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THERMOCHEMISTRY OF TANTALUM-WALL COOLING SYSTEM WITH LITHIUM AND SODIUM WORKING FLUIDS

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SUMMARY

Plots are presented which show the distribution of oxygen between liquid lithium and tantalum or niobium, and between liquid sodium and tantalum at elevated temperatures. Additional plots showing the composition of the gas phase above the solutions of oxygen and alkali metal are presented. The use of the plots is illustrated by an example tantalum heat pipe filled with lithium.

INTRODUCTION

Liquid metals as heat-transfer media have been advocated for many applications. Some of the alkali liquid metals, in particular, have vapor-pressure and heat-transfer properties favorable for use in nuclear-reactor cooling systems (ref. 1).

Because of the elevated service temperatures and the high chemical reactivity of the alkali metals, difficult materials problems in the liquid-metal cooling systems will be encountered. A continuing review of such materials problems is being conducted here at the Lewis Research Center in support of an experimental study of heat pipes for removing nuclear-reactor thermal energy. In reference 2, published solubility data for oxygen in lithium and in sodium were used to construct chemical potential diagrams. The use of the diagrams in assessing the chemical stability of systems containing refractory metal, lithium, and oxygen is illustrated by an example involving hafnium, a possible constituent of the containment structure.

Both niobium and tantalum can hold large amounts of oxygen in solution (ref. 3). Oxygen exceeding about 200 to 500 parts per million in these metals is known to result in corrosive attack by the lithium through a little-understood mechanism (ref. 4). For this reason, caution must be exercised in removing oxygen from refractory metal by the method of leaching or soaking in alkali metals.

In this report, the chemical potential data for oxygen in lithium or in sodium (ref. 2) and data for oxygen in tantalum or in niobium (refs. 3 and 5) were used to estimate the distribution of oxygen between lithium and niobium or tantalum. The information should be of use in estimating the effectiveness of methods proposed for leaching oxygen from tantalum or niobium and in setting limits on lithium purity for heat pipes.

The chemical potential diagrams from reference 2 are very tentative because of the uncertainties in the solubility-limit data and arbitrary assumptions used in their construction. The possible formation of a ternary oxide of refractory metal, alkali metal, and oxygen was not considered. Such oxides are suspected as important corrosion factors in refractory-metal - alkali-metal systems (refs. 6 and 7). Because of the importance of liquid-metal cooling systems to nuclear-reactor technology, thermochemical analyses such as the ones contained herein are required until more definitive experimental data are available.

ANALYSIS AND DISCUSSION

Reference 2 contains plots of the free-energy function

$$\left(\frac{\Delta F_T}{RT}\right)_{O_2} = \frac{\left(F_T\right)_{O_{2(g)}} - \left(F_T^o\right)_{O_{2(g)}}}{RT} = \ln p_{O_2} \qquad (1)$$

for gaseous diatomic oxygen ($O_{2(g)}$) in equilibrium with solutions containing varying mole fractions of dilithium oxide (Li_2O) in lithium or disodium oxide (Na_2O) in sodium at several temperatures T. Here, F_T is the free energy at the equilibrium condition, F_T^o is the free energy at 1 atmosphere pressure, R is the gas constant, and p is the partial pressure in atmospheres (1 atmosphere = 1.013×10^5 N/m^2).

For each liquid metal, two plots were presented in reference 2. In one plot, existing oxygen solubility data were used to determine the coefficient of a first-order term for departure from ideal solution behavior. The form of the expression for this nonideal behavior was essentially that of the regular solution (ref. 8). For the other plot, ideal solution behavior was assumed so that the sensitivity of the plots to the assumptions made in the analysis might be assessed. In the present report, only the plots for nonideal behavior derived from the oxygen solubility data will be used.

Distribution of Oxygen Between Lithium and Tantalum or Niobium

Reference 3 presents equations relating the concentration of oxygen dissolved in niobium (Nb) and tantalum (Ta) to temperature and $(\Delta F_T/RT)_{O_2}$ (eq. (1)) at equilibrium. For oxygen in niobium,

$$\left(\frac{\Delta F_T}{RT}\right)_{O_2} = 21.2 + \ln x^2_{O(Nb)} - \frac{90\ 300}{T} \tag{2}$$

and for oxygen in tantalum,

$$\left(\frac{\Delta F_T}{RT}\right)_{O_2} = 21.2 + \ln x^2_{O(Ta)} - \frac{89\ 800}{T} \tag{3}$$

where $x_{O(Ta,\,Nb)}$ is the atomic fraction of oxygen in the refractory metal indicated. Lines of $(\Delta F_T/RT)_{O_2}$ for tantalum at fixed $x_{O(Ta)}$ are superimposed in figure 1 upon a plot from reference 2 $(\Delta F_T/RT)_{O_2}$ against x and T for Li_2O in lithium. Here, x is the mole fraction of Li_2O in lithium. Lines of $(\Delta F_T/RT)_{O_2}$ for niobium (eq. (3)) lie very close to those for tantalum and are not shown. For any temperature and concentration $x_{O(Ta)}$ of oxygen in tantalum, the mole fraction x of Li_2O in solution with Li is read on the abscissa. The ordinate then gives values of the equilibrium diatomic oxygen partial pressure p_{O_2} through equation (1).

In figure 2, the data of figure 1 are replotted as lines of constant temperature, with $x_{O(Ta)}$ as the ordinate. Also shown in figure 2 are lines for niobium, rather than tantalum, in contact with the alkali metal, in which case the ordinate is interpreted as $x_{O(Nb)}$.

Figure 2 illustrates the gettering capability of lithium for oxygen. For equilibrium at 1800 K, the ratio of oxygen in tantalum to that in lithium is about 10^{-3}. At 1300 K, the ratio of oxygen in tantalum to that in lithium is about 10^{-5}.

In reference 9, some isolated theoretical and experimental values of the ratio of oxygen in refractory metals to oxygen in alkali metals (distribution coefficient) are presented. For the system Ta - O - Li at 800° C (1073 K), a value of 3×10^{-8} is calculated, which is essentially in agreement with figure 2, while the experimental value estimated from corrosion studies is listed as 0.1. If the theoretical value were actually encountered in practice, its observation would require the measurement of less than 3×10^{-5} parts per million of oxygen by weight in tantalum. Such a task would, no doubt, prove impossible. In fact, the theoretical and experimental values for the refractory-metal - alkali-metal combinations in reference 9 are only in reasonable agreement when the distribution coefficient differs from unity by less than about 2 orders of magnitude and is thus amenable to experimental determination.

Distribution of Oxygen Between Sodium and Tantalum

Figure 3, from reference 2, is a plot of $(\Delta F_T/RT)_{O_2}$ against x at various temperatures for Na_2O in sodium. Lines of constant $x_{O(Ta)}$ (eq. (2)) are also plotted in figure 3. The lines of constant $x_{O(Ta)}$ for Ta - O - Na in figure 3 have an entirely different trend than those for Ta - O - Li in figure 1. Also, for given $x_{O(Ta)}$ they are located at far lower concentrations x of alkali metal oxide in alkali metal. The data are replotted in figure 4 as lines of constant T with $x_{O(Ta)}$ as the ordinate and $x_{O(Na)}$ as the abscissa. For equilibrium from 800 to 1600 K, the ratio of oxygen in tantalum to that in sodium is about 10^{-2}. The gettering capability of sodium for the oxygen in tantalum is thus poorer than that of lithium by a factor of 10 to 10^3. This result is consistent in direction with the measured heats of formation of the compounds Na_2O and Li_2O (ref. 8).

Vapor Composition

The foregoing analysis has been concerned only with the liquid lithium or sodium phase and the solid tantalum or niobium phase. In many real situations, a gas phase of appreciable volume may also be present. The elemental composition for the vapor will generally differ from that for the solid phases. In the operation of systems such as heat pipes, a fractional distillation of the components of the condensed phase will have to be considered. In addition, if the vapor volume is very large relative to the volume of condensed phases, an accurate inventory of material in the system should include the species in the gas phase.

Any species j in the vapor phase can be expressed in terms of oxygen, refractory metal, and alkali metal atoms by a general formula typified for the Ta - O - Li system by $O_{n_{O(j)}}Li_{n_{Li(j)}}Ta_{n_{Ta(j)}}$. Thus in Li_2O, $n_{O(Li_2O)} = 1$, $n_{Li(Li_2O)} = 2$, and $n_{Ta(Li_2O)} = 0$. The density of any species j in the gas phase, by the ideal gas law, is

$$\rho_j = p_j \frac{M_j}{RT} \tag{4}$$

where R is the universal gas constant in suitable units, and M is the molecular weight of species j. The contribution of species j to the total oxygen density is

$$\rho_{O(j)} = n_{O(j)}\rho_j \frac{M_O}{M_j} \tag{5}$$

the contribution to the lithium density is

$$\rho_{Li(j)} = n_{Li(j)}\rho_{(j)}\frac{M_{Li}}{M_j} \tag{6}$$

and the contribution to the tantalum density is

$$\rho_{Ta(j)} = n_{Ta(j)}\rho_{(j)}\frac{M_{Ta}}{M_j} \tag{7}$$

The total oxygen density is then

$$D_O = \sum_j \rho_{O(j)} \tag{8}$$

the total lithium density is

$$D_{Li} = \sum_j \rho_{Li(j)} \tag{9}$$

and the total tantalum density is

$$D_{Ta} = \sum_j \rho_{Ta(j)} \tag{10}$$

The sums are over all species j in the gas phase.

Combination of equations (5) to (10) yields

$$D_O = \frac{M_O}{RT}\sum_j n_{O(j)}p_j = \frac{M_O P_O}{RT} \tag{11}$$

$$D_{Li} = \frac{M_{Li}}{RT}\sum_j n_{Li(j)}p_j = \frac{M_{Li} P_{Li}}{RT} \tag{12}$$

and

$$D_{Ta} = \frac{M_{Ta}}{RT}\sum_j n_{Ta(j)}p_j = \frac{M_{Ta} P_{Ta}}{RT} \tag{13}$$

where the effective partial pressures of oxygen, lithium, and tantalum are

$P_O = \sum_j n_{O(j)}p_j$, $P_{Li} = \sum_j n_{Li(j)}p_j$, and $P_{Ta} = \sum_j n_{Ta(j)}p_j$, respectively. For P in torr (1 torr = 1.333×10^2 N/m^2), D in grams per cubic centimeter, M in gram atomic weights, and T in degrees Kelvin, R = 62 363 (torr)(cm^3)/(mole)(K).

The evaluation of the set of equations (4) and (5) involves first the specification of x and T. Figures 1 and 3 or the computations leading thereto furnish p_{O_2}. From reference 2, the following expression for the partial pressure of the alkali metal M(M = Li, Na) above a liquid solution of the metal and its oxide M_2O can be obtained:

$$\ln p_M = \ln p_{M(l)} + \ln(1 - x) + Bx^2 \tag{14}$$

where $p_{M(l)}$ is the vapor pressure of pure liquid. Values of $p_{M(l)}$ for Li and Na are available from reference 8.

With p_M and p_{O_2} known, the remaining pressures required are given by

$$p_O = K_O \sqrt{p_{O_2}} \tag{15}$$

$$p_{MO} = K_{MO} p_M \sqrt{p_{O_2}} \tag{16}$$

$$p_{M_2} = K_{M_2} p_M^2 \tag{17}$$

$$p_{M_2O} = K_{M_2O} p_M^2 \sqrt{p_{O_2}} \tag{18}$$

where the equilibrium constants K, with the exception of K_{Li_2O}, are from reference 8. In computing K_{Li_2O}, the free-energy data for Li(g) and Li_2O(g) were from reference 10, while those for O_2 were from reference 11. For gaseous tantalum-bearing species, the partial pressures in atmospheres are (from ref. 3)

$$P_{TaO} = 1.74\times10^6 \sqrt{p_{O_2}} \exp \frac{-21\ 414}{T} \tag{19}$$

and

$$p_{TaO_2} = 1.35\times10^6 \sqrt{p_{O_2}} \exp \frac{-11\ 513}{T} \tag{20}$$

where p_{TaO} and p_{TaO_2} are in torr (1 torr = 1.333 N/m^2) and p_{O_2} is in atmospheres (1 atm = 1.013×10^5 N/m^2).

With the use of equations (4) to (20), p_{O_2} from figure 1, and B = 1.835 (from (ref. 2), computations of P_{Li}, P_O, and P_{Ta} were made for the system Ta - O - Li. Figure 5 shows $\log_{10} P_O$ and $\log_{10} P_{Li}$ against x for several temperatures. For all conditions of T and x shown in figure 5, P_O was greater than P_{Ta} by a factor of 10^8 and, therefore, P_{Ta} is not shown.

Figure 6 shows $\log_{10} P_O$ and $\log_{10} P_{Na}$ against x at several temperatures for the system Ta - O - Na, computed with the use of B = 2.0 (from ref. 2) and p_{O_2} from figure 2. For the conditions of T and x shown in figure 6, P_O was greater than P_{Ta} by a factor of 10^3 or more. No data for the molecule $Na_2O(g)$ appear in reference 10, and computations have suggested that this molecule does not exist (ref. 12). The species $Na_2O(g)$ was, therefore, not included in the sums P_O and P_{Na}.

Figures 2 and 5, or 4 and 6, suffice for determination of the distribution of total alkali metal and oxygen between the condensed and gaseous phases. The total inventory of tantalum, alkali metal, and oxygen must be specified, together with the gas volume V_g. For instance, suppose a system contains N_{Li} moles of lithium and N_O moles of oxygen in all phases,

$$N_{Li} = \left[1 - x_{O(Li)}\right] N_s + \frac{V_g P_{Li}}{RT} \tag{21}$$

$$N_O = x_{O(Li)} N_s + \frac{V_g P_O}{RT} + N_{Ta} x_{O(Ta)} \tag{22}$$

where $x_{O(Li)}$ is the atomic fraction of oxygen in solution, and N_s is the moles of solution containing oxygen and lithium. Elimination of N_s between equations (21) and (22) gives

$$N_O = \left(N_{Li} - \frac{V_g P_{Li}}{RT}\right) \frac{x}{1 + x} + \frac{V_g P_O}{RT} + N_{Ta} x_{O(Ta)} \tag{23}$$

where the atom fraction $x_{O(Li)}$ of oxygen in solution has been replaced by x, the equivalent mole fraction of Li_2O in solution. For any specified N_O, N_{Li}, N_{Ta}, V_g, and T, an iteration involving figures 2 and 5, with the constraint of equation (23) imposed, yields x, $x_{O(Ta)}$, P_{Li}, and P_O. In most practical cases, the following initial assumptions can be made, which greatly simplify the solution and render an iteration unnecessary:

$$N_{Li} >> \frac{V_g P_{Li}}{RT}$$

$$N_O >> \frac{V_g P_O}{RT} \qquad (24)$$

$$N_O >> N_{Ra} x_{O(Ta)}$$

For example, consider a tantalum-walled heat pipe operating at 1600 K, with 1.02-centimeter (0.4-in.) outer diameter and 0.102-centimeter (0.04-in.) wall. A tantalum screen of 0.71-centimeter (0.280-in.) outer diameter and 0.018-centimeter (0.007-in.) thickness with 50-percent open volume is inside. The entire passage between screen and tube, as well as the pores of the screen, is filled with lithium. The length of the pipe is sufficient to permit the tantalum in the end caps to be neglected. Assume 1000 parts per million of oxygen by weight in the system. Then, per centimeter of length, $N_O = 3.28\times10^{-04}$ gram atomic weight of O, $N_{Li} = 1.09\times10^{-2}$ gram atomic weight of Li, $N_{Ta} = 2.85\times10^{-02}$ gram atomic weight of Ta, and $V_g = 0.81$ cubic centimeters.

If the conditions specified in the inequalities (24) are assumed, equation (23) yields $x \approx 3.01\times10^{-2}$. From figure 2, $x_{O(Ta)} \approx 4.5\times10^{-6}$, and from figure 5, $P_{Li} \approx 740$ torr, and $P_O \approx 3.4\times10^{-3}$ torr. Conditions (24) are therefore satisfied. From equations (11) and (12), $D_{Li} = 5.5\times10^{-5}$ gram per cubic centimeter, and $D_O = 5.5\times10^{-10}$ grams per cubic centimeter.

CONCLUDING REMARKS

The distribution of oxygen between liquid lithium and tantalum or niobium, and between liquid sodium and tantalum at high temperature was shown. The composition of the gas phase above solutions of oxygen and alkali metal were presented. The plots were used in an example concerning a tantalum heat pipe filled with lithium. The plots are tentative because of uncertainties in the experimental data used in their construction. The importance of liquid-metal cooling systems to nuclear-reactor technology requires the use of such analyses as the one herein until better experimental data are obtained.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 7, 1972,
503-05.

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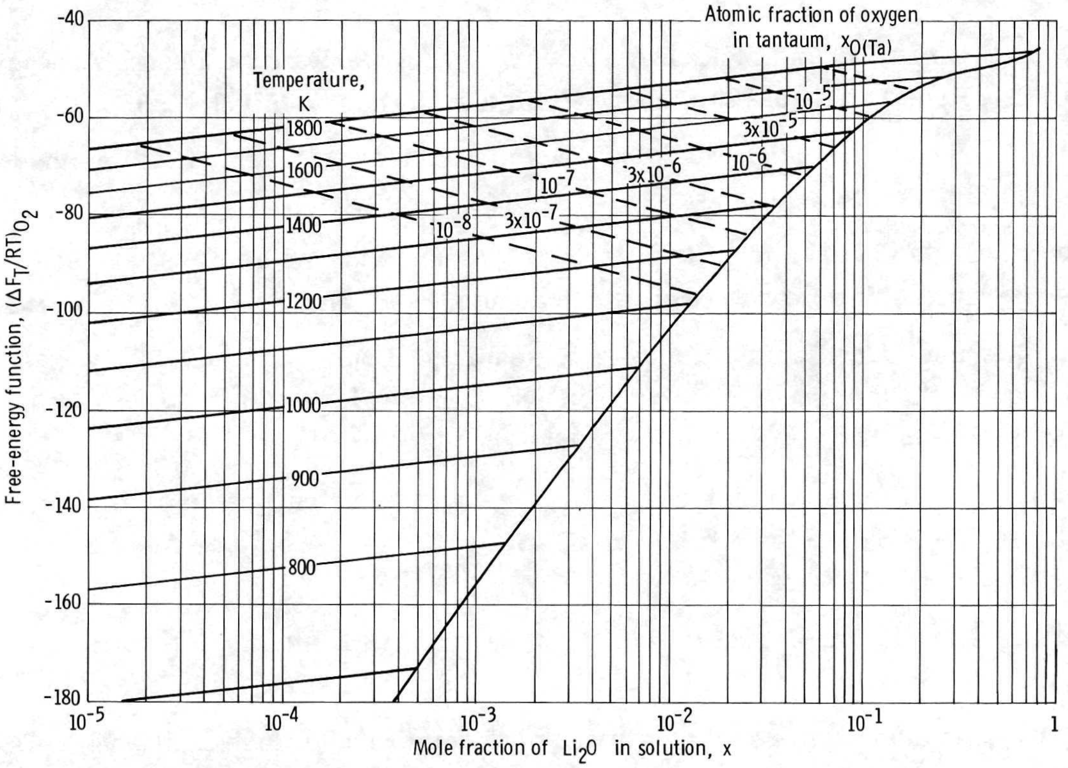

Figure 1. - Chemical potential diagram for $Li-Li_2O$ solution in equilibrium with tantalum containing dissolved oxygen.

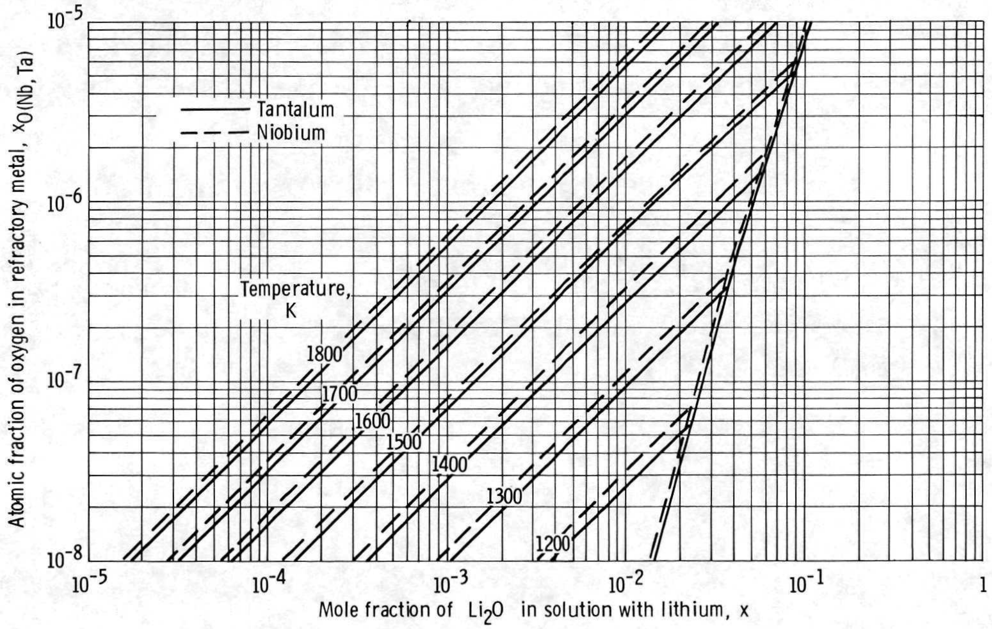

Figure 2. - Equilibrium distribution of oxygen between liquid lithium and solid tantalum or niobium at several temperatures.

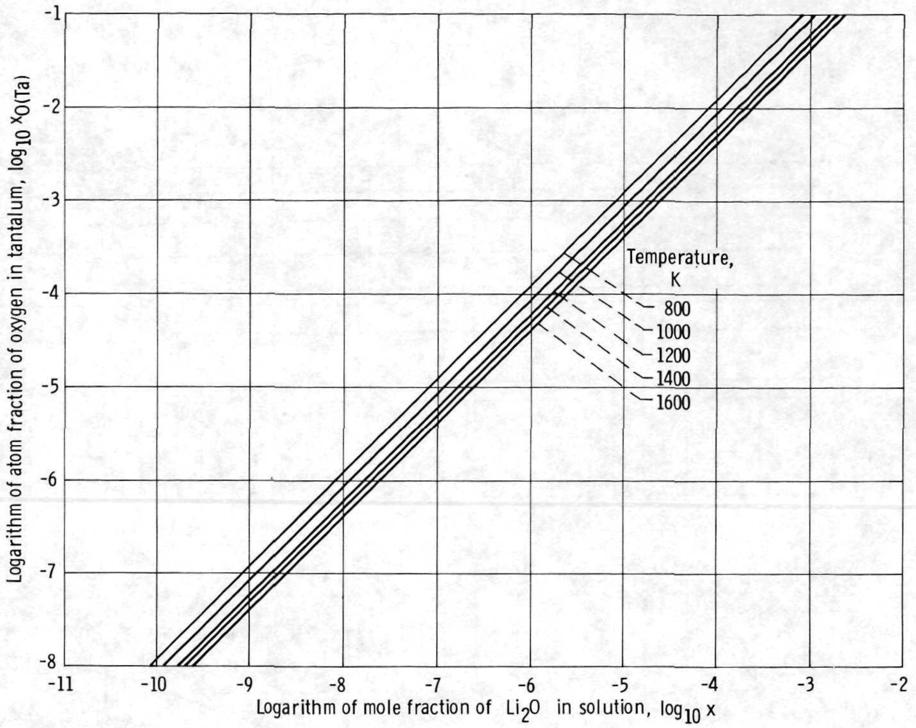

Figure 4. - Equilibrium distribution of oxygen between liquid sodium and tantalum at several temperatures.

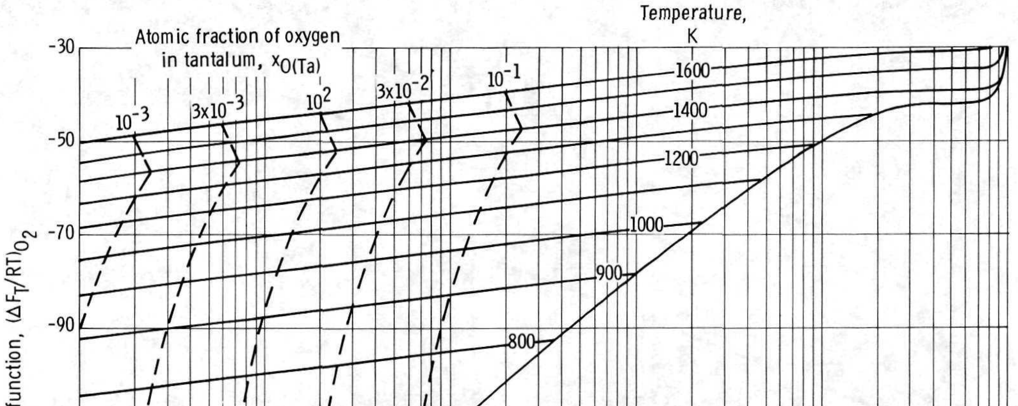

Figure 3. - Chemical potential diagram for Na-Na_2O solution in equilibrium with tantalum containing dissolved oxygen.

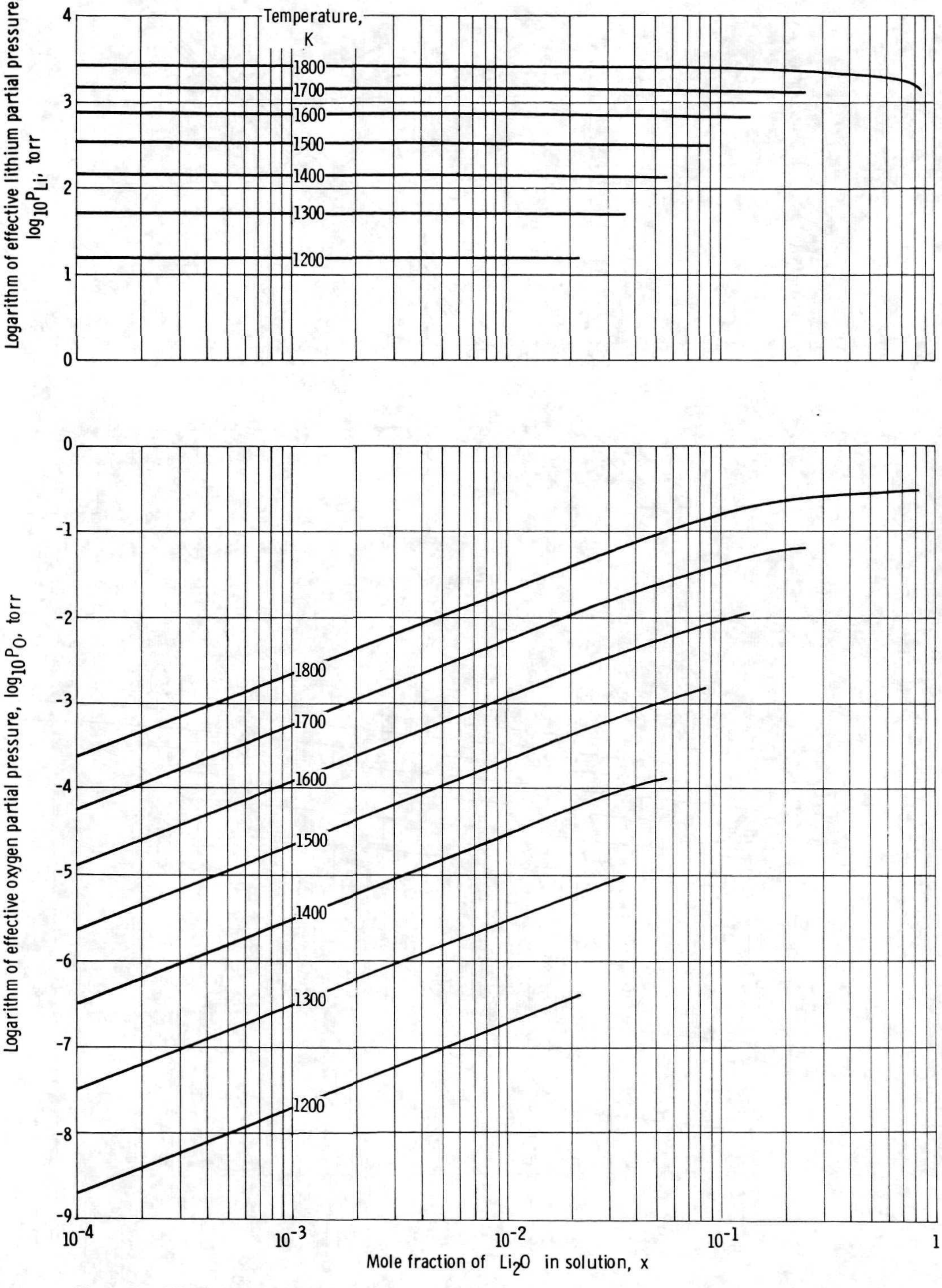

Figure 5. - Effective partial pressures of the oxygen and lithium in the vapor above solutions of oxygen and lithium.

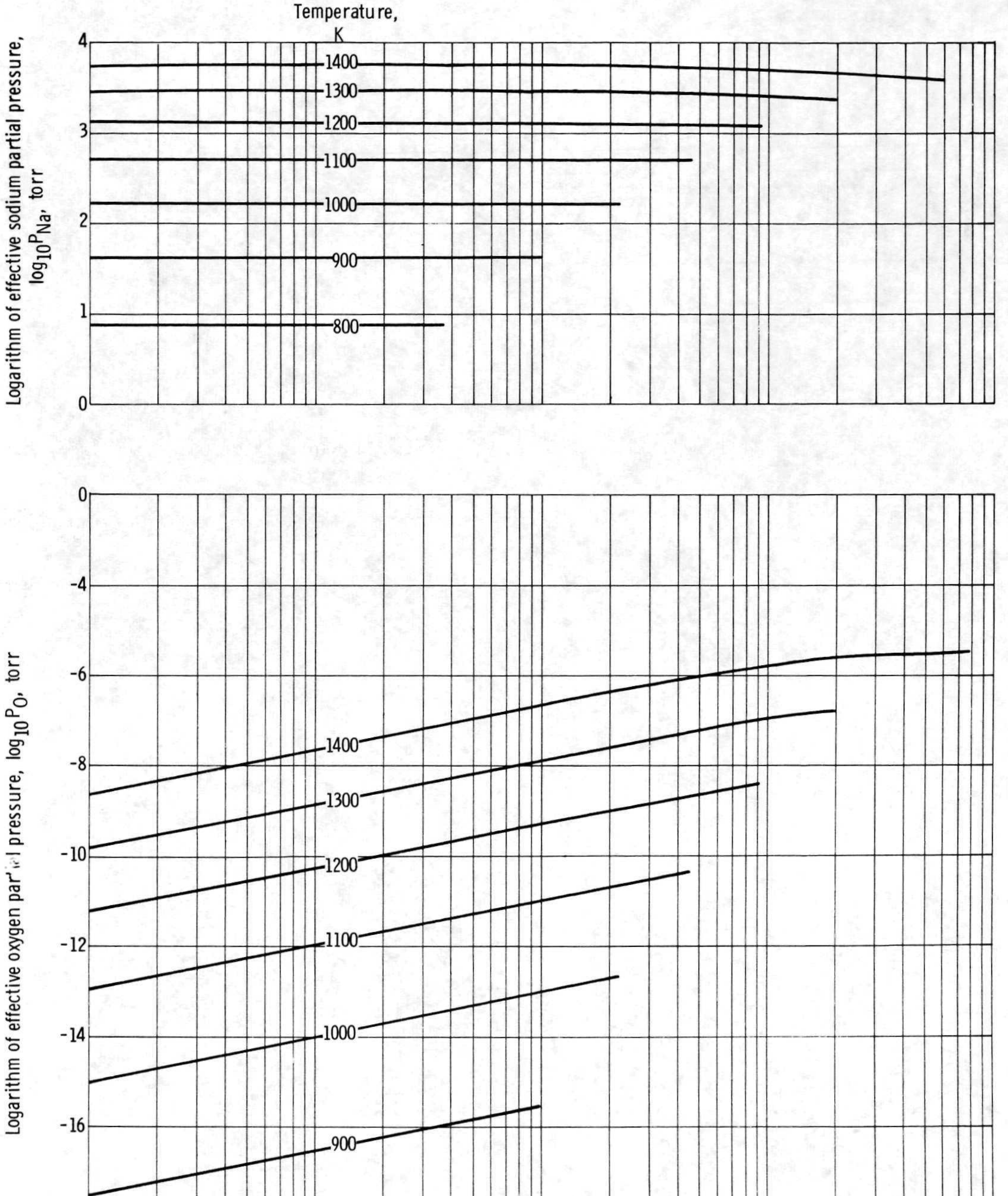

Figure 6. - Effective partial pressures of the oxygen and sodium in the vapor above solutions of oxygen and sodium.

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