 0.01% by weight of sulfur. There are no experimental data for comparison with these calculations.

Any results obtained from analyses of castings would not be comparable, as casting experiments would not be expected to yield equilibrium results. If the crucibles are porous and not well sintered, there may be particles of crucible material suspended in the metal. If the crucibles are dense and the casting time short, the melt may be considerably undersaturated. To obtain reliable solubilities, one would want to work at as high a temperature as possible in order to have an appreciable solubility to measure. One would have to guard against temperature gradients that would result in solution of the crucible at one point of contact with the melt and precipitation elsewhere. Because of this source of error, one might have to use some filtering technique to insure removal of suspended particles.

It is of interest to note that these calculations indicate that the solubility of ThS in liquid Ti or U does not change very rapidly with temperature. There is only a forty-fold increase in solubility in going from 1405 to 2500°K. In view of the uncertainties of the estimates that were necessary in these calculations, the true values might be as much as twice as large or as low as one-fifth as large as the calculated values. However, the calculations should be of the correct order of magnitude.

If one carries these calculations up to higher temperatures, where the solubility of ThS becomes larger and makes reasonable estimates of the extent of deviation from Henry's Law, one calculates that there will be a miscibility gap above the melting point of ThS with liquid metal in equilibrium with liquid ThS. At 3550°K, the atmospheric boiling point of Ti metal, liquid Ti and liquid ThS should still be immiscible. However, liquid U and liquid ThS should have become miscible at the atmospheric boiling point of liquid U. At the highest temperature at which solid ThS could conceivably have enough strength to be used as a container for the liquid metals, the solubility of ThS in liquid U or Ti would be calculated to be a mole fraction of 4×10^{-2} . This small a solubility should not reduce the vapor pressures of the metals appreciably and one should be able to readily boil these metals from ThS crucibles at reduced pressures and temperatures approaching 2700°K.

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- (2) H. A. Saller and F. A. Rough, Compilation of U. S. and U. K. Uranium and Thorium Constitutional Diagrams (First Edition), BMI-1000, June 1, 1955.