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VAPORIZATION OF ALKALI METAL OXIDES

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The vaporization of metal oxides at high temperatures may occur according to three general types of reactions: (1) by vaporization as a gaseous oxide molecule whose composition corresponds very nearly to that of a solid; (2) by vaporization with partial decomposition to a gaseous oxide molecule of composition differing from that of the solid oxide and metal, or (3) by vaporization with complete decomposition to the elements, i.e., the metal and O or O_2 as is appropriate to the temperature. As examples of the first type of vaporization one may use MoO_3, SrO, WO_3, SnO, and PbO; the second type of reaction is illustrated by Al_2O_3 and SiO_2, and the third reaction type is that shown by FeO, MnO, ZnO, CdO, and NiO.

The decision as to which reaction group is the proper one for a given oxide may be accomplished by a combination of experimental and thermodynamic procedures. It is necessary to measure experimentally the vapor pressure over the compound of interest by some reliable method; in these experiments, the Knudsen method was used, in which the weight of material effusing from a round hole of known diameter in an otherwise closed container at a given temperature, was measured over a known period of time. The problem in thermodynamics is the correlation of the measured weight losses with one of the possible methods of vaporization. The details of this procedure are described by Brewer and Mastick[19].

For the alkali metal oxides, M_2O, the question of vaporization mechanism to be settled is whether these compounds vaporize according to the reaction

$$M_2O(s) = MO(g) + M(g),$$

or

$$M_2O(s) = M_2O(g),$$

or according to the reaction

$$M_2O(s) = 2\ M(g) + 1/2\ O_2(g).$$

Previous Work

Dittmar[1] prepared Li_2O by heating the hydroxide and removing the water. Lebeau[2] made Li_2O by heating lithium carbonate to 600-800°C. and removing the CO_2. He observed that on heating at 1000°C. for one hour, complete vaporization of Li_2O occurred. De Forcrand[3] noted no weight loss on heating Li_2O for several hours at 780-800°C. Mott[4] in an early study involving the volatilities of various substances in an electric arc, has given the order of volatility of the alkali metal oxides as: $K_2O > Na_2O > Li_2O$. Lemarchands and Jacobs[5] have made estimates of the volatilities of the alkali metal oxides on the basis of comparisons of the temperature reached at a surface where the alkali metal and oxygen are in contact. This temperature is obviously some function of the volatilities of the alkali metal and the oxide. The results of their comparisons, however, must be weighed carefully since they assume MO as the volatile species and, in lieu of a properly determined constant for oxides, use one previously applied to a study of chlorides. Thomas[6] has stated that Li_2O is stable as a vapor at approximately 500°C.

Quantitative studies of the alkali metal oxides at high temperatures have not been numerous because of the corrosion problems. The main interest in these compounds has been among glass chemists and others interested in M_2O compounds with SiO_2. Kracek[7], Morey and Bowen[8], van Klooster and Jaeger[9], and others have studied the phase diagrams of the alkali metal

oxide-SiO_2 systems over fairly wide ranges of composition. Preston and Turner[10] in a series of investigations have studied the vaporization from metal oxide-silica systems including Li_2O-SiO_2, Na_2O-SiO_2, K_2O-SiO_2, and PbO-SiO_2. Their method for determination of a vapor pressure consisted basically of passing dry nitrogen gas as a carrier across the surface of a fused metal oxide-silica mixture in a Pt dish, observing how the loss of weight of material varied with the rate of flow of nitrogen, and by extrapolating the rate of weight loss to zero flow rate, i.e., equilibrium, making a computation of the vapor pressure. They also determined rates of evaporation from fused metal oxide-silica mixtures held in a static atmosphere of nitrogen. Because of the difficulty of being certain of the attainment of equilibrium, the problem of applying corrections for diffusion effects, and the necessity of considering bonding effects and the possible formation of compounds and complex ions, the vapor pressures calculated from this work are subject to doubt. In every system studied by Preston and Turner, including the PbO-SiO_2 system, the calculated vapor pressures are much higher than observed by other experimenters for the pure metal oxides, and the temperature range is too low for appreciable evaporation of SiO_2.

A recent study of the properties of pure Na_2O at high temperatures is that of Bunzel and Kohlmeyer[11]. They determined the melting point as 920°C. and stated that vaporization of Na_2O was just observable at 1350°C.

An additional reference to the vaporization of an alkali metal oxide is given in the compilation by Fischer[12] referring to unpublished data of Hartmann and Linke on Li_2O. The boiling point is given as 1573°K.

and the heat of sublimation in the range 1233-1573°K. is given as 74 kcal/mole. In a recent paper concerning the electrical conductivity of liquid metal silicates it was observed that at temperatures of about 1800°C. the vaporization of alkali metal silicates became sufficient to interfere with conductance measurements[13].

Theoretical Considerations

With this general information available on the vaporization of alkali metal oxides, Brewer and Mastick[14] carried out a calculation to determine the relative importance of the $M_2O(g)$ molecules. The various thermodynamic cycles used throughout these calculations are illustrated in Figure 1.

The theoretical treatment of the M_2O molecule was possible since an ionic model was assumed for both the gas and solid state. By using the equation for the crystal energy of an ionic solid,

$$U_o^s = \frac{NAe^2 z^2}{r_o} - \frac{B}{r_o^n} = \frac{NAe^2 z^2}{r_o}\left(1 - \frac{1}{n}\right)$$

where n is as given by Pauling[15], Brewer and Mastick showed that the agreement between calculated and experimental values of U_o^s was not very satisfactory, becoming worse with increasing atomic number. For the alkaline earth oxides CaO and SrO, good agreement was obtained if the value for E, the electron affinity of an oxygen atom for two electrons, was taken as -168 kcal/mole. This value was used in all other calculations.

Before considering the energies of $M_2O(g)$, Brewer and Mastick tried to calculate the energy of dissociation of the gaseous alkali metal halides into ions. The result of this calculation was that, when the energy of the ionic molecule was calculated only on the basis of electro-

static interactions of the ions and the influences of both van der Walls and repulsive forces were neglected, good agreement was obtained between calculated and experimental heats for the reaction

$$M(g) + X(g) = MX(g)$$

where X = Cl, Br, or I and M = Na, K, Rb, or Cs. The application of a correction term for repulsion caused a deviation somewhat greater than 10% depending on the value of n, the repulsive exponent.

It was suggested by Brewer and Mastick that for ionic molecules in the gaseous state, polarization and dispersion forces are apparently cancelled by repulsive forces. Rittner[16] has recently treated the alkali metal halide in an extensive calculation considering both polarization and repulsive effects and shown that the neglect of these two factors by Brewer and Mastick is justified since they just cancel. However, for another series of ionic molecules, the alkali metal hydrides, Klemperer and Margrave[17] have shown that for these compounds the polarization effect is less than the repulsive effect, and that a detailed calculation considering both is necessary to obtain a value for the binding energy in agreement with experimental data.

The extension of the calculation of Brewer and Mastick to M_2O molecules required knowledge of the molecular configuration. As a simple approximation the molecules were treated as a linear assemblage of three ions for which the energy of dissociation into ions is given by

$$U_o^g = \frac{7\ Ne^2}{2r_o}\left(1 - \frac{1}{n}\right) = \frac{7\ Ne^2}{2r_o} - \frac{Be^2}{r^n}$$

where n is the repulsive exponent; however, values for r_o, the interatomic distances, are not known. A procedure presented by Pauling for a crystalline

solid of the NaCl-type structure in which the potential energy of the ionic array is expressed as an electrostatic attraction term and several repulsion terms representing the various cation-anion, cation-cation, and anion-anion repulsions in terms of the ionic radii was applied to the anti-fluorite structure of the $M_2O(s)$. From this procedure, Brewer and Mastick obtained values for the interatomic distances in the hypothetical $M_2O(g)$, and with these distances were able to compute the heats of formation of these compounds. As a check the heat of formation of $CaF_2(g)$ was also computed and compared with the literature value. With these calculated heats of formation and the estimated entropy of volatilization of 40 e.u. the vapor pressure of $M_2O(g)$ molecules over the solids at 1000°K. was calculated and compared with the pressure of metal to be expected if decomposition to the elements occurred. The results of these calculations are presented in Table 1. On this basis it was to be expected that only Li_2O might vaporize as such, and that all other alkali metal oxides should vaporize by decomposition.

It is interesting to note that the results obtained in the calculations just mentioned are extremely sensitive to the value of r_g, the interatomic distance in the gas, and this quantity is not too definitely fixed by the procedure outlined above. A somewhat more reliable value for r_g would seem to be that given by considering the gaseous ionic radii found for the alkali metal ions and the halide ions by Rittner in his comprehensive study. By noting that the difference between ionic radii in solids and gases, as given by Pauling and Rittner respectively, is about 0.20 A° and extending this to the $O^{=}$ ion, one finds values for the interatomic distances in the $M_2O(g)$ molecules approximately 0.10 A. larger than those used by Brewer and Mastick. Application of these values will in every case lower the pressure of $M_2O(g)$

Table 1

Calculated Pressures of $M_2O(g)$ and $M(g)$ in Equilibrium with $M_2O(s)$ at 1000°K.*

Compound	ΔH^{vap}_{298} (M_2O (kcal/mole)	ΔF^{vap}_{298} (M_2O) (kcal/mole)	$P_{1000}(M_2O)$ (atm)	$P_{1000}(M)$ (atm)
Li_2O	59	19	10^{-4}	1×10^{-12}
Na_2O	110	70	10^{-15}	5×10^{-7}
K_2O	111	71	10^{-16}	4×10^{-5}
Rb_2O	119	79	10^{-17}	1×10^{-4}
Cs_2O	155	115	10^{-25}	2×10^{-4}

*Calculated by Brewer and Mastick[14].

to be expected at 1000°K. by several powers of ten, a change unimportant except for Li_2O where the pressure of $Li_2O(g)$ is calculated as 4×10^{-10} atm. A shift in r_g of 0.09 Å. for $Li_2O(g)$ is sufficient to make the pressure such that decomposition to the elements is the main vaporization process, and $Li_2O(g)$ only a minor vaporizing species.

A consideration of LiO(g), NaO(g), KO(g), RbO(g), and CsO(g) using the method of Rittner and assuming an ionic gas with singly charged ions shows that only for LiO(g) is there a chance of being an important vaporizing species; for the other alkali metals such oxide molecules will be far less important than the elemental species.

From the data and experiments outlined above, it is apparent that the main interest in vaporization of alkali metal oxides should lie in observation of Li_2O to find whether or not it vaporizes as $Li_2O(g)$, or LiO(g), and a check of some of the other alkali metal oxides to show that they really vaporize by decomposition to the elements.

Experimental Work

The compounds studied in this work, Li_2O and Na_2O, are extremely hygroscopic, react with CO_2 and consequently were difficult to handle. It was necessary to prepare fresh samples often and to handle them in a dry, CO_2-free atmosphere at all time. The loading of samples and transfer of materials were accomplished in a dry box with an atmosphere of argon and in the presence of molten sodium which acts both as a desiccator and as a getter for oxygen and CO_2.

(a) Preparation of Compounds

1. Li_2O

The Li_2O used for the vapor pressure runs was prepared by heating

Li_2CO_3 to about 1000°C. for 20-30 minutes and pumping off the CO_2 formed. The reaction was carried out in a Pt crucible heated inductively. It was observed that some of the Li_2CO_3 would usually melt and run over the edge of the crucible; however, there was always a clean white residue of Li_2O. X-ray studies of the powder patterns given by many samples prepared in this manner indicated the Li_2O phase present with no major impurities and a lattice constant in agreement with literature values[18]. Base titration indicated greater than 96% Li_2O in every sample.

By visual examination of the samples used for various vapor pressure runs, the temperature of melting as measured by an optical pyrometer and corrected for window absorption was in the range 1700 ± 15°K. This is lower than the value of approximately 1700°C. listed in the ICT and reported by van Klooster and Jaeger[9], but is the highest melting point of any of the alkali metal oxides.

2. Na_2O

The preparation of Na_2O is possible by several reactions:

$$NaNO_3(s) + 5\ NaN_3(s) = 3\ Na_2O(s) + 8\ N_2(g)$$

$$NaNO_2(s) + 3\ NaN_3(s) = 2\ Na_2O(s) + 5\ N_2(g)$$

$$2\ Na(s) + 1/2\ O_2(g) = Na_2O(s)$$

$$Na_2O_2(s) = Na_2O(s) + 1/2\ O_2(g)$$

$$2\ Na(l) + Na_2O_2(s) = 2\ Na_2O(s)$$

$$3\ Na(l) + NaO_2(s) = 2\ Na_2O(s)$$

$$Na(l) + NaOH(s) = Na_2O(s) + 1/2\ H_2(g)$$

In this work the first, fourth, fifth, and sixth methods were used to obtain Na_2O as indicated from X-ray diffraction patterns. The fifth and sixth reactions were used to obtain the samples of Na_2O used for the vapor pressure

runs. These preparations were carried out in the dry box with an argon atmosphere by melting the Na and heating it to 500°C. in a MgO crucible and slowly adding slightly less than the theoretical amount of either Na_2O_2 or NaO_2. A considerable evolution of heat accompanies these reactions. The excess sodium was distilled off the material in vacuum at 400-500°C. leaving only pure Na_2O since any NaOH impurity should be reduced to hydrogen gas as shown in the last reaction. X-ray powder patterns of the material containing excess Na and the pure Na_2O showed no apparent change in lattice constant indicating that at least at room temperature the solid solution of Na in Na_2O has a narrow homogeneity range. Analysis by titration showed greater than 95% Na_2O with some NaOH impurity indicated by X-ray analysis. This impurity should be removed by heating at a lower temperature than that at which vaporization of Na_2O occurs. Analysis after several vapor pressure runs indicated purities as high as 97% Na_2O. The presence of NaOH as shown by X-ray patterns is undoubtedly due to reaction with moisture on the glass capillaries used to contain the samples.

Visual examination of Na_2O samples which had been heated for different runs indicated a melting point of 1190 ± 10°K. in good agreement with the value 1193°K. reported by Bunzel and Kohlmeyer[11].

(b) Apparatus and Procedure

The apparatus used for these effusion studies has been described previously and used for various measurements[19,20]. Basically the arrangement consisted of an outer zircon crucible containing Mo radiation shields, a Pt or MgO crucible containing the material being studied, and a Mo collimating cone. This is depicted in Fig. 2. This arrangement is

supported in a large pyrex tube connected to the vacuum system and heated inductively by a coil of copper tubing. In some of the Na_2O runs at lower temperatures it was found convenient to use a quartz tube heated in a resistance furnace. The container problem for these oxides was solved satisfactorily by using Pt crucibles for the Li_2O runs and MgO crucibles for Na_2O. Spectroscopic analyses of samples heated for long periods in the temperature range concerned failed to show more than traces of the container materials.

In preparing lids for the crucibles different hole sizes were made for the effusion hole and the edges were shaped so as to give as near a knife edge as possible. A portion of the effusate from several of the Li_2O vaporization experiments was collected on a water-cooled Pt disc placed several centimeters from the top of the Mo collimating cone, weighed and titrated to give a measure of the amount and composition of material effusing, while for all the other runs the weight loss of the crucible was determined by direct weighing.

(c) Data

The vaporization of Li_2O was studied in a series of nine runs at temperatures ranging from 1532 to 1669°K. as determined by a calibrated optical pyrometer and corrected for losses due to a pyrex window. In seven of these runs only the amount of material collected on a Pt disc placed in a known position above the effusion hole was measured; in two runs both the amount collected on the Pt disc and the total weight loss of the crucible and contents were determined, and in one run only weight loss was measured. The temperature was an average temperature over the time of the run which was 1 or 2 hours and was maintained with an

accuracy of ± 10°K. for a time in which the maximum uncertainty was about three minutes. The results of these runs are given in Table 2.

Na_2O was observed over the temperature range 918-1467°K. in a series of seven runs in which only total weight loss was observed. Three of these runs at the higher temperatures were made with induction heating and lasted for relatively short times because of the high volatility of Na_2O. The four runs at the lower temperatures were made using resistance heating and were of 3 to 20 hours duration. These temperatures were maintained within ± 5°K. with a maximum uncertainty in time of about 2 minutes. The data are presented in Table 3.

Results and Conclusions

The interpretation of the data presented in Tables 2 and 3 may be made on different bases depending on the gaseous species assumed as important in the vaporization.

If one assumes that the vaporization of the oxides Li_2O and Na_2O is by decomposition to the elements and applies the Knudsen equation,

$$p = \frac{Z\sqrt{MT}}{44.331\ a.t}$$

where p = the pressure in atmospheres,

Z = the number of moles effusing,

M = the molecular weight of the effusing species,

T = absolute temperature,

a = the cross-sectional area of the effusion hole,

and t = the time in seconds, he may calculate the partial pressures of M(g) and O_2(g) over the solids as indicated by the experimental data.

Table 2

Vaporization Data on Li_2O

Run No.	T°K	Weight Effusate Collected (mg)	Li/O Effusate	Total Weight Loss (mg)	Time (sec)	Hole Area (cm^2)
1	1532	1.3	4.0	—	7,200	0.07550
7	1541	2.7	1.7	55.7	5,400	0.07550
3	1573	2.8	3.0	—	14,400	0.07550
4	1579	2.7	1.3	—	7,200	0.02836
2	1590	0.7	3.8	—	3,600	0.07550
6	1596	2.5	0.97	—	5,400	0.07550
8	1618	2.6	(2)	65.0	5,820	0.02836
5	1643	3.8	0.97	—	6,000	0.02836
9	1669	—	(2)	57.8	1,080	0.0804

(Bracketted figures indicate estimated values.)

Table 3

Vaporization Data on Na_2O*

Run No.	T°K	Total Weight Loss (mg)	Time (sec)	Hole Area (cm^2)
2	918	6.2	11,640	0.1156
5	943	7.8	64,980	0.0314
7	998	22.7	59,820	0.0314
6	1006	21.3	73,260	0.0314
4	1241	21.7	1,500	0.0855
3	1260	134.4	1,320	0.0855
1	1467	641.1	600	0.0804

* ($\frac{Na}{O}$ Ratio was not determined and was assumed to be 2/1 in all calculations on Na_2O.)

The reaction to be assumed is

$$M_2O(s) = 2\ M(g) + 1/2\ O_2(g)$$

and thus,

$$K = P_M^2\ P_{O_2}^{1/2} \quad .$$

To calculate K one must use the observed data and determine (1) the number of moles of product gases effusing from the Knudsen cell, a quantity related directly to the partial pressures of the various gases in the cell and inversely to the molecular or atomic weight of each effusing species, and (2) the ratio of metal to oxygen in the effusing gas. In lieu of this latter information from experimental data it is often assumed that the relative number of moles of each effusing species is the same as that indicated by the coefficients of these corresponding substances as written in the chemical equation describing the assumed reaction. When one observes vaporization from a solid oxide, however, the ratio of metal to oxygen atoms in the effusate may differ from that found in the solid, since most compounds show homogeneity ranges with the constituent elements at the extremes of which considerable excesses of these constituents may be present. Thus, in equilibrium with a sample on the Li-rich side of the Li-Li_2O homogeneity range, one would find a high partial pressure of Li(g) and a low partial pressure of $O_2(g)$ while the reverse would be true for a sample whose composition was on the oxygen rich side of the range. Vaporization of the solid phase under a neutral atmosphere will, of course, allow the composition to approach the constant boiling composition and thus, a series of consecutive observations on the same sample might show a fairly wide range of M/O ratios tending toward the constant boiling ratio. There is no evidence for a wide homogeneity range in either Li_2O or Na_2O and the constant

boiling composition should be near that of the solid, i.e., a M/O ratio of 2/1. When low vapor pressures are being measured and only small amounts of material are vaporized, one may find ratios varying from that indicated from preliminary considerations of homogeneity ranges. For example, in vaporizing Li_2O the Li/O ratio, as observed from experiments during which only a few milligrams of Li_2O were vaporized, varied considerably from the predicted 2/1 ratio, probably because of slight amounts of oxidation or reduction by impurities in the solid or surrounding atmosphere. Although no experimental checks were made on the Na_2O during its vaporization, it is believed that the Na/O ratio $\approx$ 2/1, particularly at the higher temperatures where the partial pressure of metal was 10^{-3} - 10^{-4} atm. and this value was assumed in all the calculations for Na_2O.

It is possible to re-write the expression for K as

$$K = P_M^{5/2} \left(\frac{\text{mol. wt. } O_2}{\text{mol. wt. } M}\right)^{1/4} \left(\frac{1}{2n}\right)^{1/2}$$

since moles $M \propto P_M/\sqrt{\text{mol. wt. } M}$,

moles $O_2 \propto P_{O_2}/\sqrt{\text{mol. wt. } O_2}$,

and moles M = 2n moles O_2 if M/O = n. This equation and the data of Tables 2 and 3 have been used to compute the experimental values of K, the equilibrium constant for decomposition of Li_2O and Na_2O to the elements, which are plotted in Figs 3 and 4. In order to obtain calculated equilibrium constants for comparison, and also to allow use of each experimental point for a determination of ΔH_0°, the heat of the decomposition reaction at absolute zero, one must use available data (and estimates) for the heat capacities of the M_2O solid phases and compute entropies, heat contents, and free energy functions for the solids. Similar data have already been tabulated for the elements[21].

The heat capacity of $Li_2O(s)$ has only been measured to 298°K.[22], and in making a reasonable estimate of the high temperature heat capacity one finds considerable lattitude available as indicated in Fig. 5. By considering the values indicated as extremes between which the true heat capacity of $Li_2O(s)$ must lie, one may compute a range of values for -log K for the decomposition reaction. This range is indicated by the cross-hatched area in Fig. 3.

Naylor[23] has estimated the high temperature heat capacity of $Na_2O(s)$ by comparison of heat capacity data on sodium silicates and titanates and the main uncertainty in the Na_2O thermodynamic functions is found above the melting point of $Na_2O(s)$ since there is no information available regarding either the heat and entropy of fusion or the heat capacity of the liquid. The following estimates were used to calculate the equilibrium constant above 920°C., the melting point of Na_2O;

$$\Delta H_{fusion} = 10 \text{ kcal/mole}$$

$$\Delta S_{fusion} = 8.4 \text{ e.u.}$$

$$C_p \quad Na_2O(l) = 24 \text{ cal/mole-deg.}$$

By using the free energy functions as calculated for the extremes of possible heat capacity values and combining these with the experimental free energies, one obtains values for ΔH_0° of vaporization of Li_2O by decomposition to the elements which are 1-6% lower than the value 214.223 kcal/mole calculated on the basis of thermochemical data[21,22]. A comparison of the experimental values of ΔH_0° for Na_2O vaporization by decomposition with that obtained from thermochemical data, $\Delta H_0^\circ = 149.10$ kcal/mole[21,24], indicates values from 2-3% low using data on $Na_2O(s)$ and from 1-2% high using data on $Na_2O(l)$ depending in the latter case on the estimated quantities listed previously for the fusion process and the liquid state.

The general range of agreement between calculated and experimental points

is within the maximum range allowable for an effusion type of experiment, and one may state that the vaporization of Li_2O and Na_2O in vacuum is mainly by decomposition to the elements although there is some indication that an oxygen containing gaseous species might be of minor importance in the Li_2O vaporization. The calculations of Brewer and Mastick[14] and others of the authors indicate that molecules of the type $M_2O(g)$ or $MO(g)$ are not important as vaporizing species even in highly oxidizing atmospheres for Na_2O, K_2O, Rb_2O, or Cs_2O. It is interesting to note that the presence of a very small amount of hydroxide impurity (1-2%) could account for the high results obtained in many of the runs on both oxides, and this possibility cannot be definitely excluded since the handling and weighing procedures involved slight but appreciable exposures to moist air.

If one treats the Li_2O data on the assumption that $Li_2O(g)$ is the main vaporizing species, and applies the Knudsen equation, the pressures calculated disagree with the pressures to be expected according to the calculations of Brewer and Mastick[14]. However, modifications of the r_g value as indicated previously could allow $Li_2O(g)$ to be of definite but slight importance in the vaporization process, and also explain the high results obtained in many of the runs on Li_2O.

Preliminary experiments have been carried out in an attempt to check the possible importance of $Li_2O(g)$ and $LiO(g)$ as vaporizing species using argon, oxygen and argon-oxygen mixtures and passing the undried gases over $Li_2O(s)$. Erratic results were observed which can most likely be explained on the basis of small amounts of water in the flow gases which volatilize the Li_2O as hydenide. A single run was made with gases dried over $CaCl_2$ and an enhanced vaporization of $Li_2O(s)$ in an oxygen atmosphere was observed at $1500^\circ - 1600^\circ K$.

Using these data, one may place the following limits on the thermodynamic properties of $Li_2O(s)$ and $LiO(g)$

	Li_2O	LiO
ΔH_f^o (Kcal/mole)	≥ 174	≥ 4
D (Kcal/mole)	≤ 270	≤ 92

where D = the dissociation energy of the gaseous molecule into atoms.

Summary

Since the observed pressures correspond very nearly to those calculated for decomposition to the elements both for Li_2O and Na_2O, it is certain that $M_2O(g)$, $MO(g)$ or any other oxide molecule must be less important vaporizing species in vacuum or neutral atmospheres than the elemental species. Thus, the alkali metal oxides must vaporize mainly by decomposition to the elements. On the basis of the experiments performed, it is impossible to state that the gaseous molecule, Li_2O, is unimportant under all conditions and it may be of some importance as a vaporizing species in atmospheres containing a high partial pressure of oxygen where decomposition to the elements is quenched. However, the theoretical calculations indicate such small partial pressures of oxides of alkali metals other than lithium, that even large errors in these calculations would not alter the conclusion that the decomposition process is the only important vaporization process for all alkali metal oxides, except possibly Li_2O, under all conditions of vaporization.

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THERMOCHEMICAL CYCLES FOR M_2O

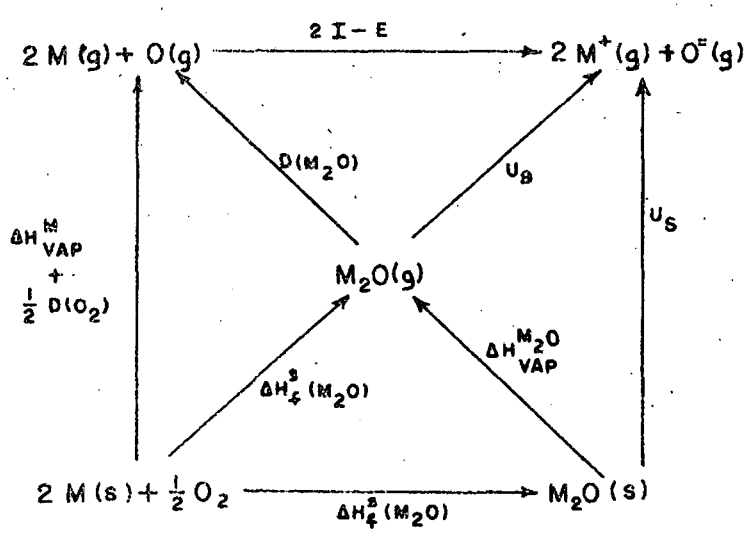


Fig.1

EFFUSION CELL

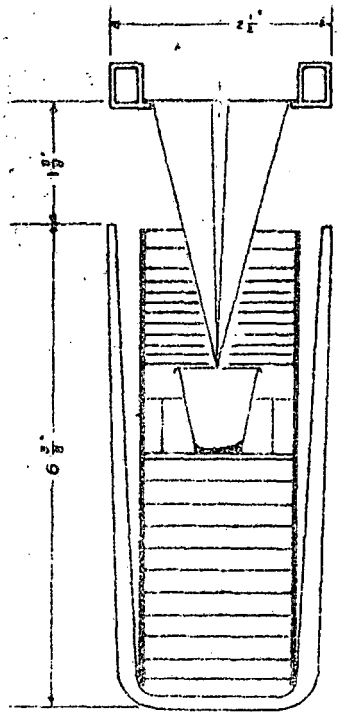
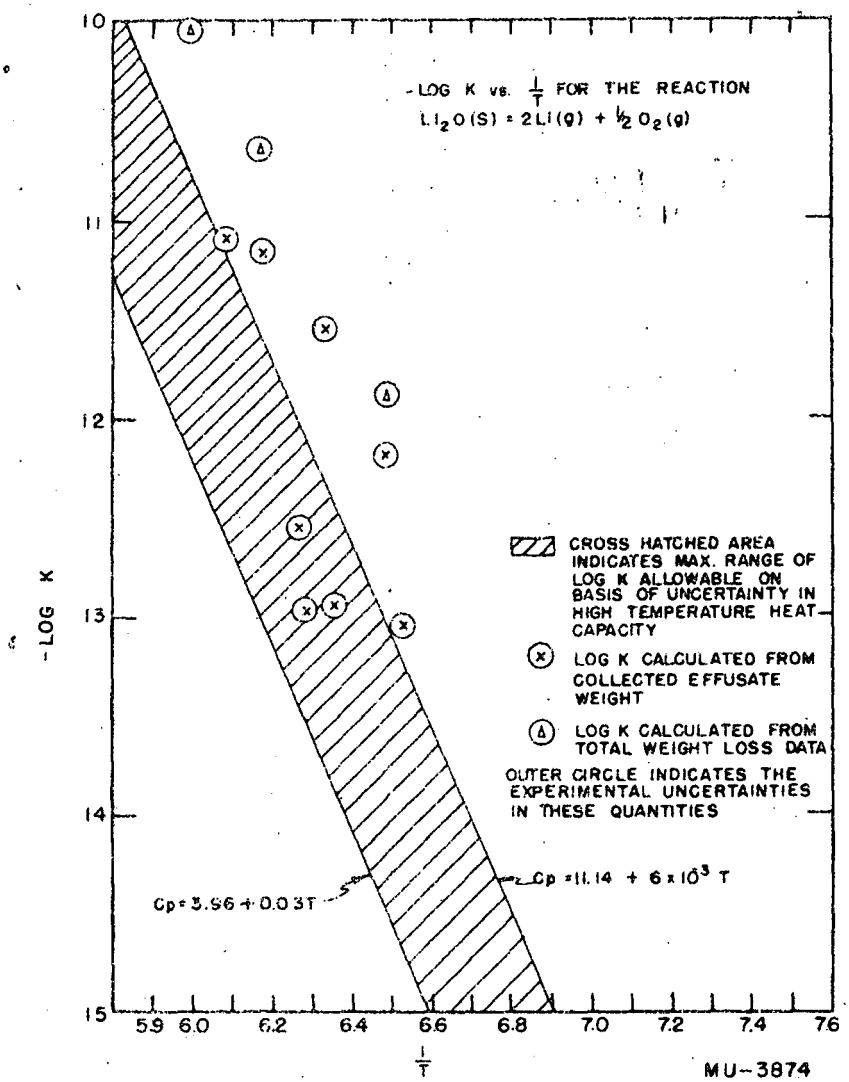
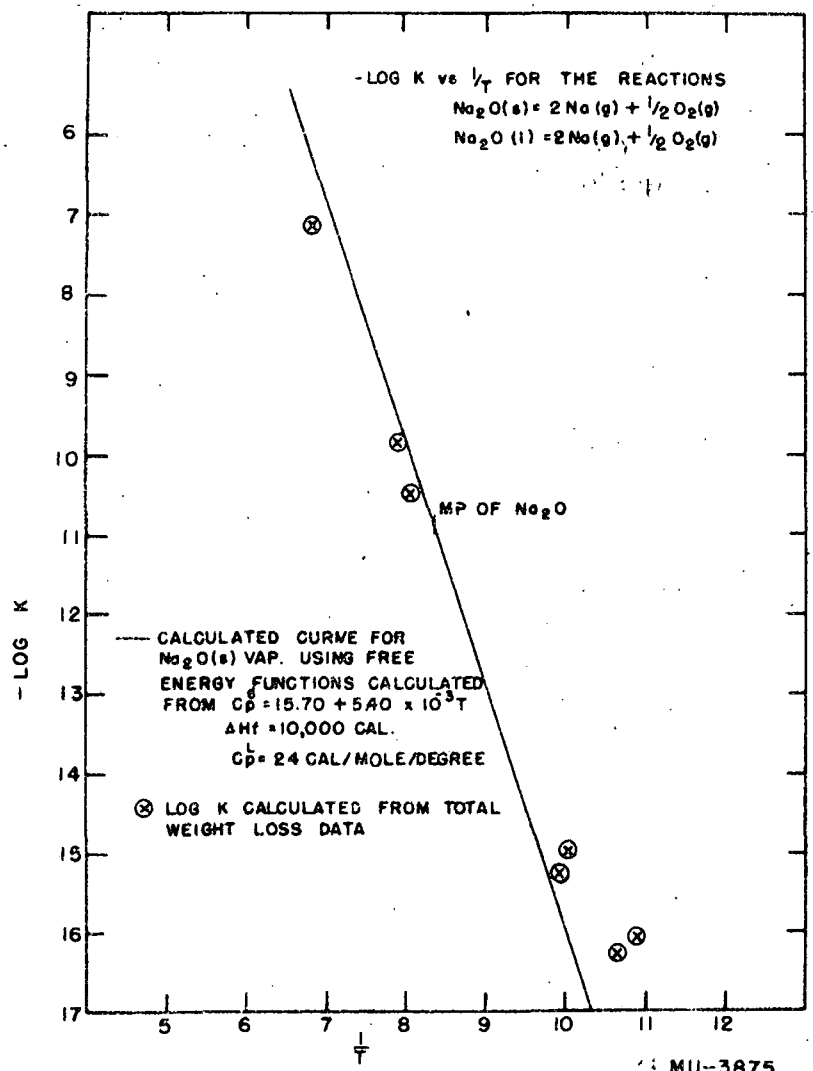


Fig.2


-LOG K vs. 1/T FOR THE REACTION
Li2O(S) = 2Li(g) + ½ O2(g)
CROSS HATCHED AREA INDICATES MAX. RANGE OF LOG K ALLOWABLE ON BASIS OF UNCERTAINTY IN HIGH TEMPERATURE HEAT CAPACITY
LOG K CALCULATED FROM COLLECTED EFFUSATE WEIGHT
LOG K CALCULATED FROM TOTAL WEIGHT LOSS DATA
OUTER CIRCLE INDICATES THE EXPERIMENTAL UNCERTAINTIES IN THESE QUANTITIES
Cp = 3.96 + 0.03T
Cp = 11.14 + 6 x 10^3 T
-LOG K
1/T
10
11
12
13
14
15
5.9
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6

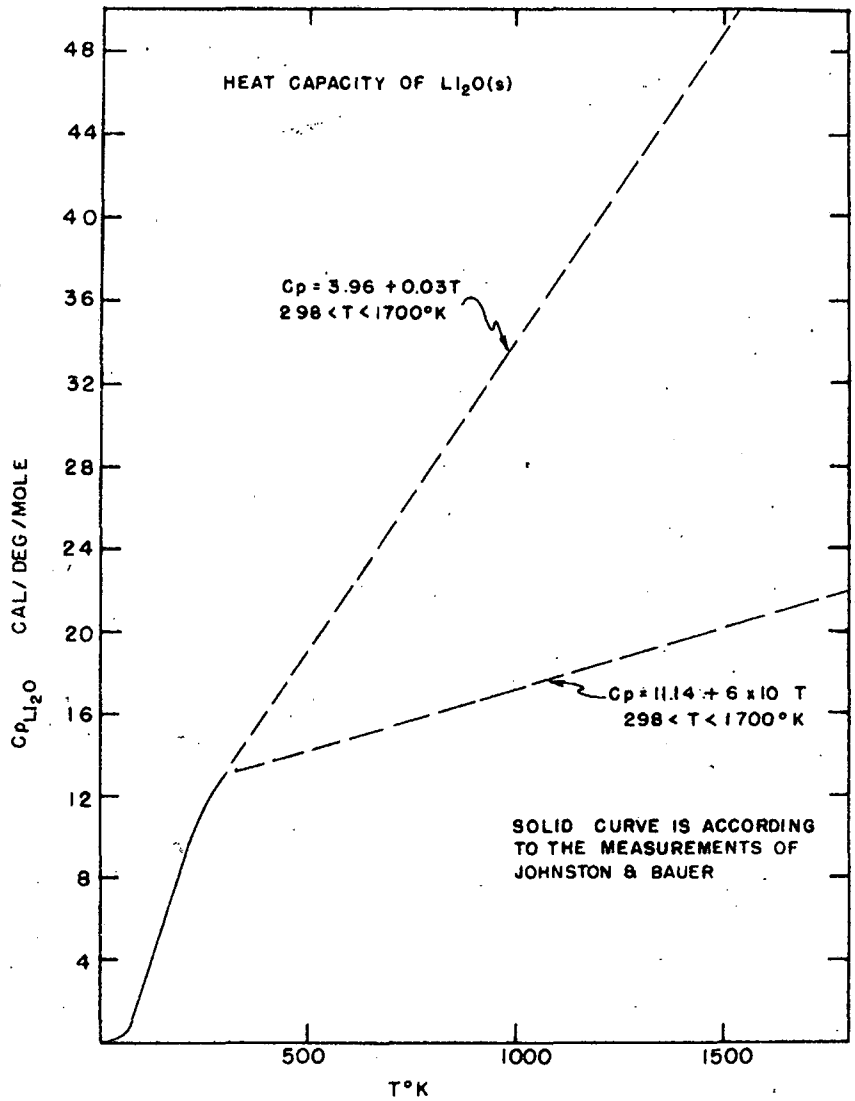
MU-3874

FIG. 3


-LOG K vs 1/T FOR THE REACTIONS
Na2O(s) = 2 Na (g) + 1/2 O2(g)
Na2O (l) = 2 Na(g) + 1/2 O2(g)
MP OF Na2O
CALCULATED CURVE FOR Na2O(s) VAP. USING FREE ENERGY FUNCTIONS CALCULATED FROM Cp° = 15.70 + 5A0 x 10^-3 T
ΔHf = 10,000 CAL.
Cp^L = 24 CAL/MOLE/DEGREE
LOG K CALCULATED FROM TOTAL WEIGHT LOSS DATA
- LOG K
1/T
6
7
8
9
10
11
12
13
14
15
16
17
5
6
7
8
9
10
11
12

MU-3875

FIG. 4


HEAT CAPACITY OF $Li_2O(s)$
$Cp = 3.96 + 0.03T$
$298 < T < 1700°K$
$Cp = 11.14 + 6 \times 10\ T$
$298 < T < 1700°K$
SOLID CURVE IS ACCORDING TO THE MEASUREMENTS OF JOHNSTON & BAUER
Cp_{Li_2O} CAL/DEG/MOLE
48
44
40
36
32
28
24
20
16
12
8
4
500
1000
1500
T°K

MU3876

FIG. 5