THERMODYNAMIC EVALUATION OF THE POSSIBILITY OF LITHIUM SUPEROXIDE PRODUCTION

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FOREWORD

The work reported herein was performed at IIT Research Institute, 10 West 35th Street, Chicago, Illinois 60616, under Contract No. AF 33(615)-2351, for the Aerospace Medical Research Laboratories, in support of Project 6373, "Equipment for Life Support," Task 637302, "Respiratory Support Equipment." The report covers the period from 1 February to 29 May 1965, and is designated Report No. IITRI-C6057-4.

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This technical report has been reviewed and is approved.

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ABSTRACT

To determine whether lithium superoxide can be produced and whether it is stable enough for use in air regeneration units of manned spacecraft, the free energy of lithium superoxide was calculated from estimated values of the heat of formation, entropy, and heat capacity. The estimates were based on graphical comparison with properties of other oxides. The heat of formation was also determined from calculation of the lattice energy by means of the Born-Haber cycle. The result was -65 kcal. The stability of lithium superoxide was deduced by comparing graphically the free energies of the oxides of lithium. The superoxide is unstable by 15 kcal from 100 to 300°K and is even more unstable at higher temperatures. Reasonably high pressure and other effects cannot overcome this instability, even at low temperature. Therefore the use of lithium superoxide for air regeneration units is not promising.

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SECTION I

INTRODUCTION

Lithium superoxide if it exists in a stable form would be of interest for air regeneration units for life support of manned aerospace flight. Lithium superoxide potentially represents the lightest alkali metal oxide in terms of weight of agent per weight of oxygen produced. Experimental efforts to produce this compound have given ambiguous results. Accordingly, this project was undertaken to estimate the thermodynamic properties of this compound. The objective was to determine whether further experimental efforts are worthwhile, to predict suitable experimental conditions, and to draw conclusions about the stability of the compound.

SECTION II

LITERATURE SEARCH

The literature on thermodynamic properties of alkali metal oxides was searched and studied to find the most reliable data to use as the basis for estimating the properties of lithium superoxide.

The following indexes to published literature and government reports were searched:

Journal	Coverage
Chemical Abstracts	1947 to March 1965
International Aerospace Abstracts	1961 to March 1965
Scientific and Technical Aerospace Reports	1960 to March 1965
Technical Abstract Bulletin	1960 to March 1965

Additional references came from our files and from review articles. For an excellent comprehensive review of the alkali metal oxides, the reader is referred to Vannerberg's article (ref. 1).

Thermodynamic data were obtained from references 1 through 16 and are summarized in Table I. When more than one value was reported in the literature, the most recent was selected. Exceptions are the heats of formation of K_2O_2 and CsO_2. For K_2O_2 the older experimental value is given in the table because it is more consistent with the trend of values for the other oxides. For CsO_2 the true value probably lies between the two experimental values.

Aside from thermodynamic predictions, the only direct evidence for the existence of lithium superoxide is in the observations of its absorption spectrum in the wavelength of visible light. Thompson and Kleinberg (ref. 17) compared the absorption of solutions made by oxidizing lithium, sodium, or potassium in liquid ammonia. The sodium and potassium superoxides were crystallized and identified, but the lithium solution decomposed when it was heated from -78 to -33°C, as indicated by the loss of the yellow color. Dr. Irvine Solomon has confirmed these observations in our laboratory.

We considered the possibility of calculating the thermodynamic properties of lithium superoxide from the observed absorption spectrum. However, the frequency of the absorption maximum apparently is a property of the superoxide ion rather than of the lithium compound itself. This is indicated by the constancy of this frequency with different cations. The same is true for the ozonides. This conforms to the general behavior of solutions of ionic compounds, in which the color is associated with the ions rather than the compound. The absorption wavelength, therefore, appears to be related to the O-O bond instead of the Li-O bond and does not indicate the strength of the Li-O bond.

SECTION III

THERMODYNAMIC PROPERTIES OF LITHIUM SUPEROXIDE

The thermodynamic properties must be estimated, since no experimental data are available. The stability and the conditions under which lithium superoxide can be formed can be predicted from the free energy of formation as a function of temperature. The free energy cannot reliably be estimated directly, but it can be calculated from other thermodynamic properties that can be estimated.

The free energy of formation at any temperature, T, is given by:

$$\Delta G_f^\circ = \Delta H_{f_{298}}^\circ + \int_{298}^{T} \Delta C_p \, dT = T\Delta S_{f_{298}}^\circ + \int_{298}^{T} \frac{\Delta C_p}{T} \, dT \qquad (1)$$

Table I

SOME THERMODYNAMIC PROPERTIES OF ALKALI METAL OXIDES

Oxide	State	Density, g/cc	Temperature, °K: Transition	Melting	Boiling	$-\Delta H^{\circ}_{f_{298}}$, kcal/mole	S°_{298}, entropy units
Li_2O	s			1854 Ref. 2	2836 Ref. 2	142.8 Ref. 3	9.056 Ref. 2
LiO	g					-20.1 Ref. 2	50.4 Ref. 2
Li_2O_2	s	2.33	498 Ref. 2	500 Ref. 2		151.7 Ref. 2	13.5 Ref. 2
LiO_2	s					(63 to 69*)	(14 to 17*)
Na_2O	s			1193 Ref. 2	>2500 Ref. 4	99.4 Ref. 2	17.99 Ref. 2
Na_2O_2	s	2.61	783 Ref. 2	948 Ref. 2		124.0 Ref. 1	22.677 Ref. 2
NaO_2	s	2.21				62.1 Ref. 5	27.7 Ref. 6
K_2O	s			>1154 Ref. 2		36.3 Ref. 2	(22.5) Ref. 2
KO	g					-10.1 Ref. 2	56.272 Ref. 2
K_2O_2	s	2.4		763		108.8 Ref. 7	(27.0) Ref. 2
KO_2	s	2.14	193.5 Ref. 2 230.9 Ref. 2	(675) Ref. 2		67.6 Ref. 2	27.888 Ref. 2
KO_3	s					62.1 Ref. 8	(30*)
Rb_2O	s			>840 Ref. 2		78.9 Ref. 6	
Rb_2O_3	s			762 Ref. 6		126 Ref. 6	
RbO_2	s	3.06		685 Ref. 6		68.8 Ref. 1	
Rb_2O_2	s	3.8		843 Ref. 1		-101.7 Ref. 1	
Cs_2O	s			894 Ref. 6	1553 Ref. 6	75.9 Ref. 6	
Cs_2O_3	s			(760) Ref. 6		135.0 Ref. 6	
CsO_2	s	3.80		705 Ref. 1		70.5 or 76 Ref. 13	
Cs_2O_2	s	4.74		863 Ref. 1		96.2 Ref. 1	
H_2O	l			273 Ref. 2	373 Ref. 2	68.32 Ref. 6	16.75 Ref. 6
H_2O_2	l			272 Ref. 2	431 Ref. 2	44.7 Ref. 6	25.3 Ref. 6
HO_2	g					-60 Ref. 9	

*Estimated by the present author.
Parentheses indicate estimated value.

where

$\Delta H^{\circ}_{f_{298}}$ = heat of formation of lithium superoxide from lithium and oxygen at 298°K.

T = temperature, °K.

ΔC_p = heat capacity difference between LiO_2 and the elements from which it is formed, cal/mol-°K. This must be known as a function of temperature.

$\Delta S^{\circ}_{f_{298}}$ = entropy difference between LiO_2 and the elements from which it is formed, cal/mol-°K.

The heat of formation is the most critical property to be estimated, since of all the terms in Equation 1 it makes the largest contribution to the free energy. A computer program is available that performs the integrations in Equation 1 and gives a graph of ΔG_f versus temperature.

The heat of formation was estimated by two graphic methods and by a Born-Haber cycle calculation. The results agreed so well that a definite conclusion about the stability could be drawn. Of the three methods, the Born-Haber cycle is the most reliable, for the reasons explained below.

Heat of Formation - Graphic Methods

The best available summary of methods of estimating thermodynamic properties is given in a book by Kubaschewski and Evans (ref. 6). For example, they describe a method for estimating the heat of formation by comparison with other oxides of the same metal. Figure 1 makes use of this method. In this graph the heats of formation are plotted against the molar composition of the oxide, expressed in percent oxygen. The heats are in units of kilocalories per gram-atom (thus the atomic heat of Li_2O is one-third that of the molecular heat of Li_2O). In Figure 1 the heats of Li_2O, Li_2O_2, and O_2 fall on an almost straight line. This gives us some confidence to interpolate the heat of formation of LiO_2 as -24.5 kcal/g-atom, or -74 kcal/g-mole.

Another method of estimation compares the oxides of lithium with those of the other alkali metals. Figure 2 is a graphic comparison from Kubaschewski and Evans (ref. 6), to which additional oxides have been added. If lithium is the terminal member of the series, the problem is to extrapolate the curve without knowing whether it will go up or down. If hydrogen could be considered part of the series, the data would bracket lithium.

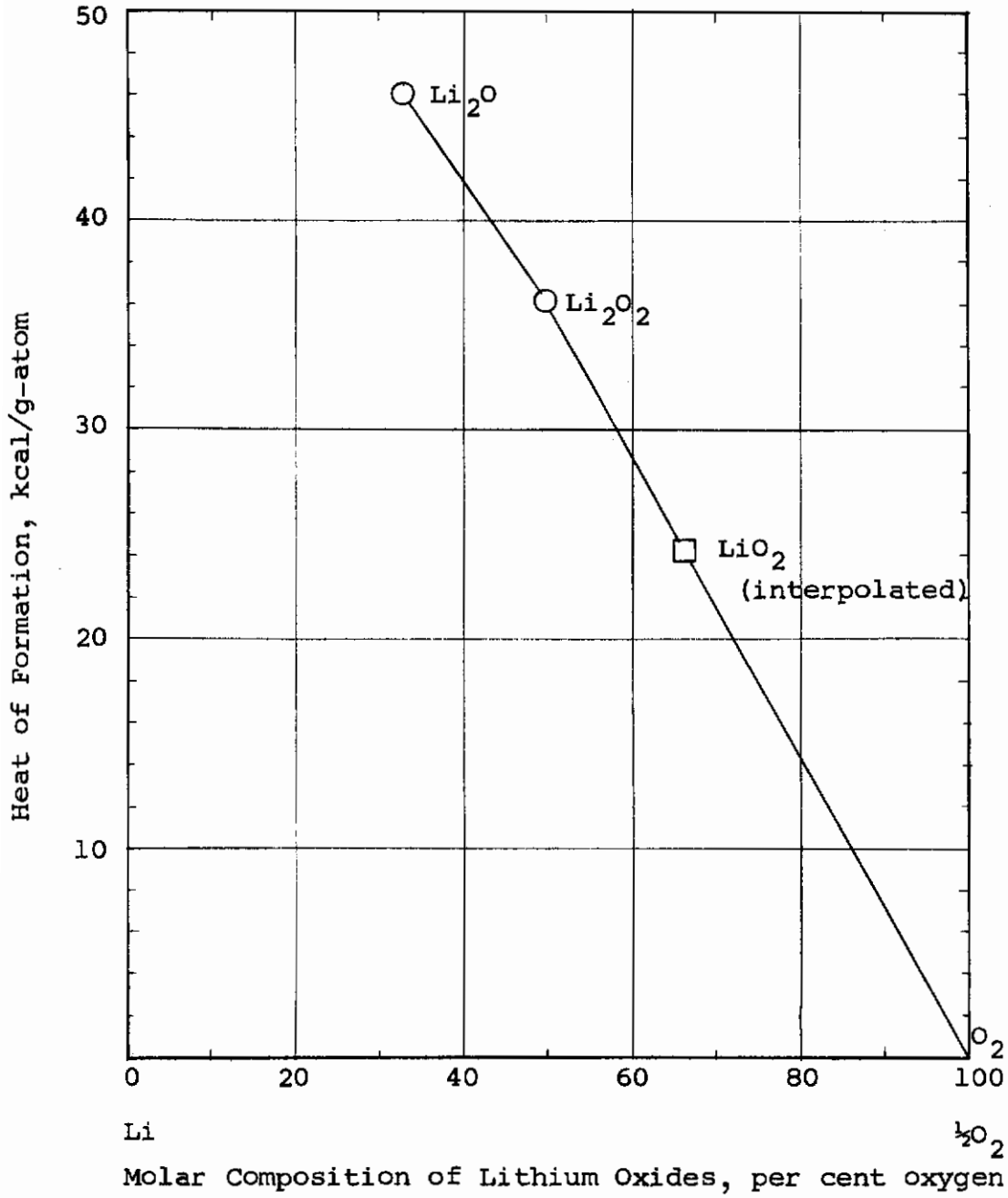


Figure 1. ESTIMATION OF HEAT OF FORMATION OF LITHIUM SUPEROXIDE FROM HEATS OF OTHER LITHIUM OXIDES

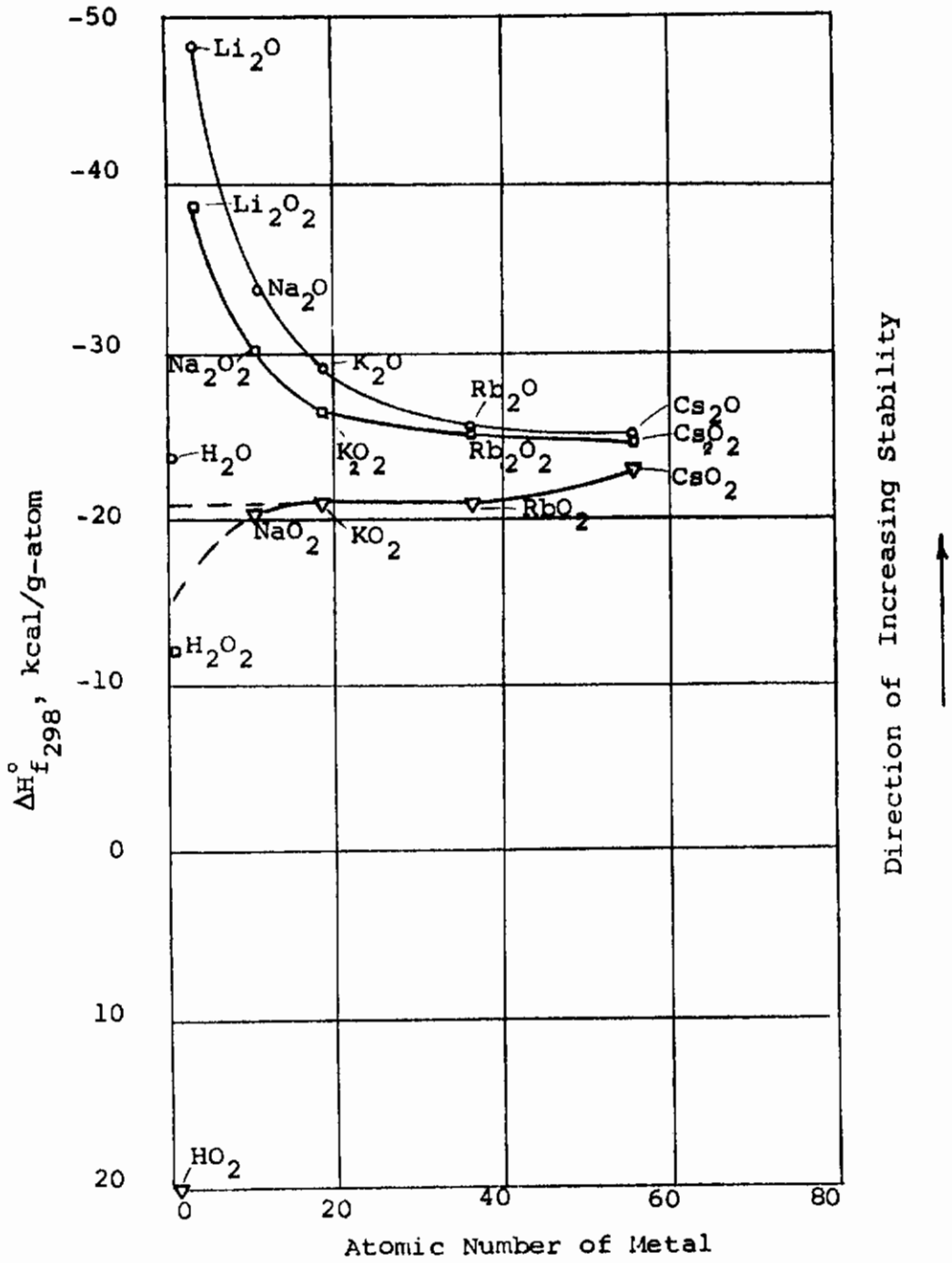


Figure 2. HEATS OF FORMATION OF OXIDES OF ALKALI METALS AND HYDROGEN

However, the data for oxides of hydrogen lie far below the curves for the metals. Perhaps hydrogen is anomalous and should be ignored. If so, the most probable value for lithium superoxide is -20 kcal/g-atom, or -60 kcal/g-mole. It could lie between -45 and -65.

Heat of Formation - Born-Haber Cycle Calculations

The heat of formation of a compound can be related to the lattice energy by the Born-Haber cycle. This method is useful because the lattice energy can be estimated or calculated from theory more reliably than the heat of formation. The Born-Haber cycle for lithium superoxide is defined in Figure 3.

The desired quantity is the heat of formation of lithium superoxide from the elements. This can be calculated from the lattice energy if the other quantities are known. The other quantities in the cycle are not properties of lithium superoxide but of lithium and oxygen, and so they can be determined from sources other than experiments on lithium superoxide.

The lattice energy of an ionic crystal is the energy released if the constituent ions are brought together. This energy is primarily the result of the coulombic attraction due to the charges on the ions. The energy can be calculated according to a method reviewed by Kittel (ref. 18). The method is valid for ionic crystals only, but lithium superoxide is believed to be strongly ionic, according to evidence reviewed by Vannerberg (ref. 1).

The formula for lattice energy is:

$$U_0 = \frac{N\alpha e^2}{R_0}\left(1 - \frac{1}{n}\right) \qquad (2)$$

where

U_0 = lattice energy, cal/mole

N = Avogadro's number, 6.023×10^{23}/mole

α = Madelung constant

e = charge on electron = 4.8×10^{-10} dynes$^{\frac{1}{2}}$/cm

R_0 = nearest neighbor distance between ions in the crystal, A

n = exponent in the law of repulsive force between ions

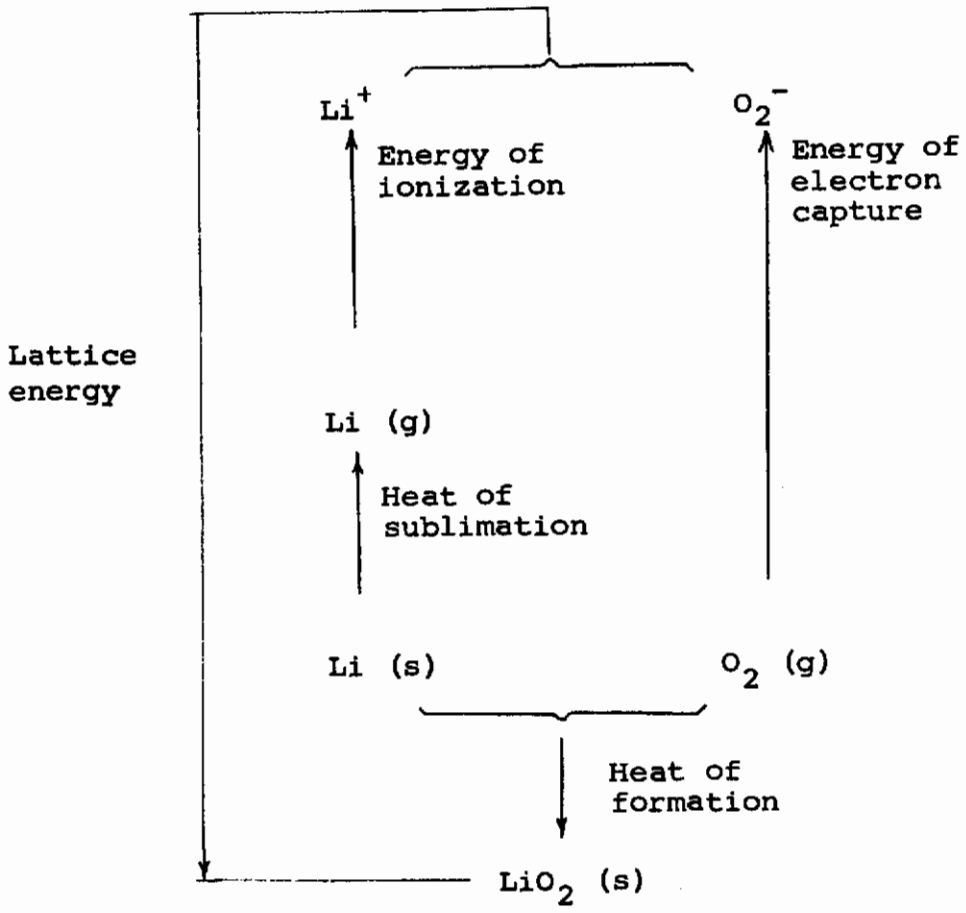


Figure 3. BORN-HABER CYCLE FOR LITHIUM SUPEROXIDE

Both α and R_0 vary from substance to substance, while n is generally equal to about 10. The Madelung constant, α, is determined by carrying out a difficult summation of interactions between ions over the whole crystal structure. It is known for common crystal structures and does not vary greatly.

In order to determine R_0 and α it is necessary to investigate the crystal structure of the material. We reviewed the crystal data for all the alkali metal superoxides in order to estimate the properties of lithium superoxide. Vannerberg (ref. 1) reviewed the published x-ray diffraction studies on the structure of these substances, but his summary is not too clear.

The superoxides of the larger cations, potassium, rubidium, and cesium, have tetragonal structures with the ions located in similar positions to those in the sodium chloride lattice. The sodium chloride lattice is face-centered cubic, not tetragonal; and the superoxides thus look like a face-centered cubic lattice slightly elongated in one direction. The structure is shown in Figure 4.

The superoxide ion is composed of two oxygen atoms; each superoxide ion is surrounded by cations as shown in Figure 5. The shortest distance, 2.71 A, is a typical K-O distance, but because of the unsymmetry of the superoxide ion, we cannot expect to apply the usual ionic radii to this type of crystal structure.

Sodium superoxide has several crystalline forms, depending on the temperature. At room temperature it has a face-centered cubic structure, described by Carter and Templeton (ref. 20). The superoxide ion still lies on the cube edge between cations, but instead of being oriented in line with the edge it is oriented in the direction of a cube diagonal, and it undergoes some hindered rotation. At a lower temperature, -50°C, the orientation changes and the rotation stops. The structure is then like that of pyrite, in which the oxygen atoms are on a face-centered cubic structure, and the cations are also on a cubic structure displaced from the oxygen atoms by an amount that is not a simple fraction of the crystal cell dimension. At a still lower temperature the structure changes to an orthorhombic marcasite structure.

According to Templeton and Dauben (ref. 21), the difference in crystal structure between the various alkali metal superoxides is due to the different sizes of the cations. The larger potassium ion gives the superoxide ion more room, so it can orient along the crystal axis in response to coulombic attraction. In sodium superoxide repulsive forces dominate, leading to a different orientation of the superoxide ion. However, the potassium superoxide changes to a face-centered cubic structure at a temperature of 60 to 100°C. This is due to increased thermal energy of the atoms in the lattice.

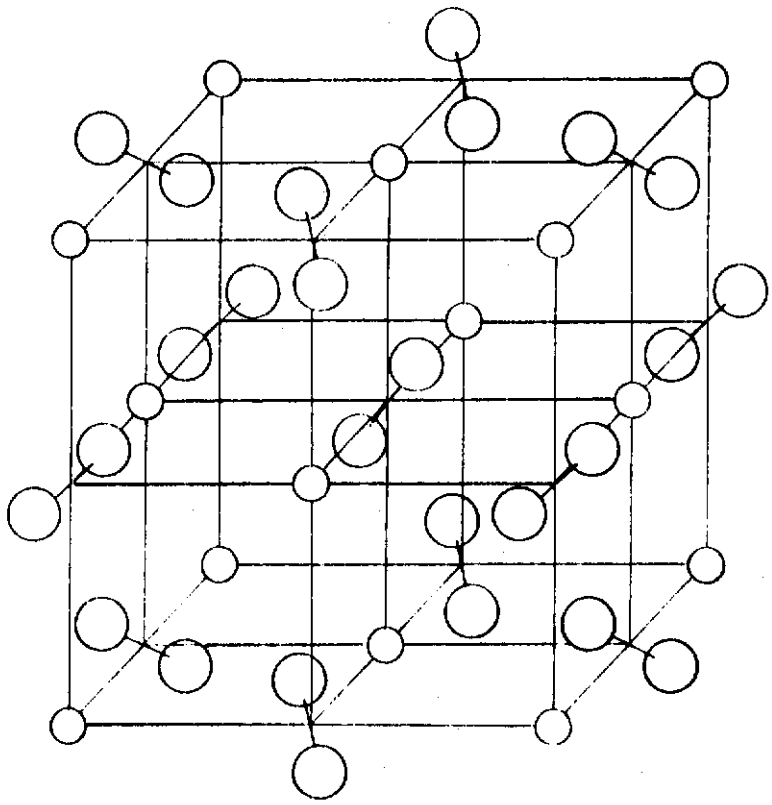
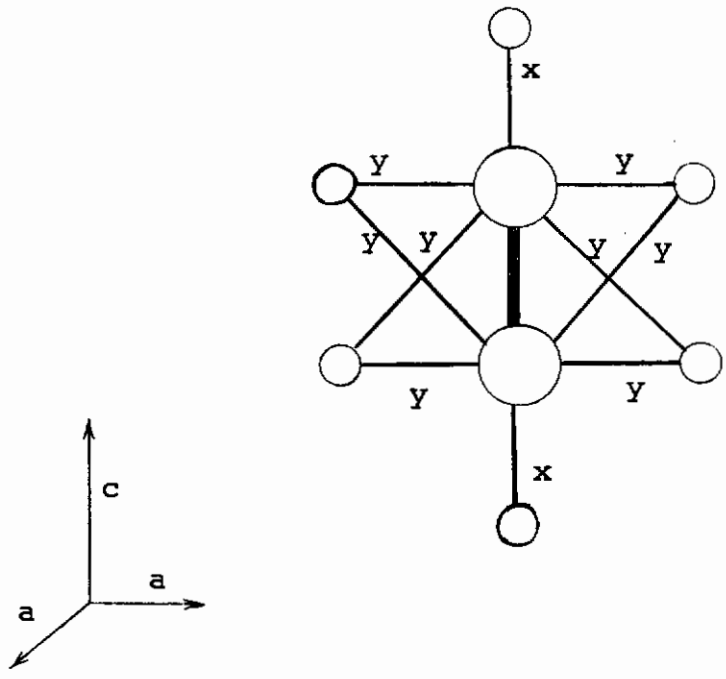


Figure 4. STRUCTURE OF SODIUM SUPEROXIDE



o Potassium

o Oxygen

x = 2.71 A

y = 2.92 A

Figure 5. STRUCTURE OF THE SUPEROXIDE ION
(Adapted from ref. 19)

In the tetragonal cell the cation is surrounded by 10 superoxide ions. In the cubic cell the cation is surrounded by only six superoxide ions. This is another reflection of the effect of cation size on the stable crystalline form. From this, Vannerberg (ref. 1) concluded that lithium superoxide can exist only in the cubic form, since lithium is even smaller than sodium. Furthermore, the lithium ion is so small that it is questionable whether six superoxide ions can fit around it without touching. However, we cannot draw a definite conclusion, because the normal ionic radii determined as averages from many other crystals may not apply to lithium superoxide. Different investigators (ref. 22) have arrived at different normal ionic sizes for lithium, varying from 0.60 to 0.71. Vannerberg (ref. 1) concluded that 0.66 is the minimum size of cation around which six superoxide ions could fit.

The lattice energy of alkali metal superoxides can be calculated from the crystallographic data in Table II. The value of the Madelung constant depends on the crystalline form. For a face-centered cubic structure it is 1.75. R_0 is defined as the nearest distance between superoxide ions and cations. For a face-centered cubic crystal there is a cation at each cube corner and an anion in the middle of certain cube edges. Therefore R_0 is half the cube edge, or half of dimension a in Table II. Substituting these values in Equation 2 gives the values labeled U_0 in Table III for NaO_2 and KO_2.

Evans and Uri (ref. 24) calculcated lattice energies for the tetragonal forms of KO_2, RbO_2, and CsO_2. They calculated the Madelung constant for this crystal structure to be 1.644 when R_0 is half of dimension a in Table II. The result for KO_2 agrees remarkably well with the value of U_0 calculated by the present author for the face-centered cubic structure. The difference in heat of formation between these two structures is expected to be negligible compared with the uncertainty of this calculation.

The remaining quantities needed to calculate the heat of formation of the superoxides are given in Table III. All these are known accurately except the radii of the cations and the electron affinity of the superoxide ion, $\Delta H_f\ O_2^-$. Pritchard (ref. 25) and Buchel'nikova (ref. 26) both reviewed the data on the electron affinity. The negative of this quantity is the energy released when an oxygen molecule combines with an electron. There are several means to measure it directly, and these authors concluded that the most probable value is -20 ± 3 kcal.

This value could be used to calculate the heat of formation of the alkali metal superoxides. According to the Born-Haber cycle this is the sum of columns 4 to 7 of Table III. Conversely, the experimental value for the heat of formation was used to compute the electron affinity. The latter approach

Table II

CRYSTALLOGRAPHIC DATA FOR ALKALI METAL SUPEROXIDES

Substance	Form	Temp., °C	Cell Dimensions, A		Density, g/cc
			a	c	
LiO_2	Face-centered cubic				
NaO_2	Face-centered cubic	25	5.49		2.21
NaO_2	Cubic	-70	5.46		
NaO_2	Orthorhombic	-77			
KO_2	Face-centered cubic	80	6.09		2.13
KO_2	Tetragonal	25	5.71	6.70	2.17
RbO_2	Tetragonal	25	6.01	7.04	3.07
CsO_2	Tetragonal	25	6.29	7.28	3.80

Table III

DATA FOR BORN-HABER CALCULATIONS

Oxide	Cationic Radius, A	Face-Centered Cubic Crystal Dimension, A	$\Delta H^\circ_{subl.\ metal}$, kcal/mole at 25°C	$\Delta H^\circ_{f_{M^+}}$, kcal/mole **	U_0, kcal/mole	$\Delta H^\circ_{f_{O_2^-}}$, kcal/mole ***	$\Delta H^\circ_{f_{MO_2}}$, kcal/mole Calc.*	$\Delta H^\circ_{f_{MO_2}}$, kcal/mole Exptl.
LiO_2	0.63 Ref. 22 0.70 Ref. 22	4.86* 5.06*	38.6 Ref. 6	126.7 Ref. 23	-216* -210*	-18.5	-69 -63	
NaO_2	0.95 Ref. 22	5.49 Ref. 1	26.35 Ref. 6	119.5 Ref. 23	-191*	-18.5	-63.6	-62.5
KO_2	1.33 Ref. 22	6.09 Ref. 1	21.5 Ref. 6	101.3 Ref. 23	-172* Ref. 24	-18.5	-67.7	-67.6
RbO_2	1.48 Ref. 22		20.5 Ref. 6	97.7 Ref. 23	-168 Ref. 24	-18.5	-68.3	-68.8
CsO_2	1.69 Ref. 22		18.8 Ref. 6	91.0 Ref. 23	-165 Ref. 24	-18.5	-73.7	-70.5 or -76

*Calculated by the present author.

**Converted from 0 to 298°K by adding -1.5 kcal.

***Mean value chosen to best fit all the data.

gave a mean value of -18.5, which is in excellent agreement with the directly measured value. That this value is consistent with the data for all four of these compounds can be seen by comparing the experimental and calculated values of their heats of formation, given in the last two columns of Table III. Evans and Uri (ref. 24) also calculated the electron affinity. Their result was slightly lower and less consistent among the various compounds because they used different values of other quantities in Table III.

Since these results agreed so well, it was possible to make a similar calculation of the lattice energy and the heat of formation of lithium superoxide. The problem really was one of estimating the size of the lithium ion in the superoxide lattice. The ionic size varies from 0.60 to 0.71 Å, depending on which of the lithium compounds is considered and on which anion is chosen as a standard. The radii given in Table III for potassium, rubidium, and cesium were consistent with the measured a dimensions of the tetragonal superoxide crystals. However, the sizes of the face-centered cubic crystals of sodium and potassium were not consistent with the cationic radii given in Table III; the discrepancy was 0.08 Å.

This makes the extrapolation to lithium somewhat uncertain. Nevertheless, there is some limit to the error that can be introduced by the uncertainty in the size of the lithium ion, although it is difficult to assign an uncertainty to the estimates of the heat of formation based on other methods. Therefore, the Born-Haber method is the most reliable.

Table III lists two probable values for the radius of the lithium ion. Depending on which radius is chosen, the heat of formation is calculated to be -63 or -69 kcal/mole. A value of -65 ± 5 kcal is recommended.

Entropy

The entropy of lithium superoxide was estimated from the entropies of the sodium and potassium compounds. According to Kubaschewski and Evans (ref. 6), each atom or radical in the molecule makes a contribution to entropy that is independent of the other atoms (provided that compounds are compared in which the other atoms have the same valence). The contributions for the alkali metals are:

Li	3.5
Na	7.5
K	9.2
Rb	11.9
Cs	13.6

The contribution for the superoxide radical was found by subtracting 7.5 and 9.2 from the entropies of sodium and potassium superoxides, respectively, giving 19.5 as an average contribution. Adding this to 3.5 gave 23 for the entropy of lithium superoxide.

Heat Capacity

The heat capacity of lithium superoxide was assumed to equal that of sodium superoxide, neglecting local peaks due to crystalline phase transitions in sodium superoxide. Such transitions are not expected for lithium superoxide, since only the face-centered cubic form may possibly allow enough room for the superoxide ion to exist.

SECTION IV

FREE ENERGY OF LITHIUM SUPEROXIDE

When free energy is to be evaluated at temperatures other than the base temperature, 298°K, it is convenient to express the right side of Equation 1 as an integral involving heat capacities, heats of transition, and base values at 298°K. The resulting expressions are tedious to evaluate. Numerical errors are difficult to avoid and are often found even in published results. A computer program was therefore prepared to carry out the integration. It is based on the equations derived by Glassner (ref. 10) and given below.

The heat capacities of the substance and its constituent elements must be given in the following form:

$$C_p = a + b \times 10^{-3} T + c \times 10^{-6} T^2 + \frac{d \times 10^5}{T^2} \qquad (3)$$

where

C_p = heat capacity, cal/mole-°K

T = temperature, °K

a, b, c, d = empirical coefficients, not all zero.

The following properties must also be given:

$\Delta H^\circ_{f_{298}}$ = heat of formation of the substance from the elements in the standard state at 298°K

S°_{298} = entropy of the substance and its constituent elements in the standard state at 298°K

ΔH_{TR} = heat of transition of the substance and its constituent elements at given transition temperatures, cal/mole

The program computes the coefficients of the following expression derived by Glassner (ref. 10):

$$\Delta G_f = \Delta H^{\circ}_{f_{298}} - \Delta a\ T\ \ln T - \frac{1}{2}\Delta b \times 10^{-3} T^2$$

$$- \frac{1}{6}\Delta c \times 10^{-6} T^3 - \frac{\frac{1}{2}\Delta d \times 10^5}{T} - T\,\Delta(B - a) + \Delta A \qquad (4)$$

where

Δa, Δb, Δc, and Δd = stoichiometric sums of a, b, c, and d.

The expressions $-\Delta A$ and $-\Delta B$ are similarly defined in terms of A and B, which are given below:

$$A = 298a + \tfrac{1}{2}b \times 10^{-3} \times 298^2 + \frac{1}{3} c \times 10^{-6} \times 298^3$$

$$- \frac{d \times 10^5}{298} \qquad (5)$$

Above a transition temperature, A in Equation 4 is replaced by A':

$$A' = A + (a' - a)T_{TR} + \tfrac{1}{2}(b' - b) \times 10^{-3} T_{TR}^2$$

$$+ \frac{1}{3}(c' - c) \times 10^{-6} T_{TR}^3 - \frac{(d' - d) \times 10^5}{T_{TR}} - \Delta H_{TR} \qquad (6)$$

where primes refer to conditions above the transition temperature, T_{TR}.

$$B = - S^{\circ}_{298} + a \ln 298 + b \times 10^{-3} \times 298 + \tfrac{1}{2}c \times 10^{-6}$$

$$\times 298^2 - \frac{\frac{1}{2}d \times 10^5}{298^2} \qquad (7)$$

$$B' = B + (a' - a) \ln T_{TR} + (b' - b) \times 10^{-3} T_{TR}$$

$$+ \tfrac{1}{2}\ (c' - c) \times 10^{-6} T_{TR}^2 - \frac{\frac{1}{2}(d' - d) \times 10^5}{T_{TR}^2}$$

$$- \frac{\Delta H_{TR}}{T_{TR}} \qquad (8)$$

In terms of the same coefficients, the heat of formation at any temperature is then:

$$\Delta H_f = \Delta H^{\circ}_{f_{298}} + \Delta a\, T + \tfrac{1}{2}\,\Delta b \times 10^{-3} T^2 + \tfrac{1}{3}\,\Delta C \times 10^{-6} T^3 - \frac{\Delta d \times 10^5}{T} + \Delta A \qquad (9)$$

The given data can be expressed on a mole or a gram-atom basis or a multiple thereof, but the basis must be specified. The program converts all data to a common basis of a gram-atom of each element or, in the case of a compound, of the amount of compound equivalent to a gram-atom in the following reaction:

$$\frac{1}{n} D_n + \frac{q}{mp} A_m \longrightarrow \frac{1}{p} D_p A_q \qquad (I)$$

where

D_n = proton donor molecule with n atoms

A_m = proton acceptor molecule with m atoms

D_pA_q = a compound.

The data supplied to this computer program are listed in Table IV. Table V gives the integrated results, in terms of the coefficients in Equation 4. Thus it was possible to calculate the free energy of formation of any of the lithium oxides at any temperature from 100 to 1000°K by substituting the coefficients from Table V in Equation 4. The results are plotted in Figure 6.

SECTION V

STABILITY OF LITHIUM SUPEROXIDE

A compound is stable under certain conditions if no reaction by which it may decompose has negative free energy. Lithium superoxide may decompose, giving oxygen and either of the lower oxides according to the reactions:

$$LiO_2 \longrightarrow \tfrac{1}{2}Li_2O_2 + \tfrac{1}{2}O_2 \qquad (II)$$

$$LiO_2 \longrightarrow \tfrac{1}{2}Li_2O + 3/4\ O_2 \qquad (III)$$

Table IV

THERMODYNAMIC PROPERTIES OF LITHIUM AND ITS OXIDES

Substance	Phase	Temp. Range, °K	Heat of Transition, kcal/mole	Entropy at 298°K, EU	Coefficients of Heat Capacity Equation 3			
					a	b	c	d
Li	s	100 to 330	0	6.954	-1.3	44.5	-68.9	0
	s	330 to 454 (mp)	0.717		1.64	11.1	0	0.84
	l	454 to 1638			6.78	0	0	0.99
O_2	g	100 to 330	0	53.286	7	0	0	0
	g	330 to 1843 (mp)	0		7.16	1	0	-.4
Li_2O	s	100 to 330	0	9.056	-10.1	154	-256	0
	s	330 to 1843 (mp)			14.94	6.08	0	-3.38
Li_2O_2	s	100 to 330	0	13.5	0.1	100	-125	0
	s	330 to 2000			18.5	1	0	0
LiO_2	s	100 to 400	0	15	4.4	8.8	-110	0
	s	400 to 1000			22	0	0	0

Table V

THERMOCHEMICAL PROPERTIES OF LITHIUM OXIDES

Reaction	Transition Temp., °K	$\Delta H^{\circ}_{f_{298}}$, kcal/mole	$\Delta G^{\circ}_{f_{298}}$, kcal/mole	Coefficients in Free Energy Equation Δa	Δb	Δc	Δd	ΔA, cal/mole	ΔB, EU
$\frac{1}{2}Li_2O \rightarrow Li + \frac{1}{4}O_2$	100- 330	-71.5	-66.8	-5.5	32.5	-59.1	0	717	8.52
	330- 454			4.04	-8.3	0	-2.43	-947	-37.66
	454-1638			-1.1	2.8	0	-2.58	-508	-12.87
$\frac{1}{2}Li_2O_2 \rightarrow Li + \frac{1}{2}O_2$	100- 330	-75.5	-67.5	-2.15	5.5	6.40	0	340	-16.52
	330- 454			4.03	-11.1	0	-0.64	-489	-46.83
	454-1638			-1.11	0	0	-0.79	-550	-22.04
$LiO_2 \rightarrow Li + O_2$	100- 330	-65.0	-52.8	-1.3	-35.7	-41.1	0	2335	-25.37
	330- 400			-4.4	3.3	-110.0	-0.44	1463	-14.54
	400- 454			13.2	-12.1	0	-0.44	-4879	-125.3
	454-1000			8.06	-1.0	0	-0.59	-4439	-100.5

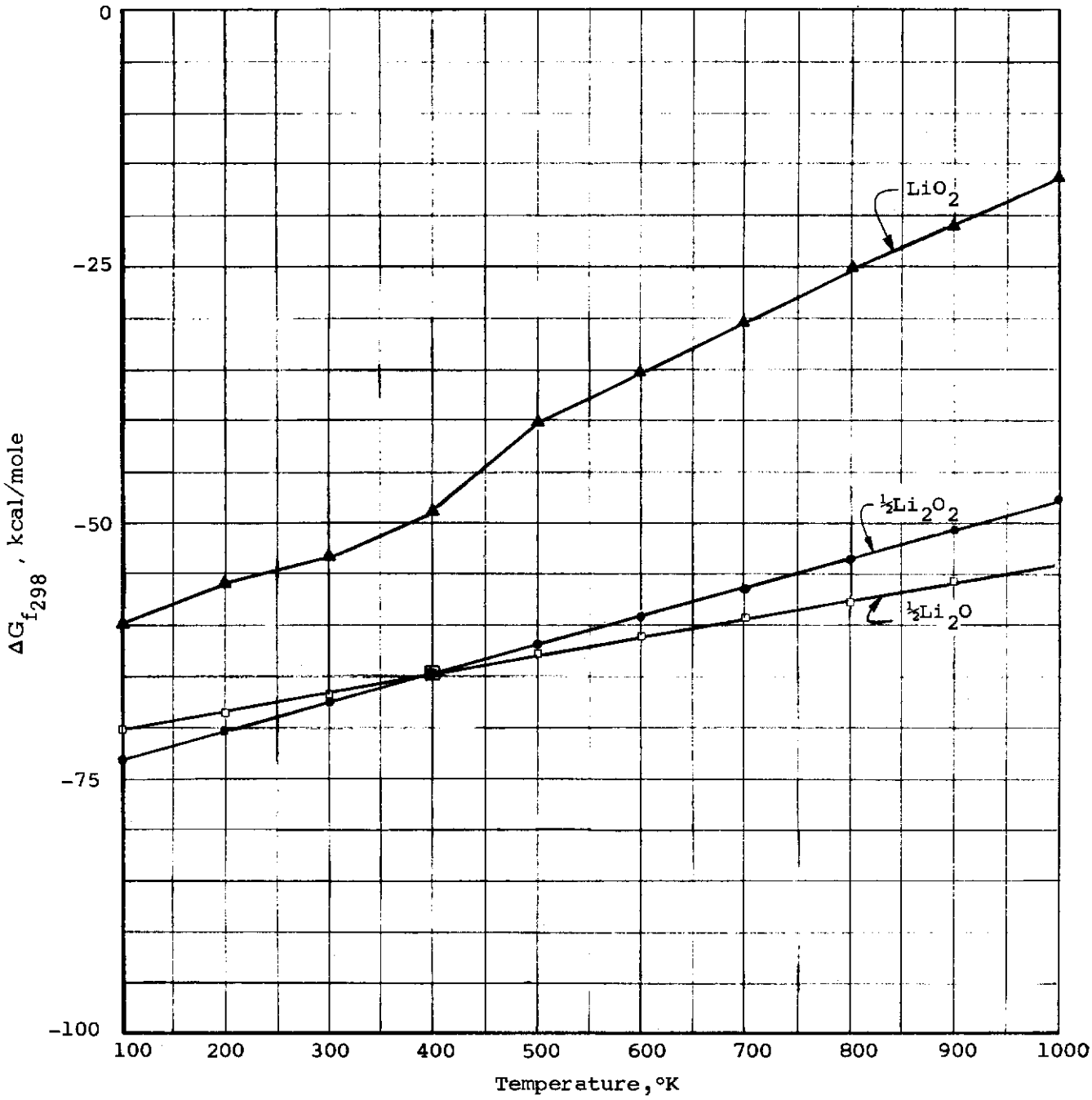


Figure 6. FREE ENERGIES OF LITHIUM OXIDES

The free energies of these reactions can be read from Figure 6, since they represent the vertical distance between the curves corresponding to the two oxides involved. Note that the oxide with the lowest curve at any temperature is the most stable. According to this, lithium peroxide is most stable below 400°K (127°C), while the monoxide is most stable at higher temperatures. Furthermore, the free energy curve is such that there is no increase in stability of the superoxide as the temperature is lowered below 300°K. This behavior is somewhat unusual, since the stability usually shifts toward higher oxides at lower temperatures.

The effect of pressure of oxygen on the stability can be calculated from the relation between free energy change and the equilibrium constant, K:

$$\Delta G = -RT \ln K \qquad (10)$$

where R = 1.987 cal/mole-°K. For example, for reaction (III)

$$K = (P_{O_2})^{3/4}.$$

Every tenfold increase in the pressure of oxygen gives the following decrease in ΔG at 300°K

$$\Delta G = -1.987 \times 400 \times \ln (10)^{3/4} = 1250 \text{ cal} = 1.25 \text{ kcal}$$

Thus, to overcome the 15 kcal difference in free energy between these compounds, a pressure of

$$10^{15/1.25} = 10^{12} \text{ atmospheres of oxygen}$$

would have to be applied. This result explains the failure of attempts to form lithium superoxide by exposing the peroxide to oxygen under pressure. Similar calculations show that at other temperatures, even higher oxygen pressure is required.

Substances can be stabilized by putting them into solution. When a solution is saturated, the solute has the same free energy as the crystalline form of the material, since the two forms are in equilibrium. At lower concentrations the free energy differs by:

$$\Delta G = RT \ln(C/C_s) \qquad (11)$$

where

C = concentration

C_s = saturated concentration

At 300°K a tenfold dilution changes ΔG by 1.4 kcal. Clearly lithium superoxide molecules can exist in solution only in extreme dilution. The superoxide ion can exist in higher concentrations because there is a free energy change when ionization occurs. Infrared spectra of solutions in liquid ammonia show that significant concentrations of ions can be produced, but no other conclusions can be drawn without further data.

Substances can be stabilized by putting them into solid solution. For example, phase data have shown the existence of solutions of sodium superoxide in sodium peroxide. Equation 11 shows that no significant concentration of lithium superoxide can be stabilized in this way. This conclusion might be different if a mixed compound that has a definite heat and free energy of formation is formed. Such compounds do not usually have sufficient free energy to overcome the instability of lithium superoxide.

This investigation does not rule out the possibility of the existence of a unique crystalline form of lithium superoxide different from any of the other alkali metal superoxides. Such a form could have different thermodynamic properties. However, the chance that such an unusual form exists is remote, and there is no evidence to suggest it.

SECTION VI

CONCLUSIONS

The thermodynamic properties of lithium superoxide were estimated. The most important term in the free energy is the heat of formation. The best estimate of heat of formation was based on the Born-Haber cycle and a lattice energy calculation, and gave the result -65 kcal. The estimated uncertainty in this value is $\pm$ 5 kcal. An estimate based on a simple interpolation gave -74 kcal $\pm$ 10 kcal, in fair agreement with the Born-Haber result. From the Born-Haber result and other estimated data the free energy at room temperature is -53 $\pm$ 5 kcal.

Consideration of the free energies of various decomposition reactions showed that the tendency to decompose corresponds to 15 kcal. This tendency is so much greater than the uncertainty of the estimates that lithium superoxide can be considered unstable at all temperatures. Furthermore, none of the usual methods of promoting stability are sufficiently effective to overcome this instability. Further attempts to prepare it do not appear promising. Even if the compound were prepared, it would tend to decompose spontaneously. It would not be safe to carry such an unstable compound in a manned space cabin.

Further efforts to reduce the weight necessary to carry along oxygen for air regeneration should be turned in other directions.

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13. ABSTRACT

To determine whether lithium superoxide can be produced and whether it is stable enough for use in air regeneration units of manned spacecraft, the free energy of lithium superoxide was calculated from estimated values of the heat of formation, entropy, and heat capacity. The estimates were based on graphical comparison with properties of other oxides. The heat of formation was also determined from calculation of the lattice energy by means of the Born-Haber cycle. The result was -65 kcal. The stability of lithium superoxide was deduced by comparing graphically the free energies of the oxides of lithium. The superoxide is unstable by 15 kcal from 100 to 300°K and is even more unstable at higher temperatures. Reasonably high pressure and other effects cannot overcome this instability, even at low temperature. Therefore the use of lithium superoxide for air regeneration units is not promising.

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