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Theoretical Calculation of the Stability of Solid and Gaseous Species in the Alkali and Alkaline Earth Oxide Systems

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1. Introduction.

The oxides of the elements in the first two columns of the Periodic Table were chosen as the subject of this treatment primarily because of the apparent ionic character of the bonding shown by these elements which greatly simplifies theoretical attack, and secondly, since the information in the literature concerning the stability of the gaseous species studied herein is very limited it is considered that these calculations will be a practical addition to the existing thermochemical data of gaseous oxides.

In this development, ionic models are assumed for the solid and gaseous states; these models are then subjected to theoretical calculations of stability which are compared with experimental values for the stability of the specific model or one of the same coulombic nature.

Two empirical expressions[1] for dealing with the mutual repulsive potential existant between ions were investigated, namely the Born expression

$$V_r = \frac{b}{r^n} \tag{1}$$

and the Born and Mayer exponential expression

$$V_r = ae^{\frac{-r}{\rho}} \tag{2}$$

Here, b and n are constants and r is the distance between the ions, ρ is taken in Eq. (2) as 0.345×10^{-8} if a is determined as a function of the valences, the number of valence electrons and the ionic radii of the two ions. While the potential of the type given in Eq. (2) leads to a more satisfactory value of the repulsion and has the further merit of having some theoretical foundation, it was

found that Eq. (1) was not only convenient to apply but also was of sufficient accuracy in view of the fact that in many cases the radii of ions in the solid and gaseous state were necessarily estimated. The latter uncertainty was indeed of such a nature to allow the combination of secondary forces such as those arising from polarization, distortion and slight covalency to be neglected. Actually then, this treatment deals with the coulombic force and the apparent repulsive force between ions the latter function being of such nature to give agreement between theoretical and experimental heats of formation.

Thus the expressions given by Pauling[2] for the calculation of interionic forces and crystal energy are adopted, herein, following Born, the mutual potential energy of two ions is written as

$$V_{ij} = \frac{z_i z_j e^2}{r_{ij}} + \frac{b_{ij} e^2}{r_{ij}^n} \qquad (3)$$

and the total potential energy of an ionic crystal by incorporation of the appropriate geometrical factor A (Madelung constant) is given as

$$V = -\frac{Ae^2z^2}{R} + \frac{Be^2}{R^n} \qquad (4)$$

In Eq. (3) z_i and z_j refer to the algebraic value of the valence of the ion, b is an appropriate constant and r_{ij} the distance between the ions, or, more appropriately, the sum of their radii. In Eq. (4) z is the largest common factor of the valences of the ions, A is the Madelung constant and R is a crystal dimension appropriate to the value of A used. In this work both the anion-cation distance and the unit cell side length for cubic systems has been applied. It is convenient to eliminate the repulsive constant B from Eq. (4) by allowing $\frac{dV}{dR} = 0$ at $R = R_0$, the equilibrium distance. Thus, by substitution in Eq. (4), one obtains for the crystal energy

$$U_o = \frac{NAe^2z^2}{R_o}\left(1 - \frac{1}{n}\right) \qquad (5)$$

The values for the repulsive exponent n are given by Pauling for crystals of mixed ion type:

Ion Type	n
He	5
Ne	7
Ar, Cu^+	9
Kr, Ag^+	10
Xe, Au^+	12

An average value is taken for the specific case, i.e., 6 for LiF.

In order to calculate the desired heats of formation use is made of the familiar Born-Haber cycle:

$$\begin{array}{ccc} MX(c) & \xrightarrow{U_o} & M^+(g) + X^-(g) \\ \uparrow \Delta H & & \downarrow -I + E \\ M(c) + \frac{1}{2}X_2(g) & \xleftarrow{-S - \frac{1}{2}D} & M(g) + X(g) \end{array} \qquad (6)$$

Here U_o is the crystal energy given by Eq. (5), I the ionization potential of the metal M(g), E the electron affinity of X(g), S the heat of sublimation of the metal, D the heat of dissociation of $X_2(g)$, and ΔH the heat of formation of crystalline MX from the elements M(c) and $\frac{1}{2}X_2(g)$. All heats and energy terms will be given in kcal/mole. The values of all the energy terms in the cycle should be taken at the same temperature. It will be noted in the following that heats of formation are calculated for 0° K and 298.1° K as is convenient for sake of comparison. For the values of I and E one adds 1.481 kcal/mole per charge on the ion to the 0° K value to obtain the value appropriate to 298.1° K. For correction of the other values estimated

ΔC_p values are applied since this is in general a small correction. The values for U_o are calculated for the interionic distances measured at room temperature, thus no correction is applied. When Eq. (5) is applied to gaseous molecules it is assumed that the interionic distances measured spectroscopically apply to the ground state and that they are valid for 0° K and 298.1° K calculations within the desired accuracy.

Eq. (6) is so written that the sum of the energy terms around the cycle is equal to zero. Thus

$$\Delta H = S + I + \frac{1}{2}D - E - U_o \qquad (7)$$

In applying this cycle to oxides one must choose a most probable value for electron affinity of O(g) for two electrons since an experimental value is not available. In this work the value -168 kcal/mole is used throughout. A discussion of this choice is given in a later section. The experimentally determined values for the terms on the right side of Eq. (7) (excepting U_o and E as explained above) are available.[3],[4],[9]

2. Solid State.

The applicability of the foregoing theory was first investigated with respect to the solid state alkali and alkaline earth oxides. In these cases the heat of formation of the solids are known[5], and Eq. (7) is applied to obtain the experimental U_e and Eq. (5) gives the theoretical U_o, wherein

$$\frac{Ne^2}{1\text{Å}} = 329.7 \text{ kcal/mole}$$

The results of these calculations are given in Table I and Table II. While U_e and U_o both designate the lattice energy of the crystal the

distinction by subscript is made to distinguish the one (U_e) derived from the Born-Haber cycle by application of experimentally determined quantities from that (U_o) calculated by use of Eq. (5).

An inspection of Tables I and II clearly shows the trend in both series of theoretical values which become smaller than the experimental with increasing atomic weight. Indeed, in the alkaline earth series the trend is so pronounced that the lighter members have U_o values indicating greater stability than that found experimentally. If the assumption of coulombic bonding is valid, it is necessary to discuss this trend in terms of the validity of the repulsive function and the neglect of secondary bonding forces.

It is unlikely that Van der Waals forces and those due to polarisation will account for the 44 kcal divergence found for Rb_2O, although these forces do become of greater importance with increasing cation size. Since very little is known concerning the true character of the repulsive function, one is led to the conclusion that the function and values for the repulsive exponent given by Pauling does not afford a correlation much better than that given here. In Table II, U_o exceeds U_e for the probable reason that the repulsive energy given by Eq. (5) is actually too low since in these cases the doubly charged ions may exert enough attractive force to cause kernel repulsion in the smaller cations. This, of course, would demand a different value of n than that which is given by Pauling.

Thus, within the uncertainty of the repulsive potential it can be assumed that bonding in these crystalline oxides is predominately ionic. It is of interest to note that the repulsive potential gives an apparent fit between CaO and SrO. If one applies Eq. (6) to these compounds to obtain E for O(g) for two electrons one obtains the value -168 kcal/mole, which is in agreement with the value given by

Table I

Crystal	a_o	n	U_A	2I	2S
Li_2O	4.619	6.0	693	251.5	73.9
Na_2O	5.55	7.0	593	239.9	51.9
K_2O	6.436	8.0	522	203.1	43.0
Rb_2O	6.74	8.5	503	195.5	41.0

Crystal	$\frac{1}{2}D$	$-E$	$-\Delta H$	U_e	U_e-U_o
Li_2O	59.3	168	142.3	695	2
Na_2O	59.3	168	102.9	622	29
K_2O	59.3	168	86.2	560	38
Rb_2O	59.3	168	82.9	547	44

Table II

Crystal	a_0	n	U_0	I	S
BeO	2.695	6.0	1099	636.1	80.0
MgO	4.203	7.0	941	524.5	55.9
CaO	4.797	8.0	841	416.0	42.6
SrO	5.144	8.5	791	386.9	39.2
BaO	5.523	9.5	748	352.1	42.0

Crystal	$\frac{1}{2}D$	$-E$	$-\Delta H$	U_e	U_e-U_0
BeO	59.5	168	147	1090	-9
MgO	59.5	168	143.8	931	-10
CaO	59.5	168	151.7	838	-3
SrO	59.5	168	140.8	794	3
BaO	59.5	168	133	754	6

Sherman.[6] For this reason this value for the electron affinity of O(g) has been used throughout this paper.

3. Gaseous Alkali Halides.

Having established the ionic model as being satisfactory for the solid state oxides and noting the weakness of the repulsive function when applied to divalent ions, the gaseous molecules are next inspected concerning the validity of the ionic model. In this case, recourse is had to the gaseous alkali halides since thermochemical values for the heat of the reaction M(g) + X(g) = MX(g) are available.[7],[9] Use is made again of Eq. (5) to determine the heat of dissociation, however in this case the Madelung constant will be unity and one must investigate the appropriate magnitude of the repulsive energy contribution. Table III gives the results of these calculations for 0° K in which allowance was made first for no repulsion and then for repulsion calculated using a value of n for the crystalline state of the species. The values for the equilibrium bond distance are taken from spectroscopic data.[8] The values for the electron affinities of the X(g) and ionization potential of the M(g) are given by Brewer, et al.[9] Use is made of a modified Born-Haber cycle in the calculation of the heat of reaction, which is given as

$$\begin{array}{ccc} MX(g) & \xrightarrow{U_o} & M^+(g) + X^-(g) \\ & \nwarrow \Delta H & \swarrow -I + E \\ & M(g) + X(g) & \end{array}$$

The theoretical and experimental agreement are very good with no repulsive contribution which, when applied, lowers the theoretical values by about 10 kcal. Considering the smaller interionic distance

Table III

Gas	r_e	n	U_o	$-\Delta H$ Crystal Repulsion	$-\Delta H$ No Repulsion	$-\Delta H$ Experimental
NaCl	2.51	8.0	115	82	98	96
NaBr	2.64	8.5	110	72	87	85
NaI	2.83	9.5	105	58	70	69
KCl	2.79	9.0	105	92	104	101
KBr	2.94	9.5	100	81	93	91
KI	3.13	10.5	95	67	77	79
RbCl	2.89	9.5	102	92	104	108
RbBr	3.06	10.0	97	82	93	93
RbI	3.26	11.0	92	68	77	79
CsCl	3.06	10.5	98	94	104	106
CsBr	3.14	11.0	96	87	96	94
CsI	3.41	12.0	89	71	79	81

M(g)	I
Li	124.3
Na	118.5
K	100.1
Rb	96.3
Cs	89.8

X(g)	E
Cl	85.8
Br	80.5
I	72.4

in the gas relative to the solid state one might expect a greater repulsive energy in the former state. However, two factors apparently mask this effect. First, the ion in the solid is probably held in a symmetrical configuration by the semi-infinite lattice of charges surrounding it such that only slight distortion occurs. In the gaseous distortion of the positive and negative ions may occur to a great extent thus increasing the bonding energy which, supplemented by increased dispersion forces, apparently cancels the repulsive force. The second factor is that the actual magnitude of the repulsive force is less in the gaseous state since repulsion occurs with only one neighbor, while in the solid state six nearest neighbors are involved, so again the repulsive effect is apparently diminished with respect to this calculation.

Hence, it appears that the ionic model is valid for these univalent gaseous molecules and the use of Eq. (5) making no allowance for repulsion may be made in such cases.

4. Gaseous Alkali Oxides.

In the calculation of the heats of formation of the gaseous alkali oxides the model developed above is used; namely, it is assumed that the two alkali atoms have unit positive charge and the oxygen atom is doubly charged of opposite sign. Furthermore, the molecule is treated as a linear assemblage of the three ions. The latter is of importance in the application of Eq. (5) since the Madelung constant for the mutual coulombic attractions and repulsions for such a linear ionic molecule will be $\frac{7}{2}$, as follows:

$$e^2\left[\frac{z_1 z_2}{r_0} + \frac{z_1 z_3}{r_0} - \frac{z_1 z_1}{2r_0}\right] = e^2\left[-\frac{4}{r_0} + \frac{1}{2r_0}\right] = -\frac{7}{2}\frac{e^2}{r_0}$$

which leads to a value of the mutual potential energy between the ions

$$V = -\frac{7}{2}\frac{e^2}{R} + \frac{Be^2}{R^n}$$

Upon differention, allowing $\left.\frac{dV}{dR}\right|_{R=R_0} = 0$ and substituting the expression for B back into this potential equation (See Pauling's text, page 339) one obtains

$$U_0 = \frac{7}{2}\frac{Ne^2}{R_0}\left(1 - \frac{1}{n}\right) \tag{8}$$

for the energy of dissociation into the gaseous ions in accord with Eq. (5).

The experimental values for the interatomic distances in these gaseous molecules are not available. In order to obtain these data a theoretical method was developed and applied. Pauling[10] gives a more detailed discussion of the energy per molecule for a crystal of the sodium chloride structure containing univalent cations and anions with radii r_+ and r_- respectively, leading to the expression

$$V = -\frac{Ae^2}{R} + 6B_0e^2\frac{(r_+ + r_-)^{n-1}}{R^n} + 6\cdot 1.25\, B_0e^2\frac{(2r_+)^{n-1}}{(\sqrt{2}\,R)^n}$$

$$+ 6\cdot 0.75\, B_0e^2\frac{(2r_-)^{n-1}}{(\sqrt{2}\,R)^n} \tag{9}$$

The first term on the right, containing the Madelung constant, is the coulombic energy, R being the minimum cation-anion distance. The second term represents the repulsion between each cation and its six anion neighbors, the third term the repulsion of each cation and its nearest six cation neighbors at the distance $\sqrt{2}\,R$, and the fourth term the repulsion of anion-anion neighbors at the distance $\sqrt{2}\,R$. The constants 1.25 and 0.75 appearing in terms three and four respectively are quantum-mechanically derived values for the weight of cation-cation and anion-anion interaction relative to the cation-anion

interaction of weight unity. B_o is a characteristic repulsive coefficient. Eq. (9) is rewritten as

$$V = -\frac{Ae^2}{R} + \frac{6B_o e^2}{R^n}\left[(r_+ + r_-)^{n-1} + \frac{1.25(2r_-)^{n-1}}{(\sqrt{2})^n} + 0.75\,\frac{(2r_-)^{n-1}}{(\sqrt{2})^n}\right]. \tag{10}$$

which is analogous to Eq. (4). Accordingly, differentiation leads to an equilibrium value of R

$$R_o = (r_+ + r_-)\,F(\rho) \tag{11}$$

in which $F(\rho)$ is a function of the radius ratio $\rho = r_+/r_-$. The values of the constants r_+ and r_- are given in Pauling's text. $F(\rho)$ has the form

$$F(\rho) = \left(\frac{6nB_o}{A}\right)^{\frac{1}{n-1}}\left[1 + \frac{1.25}{(\sqrt{2})^n}\left(\frac{2\rho}{\rho+1}\right)^{n-1} + \frac{0.75}{(\sqrt{2})^n}\left(\frac{2}{\rho+1}\right)^{n-1}\right]^{\frac{1}{n-1}} \tag{12}$$

A similar expression may be derived for the fluorite structure which is that assumed by the crystalline alkali oxides. In accord with Eq. (9) this structure gives for the total energy per molecule

$$V = \frac{-Ae^2z^2}{R} + 8B_o e^2\,\frac{(r_+ + r_-)^{n-1}}{R^n} + 12\cdot 1.25\,B_o e^2\,\frac{(2r_+)^{n-1}}{(1.155\,R)^n} + 12\cdot 0.75\,B_o e^2\,\frac{(2r_-)^{n-1}}{(1.633\,R)^n} \tag{13}$$

The terms in Eq. (13) have the same respective significance as those in Eq. (9). It follows then, analogously to Eqs. (11) and (12) that the equilibrium value of R_c in the crystal is given by

$$R_c = (r_+ + r_-)\left(\frac{nB_o}{Az^2}\right)^{\frac{1}{n-1}}\left[8 + \frac{15}{(1.155)^n}\left(\frac{2\rho}{\rho+1}\right)^{n-1} + \frac{9}{(1.633)^n}\left(\frac{2}{\rho+1}\right)^{n-1}\right]^{\frac{1}{n-1}} \tag{14}$$

In exactly the same manner the following expressions may be developed for the gaseous M_2O linear molecule

$$V = -\frac{7}{2}\frac{e^2}{R_g} + 2B_o e^2 \frac{(r_+ + r_-)^{n-1}}{R_g{}^n} \tag{15}$$

By differentiation and equating $\frac{dV}{dR}$ to zero one obtains

$$R_g = \left(\frac{4nB_o}{7}\right)^{\frac{1}{n-1}} (r_+ + r_-) \tag{16}$$

If, now, one assumes the value of the characteristic repulsive coefficient B_o to be the same for the crystalline and gaseous state as well as assuming constancy of the ionic radii constants and the repulsive exponent, the ratio of the equilibrium bond distance in the gaseous molecule to the known distance in the crystal may be written as

$$\frac{R_g}{R_c} = \left(\frac{4A}{7}\right)^{\frac{1}{n-1}}\left[8 + \frac{15}{(1.155)^n}\left(\frac{2\rho}{\rho+1}\right)^{n-1} + \frac{9}{(1.633)^n}\left(\frac{2}{\rho+1}\right)^{n-1}\right]^{-\frac{1}{n-1}} \tag{17}$$

Having this value of R_g one may apply Eq. (8), using the crystal value of n to remain consistent, to calculate the heat of formation desired. In order to test this theoretical approach, the heat of formation of $CaF_2(g)$ was calculated and compared to the experimental value.[3],[4],[7],[9] Table IV gives the results of these calculations, in which use is made again of the modified Born-Haber cycle for the reaction $2M(g) + X(g) = M_2X(g)$. The value of 97 kcal/mole for the electron affinity of F(g) is used to remain consistent with the heat

Table IV

Gas	A	R_c	n	R_g	U_o	I	E	$-\Delta H_{298}$
CaF_2	5.039	2.36	8.0	1.99	507	416	97	285
Li_2O	5.039	2.00	6.0	1.52	633	126	-168	213
Na_2O	5.039	2.40	7.0	1.94	510	120	-168	102
K_2O	5.039	2.79	8.0	2.27	446	102	-168	74
Rb_2O	5.039	2.92	8.5	2.37	424	98	-168	60
Cs_2O	4.116	3.09	9.5	2.78	425	91	-168	75

of dissociation of $F_2(g)$ [4] of 64 kcal/mole, which gives for the reaction $Ca(g) + F_2(g) = CaF_2(g)$, $\Delta H_{298} = -221$ kcal/mole. This is to be compared with the thermochemical value $\Delta H_{298} = -226$ kcal/mole.

Since the theory affords a reasonable check with experiment in the case of $CaF_2(g)$, the calculations are extended in order that the stability of the gaseous oxides relative to dissociation into gaseous atoms may be estimated. Using $\frac{1}{2}D_0$ for $O_2(g)$ equal to 59 kcal/mole,[4] and known heats of formation[5] of the solid oxides and estimating the entropy of volitilization as 30 e. u., the vapor pressures of the oxides at 1000° K are calculated. From the free energy values[3] for the gaseous alkali atomic species the vapor pressure of the metal over the oxide is calculated for 1000° K, the appropriate species for gaseous oxygen being incorporated at the derived pressures. These results are given in Table V.

It is seen, in accord with scanty experimental evidence, that $Li_2O(s)$ vaporises without dissociation to the gaseous metal and oxygen.

5. Gaseous and Solid Alkaline Earth Suboxides.

The methods used in the preceding section are now applied to the investigation of the significance of alkaline earth suboxide species in the solid and gaseous state. Since no experimental data exist for these species, it is necessary to estimate the properties of the crystalline state. Recourse is again had to Pauling's text (pg. 346) in which univalent crystal radii of ions are given. Now these radii are calculated by the use of screening constants such that they are primarily appropriate to the alkali and halogen atoms when they are in the sodium chloride crystal structure. That is, they are radii for the ionic state which results in the rare gas structure, but are

Table V

Gas	$-\Delta H_{298}(s)$ Std. state	$2\Delta H_{298}$ Sublimation	ΔH_{298} Volatilisation	ΔF_{1000}
Li_2O	142	65	53	23
Na_2O	100	46	103	73
K_2O	86	38	86	56
Rb_2O	83	36	118	88
Cs_2O	82	33	99	69

Gas	$P_{1000}(M_2O)$	$P_{1000}(M)$
Li_2O	1.0×10^{-5} atm.	2.0×10^{-14} atm.
Na_2O	1.1×10^{-16}	8.6×10^{-9}
K_2O	1.3×10^{-11}	1.1×10^{-8}
Rb_2O	6.4×10^{-20}	1.2×10^{-7}
Cs_2O	1.8×10^{-15}	1.2×10^{-7}

calculated on the assumption that they enter into coulombic interaction as a univalent ion. Hence the radii given for the univalent alkaline earths are smaller than those to be expected in the actual case since allowance is not made for the remaining 1s electron. If these radii are used in the coulombic functions used herein, the calculated stability of the suboxide will be favored. Since the results indicate a great instability and furthermore, since it is difficult to arrive at a better figure for these univalent radii the radii given by Pauling are used in the following.

From the probable radii ratios it is assumed that these suboxides assume the fluorite structure. Thus one has assembled the radii, Madelung constant and repulsive exponents necessary to conduct the same calculations carried out in the preceding section. The results of these calculations are given in Table VI. The heat of formation given in the last column on the right is for the reaction $2M(g) + O(g) = M_2O(g)$.

Having available the experimental heats of formation of the solid[5] and gaseous[11] alkaline earth oxides the free energies for the following reactions were calculated using the estimated entropies shown after the reaction:

$M_2O(s) = M(s) + MO(s)$	$\Delta S \cong 0$	298.1° K
$M_2O(g) = M(g) + MO(g)$	$\Delta S \cong 25$	2000° K

In order to calculate the ΔF at 2000° K the expression $\Delta F_{2000} = \Delta H_{298} - 2000\ (\Delta S)$ which treats the ΔC_p as zero was used. The heats of formation of the species $M_2O(s)$ from standard elements $2M(s) + \frac{1}{2}O_2(g) = M_2O(s)$ were calculated by application of Eqs. (5) and (6). Table VII gives these results. It will be noted that the heats of formation in this table for the solids at 298.1° K are

Table VI

Gas	A	R_c	n	R_g	U_c	I	-E	$-\Delta H_{298}$
Be_2O	5.039	1.84	6.0	1.38	707	214	168	101
Mg_2O	5.039	2.22	7.0	1.79	562	175	168	34
Ca_2O	5.039	2.58	8.0	2.14	482	140	168	24
Sr_2O	5.039	2.72	8.5	2.26	461	131	168	21
Ba_2O	5.039	2.93	9.5	2.45	433	120	168	15

Table VII

Oxide	$\Delta H_{298}(s)$ M_2O	$-\Delta H_{298}(s)$ MO	$-\Delta F_{298}(s)$
Be_2O	62	147	209
Mg_2O	7	144	151
Ca_2O	29	152	181
Sr_2O	27	141	168
Ba_2O	44	133	177

Oxide	$-\Delta H_{298}(g)$ M_2O	$-\Delta H_{298}(g)$ MO	$-\Delta F_{2000}(g)$
Be_2O	101	129	78
Mg_2O	34	71	87
Ca_2O	24	125	151
Sr_2O	21	109	138
Ba_2O	15	131	168

from the standard elements, whereas the heats given for the gaseous oxides at 298.1° K are for formation from M(g) and O(g). This is simply a matter of convenience in choosing standard state.

From the magnitudes of the free energies resulting from these calculations one is led to the conclusion that, despite the approximations involved, it is very unlikely that these suboxide species can be of any significance in either the solid or gaseous state.

6. Gaseous Divalent Ionic Species.

An attempt has been made to extend these calculations to the doubly charged anion-cation type of gaseous molecule such as one might expect would be the case for the gaseous alkaline earth oxides. The calculations involved the use of Eq. (5) and the modified Born-Haber cycle leading to the heat for the reaction
M(g) + O(g) = MO(g).

The first model assumed was that of doubly charged anion and cation and three values for the repulsive contribution to the bonding energy were investigated: (1) no repulsion, (2) repulsion resulting from the use of a value of the repulsive exponent, n, equal to that appropriate for the crystalline state, and (3) a value of n_g for the gaseous molecule derived from the use of expressions similar to Eq. (9). In each case the resulting heat is compared to the thermochemical value.

A short discussion of the method involved in deriving the value of n_g, in case (3) may be of interest. In the case of the alkaline earth oxides the bond distance in both the solid[12] and gaseous[8] states are available. Since Eq. (9) is derived for the sodium chloride structure which is that assumed by the alkaline earth oxides (excepting BeO), it may be combined with the similar

equations for the gaseous molecule which are

$$V_g = -\frac{4e^2}{R} + B_o e^2 \frac{(r_+ + r_-)^{n_g-1}}{R^{n_g}}$$

$$R_o = (r_+ + r_-)\left(\frac{n_g B_o}{4}\right)^{\frac{1}{n_g-1}} \qquad (18)$$

Designating the equilibrium distance in the solid and gas R_c and R_g respectively one may divide Eq. (18) by Eq. (11) which now contains the appropriate factor of four for the divalent charges and solve for n_g:

$$n_g\left(\frac{1}{n_g-1}\right) = \left(\frac{R_g}{R_c}\right)\left(\frac{6n_c}{A_c}\right)^{\frac{1}{n_c-1}}\left[1 + \frac{1.25}{(\sqrt{2})^{n_c}}\left(\frac{2\rho}{\rho+1}\right)^{n_c-1} + \frac{0.75}{(\sqrt{2})^{n_c}}\left(\frac{2}{\rho+1}\right)^{n_c-1}\right]^{\frac{1}{n_c-1}}$$

which should give a repulsive coefficient suitable for incorporation in the calculations for these gaseous molecules. Table VIII gives the values calculated for the alkaline earth oxides.

These results indicate that these empirical formulae require the repulsive contribution to the bond energy to decrease rapidly with increasing cation radius.

The heats of formation of the gaseous oxides from the gaseous elements calculated assuming doubly charged ions with these three repulsive contributions are compared with the thermochemical values[11] in Table IX.

The ionization potentials of the gaseous metals were taken from Brewer, et al[8] and the electron affinity of O(g) is taken as -168 kcal/mole in the calculation of these heats.

Table VIII

Gas	R_g	R_c	n_c	A_c	f	n_g
BeO	1.33	1.64	6.0	1.641	0.221	5.35
MgO	1.60	2.10	7.0	1.747	.464	7.3
CaO	1.75	2.40	8.0	1.747	.707	16.5
SrO	1.83	2.57	8.5	1.747	.807	31.4
BaO	1.80	2.76	9.5	1.747	.965	>648

Table IX

Gas	R_K	n_c	U_o	-ΔH Exper.
BeO	1.33	6.0	825	< 129
MgO	1.60	7.0	707	71
CaO	1.75	8.0	668	129
SrO	1.83	8.5	637	109
BaO	1.80	9.5	658	131

Gas	-ΔH No Repulsion	-ΔH Crystal Repulsion	-ΔH Gas Repulsion
BeO	189	22	3
MgO	134	16	21
CaO	172	85	126
SrO	170	84	157
BaO	216	139	216

An inspection of Table IX shows no agreement between the experimental and theoretical values. In view of the large thermodynamic instability of $O^{=}(g)$ ion the next model investigated was that in which the bonding was coulombic in nature, resulting from unit positive and negative charges on the cation and anion respectively.

The heats for the reaction $M(g) + O(g) = MO(g)$ calculated for this model are given in Table X.

The values for R_g and n_c are given in Table IX. The ionization potentials are given by Herzberg[13] and the electron affinity of O(g) for one electron is given by Brewer, et al.[9]

In Table X apparent agreement is seen with respect to the order of magnitude and trend when no allowance is made for repulsion. The use of the n_c values again lead to no agreement.

At the present writing the apparent agreement is regarded as being essentially fortuitous since there is no theoretical basis for the type of bonding assumed here. Actually, these results are interpreted as an illustration of the failure of the existing formulations of the repulsive energy when ions or atoms are subjected to high compression. That such compression occurs in these gaseous molecules follows from the short bond distance and the high attractive forces existant between the doubly charged ions.

The failure of the Born expression for the force between ions has been observed by Bridgman[14] by the researches utilizing high pressures. It is illuminating to quote from his review:

"One aspect of the method of treatment followed by Born is conventional in practically all derivations of an equation of state, whether or not intended to be applicable to high pressures and condensed phases, namely the assumption of a 'law of force' between atoms, a function only of the distance of separation of atomic

Table X

Gas	U_o	$-\Delta H$ Exper.	$-\Delta H$ No Repulsion	$-\Delta H$ Crystal Repulsion
BeO	206	129	105	63
MgO	177	71	102	73
CaO	164	<129	119	95
SrO	160	109	121	100
BaO	164	131	134	115

centers. In view of the failure of all attempts to reproduce more than the first derivative of volume with respect to pressure the question presents itself as to how far the action between atoms in condensed phases under variations of temperature and pressure can be represented by 'a law of force.' In assuming a law of force of the form, for example, $-a/r^2 + b/r^n$, we are evidently maintaining that the behavior of the entire assemblage of atoms can be found by postulating that each atom of every pair of atoms acts on the other with the force given, irrespective of the presence of other atoms, in all orientations (orientation is not a factor for the type of ions just considered, which by wave mechanics have spherical symmetry), and at all distances. The assumption of a law of force of the form given certainly corresponds to the facts from the point of view of one very important first approximation. For two atoms acting on each other with a force of this character may be brought indefinitely close together by the action of sufficiently large forces, that is, such atoms are not rigid but are effectively deformable, as is demanded by many lines of experimental evidence. But the question is, how much further is the approximation represented by such a law valid. . . . . Into this law of force will certainly enter the distribution of the electrons within the atoms. The law of force may remain good as long as the distribution of electrons remains fixed or as long as the electron distribution is not fixed uniquely on the distance r, as when pressure is changed at constant temperature. But if the electron distribution is not fixed uniquely by r, a possibility which we must recognize if both pressure and temperature are allowed to vary, then we must be prepared to find that the interaction cannot be described in terms of constants and r only, that is, we must be prepared to find that there is no 'law of force.' Doubtless in

a sufficiently narrow range the assumption of a law of force is a valid approximation."

8. Summary.

Normal ionic bonding is assumed to exist between the atoms in the gaseous alkali halides, alkali oxides and alkaline earth suboxides as well as for the solid state of the last species. The empirical repulsive function suggested by Born and the values of the repulsive exponent given by Pauling are applied in the calculation of the heat of formation of the gaseous and solid oxide species mentioned.

In order to establish empirically a function which appears to represent the repulsive contribution to the bonding energy of these gaseous species, variations of the repulsive exponent are introduced into the theoretical calculation for gaseous species whose thermochemical heats of formation are known. To substantiate the assumption of ionic bonding in the gaseous species, the lattice energy of the alkali oxides and alkaline earth oxides are calculated theoretically assuming complete ionic bonding and compared to the value of the lattice energy obtained from experimental data by use of the Born-Haber cycle.

In the case of the lattice energy calculations, the value of -168 kcal/mole was chosen for the electron affinity of O(g) for two electrons, and this value is used consistently throughout this paper. In general, good agreement is had between the theoretical and experimental results; however, it is to be noted that Pauling's values for the repulsive exponent do not give an exceptionally good fit for either series as there is a definite trend which, on the basis of ionic bonding, indicates the theory affords too much repulsive energy

for the higher molecular weight members. Furthermore, in the lighter members of the alkaline earth series one is led to the conclusion that kernel repulsion is of significance due to the close contact induced by the doubly charged ions which is not accounted for by the theory which in these cases then gives values for the lattice energy higher than that obtained experimentally. However, from these results it may be assumed that the bonding in these solids is predominately ionic.

It is found that the calculated heats of formation of the gaseous alkali halides assuming a very large value for the repulsive exponent, i.e., a negligible repulsive energy contribution to the ionic bonding, agree exceedingly well with the experimental value, whereas the calculations which include the value of the exponent given for the solid state are in disagreement by about 10 kcal/mole. It is concluded that two effects are masking the actual repulsive energy in these systems: (1) a great deal more distortion of the ions probably occurs in the gaseous state leading to higher attractive potential than that of coulombic alone, and (2) the actual expected magnitude of the repulsive forces in the gaseous molecule will be lower than that per molecule in the solid since six neighbors about each ion are involved in repulsion in the solid whereas only one is involved in the gaseous state. This is true even though the actual repulsion per contact is greater in the gaseous molecule. Thus it is probable that the increased attraction due to distortion essentially equalizes the repulsive force, both of these being relatively small.

In order to establish the heats of formation of the gaseous alkali oxides, it is first necessary to develop a theoretical method which enables one to calculate the bond distances in these molecules

since these data are not available from spectroscopic data. Such a method is developed through application of a detailed expression given by Pauling for the solid state of NaCl type lattice which involves the coulombic attraction and quantum-mechanically weighted anion-anion, anion-cation, and cation-cation repulsions. This expression is changed in order to be appropriate for the CaF_2 structure and a similar expression is established for the gaseous molecule. Assuming the repulsive constants between the ions to be the same in both states and knowing the bond distance in the solid, the distances for the gaseous molecules are obtained. In the calculation of the heat of formation of the gaseous compounds the value of the repulsive exponent used is that given by Pauling. This was done originally to remain consistent with the same usage which was made in the derivation of the gaseous bond distances, and is substantiated by a check calculation of the heat of formation of gaseous CaF_2 which gives -221 kcal/mole and is to be compared with the thermochemical value, -226 kcal/mole.

Having calculated the heats of formation of the gaseous alkali oxides by this method, having available the heats for the solids and estimating the entropy of volatilization of the oxide to be 30 e.u., the vapor pressure of the gaseous oxide and that of the gaseous metal in equilibrium with the solid at 1000° K are obtained. It is found that in accord with scanty experimental evidence, $Li_2O(s)$ vaporizes undissociated whereas the remaining members of the series dissociate to the metal and oxygen upon volatilization.

In order to calculate the stability of solid and gaseous alkaline earth suboxides with respect to disproportionation to the metal and normal oxide, the lattice energy was calculated assuming a fluorite structure and applying Pauling's univalent ionic radii

and repulsive exponents. The heat of formation of the gaseous suboxides were obtained by the method described in the alkali oxide calculations.

Having available the experimental heats of formation of the solid and gaseous alkaline earth oxides the free energies for the following reactions were calculated using the estimated entropies shown after the reaction:

$$M_2O(s) = M(s) + MO(s) \qquad \Delta S = 0$$

$$M_2O(g) = M(g) + MO(g) \qquad \Delta S = 25$$

In the case of the solid state reaction at 298.1° K the free energies for the series fall between -151 and -209 kcal/mole, and in the gaseous state reaction at 2000° K the free energy values fall between -78 and -168 kcal/mole. From this it is concluded that despite the assumptions made in the calculations these large values strongly indicate that the alkaline earth suboxides are not significant species in either the solid or gaseous state.

When attempting to apply these methods to the gaseous alkaline earth oxides it is found that the simple Born expression does not afford a good fit to the known bond energies if one assumes the cation and anion to be doubly charged. Actually, a closer fit is obtained if the repulsion is assumed to be negligible and further, that the cation and anion are singly charged. From an investigation of the results of these calculations and the findings of Bridgman in high pressure researches it is concluded that in such molecules where the mutual penetration is high, because of the large coulombic force arising from doubly charged ions, the simple repulsive "law of force" such as given by Born no longer applies. Bridgman comes to the same conclusion in studying ionic compressions due to externally

applied pressure; namely, that the simple functions of the distance between the ions are a good empirical fit over a short range of the distance and fail badly when applied to extreme cases. This is the situation which obtains in the case of the alkaline earth oxides. The Born expression affords a good fit in the solid state since the equilibrium interionic distances do not involve extreme interpenetration by virtue of the semi-infinite lattice of positive and negative charges about any one ion. In the gaseous state, however, only the coulombic force between the cation and anion are acting which leads to a much closer approach of the two ions relative to that in the solid state as is actually shown from the spectroscopically determined bond distance.

Thus, calculations using the methods developed herein cannot be made for gaseous molecules whose bonding is coulombic resulting from charges on the ions of magnitude two or greater since the repulsive "law of force" which is the basis of the theory presumably does not apply to these systems.

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