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MEMORANDUM

SIMPLIFIED THERMOCHEMISTRY
OF OXYGEN IN LITHIUM AND SODIUM
FOR LIQUID METAL COOLING SYSTEMS

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16. Abstract

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SUMMARY

Plots of oxygen chemical potential against composition of lithium - oxygen solutions and sodium - oxygen solutions for a range of temperature were constructed. For each liquid metal two such plots were prepared. For one plot ideal solution behavior was assumed. For the other plot, existing solubility limit data for oxygen in the liquid metal were used to determine a first-order term for departure from ideality.

The use of the plots in evaluating the oxygen gettering capability of refractory metals in liquid metal cooling systems is illustrated by a simple example involving lithium, oxygen, and hafnium.

INTRODUCTION

The use of liquid alkali metals as high temperature heat transfer media is being extensively investigated. Familiar applications include forced convection cooling loops in nuclear reactors. Recently, heat pipes containing alkali metals have been proposed as a means of removing reactor heat (ref. 1).

Because of the elevated temperature in these systems and the high chemical reactivity, some rather difficult materials problems are encountered. For instance, corrosion of containment vessels by the liquid is observed. Solution of the vessel wall by the liquid metal has been studied (ref. 2) and found to be aggravated by small amounts of oxygen dissolved in the wall material (ref. 3). The formation of a soluble ternary oxide of the refractory and alkali metals is suspected as part of the corrosion mechanism (refs. 4 and 5) for some refractory metals.

Because oxygen in liquid metals at elevated temperatures is apparently a cause of corrosion, various schemes have been proposed for alleviating the problem. The alloying of oxygen-gettering elements with the metals used in containment vessel walls (ref. 6) and the use of gettering traps have been proposed.

The success of such methods depends on the relative chemical potentials of oxygen in the liquid metal and in the gettering materials. An estimation of the chemical potential of oxygen in the liquid metal becomes necessary in assessing the feasibility of gettering methods.

No direct measurement of the chemical potentials of oxygen in the liquid metals is known to exist. This information must therefore be inferred from solubility limit data for oxygen in the liquid metals. This task is undertaken in the present report for lithium and sodium, two coolants of considerable interest for nuclear reactor application.

The present report contains plots of chemical potentials for oxygen dissolved in lithium and in sodium as functions of temperature and concentration of oxygen in solution. For each liquid metal two such plots were prepared. The assumption of ideal solution behavior was made in constructing one plot. For the other plot existing oxygen solubility limit data was used to determine the coefficient of a first order term for departure from ideality. The form of the expression used for this nonideal correction was essentially that of the regular solution (ref. 7). The use of the chemical potential diagrams in assessing chemical stability of a system containing refractory metal, alkali metal and oxygen is illustrated by an example involving hafnium.

Because of the uncertainties in the solubility limit data analyzed and the arbitrary nature of some of the assumptions, thermochemical data herein for the nonideal case is at best very tentative. The ideal case has been included for comparison so that the sensitivity of the computed thermochemical results to the assumptions made in the analysis can be assessed. The potential importance of liquid metal cooling systems to nuclear reactor technology makes such tools as devised here for the analysis of thermochemical problems necessary until more definitive information is available.

ANALYSIS AND DISCUSSION

Coordinates of temperature - composition phase diagrams have sometimes been used to determine the thermochemical properties of solution phases. Various analytical methods have been devised for this task, some of them suitable for binary metallic systems (refs. 8 to 10) and some for multicomponent systems (refs. 11 and 12). The methods consist of determining the values of constants in Taylor series or similar expansions relating the chemical potentials of the solution components to composite-variables.

In a study (ref. 13) related to the present one, the thermochemical properties of a system containing cesium and oxygen was computed from an experimental phase diagram (ref. 14). This diagram covered a far greater composition range than the solubility limit data available for oxygen in lithium and in sodium. The method of references 8 to 10 as used in reference 13 is not suitable for oxygen in lithium and in sodium.

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A very elementary approach will be employed herein. The first assumption made is that the components of the lithium - oxygen and sodium - oxygen systems are Li, Li_2O and Na, Na_2O. Experimental evidence shows the presence of O^{--} ions in liquid alkali metal systems containing oxygen (refs. 15 to 17). Even a small concentration of such ions might affect the electrical conductivity (ref. 17) or play a role in the kinetics of the corrosion mechanism (refs. 15 and 18). The absence of any quantitative data for concentrations of O^{--} relative to total oxygen in liquid lithium or sodium precludes considering the effect here.

The second simplifying assumption is the applicability of the so-called regular solution approximation in a modified form. Regular solution behavior has been found in many binary systems involving metallic species (ref. 19). In systems exhibiting this behavior, μ_a and μ_b of species a and b are given by

$$\mu_a = \mu_a^O + RT \ln(1 - x) + Lx^2 \tag{1}$$

$$\mu_b = \mu_b^O + RT \ln x + L(1 - x)^2 \tag{2}$$

where μ^O designates the free energy of the pure liquid at the temperature T in question, x is the atom fraction of b in solution, and R is the gas constant. Ideal solution behavior occurs when the interaction parameter L is zero.

Sometimes nonideality in solutions is handled by defining activity coefficients γ_a and γ_b such that (ref. 20)

$$\mu_a = \mu_a^O + RT \ln \gamma_a y \tag{3}$$

$$\mu_b = \mu_b^O + RT \ln \gamma_b x \tag{4}$$

where x = 1 - y. The parameters γ_a and γ_b generally vary with x. If $\gamma_a \rightarrow$ constant as $y \rightarrow 0$, Henry's law is said to be obeyed in the limit. If $\gamma_a \rightarrow 1$ as $y \rightarrow 1$, Raoult's law for ideal behavior is obeyed in the limit. Similar considerations apply to γ_b. The behavior of equations (1) and (2) in the foregoing limits is seen to be nearly the same as that of equations (3) and (4). The principle difference is that L either is assumed constant or has a temperature dependence of the form $L = L_0 + L_1T$ (ref. 19).

The modification adopted here consists of setting $L_0 = 0$. Equations (1) and (2) then become

$$\mu_a = \mu_a^O + RT \left[\ln(1 - x) + Bx^2\right] \tag{5}$$

$$\mu_b = \mu_b^o + RT\left[\ln x + B(1 - x)^2\right] \tag{6}$$

This modification will be shown to be advantageous in handling the experimental data for oxygen in lithium.

Oxygen in Lithium

Measurements of the solubility of oxygen in lithium are reported in reference 21. Solid dilithium oxide was placed in contact with lithium. The amount of oxygen remaining in the lithium after filtration was then determined by analysis. Table I presents the results from reference 21.

The oxygen concentrations are also converted in table I to equivalent mole fractions x of dilithium oxide (Li_2O) in a solution of Li_2O and lithium. This is consistent with the assumption herein that all dissolved oxygen is in Li_2O.

At the condition of saturation, Li_2O in the solid phase must be in equilibrium with Li_2O in solution, and the free energy $\left(F_T^o\right)_{Li_2O(c)}$ of crystalline Li_2O must equal the chemical potential of dissolved Li_2O.

Equations (2) and (6) for b as Li_2O were evaluated for parameters L and B from the x data in table I. Free energies of fusion, $\left(\Delta F_T^o\right)_{Li_2O(c,1)}$, for Li_2O from reference 22 used in the computations represent an extrapolation into the supercooled region for $Li_2O(1)$ since the temperatures are below the freezing point. The resulting L from equation (2) and B from equation (6) are listed in table I.

The mean value of B for the data in table I is 1.835 with a standard deviation of 0.221. No single satisfactory mean value of L can be determined from the data. If L is permitted to vary linearly with temperature, a much better fit can be achieved, the correlation being $L = -1950 + 6.96\,T$. At the melting point of Li_2O, 1843 K (refs. 17 and 19), the value of L is about 9970.

Allowable values of L and B are limited by theoretical considerations discussed in the appendix. The maximum allowable value of B is shown there to be 2. The maximum allowable value of L at the melting point is about 7300. Since the value of L extrapolated from the experimental data exceeds this, the B formulation of equations (5) and (6) was used herein with $B = 1.835$.

The solubility limit x_{sat} for Li_2O in lithium computed from equation (6) using this B with $\left(\Delta F_T^o\right)_{Li_2O(c)}$ from reference 22 is shown in figure 1 against reciprocal temperature. Also shown are the experimental data points from reference 21 used in determining B. The ideal solubility limit determined from equation (6) by setting $B = 0$ is shown. In the temperature range of the experimental data about two-thirds of a decade separates the ideal and nonideal solubilities.

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Equations (5) and (6) with $B = 1.835$ together describe the thermochemical properties of the Li - Li_2O system. For convenience in studies involving the presence of oxidizable materials, the thermochemical base is changed from $Li_2O(s)$ and $Li(s)$ to an atmosphere of diatomic oxygen in equilibrium with the Li - Li_2O solution. For the reaction
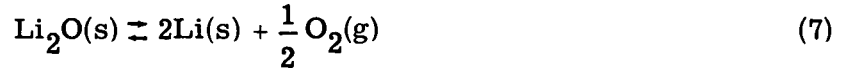
$$Li_2O(s) \rightleftharpoons 2Li(s) + \frac{1}{2}O_2(g) \tag{7}$$

thermochemical equilibrium requires that

$$\mu_{Li_2O(s)} = 2\mu_{Li(s)} + \frac{1}{2}\mu_{O_2(g)} \tag{8}$$

Here,

$$\mu_{O_2(g)} = \left(F_T^O\right)_{O_2} = \left(F_T^O\right)_{O_2} + RT \ln p_{O_2} \tag{9}$$

where the pressure p for thermochemical purposes is in atmospheres (1 atm = 1.013×10^5 N/m). Combination of equations (5), (6), and (9) yields

$$\ln p_{O_2} = \left(\frac{\Delta F_T^O}{RT}\right)_{O_2} = \left(\frac{\Delta F_f^O}{RT}\right)_{Li_2O(c)} + \left(\frac{\Delta F_T^O}{RT}\right)_{Li_2O(c,l)} + \ln \frac{x}{(1-x)^2} + B(1 - 2x - x^2) \tag{10}$$

where the standard state free energy of formation of $Li_2O(c)$ is

$$\left(\Delta F_f^O\right)_{Li_2O(c)} = \left(F_T^O\right)_{Li_2O(c)} - 2\left(F_T^O\right)_{Li(l)} - \frac{1}{2}\left(F_T^O\right)_{O_2} \tag{11}$$

Values of $\left[\left(F_T^O\right) - \left(H_{298}^O\right)\right]/T$ for $Li_2O(c)$ and Li(c,l) were taken from reference 22, while $\left[\left(F_T^O\right) - H_{298}^O\right]/T$ for $O_2(g)$ and $\left(H_{f,298}^O\right)_{Li_2O(c)}$ were from reference 23. A plot of equation (10) appears as figure 2(a) herein. Figure 2(a) shows $\left(\Delta F_T^O/RT\right)_{O_2}$ against mole fraction of Li_2O in solution, for several temperatures.

By setting $B = 0$ equation (10) was also evaluated for the ideal case. The results are shown as figure 2(b). Comparison of figures 2(a) and (b) reveals that $\left(\Delta F_T^O/RT\right)_{O_2}$ is higher (less negative) by about 4 units in the nonideal case. This amounts to about

23 000 joules per mole (5500 cal/mole) at 700 K and about 59 000 joules per mole (14 000 cal/mole) at 1800 K.

Oxygen in Sodium

Many determinations have been made of the solubility of oxygen in sodium. Reference 16 summarizes and discusses data of many investigators taken prior to 1966. This body of data together with subsequent information was evaluated critically in reference 24. The following standard equation for the solubility of oxygen in sodium was recommended as a result of the evaluation:

$$\log_{10} s = 6.239 - \frac{2447}{T} \tag{12}$$

where s is weight parts per million of oxygen in sodium. Converted to mole fraction x of sodium oxide in solution equation (12) gives

$$\log x = 14.37 - \frac{5634}{T} \tag{13}$$

By using equation (13) together with equation (6) and values of $\left(\Delta F_T^0\right)_{Na_2O(c,l)}$ from reference 22, B was evaluated at several temperatures encompassing the range covered by the many investigators whose data contributed to the construction of equation (12). These temperatures and the corresponding values of B are 400 K, 1.75; 500 K, 1.92; 600 K, 2.13; 700 K, 2.33; 800 K, 2.53. The mean of these values of B is 2.13.

While B is understood to be a constant, the values determined from the curve fit of reference 24 show a decided trend with temperature. Another approach would have been to solve for B for each data point used in constructing equation (12) and to take the mean. The amount of scatter in the data together with the number of assumptions involved in the present analysis makes such an effort unwarranted.

The mean B of 2.13 deduced from equation (12) exceeds the maximum allowable value of 2 discussed in the appendix. For the Na - Na_2O studies herein a value of B = 2 will be adopted.

Figure 3 shows the solubility limit x_{sat} against reciprocal temperature for Na_2O in sodium, computed from equation (6) using a B of 2 and $\left(\Delta F_T^0\right)_{Na_2O(c,l)}$ from reference 22. The ideal solubility limit found by setting B = 0 in equation (6) is also shown, together with equation (13) from reference 16.

Figure 4(a) is a plot of $\left(\Delta F^O_R / RT\right)_{O_2}$ against mole fraction of Na_2O in solution with sodium at several temperatures for oxygen in equilibrium with the solution. The data were computed for $B = 2$, the nonideal case, using equation (10), with thermochemical data from reference 22. Figure 4(b) is the corresponding plot for $B = 0$, the ideal case.

Example Using Oxygen-Contaminated Lithium in Contact with Hafnium

The use of figures 2 and 4 in evaluating the chemical stability of a system containing a refractory metal in contact with oxygen-contaminated lithium can be illustrated by an example involving hafnium. Hafnium is a common constituent of alloys that are being considered for structures containing liquid alkali metal coolants. The hafnium in part is intended as a getter to counter oxidation of the other alloying constituents.

The equilibrium between $HfO_2(c)$ and $Li_2O(s)$ is expressed as

$$2Li_2O(s) + Hf(c) \rightleftarrows HfO_2(c) + 4Li(s) \tag{14}$$
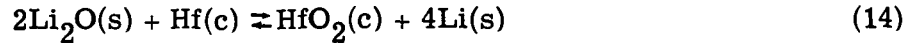
which requires that

$$2\mu_{Li_2O(s)} + \left(F^O_T\right)_{Hf(c)} = \left(F^O_T\right)_{HfO_2(c)} + 4\mu_{Li(s)} \tag{15}$$

Equilibrium (14) can be expressed as the sum of the following equilibria:

$$2Li_2O(s) \rightleftarrows 4Li(s) + O_2(g) \tag{16}$$

$$Hf(c) + O_2(g) \rightleftarrows HfO_2(c) \tag{17}$$

The condition for equilibrium (16) to exist is given by equation (8), which can be reexpressed as

$$2\mu_{Li_2O(s)} - 4\mu_{Li(s)} - \left(F^O_T\right)_{O_2(g)} = \left(\Delta F_T\right)_{O_2(g)} \tag{18}$$

For equilibrium (17) to exist,

$$\left(F^O_T\right)_{Hf(c)} + \left(F_T\right)_{O_2(g)} = \left(F^O_T\right)_{HfO_2(c)} \tag{19}$$

Subtracting $\left(F_T^O\right)_{O_2(g)}$ from both sides of equation (19) gives

$$\left(\Delta F_T^O\right)_{HfO_2(c)} = \left(\Delta F_T\right)_{O_2(g)} \qquad (20)$$

where $\left(\Delta F_f^O\right)_{HfO_2}$ is the standard state free energy of formation for $HfO_2(c)$. When $\left(\Delta F_T\right)_{O_2(g)}$ in equations (18) and (20) are equal, these equations can be combined to obtain equation (15), the condition for equilibrium (14). A line of $\left(\Delta F_T/RT\right)_{O_2(g)} = \left(\Delta F_f^O/RT\right)_{HfO_2(c)}$ (see eq. (20)) is plotted on figure 2(a) for nonideal solution behavior, and on figure 2(b) for ideal solution behavior. The HfO_2 data are from reference 25. The line and its x coordinate will henceforth be designated as $x(HfO_2)$.

For Na_2O in solution (fig. 4) the line for $x(HfO_2)$ cannot be plotted since its small magnitude places it too far to the left. The effectiveness of hafnium in gettering oxygen from sodium is thus illustrated to be much greater than in gettering oxygen from lithium.

For Li_2O concentrations to the left of the line $x(HfO_2)$ on figure 2, $HfO_2(c)$ will not be stable, while to the right of the line it will be. To determine on which side of the line $x(HfO_2)$ a given Li - Hf - O system lies, an inventory must be made of the total moles of lithium (N_{Li}), of hafnium (N_{Hf}), and of atomic oxygen (N_O) in the system. All phases and all compounds must be considered in the inventory. For this example the gas volume will be assumed small enough to contain negligible material.

A simple criterion for the stable existence of $HfO_2(c)$ can be readily derived. In the presence of stable $HfO_2(c)$ the excess oxygen forms Li_2O, the number of moles of which are

$$N_{Li_2O} = N_O - 2N_{Hf} \qquad (21)$$

Of the total amount of lithium, N_{Li} in the system, the amount as free lithium is

$$N'_{Li} = N_{Li} - 2N_{Li_2O} \qquad (22)$$

The number of moles of solution is

$$N_{Sol} = N'_{Li} + N_{Li_2O} \qquad (23)$$

The mole fraction x of Li_2O in solution is then

$$x = \frac{N_{Li_2O}}{N_{Sol}} = \frac{N_O - 2N_{Hf}}{N_{Li} + 2N_{Hf} - N_O} \tag{24}$$

For $HfO_2(c)$ to be thermochemically stable

$$x \geq x(HfO_2)$$

or

$$\frac{N_O - 2N_{Hf}}{N_{Li} + 2N_{Hf} - N_O} \geq x(HfO_2) \tag{25}$$

If criterion (25) is not satisfied, $HfO_2(c)$ cannot be stable. In such a case the concentration x will be less than $x(HfO_2)$.

The example for HfO_2 can be extended to other hafnium oxides and to solutions of oxygen in hafnium when currently unavailable thermochemical data become available. Recently the compounds $Hf_3O(c)$ and $Hf_6O(c)$ have been identified (ref. 26). Lines for these compounds should lie to the left of $HfO_2(c)$ in figure 2. Solid hafnium can contain up to 7 percent oxygen in solution (ref. 26). The lines of $(\Delta F_T/RT)O_2$ for varying concentrations of dissolved oxygen in hafnium will lie still further to the left of $x(HfO_2)$ in figure 2.

Hafnium as a minority element in some refractory metal alloys such as T-111 (tantalum - 8 tungsten - 2 hafnium) is in a single phase solution. For this case $(F_T^O)_{Hf(c)}$ in equation (15) must be replaced by a chemical potential pertaining to hafnium in the metal solution. An additional complication is the possible formation and solution of Li_2HfO_3 in lithium (ref. 2).

The foregoing example, despite the dearth of thermochemical data for hafnium oxides and for oxygenated lithium, illustrates the procedures involved in estimating the effectiveness of getters for removing oxygen from alkali metals. The constructions in figure 2 provide a first order estimate of this gettering effectiveness for the Hf - O - Li system.

CONCLUDING REMARKS

Plots of oxygen chemical potential against composition were presented for solutions of oxygen in lithium and in sodium at several temperatures. Because of the uncertainties in the experimental data used to construct the diagrams for nonideal solution behavior and the assumptions required, plots were also presented for ideal solution behavior.

Comparison of the results for the ideal and nonideal cases gives an indication of the sensitivity of the thermochemical results to the assumptions made in the nonideal analysis. The potential importance of liquid alkali metals in nuclear reactor cooling systems justifies the use of the tentative data presented herein in analyzing problems involving oxygen contamination until better data can be derived.

Lewis Research Center,
    National Aeronautics and Space Administration,
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            503-25.

APPENDIX - UPPER LIMITS OF L AND B

Upper limits of L and B are imposed by thermochemical requirements. At fixed temperature

$$\mu_b \leq \left(F_T^O\right)_{b(c)} \tag{A1}$$

for $x \leq x_{sat}$. Otherwise, the purported x_{sat} must be conceded to be erroneous and the saturation line at that temperature shifted to a smaller value of x where μ_b does indeed equal $\left(F_T^O\right)_{b(c)}$. Figure 5(a) illustrates the situation which would exist in such a case. This figure is drawn in such a manner as to suggest that one requirement for the saturation point x_{sat} is that the variation of μ_b with x be monotonic at $x \leq x_{sat}$. For equation (2) to be monotonic,

$$\left(\frac{\partial \mu_b}{\partial x}\right)_T = \frac{RT}{x} - 2(1 - x)L \geq 0 \tag{A2}$$

for $x \leq x_{sat}$.

A possible variation in μ_b which satisfies inequality (A1) but not inequality (A2) is sketched in figure 5(b). The situation depicted requires that a point of inflection lie between two real roots of inequality (A2). For a point of inflection

$$\left(\frac{\partial^2 \mu_b}{\partial x^2}\right)_T = -\frac{RT}{x^2} + 2L = 0 \tag{A3}$$

the only positive abscissa of which is

$$x = \sqrt{\frac{RT}{2L}} \tag{A4}$$

The locations of the maxima or minima of inequality (A2), where $(\partial \mu_b / \partial x)_T = 0$, are

$$x = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - \frac{2RT}{L}} \tag{A5}$$

If the point of inflection is to lie between the roots of $\partial \mu_b / \partial x$ as depicted, equations (A4) and (A5) require that

$$\sqrt{\frac{RT}{2L}} \geq \frac{1}{2} - \frac{1}{2}\sqrt{1 - \frac{2RT}{L}} \tag{A6}$$

or

$$\sqrt{1 - \frac{2RT}{L}} \geq 1 - 2\sqrt{\frac{RT}{2L}} \tag{A7}$$

Squaring equation (A7) gives

$$1 - \frac{2RT}{L} \geq 1 - 4\sqrt{\frac{RT}{2L}} + \frac{2RT}{L} \tag{A8}$$

and

$$4\sqrt{\frac{RT}{2L}} \geq \frac{4RT}{L} \tag{A9}$$

Squaring again and rearranging result in

$$\frac{L}{RT} \geq 2 \tag{A10}$$

However, for real x, equation (A5) requires that $L/RT \leq 2$. Except for the special case $L/RT = 2$, $x = 1/2$ these are contradictory requirements. The conclusion follows that the situation in figure 5(b) cannot exist for chemical potentials obeying equation (2). The variation of μ_b with x must therefore be monotonic, with inequality (A2) applying for $x \leq x_{sat}$.

From inequality (A2)

$$L \leq \frac{RT}{2x(1 - x)} \tag{A11}$$

The minimum value of the right side, occurring at $x = 1/2$, is $2RT$. Therefore, the maximum allowed value of L is $L \leq 2RT$.

Precisely the same arguments, applied to equation (6), give $B \leq 2$.

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TABLE I. - ANALYSIS OF SOLUBILITY DATA FOR

OXYGEN IN LITHIUM FROM REFERENCE 21

| Temperature, ^{o}C	Oxygen in lithium, wppm	Mole fraction of Li_2O in solution, x	L	B
250	58	2.516×10^{-6}	2185	2.102
	74	3.210	1932	1.858
	85	3.687	1788	1.720
	92	3.990	1706	1.641
	96	4.164	1662	1.598
	101	4.381	1609	1.547
	109	4.728	1529	1.471
	121	5.248	1421	1.367
300	176	7.634×10^{-6}	2190	1.923
	190	8.241	2103	1.846
	193	8.371	2085	1.830
	205	8.892	2016	1.770
	212	9.195	1978	1.736
	214	9.282	1967	1.727
	214	9.282	1967	1.727
	237	1.028×10^{-4}	1851	1.625
	253	1.097	1776	1.560
350	348	1.510×10^{-4}	2483	2.005
	368	1.596	2415	1.950
	374	1.622	2395	1.934
	383	1.661	2365	1.910
	392	1.700	2337	1.887
	396	1.718	2324	1.876
400	477	2.069×10^{-4}	3165	2.366
	529	2.295	3027	2.262
	604	2.620	2849	2.130
	729	3.163	2598	1.942
	730	3.167	2596	1.941
	761	3.302	2540	1.899
	766	3.323	2532	1.893
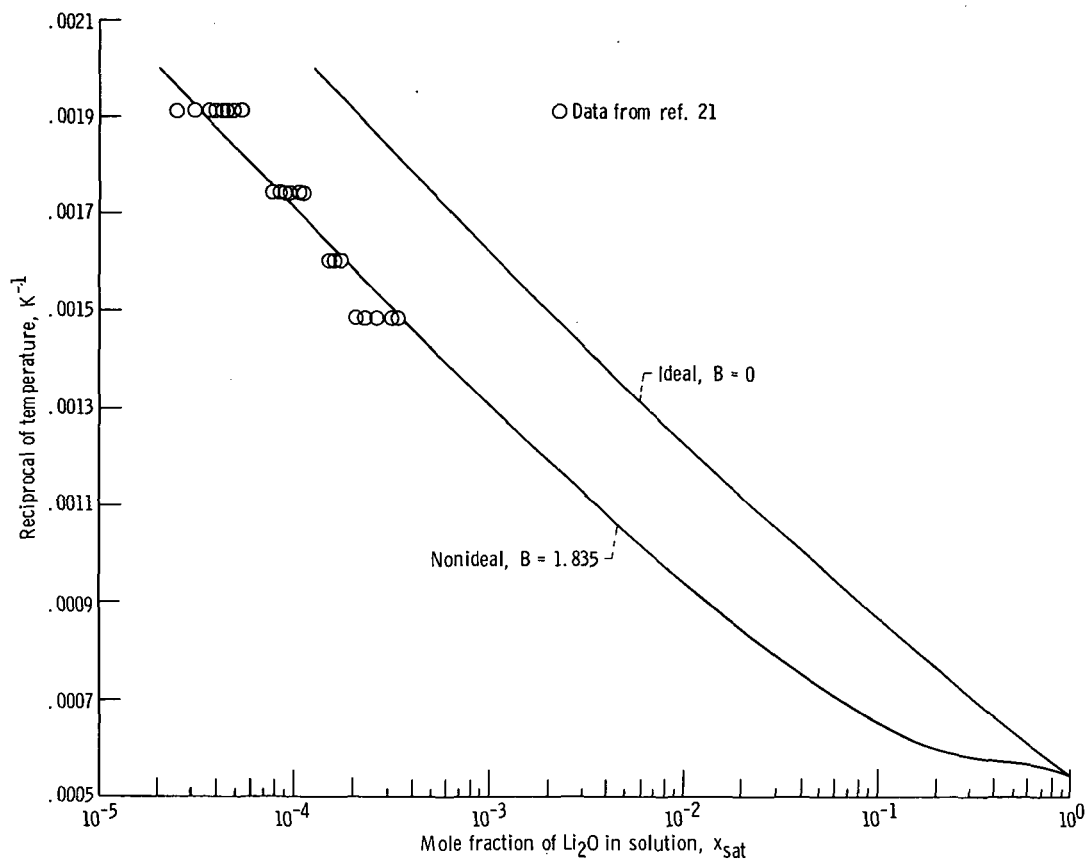
Figure 1. – Solubility limit for Li_2O in liquid lithium x_{sat} against reciprocal temperature $1/T$.
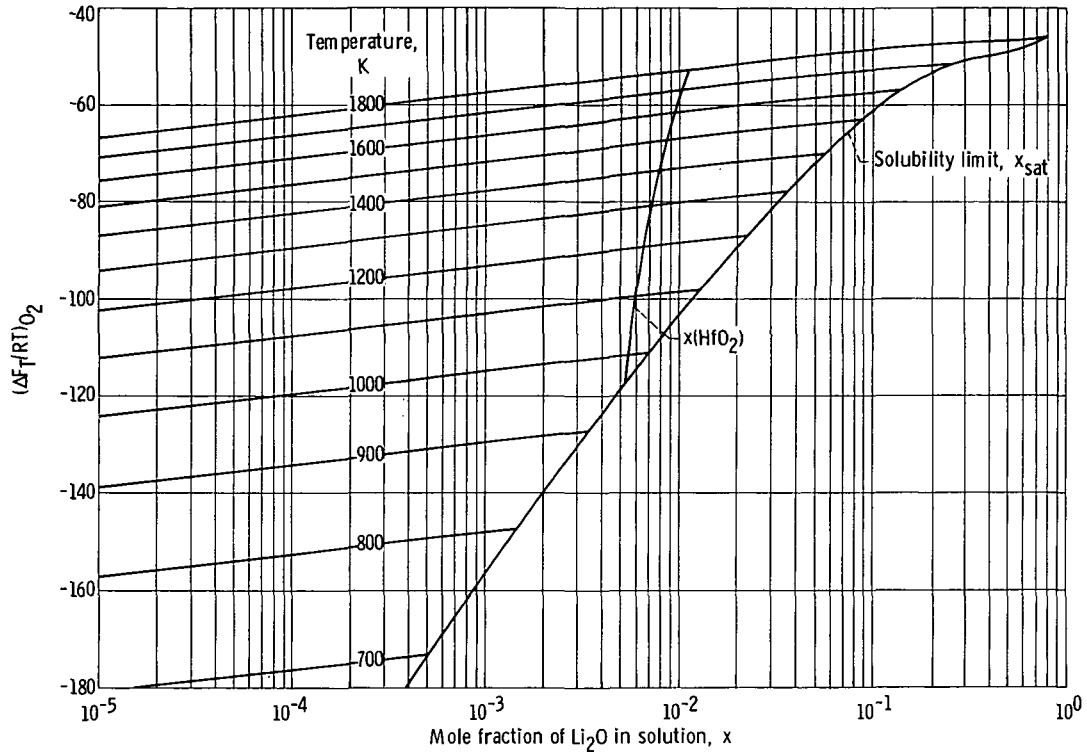
(a) Nonideal case, $B = 1.835$.

Figure 2. - Chemical potential diagram for diatomic oxygen in equilibrium with a solution of lithium and Li_2O.

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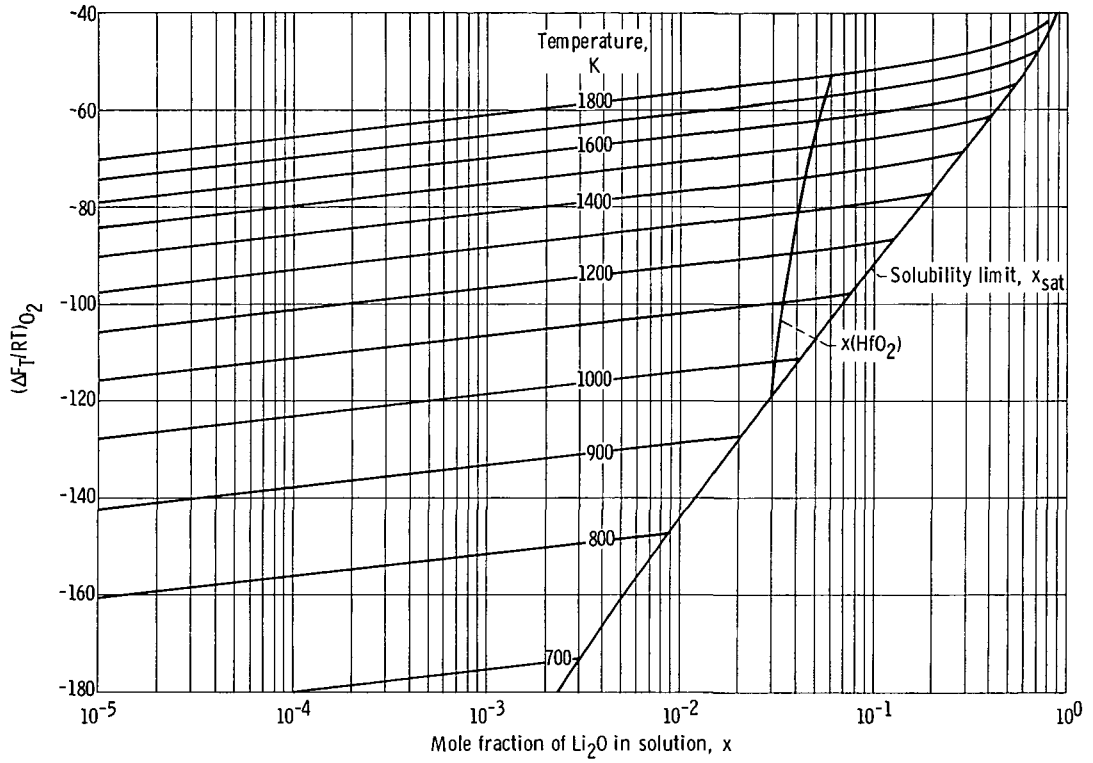
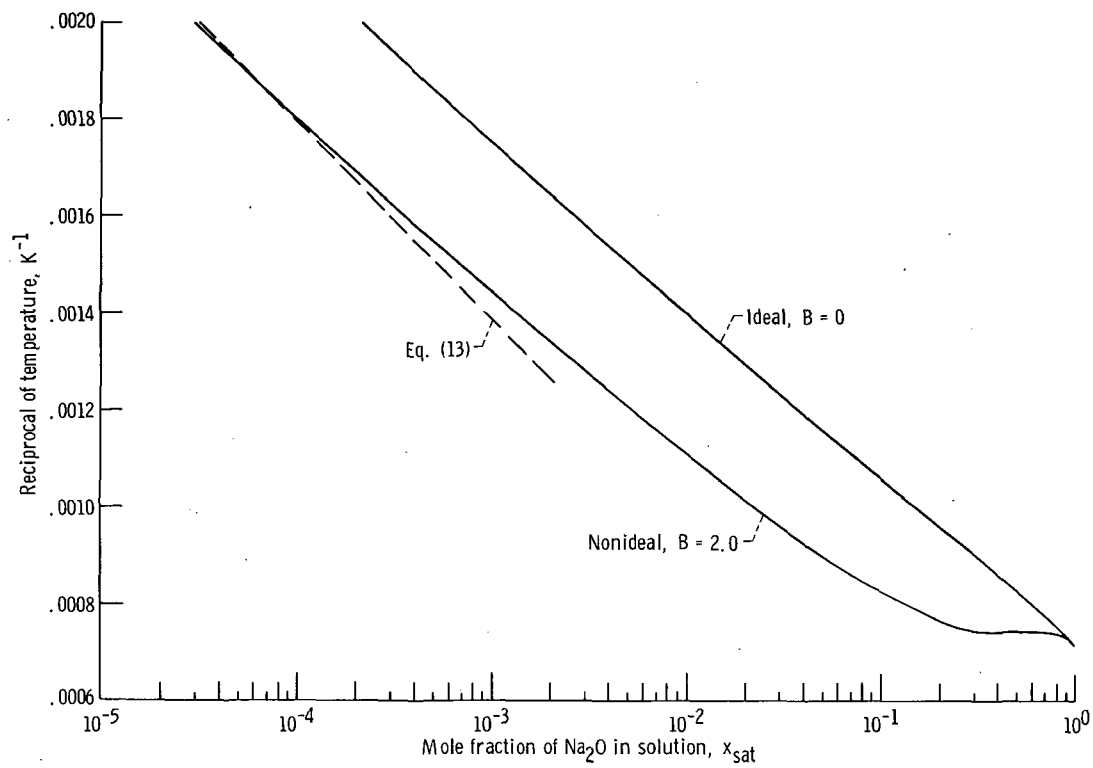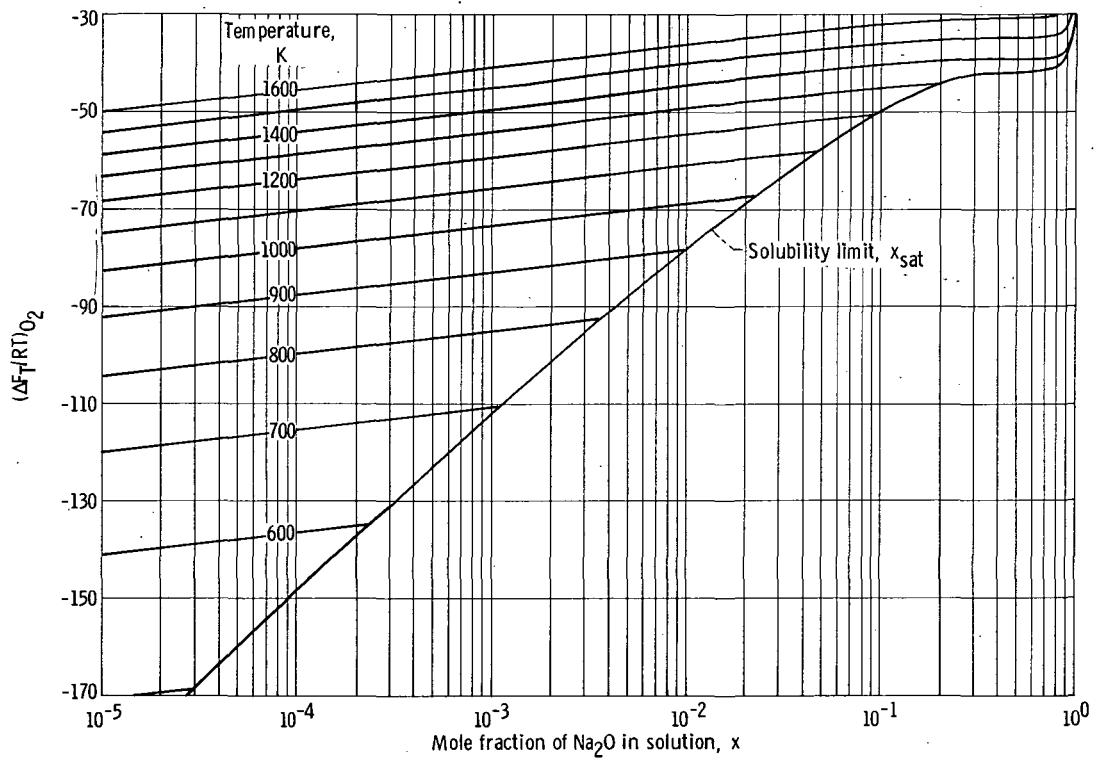(b) Ideal case, B = 0.
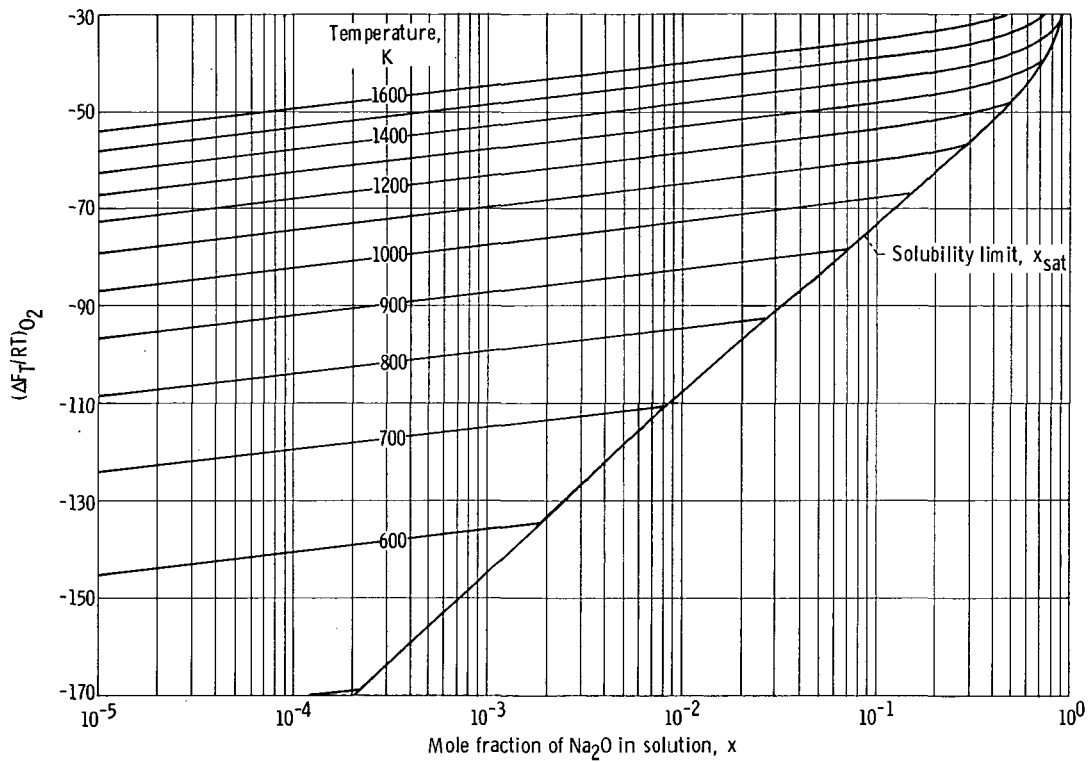
Figure 2. – Concluded.

Figure 3. – Solubility limit for Na_2O in liquid sodium x_{sat} against reciprocal temperature $1/T$.

(a) Nonideal case, B = 2.0.

Figure 4. - Chemical potential diagram for diatomic oxygen in equilibrium with a solution of sodium and Na_2O.
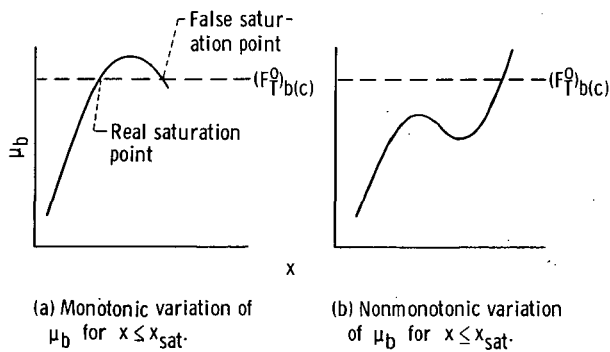
(b) Ideal case, B = 0.

Figure 4. – Concluded.

(a) Monotonic variation of μ_b for $x \leq x_{sat}$.

(b) Nonmonotonic variation of μ_b for $x \leq x_{sat}$.

Figure 5. – Some modes of variation of μ_b with x.

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