

As a rule, the intermediate melting forms of the triglycerides, when isolatable, possess somewhat higher dielectric constants than the highest melting forms, at least near their melting points. Instead of being nearly constant with temperature, their dielectric constants rise gradually with increasing temperature (Figs. 5 and 7). The same behavior was observed for a number of *n*-alkyl brom-

ides¹⁸ which were found to exist in two solid modifications. Since metastable forms might be expected to consist of more loosely packed structures than stable forms, the gradual rise in dielectric constant could well be the result of the gradual increase in orientational freedom as the melting point is approached.

(18) R. W. Crowe and C. P. Smyth, *THIS JOURNAL*, **72**, 1098 (1950).
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Theoretical Calculation of the Stability of Solid and Gaseous Alkali and Alkaline Earth Oxides²

BY LEO BREWER AND DONALD F. MASTICK³

A theoretical method is described for calculation of stabilities of gaseous alkali oxides and solid and gaseous alkaline earth suboxides. Results of the theory are compared with existing experimental data. Calculations indicate that at 1000°K. all the gaseous alkali oxides except Li₂O are unstable with respect to dissociation, and that the alkaline earth suboxides are unstable toward disproportionation in both gaseous and solid states. The method is not applicable to divalent gaseous oxides such as the alkaline earth oxides because of the high attractive forces between the doubly charged ions.

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 their apparent ionic bonding 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 the following, ionic models are assumed for the solid and gaseous states; on this basis calculations of stability are made which are compared with experimental values for the stability of the specific molecule or one of the same coulombic nature.

Two empirical expressions⁴ for dealing with the mutual repulsive potential existent between ions were investigated, namely, the Born expression

$$V_r = b/r^n \quad (1)$$

and the Born and Mayer exponential expression

$$V_r = ae^{-r/\rho} \quad (2)$$

Here, *b* and *n* are constants and *r* is the distance between the ion, *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, 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.

The expressions given by Pauling⁵ for the calculation of interionic forces and crystal energy are adopted. The mutual potential energy of two ions is written as

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

and the total potential energy of an ionic crystal by incorporation of the appropriate geometrical factor *A* is given as

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

In Eq. (3) *z_i* and *z_j* refer to the algebraic value of the valence of the ions, *b* is an appropriate constant and *r_{ij}* the distance between the ions. 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. It is convenient to eliminate the repulsive constant *B* from Eq. (4) by allowing *dV/dR* = 0 at *R* = *R*₀, the equilibrium distance. Thus, by substitution in Eq. (4), one obtains for the crystal energy

$$U_0 = \frac{NAe^2 z^2}{R_0} \left(1 - \frac{1}{n}\right) \quad (5)$$

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

| Ion type | <i>n</i> | Ion type | <i>n</i> |
|---------------------|----------|---------------------|----------|
| He | 5 | Kr, Ag ⁺ | 10 |
| Ne | 7 | Xe, Au ⁺ | 12 |
| Ar, Cu ⁺ | 9 | | |

(5) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, Chapter X.

(1) This document is based in part on work performed under Contract No. W-7405-eng-48B for the Atomic Energy Commission.

(2) Abstracted in part from the thesis submitted by Donald F. Mastick in partial satisfaction of the requirements for the degree of Doctor of Philosophy in chemistry at the University of California. Presented before the Inorganic and Physical Division of the American Chemical Society at the 116th National Meeting at Atlantic City, N. J., September, 1949.

(3) Atomic Energy Commission Fellow in chemistry, 1948-1949.

(4) F. Seitz, "The Modern Theory of Solids," Chapter II, McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

TABLE I

| Crystal | a_0 | n | U_0 | $2I$ | $2S$ | $1/2D$ | $-E$ | $-\Delta H_{298}$ | U_0 | $U_0 - U_e$ |
|-------------------|-------|-----|-------|-------|------|--------|------|-------------------|-------|-------------|
| Li ₂ O | 4.619 | 6.0 | 693 | 248.5 | 73.9 | 59.3 | 168 | 142.3 | 692 | 1 |
| Na ₂ O | 5.55 | 7.0 | 593 | 236.9 | 51.9 | 59.3 | 168 | 102.9 | 619 | 26 |
| K ₂ O | 6.436 | 8.0 | 522 | 200.1 | 43.0 | 59.3 | 168 | 86.2 | 557 | 35 |
| Rb ₂ O | 6.74 | 8.5 | 503 | 192.5 | 41.0 | 59.3 | 168 | 82.9 | 544 | 41 |

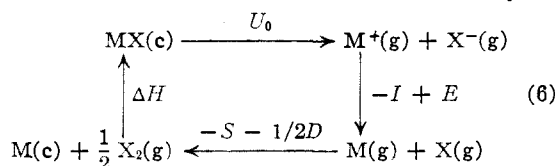
TABLE II

CALCULATED CRYSTAL ENERGIES OF ALKALINE EARTH OXIDES (U_0) AND COMPARISON WITH EXPERIMENTAL CRYSTAL ENERGIES (U_e)

| Crystal | a_0 | n | U_0 | I | S | $1/2D$ | $-E$ | $-\Delta H_{298}$ | U_0 | $U_0 - U_e$ |
|---------|-------|-----|-------|-------|------|--------|------|-------------------|-------|-------------|
| BeO | | 6.0 | 1099 | 634.6 | 80.0 | 59.3 | 168 | 147 | 1089 | -10 |
| MgO | 4.203 | 7.0 | 941 | 522.8 | 35.9 | 59.3 | 168 | 143.8 | 930 | -11 |
| CaO | 4.797 | 8.0 | 841 | 414.5 | 42.6 | 59.3 | 168 | 151.7 | 836 | -4 |
| SrO | 5.144 | 8.5 | 791 | 385.4 | 39.2 | 59.3 | 168 | 140.8 | 793 | 2 |
| BaO | 5.523 | 9.5 | 748 | 350.7 | 42.0 | 59.3 | 168 | 133 | 753 | 5 |

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



Here U_0 is the crystal energy given by Eq. (5), I the ionization potential of the metal $\text{M}(g)$, E the electron affinity of $\text{X}(g)$, S the heat of sublimation of the metal, D the heat of dissociation of $\text{X}_2(g)$ and ΔH the heat of formation of crystalline MX from the elements $\text{M}(c)$ and $1/2 \text{X}_2(g)$. 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. However, the values of I and E for 0°K . may be used at other temperatures since their changes cancel one another. U_0 from Eq. (5) should be increased by about one kcal. at 298°K . but this correction will be neglected. For correction of the other values estimated ΔC_p values are applied since this is, in general, a small correction. 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.

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

$$\Delta H = S + I + 1/2D - E - U_0 \quad (7)$$

In applying this cycle to oxides one must choose a most probable value for electron affinity of $\text{O}(g)$ 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_0 and E as explained above) are available.^{6,7,8}

(6) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, National Nuclear Energy Series, Vol. 19B, paper 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

(7) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, *ibid.*, paper 5.

(8) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, *ibid.*, paper 6.

Results and Discussion

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,⁹ and Eq. (7) is applied to obtain the experimental U_e and Eq. (5) gives the theoretical U_0 , wherein

$$Ne^2/1\text{\AA} = 329.7 \text{ kcal./mole}$$

The results of these calculations are given in Table I and Table II for 298°K .

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_0 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 polarization will account for the 41 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 the values for the repulsive exponent given by Pauling do not afford a correlation much better than that given here. In Table II, U_0 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 exert enough attractive force to cause kernel repulsion in the case of the smaller cations.

It will be noted that the repulsive potential gives an apparent fit between CaO and SrO . If one applies Eq. (6) to these compounds to obtain the electron affinity of $\text{O}(g)$ for two electrons, one obtains the average value -168 kcal./mole, which is in agreement with the value given by Sherman.¹⁰ This value for the electron affinity of $\text{O}(g)$ has been used throughout.

Gaseous Alkali Halides.—Having considered the ionic model for the solid state oxides and noting the weakness of the repulsive function

(9) L. Brewer, "The Thermodynamic Properties of the Oxides," Declassified Atomic Energy Paper UCRL-104, (1946).

(10) J. Sherman, *Chem. Revs.*, 11, 93 (1932).

when applied to divalent ions, the gaseous alkali halides are first investigated since thermochemical values for the heat of the reaction $M(g) + X(g) = MX(g)$ are available.^{8,11} 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, secondly, for repulsion calculated using a value of n for the crystalline state of the ionic species. The values for the equilibrium bond distance are taken from spectroscopic data.¹² The values for the electron affinities of $X(g)$ and ionization potential of the $M(g)$ are given by Brewer, *et al.*⁸ Use is made of a modified Born-Haber cycle in the calculation of the heat of reaction

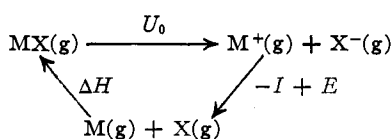


TABLE III

CALCULATED HEATS OF DISSOCIATION OF GASEOUS ALKALI HALIDES AND COMPARISONS WITH EXPERIMENTAL VALUES:

| Gas | r_0 | n | U_0 | ΔH_0 , crystal repul- sion | ΔH_0 , no repul- sion | ΔH_0 , experi- mental |
|------|-------|------|-------|---|--|-------------------------------------|
| NaCl | 2.51 | 8.0 | 115 | 82 | 98 | 98 |
| NaBr | 2.64 | 8.5 | 110 | 72 | 87 | 86 |
| NaI | 2.90 | 9.5 | 102 | 55 | 67 | 70 |
| KCl | 2.79 | 9.0 | 105 | 92 | 104 | 101 |
| KBr | 2.94 | 9.5 | 100 | 81 | 93 | 90 |
| KI | 3.23 | 10.5 | 92 | 64 | 74 | 74 |
| RbCl | 2.89 | 9.5 | 102 | 92 | 104 | 105 |
| 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 | X(g) | E |
|------|-------|------|------|
| Na | 118.5 | Cl | 85.8 |
| K | 100.1 | Br | 80.5 |
| Rb | 96.3 | I | 72.4 |
| Cs | 89.8 | | |

The theoretical and experimental agreement are quite good with no repulsive contribution which, when applied, lowers the theoretical values by about 10 kcal. Considering the smaller interionic distance 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 held in a symmetrical configuration by the semi-infinite lattice of charges surrounding it such that only slight distortion occurs. In the gaseous state distortion of the positive and negative ions may occur to a great extent thereby increasing the bonding energy which, supplemented by increased dispersion

(11) L. Brewer, *Nuclear Energy Series*, Vol. 19B, paper 7.

(12) G. Herzberg, "Molecular Spectra and Molecular Structure, Vol. I," D. Van Nostrand Co., New York, N. Y., 1950.

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 apparent repulsive effect is diminished in this calculation. Hence, it appears that the ionic model is valid for these univalent gaseous molecules and Eq. (5) may be used, with no allowance for repulsion. Townes and Daily¹⁸ confirm this.

Gaseous Alkali Oxides.—In the calculation of the heats of formation of the gaseous alkali oxides the model developed above is used. It is assumed that the 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 Madelung constant for the mutual coulombic attractions and repulsions for such a linear ionic molecule is 7/2, which leads to a value of the mutual potential energy between the ions

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

Upon differentiation, allowing $dV/dR|_{R=R_0} = 0$, and substituting the expression for B back into this potential equation one obtains

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

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 applied. Pauling⁵ 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

$$V = -\frac{Ae^2}{R} + 6B_0e^2 \frac{(r_+ + r_-)^{n-1}}{R^n} + 6 \times 1.25 B_0e^2 \frac{(2r_+)^{n-1}}{(\sqrt{2}R)^n} + 6 \times 0.75 B_0e^2 \frac{(2r_-)^{n-1}}{(\sqrt{2}R)^n} \quad (9)$$

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_0 is a characteristic repulsive coefficient. Equation (9) is rewritten as

$$V = -\frac{Ae^2}{R} + \frac{6B_0e^2}{R^n} \left[(r_+ + r_-)^{n-1} + \frac{1.25(2r_+)^{n-1}}{(\sqrt{2})^n} + 0.75 \frac{(2r_-)^{n-1}}{(\sqrt{2})^n} \right] \quad (10)$$

(13) C. Townes and B. Daily, *J. Chem. Phys.*, **17**, 782 (1949).

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

$$R_0 = (r_+ + r_-)F(\rho) \quad (11)$$

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

$$F(\rho) = \left(\frac{6nB_0}{A}\right)^{\frac{1}{n-1}} \left[1 + \frac{1.25}{(\sqrt{2})^n} \left(\frac{2\rho}{\rho+1}\right)^{n-1} + \frac{0.75}{(\sqrt{2})^n} \left(\frac{2}{\rho+1}\right)^{n-1} \right]^{\frac{1}{n-1}} \quad (12)$$

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

$$V = \frac{-Ae^2z^2}{R} + 8B_0e^2 \frac{(r_+ + r_-)^{n-1}}{R^n} + 12 \times 1.25B_0e^2 \frac{(2r_+)^{n-1}}{(1.155R)^n} + 12 \times 0.75B_0e^2 \frac{(2r_-)^{n-1}}{(1.633R)^n} \quad (13)$$

It follows then, analogously to Eq. (11) and (12), that the equilibrium value of R_c in the fluorite crystal is given by

$$R_c = (r_+ + r_-) \left(\frac{nB_0}{Az^2}\right)^{\frac{1}{n-1}} \left[8 + \frac{15}{(1.155)^n} \left(\frac{2\rho}{\rho+1}\right)^{n-1} + \frac{9}{(1.633)^n} \left(\frac{2}{\rho+1}\right)^{n-1} \right]^{\frac{1}{n-1}} \quad (14)$$

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

$$V = -\frac{7e^2}{2R_g} + 2B_0e^2 \frac{(r_+ + r_-)^{n-1}}{R_g^n} \quad (15)$$

By differentiation and equating dV/dR to zero one obtains

$$R_g = \left(\frac{4nB_0}{7}\right)^{\frac{1}{n-1}} (r_+ + r_-) \quad (16)$$

If, now, one assumes the value of the characteristic repulsive coefficient B_0 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

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

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. Table IV gives the results of these calculations, in which use is made again of the modified Born-Haber cycle for the reaction $2M(g) + X(g) = M_2X(g)$. In order to test this theoretical approach, the heat of formation of $CaF_2(g)$ was calculated and compared to the experimental value.^{6,7,8,11} The value of 80 kcal./mole for the electron affinity of $F(g)$ is used to remain consistent with the heat of dissociation of $F_2(g)$ of 33 kcal./mole, which gives for the reaction $Ca(g) + F_2(g) = CaF_2(g)$, $\Delta H_{298} = -219$ kcal./mole. This is to be compared with the thermochemical value $\Delta H_{298} = -226$ kcal./mole.

TABLE IV
CALCULATED HEATS OF FORMATION OF GASEOUS CaF_2 AND ALKALI OXIDES

| Gas | A | R_c | n | R_g | U_0 | I | E | $-\Delta H_{298}$ |
|---------|-------|-------|-----|-------|-------|-----|------|-------------------|
| CaF_2 | 5.039 | 2.36 | 8.0 | 1.99 | 507 | 415 | 80 | 252 |
| Li_2O | 5.039 | 2.00 | 6.0 | 1.52 | 633 | 124 | -168 | 217 |
| Na_2O | 5.039 | 2.40 | 7.0 | 1.94 | 510 | 119 | -168 | 104 |
| K_2O | 5.039 | 2.79 | 8.0 | 2.27 | 446 | 100 | -168 | 78 |
| Rb_2O | 5.039 | 2.92 | 8.5 | 2.37 | 424 | 96 | -168 | 64 |
| Cs_2O | 4.116 | 3.09 | 9.5 | 2.78 | 372 | 90 | -168 | 24 |

Since the theory affords a reasonable agreement with experiment in the case of $CaF_2(g)$, the calculations were extended in order that the stability of the gaseous oxides relative to dissociation into gaseous atoms may be estimated. Using $1/2D_0$ for $O_2(g)$ equal to 59 kcal./mole,⁷ and known heats of formation⁹ of the solid oxides and estimating the entropy of volatilization as 40 e.u., the vapor pressures of the oxides at 1000°K. are calculated. From the free energy values⁶ 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.

TABLE V
CALCULATED VAPOR PRESSURES OF ALKALI OXIDE AND ALKALI METAL IN EQUILIBRIUM WITH SOLID ALKALI OXIDE AT 1000°K.

| Gas | $-\Delta H_{298}$ $M_2O(g)$ | $-\Delta H_{298}$ $M_2O(s)$ | ΔH_{1000} vola- tiliza- tion | ΔF_{1000} vola- tiliza- tion | $P_{1000}(M_2O)$, atm. | $P_{1000}(M)$, atm. |
|---------|--------------------------------|--------------------------------|---|---|----------------------------|-------------------------|
| Li_2O | 217 | 276 | 59 | 19 | 10^{-4} | 1×10^{-13} |
| Na_2O | 104 | 214 | 110 | 70 | 10^{-16} | 5×10^{-7} |
| K_2O | 78 | 189 | 111 | 71 | 10^{-16} | 4×10^{-6} |
| Rb_2O | 64 | 183 | 119 | 79 | 10^{-17} | 1×10^{-4} |
| Cs_2O | 24 | 179 | 155 | 115 | 10^{-25} | 2×10^{-4} |

It is seen, in accord with scanty experimental evidence, that $Li_2O(s)$ vaporizes without dissociation.

Gaseous and Solid Alkaline Earth Suboxides.—The methods used in the preceding section are now applied to the 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 (p. 346) in which univalent crystal radii of ions are given. These radii are calculated by the use of screening constants such that they are appropriate to the alkali and halogen atoms in the sodium chloride crystal structure. That is, they are radii for ions having the rare gas structure, but are 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 given, the calculated stability of the suboxide will be favored. Since the results indicate a great instability and since it is difficult to arrive at a better figure for these univalent radii, the values given by Pauling are used.

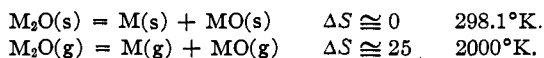
From the probable radii ratios it is assumed that these suboxides assume the fluorite structure. The results of the calculations are given in Table VI. The heat of formation given in the last column on the right is for the reaction $2M(g) + O(g) = M_2O(g)$.

TABLE VI

CALCULATED HEATS OF FORMATION OF ALKALINE EARTH SUBOXIDES, $2M(g) + O(g) = M_2O(g)$

| Gas | A | R _c | n | R _g | U ₀ | I | -E | -ΔH ₂₉₈ |
|-------------------|-------|----------------|-----|----------------|----------------|-----|-----|--------------------|
| Be ₂ O | 5.039 | 1.84 | 6.0 | 1.38 | 707 | 214 | 168 | 101 |
| Mg ₂ O | 5.039 | 2.22 | 7.0 | 1.79 | 562 | 175 | 168 | 34 |
| Ca ₂ O | 5.039 | 2.58 | 8.0 | 2.14 | 482 | 140 | 168 | 24 |
| Sr ₂ O | 5.039 | 2.72 | 8.5 | 2.26 | 461 | 131 | 168 | 21 |
| Ba ₂ O | 5.039 | 2.93 | 9.5 | 2.45 | 433 | 120 | 168 | 15 |

Having available the experimental heats of formation of the solid⁹ and gaseous¹⁴ alkaline earth oxides, the free energies for the following reactions were calculated using the estimated entropies shown after the reaction



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 Eq. (5) and (6). Table VII gives these results.

TABLE VII

CALCULATED FREE ENERGIES OF DISPROPORTIONATION OF SOLID AND GASEOUS ALKALINE EARTH SUBOXIDES AT 298°K. AND 2000°K. $M_2O(s) = M(s) + MO(s)$, $M_2O(g) = M(g) + MO(g)$

| Oxide | -ΔF ₂₉₈ (g) | -ΔF ₂₀₀₀ (g) |
|-------------------|------------------------|-------------------------|
| Be ₂ O | 209 | 78 |
| Mg ₂ O | 151 | 136 |
| Ca ₂ O | 181 | 146 |
| Sr ₂ O | 168 | 140 |
| Ba ₂ O | 177 | 168 |

From 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.

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 would expect to 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 re-

(14) L. Hultdt and A. Lagerqvist, *Arkiv Fysik*, 3, Nr. 37, 1-4 (1950), give heats for reaction $M(g) + O(g) = MO(g)$, 298°K., for MgO and CaO. The remaining values are from a yet unpublished paper by L. Brewer where all the data in the literature have been reviewed and recalculated.

sulting from the use of a value of the repulsive exponent, n , 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. (17). In each case the resulting heat is compared to the thermochemical value, as given in Table VIII.

TABLE VIII

CALCULATED HEATS OF FORMATION OF GASEOUS ALKALINE EARTH OXIDES ASSUMING DIFFERENT IONIC REPULSIVE TERMS. COMPARISON WITH EXPERIMENTAL VALUE $M(g) + O(g) = MO(g)$

| Gas | R _g | n _c | n _g | U ₀ | -ΔH ₂₉₈ no repul- sion | -ΔH ₂₉₈ crys- tal repul- sion | -ΔH ₂₉₈ gas repul- sion | -ΔH ₂₉₈ experi- mental |
|-----|----------------|----------------|----------------|----------------|-----------------------------------|--|------------------------------------|-----------------------------------|
| BeO | 1.33 | 6.0 | 5.4 | 826 | 188 | 13 | 5 | 129 |
| MgO | 1.75 | 7.0 | 4.0 | 645 | 62 | -46 | -126 | 120 |
| CaO | 1.78 | 8.0 | 14.5 | 649 | 157 | 66 | 107 | 120 |
| SrO | 1.92 | 8.5 | 18.4 | 607 | 136 | 54 | 97 | 111 |
| BaO | 1.94 | 9.5 | 41 | 609 | 161 | 90 | 144 | 131 |

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.

An inspection of Table VIII 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 IX. The values for R_g and n_c are given in Table VIII, and the electron affinity of O(g) for one electron is given by Brewer, *et al.*⁸

In Table IX 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 leads to no agreement.

TABLE IX

CALCULATED HEATS OF FORMATION OF GASEOUS ALKALINE EARTH OXIDES FROM GASEOUS ELEMENTS ASSUMING UNIT CHARGE ON IONS: $M(g) + O(g) = MO(g)$

| Gas | U ₀ | -ΔH ₂₉₈ exptl. | -ΔH ₂₉₈ no repul- sion | -ΔH ₂₉₈ crystal repul- sion |
|-----|----------------|---------------------------|-----------------------------------|--|
| BeO | 206 | 129 | 105 | 63 |
| MgO | 161 | 120 | 84 | 57 |
| CaO | 162 | 120 | 116 | 93 |
| SrO | 152 | 111 | 112 | 92 |
| BaO | 152 | 131 | 121 | 103 |

This agreement is regarded as being fortuitous although Hultdt and Lagerqvist¹⁴ claim a triplet ground state for the alkaline earth oxides which would correspond to this singly charged ionic model. Actually, these results are interpreted as an illustration of the failure of the existing formulations of the repulsive energy when ions or atoms are subject to high compression. That such compression occurs in these gaseous molecules follows from the short bond distance and the high attractive forces between the doubly charged ions. The failure of the Born expression for the force between ions has been ob-

served by Bridgman¹⁵ in researches utilizing high pressures. He has been led to the conclusion that

(15) P. W. Bridgman, *Rev. Mod. Phys.*, **7**, 1 (1935).

no simple "law of force" can adequately represent the repulsive force between atoms.

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Kinetics of the Acid Decomposition of Sodium Thiosulfate in Dilute Solutions

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The kinetics of the acid decomposition of sodium thiosulfate in dilute solution has been reinvestigated spectrophotometrically at constant ionic strength. Measurements made at $\lambda = 4000 \text{ \AA}$. show that the time of formation of discrete particles of colloidal sulfur after mixing of reagents depends approximately on $(\text{H}^+)_{0,1/2}$ and $(\text{S}_2\text{O}_3^-)_0 > 1$. The resultant data have been analyzed in conjunction with the facts that the decomposition shows a positive primary salt effect and that thiosulfuric acid is not completely dissociated with respect to its second ionization. By assumption of a bimolecular mechanism between HS_2O_3^- and S_2O_3^- with an intermediate complex whose first order specific rate constant (k_2) is comparable to the bimolecular specific rate constant (k_1) kinetic equations have been derived that express the experimental results reasonably well. The values of k_1 and k_2 calculated are 0.31 and 0.14, respectively. Iodine and acid-base titrations during the course of the reaction show that although sulfite ion is produced in significant amounts in the early stages of the decomposition the production of polythionates is insignificant in dilute solutions.

Sulfur hydrosols² prepared from dilute sodium thiosulfate and strong acids arise from the molecularly dispersed sulfur produced by a reaction whose velocity is given approximately by $k(\text{Na}_2\text{S}_2\text{O}_3)^{1/2}(\text{HCl})^{1/2}$. Such a rate equation is difficult to interpret mechanistically. Simultaneously a side reaction, producing pentathionic acid instead of sulfur, has been stated to occur in appreciable amounts according to the stoichiometric equation



The present investigation of this system has given results that are interpretable in terms of a bimolecular reaction between HS_2O_3^- and S_2O_3^- and shows that this reaction proceeds without the complication of an appreciable amount of the side reaction (1) in the early stages.

Experimental.—C.P. sodium thiosulfate recrystallized from ethanol-water solutions was standardized against re-sublimed I_2 in KI for which C.P. KIO_3 was the primary standard. A 1% starch solution was the indicator in all cases.

The HCl solutions were made up by dilution of the concentrated acid and standardized against standard NaOH for which potassium acid phthalate was the primary standard. Phenolphthalein was the indicator.

The KCl used for adjusting ionic strengths was the C.P. salt, dried for 24 hours in an oven at 110° , and then weighed out. The concentration of the resulting solution was re-standardized according to the Mohr method for soluble chlorides using standard AgNO_3 , with K_2CrO_4 as the indicator.

Solutions of various concentrations of acid and thiosulfate and enough KCl to ensure equality of ionic strengths throughout all runs were mixed as rapidly as possible and the resulting solutions examined by means of a Beckman spectrophotometer (model DU) for the first appearance of turbidity signifying the formation of discrete particles of super-cooled liquid sulfur. The wave length used was 4000 \AA ., the lowest value to which sulfur is transparent. The temperature was $25 \pm 0.02^\circ$ and the cell length was 10 cm. The time of appearance of the Tyndall beam as a function of the concentration of reagents is shown in Table III and plotted graphically in Fig. 1 where the product $\{(\text{H}^+)_{0,1/2}\}$ is plotted versus $(\text{H}^+)_{0,1/2}$. Figure 2 shows the variation of the slopes of Fig. 1 as a function of the thiosulfate concentration. These figures represent only empirical relationships facilitating the correlation of data between initial concentra-

tion of reagents and the time of appearance of the Tyndall beam.

Derivation of Rate Equations.—Any interpretation of the data must begin with the consideration of two important observations. The first is that actual measurements show that the hydrogen ion activity measured immediately upon mixing of reagents is significantly smaller than that calculated on the basis of the concentration of acid added and the known activity coefficient. This indicates that some species is either present initially or produced extremely rapidly which results in the immediate removal of some of the hydrogen ion. Since no significant amount of S_2O_3^- is decomposed, no significant quantity of sulfite ion can exist in these early stages. The loss in hydrogen ion activity is due then to the formation of $\text{H}_2\text{S}_2\text{O}_3$ and HS_2O_3^- . Previous investigators^{3,4} report the value of the first dissociation constant (K_1) to be of the order of 0.45 and the second (K_2) equal to 0.01 for dilute solutions and 0.062 for moderately concentrated sodium thiosulfate solutions. These values show that $\text{H}_2\text{S}_2\text{O}_3$ is a strong acid only with respect to the first dissociation and that the second equilibrium must be considered in any rate equation derived. By designating the initial concentrations of reagents added (H^+ and S_2O_3^-) with zero subscripts the expression for the second equilibrium constant is

$$K_2 = \frac{\{(\text{H}^+)_{0,1/2} - (\text{HS}_2\text{O}_3^-)\} \{(\text{S}_2\text{O}_3^-)_0 - (\text{HS}_2\text{O}_3^-)\}}{(\text{HS}_2\text{O}_3^-)} \quad (2)$$

Neglecting $(\text{HS}_2\text{O}_3^-)^2$ and simplifying gives, for the amount of bithiosulfate ion

$$(\text{HS}_2\text{O}_3^-) = \frac{(\text{H}^+)_{0,1/2} (\text{S}_2\text{O}_3^-)_0}{K_2 + (\text{H}^+)_{0,1/2} + (\text{S}_2\text{O}_3^-)_0} \quad (3)$$

and since

$$(\text{S}_2\text{O}_3^-) = (\text{S}_2\text{O}_3^-)_0 - (\text{HS}_2\text{O}_3^-)$$

the amount of free thiosulfate ion as a function of initial reactants is

$$(\text{S}_2\text{O}_3^-)_0 - \frac{(\text{H}^+)_{0,1/2} (\text{S}_2\text{O}_3^-)_0}{K_2 + (\text{H}^+)_{0,1/2} + (\text{S}_2\text{O}_3^-)_0} \quad (4)$$

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(2) E. M. Zaiser and V. K. La Mer, *J. Colloid Sci.*, **3**, 571 (1948).

(3) K. Jellinek, *Z. physik. Chem.*, **76**, 257 (1911).

(4) I. Kolthoff, *Rec. trav. chim.*, **43**, 216 (1924).