

Heat of Formation of O^{2-} *

EDWARD S. GAFFNEY AND THOMAS J. AHRENS

Seismological Laboratory, California Institute of Technology, Pasadena, California 91107

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A series of Born-Mayer-type calculations are used to calculate the lattice energies of simple oxides (MgO, BeO, CaO, and ZnO). Repulsion and other non-Coulombic contributions to the lattice energy are obtained using thermodynamic and recent ultrasonic data for the bulk moduli and the isothermal pressure and temperature derivatives of the elastic constants. Using thermochemical data for the heat of formation of MgO, CaO, and BeO and their cations, the heat of formation of O^{2-} , $\Delta H_f^\circ(O^{2-})$, is calculated to be 197 ± 5 kcal/mole. Using the largest value of $\Delta H_f^\circ(O^{2-})$, obtained for MgO, presumably the most ionic of the crystals treated, a value of 202.3 kcal/mole is obtained. These values are believed to be more accurate than earlier values given by Morris and by Huggins and Sakamoto who obtained 210 ± 6 and 221 ± 15 kcal/mole. The anomalously low value calculated for $\Delta H_f^\circ(O^{2-})$ for ZnO is believed to result from a substantial covalent contribution in the Zn-O bond in this oxide.

INTRODUCTION

The Born-Haber cycle can be used to calculate the heat of formation of essentially ionic crystals such as the alkali halides.^{1,2} In the case of the alkali halides (MX), the heat of formation is readily calculable because the relevant electron affinities ($X + e^- \rightarrow X^-$) are known. However, similar efforts for oxides (MO) have been less successful largely because an accurate value for the affinity of oxygen for two electrons ($O + 2e^- \rightarrow O^{2-}$) has not been available. Huggins and Sakamoto³ and Morris⁴ have calculated the heat of formation of the O^{2-} ion [$\Delta H_f^\circ(O^{2-})$] using enthalpies of formation of the cations and oxides and calculating the lattice energies of alkaline earth oxides and alkali

oxides, respectively. New bulk modulus measurements, only recently available, make it possible to substantially improve on the previous calculations.

CALCULATIONS

The two approaches to lattice energy calculations involve treating the oxides as groups and using a common repulsion parameter weighted by the constant energy radii (Huggins-Mayer⁵ approach) or individually evaluating the repulsion parameter from bulk modulus data (Born-Mayer approach¹). Previously, Huggins and Sakamoto³ used a Huggins-Mayer form for the repulsion energy and a resulting equation for the lattice energy of the form:

$$W_L = -\frac{A_R q^2}{R} - \frac{C_R}{R^6} - \frac{D_R}{R^8} + c_+ - M \exp\left[\frac{(R_A + R_B - R)}{\rho}\right] + \frac{1}{2} M' \left\{ c_{--} \exp\left(\frac{(2R_B - k_2 R)}{\rho}\right) + c_{++} \exp\left(\frac{(2R_A - k_2 R)}{\rho}\right) \right\}, \quad (1)$$

where A_R is the Madelung constant, q^2 is product of the anion and cation charges, R is the nearest-neighbor distance, C_R and D_R are van der Waals dipole and quadrupole constants, c_{++} , c_{+-} , c_{--} are the overlap repulsion factors, M and M' are the number of closest unlike and like ions, r_A and r_B are the constant energy radii for the positive and negative ion, k_2 is the ratio of shortest distance between like neighbors to unlike neighbors, and ρ is a repulsion constant.

The heat of formation of O^{2-} is obtained from

$$\Delta H_f^\circ(O^{2-}) = \Delta H_f^\circ(\text{oxide}) - \Delta H_f^\circ(\text{cation}) - (W_L - 5RT). \quad (2)$$

* Contribution No. 1605, Division of Geological Sciences, California Institute of Technology, Pasadena, Calif.

¹ M. P. Tosi, *Solid State Phys.* **16**, 1 (1964).

² T. C. Waddington, *Advan. Inorg. Chem. Radiochem.* **1**, 157 (1959).

³ M. L. Huggins and Y. Sakamoto, *J. Phys. Soc. Japan* **12**, 241 (1957).

⁴ D. F. C. Morris, *Proc. Roy. Soc. (London)* **A242**, 116 (1957); *Acta Cryst.* **11**, 163 (1958); *J. Phys. Chem. Solids* **5**, 264 (1958).

In the absence of good bulk moduli for the oxides, except for MgO, they were not able to directly calculate an appropriate repulsion parameter, ρ , and thus assumed it to be either 0.333 Å as in alkali halides or 0.4 Å as in MgO. Using these values they obtained $\Delta H_f^\circ(O^{2-}) = 221 \pm 15$ kcal/mole. All of the uncertainty was ascribed to uncertainty in ρ . The various oxides gave different values for $\Delta H_f^\circ(O^{2-})$ and it was assumed that the largest was the true value. The lower values of $\Delta H_f^\circ(O^{2-})$ calculated by Huggins and Sakamoto for BeO, CaO, SrO, and BaO were largely accounted for by covalent bonding effects. Morris⁴ obtained the value 210 ± 6 kcal/mole from the oxides of Na, K, and Rb with $\rho = 0.333$ Å.

Precise data on bulk moduli based on ultrasonic measurements on single crystals or dense polycrystalline aggregates have recently been published for BeO,⁶

⁵ M. L. Huggins and J. E. Mayer, *J. Chem. Phys.* **1**, 643 (1933).

⁶ N. Soga, *J. Am. Ceram. Soc.* (to be published).

MgO,⁷ CaO,⁸ and ZnO.⁹ In addition to bulk moduli, the pressure and temperature derivatives of the bulk moduli were measured in the same experiments. The Debye temperatures for these oxides can be calculated from the same data. These results thus make it possible to employ a Born-type treatment¹ of the ionic and repulsion energy, coupled with a Mie-Gruneisen

equation of state for the thermal energy to calculate the lattice energies of these four simple oxides. Using a refined lattice energy calculation we can then hope to substantially increase the accuracy of the determination in $\Delta H_f^\circ(O^{2-})$.

The results discussed below were obtained by the following equations for lattice energy¹:

$$W_L = -\frac{A_R q^2}{R} \left(1 - \frac{\rho}{R}\right) - \frac{3V\alpha K}{R/\rho} \frac{W_{\text{vib}}}{C_V} - \frac{C_R}{R^6} \left(1 - \frac{6\rho}{R}\right) - \frac{D_R}{R^8} \left(1 - \frac{8\rho}{R}\right) + W_{\text{vib}}, \quad (3)$$

where W_L represents the energy at 298°K relative to the ion gas at 0°K. The quantity R/ρ is given by

$$\frac{R}{\rho} = \left[9VKF + 2\frac{A_R q^2}{R} + 42\frac{C_R}{R^6} + 72\frac{D_R}{R^8}\right] / \left[\frac{A_R q^2}{R} + 6\frac{C_R}{R^6} + 8\frac{D_R}{R^8} - 3V\alpha K \frac{W_{\text{vib}}}{C_V}\right], \quad (4)$$

where

$$F = 1 - \frac{W_{\text{vib}}}{C_V} \left[\frac{1}{K} \left(\frac{\partial K}{\partial T}\right)_P + \alpha \left(\frac{\partial K}{\partial P}\right)_T - \frac{2}{3}\alpha \right] + \frac{V\alpha^2 K}{C_V^2} \left[TC_V - W_{\text{vib}} - \frac{TW_{\text{vib}}}{C_V} \left(\frac{\partial C_V}{\partial T}\right)_V \right], \quad (5)$$

and K is the isothermal bulk modulus, ρ is the repulsive parameter, V is the molecular volume, α is the thermal expansivity, W_{vib} is the vibrational energy, C_V is the heat capacity at constant volume. The values of these parameters which we have used are given in Table I. W_{vib} , C_V , and $(\partial C_V/\partial T)_V$ were calculated from the Debye theory using the Debye temperature shown. Madelung constants are taken from the review article of Waddington,² C_R and D_R were taken from Huggins and Sakamoto³ for BeO, MgO, and CaO and were estimated by the authors for ZnO.

RESULTS

Values of W_L for BeO, MgO, CaO, and ZnO have been calculated using Eq. (3). The value for each term in Eq. (3) (except for W_{vib} which is negligible), as well as the total, is given in Table II. Note that the Coulombic contribution is about 120% of W_L while the repulsion contribution is about 20%. The effect of the other terms is very small. If we use the simple form

$$W_L = -(A_R q^2/R)[1 - (\rho/R)],$$

where

$$R/\rho = (9VRK/A_R q^2) + 2,$$

which is strictly appropriate only for a 0°K crystal with no zero-point energy and no van der Waals energy the values of W_L are only about 1 kcal/mole larger than those obtained by using Eqs. (3)–(5).

The value of $\Delta H_f^\circ(O^{2-})$ is obtained by substituting our result for W_L and the appropriate thermochemical data (Table III) into Eq. (2). Also shown in the same table are the results of Huggins and Sakamoto.³

DISCUSSION

If, following Huggins and Sakamoto, we assume that the compound with the largest $\Delta H_f^\circ(O^{2-})$ is the most ionic then MgO is the most ionic and our best estimate of $\Delta H_f^\circ(O^{2-})$ will correspond to the result for MgO which is 202.3 kcal/mole. It follows that the lower values of $\Delta H_f^\circ(O^{2-})$ obtained for the other compounds reflect the effects of covalent bonding. These effects are -4.8 kcal/mole for BeO, -9.8 kcal/mole for CaO, and -25.4 kcal/mole for ZnO. These relative degrees of covalency are not as we would predict from a table of electronegativities such as that of Pauling.¹⁰ (The experimental lattice parameters and bulk moduli used in the calculations, are themselves affected by the presumably weak covalent bonds.)

Another approach would be to use the mean of the calculated values for $\Delta H_f^\circ(O^{2-})$ as our best estimate. In this case, the value calculated from ZnO should be excluded from the average because of the anomalous oxygen coordination of Zn^{2+} relative to its size. In ZnO, as in almost all other occurrences of Zn^{2+} in oxides, the Zn^{2+} (ionic radius 0.7 Å) is surrounded by only four oxygens whereas a well-behaved ion of the same size (e.g., MgO, 0.6 Å; Fe, 0.76 Å) will be surrounded by six oxygens. This coordination anomaly can be most easily explained by assuming that the ZnO bonds have a fairly large covalent character.) Upon averaging the results from CaO, MgO, and BeO gives $\Delta H_f^\circ(O^{2-}) = 197 \pm 5$ kcal/mole. This uncertainty reflects the spread in the calculated values and not the experimental uncertainty of the crystal data.

The foregoing discussion has ignored the effects of higher-order terms in the multipole expansion of the coulombic field at lattice sites. Such terms are not large

⁷ O. L. Anderson and P. Andreatch, Jr., *J. Am. Ceram. Soc.* **49**, 404 (1966).

⁸ N. Soga, *J. Geophys. Res.* **73**, 5385 (1968).

⁹ N. Soga and O. L. Anderson, *J. Appl. Phys.* **38**, 2985 (1967).

¹⁰ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N.Y., 1960).

TABLE I. Thermal, elastic, and structural data used to calculate lattice energies.

	Θ (°K)	$10^6\alpha$ (°K) ⁻¹	C_V cal/mole·°K	W_{vib} cal/mole	$(\partial C_V/\partial T)_V$ cal/mole·(°K) ²	
A. Thermal data						
BeO	1274	17.7 ^a	5.52	0.071	0.023	
MgO	941	31.5 ^b	7.58	0.164	0.021	
CaO	654	28.1 ^c	9.49	0.327	0.014	
ZnO	410	15.0 ^d	10.85	0.572	0.006	
B. Elastic data						
	K_T (Mb)	$(\partial K_T/\partial P)_T$	$(\partial K_T/\partial T)_P$ (10 ⁻³ Mb/°)			
BeO	2.157	5.5	-0.17			
MgO	1.599	4.52	-0.24			
CaO	1.049	5.26	-0.18			
ZnO	1.389	4.8	-0.15			
C. Structural data						
	Structure	V (Å ³)	R (Å)	A_R	C_R (10 ⁻⁶⁰ erg·cm ⁶)	D_R (10 ⁻⁷⁶ erg·cm ⁸)
BeO	Wurtzite	13.77	2.3968	2.3761	84.8	39.8
MgO	Halite	18.67	2.6529	2.2018	188	107.9
CaO	Halite	27.83	3.0304	2.2018	540	526.9
ZnO	Wurtzite	23.74	1.8740	2.4007	245.8	187.6

^a R. E. Fryxell and B. A. Chander, J. Am. Ceram. Soc. **47**, 283 (1964).^b G. K. White and O. L. Anderson, J. Appl. Phys. **37**, 430 (1966).^c B. J. Skinner, Geol. Soc. Am. Mem. **97**, 75 (1966).^d R. J. Beals and R. L. Cook, J. Am. Ceram. Soc. **40**, 279 (1957).

TABLE II. Lattice energy terms.

Crystal	Coulombic ^a (kcal/mole)	Repulsion ^b (kcal/mole)	Thermal ^c (kcal/mole)	van der Waals ^d (kcal/mole)	Lattice energy total (kcal/mole)
BeO	-1317.31	263.77	-0.16	1.62	-1052.1
MgO	-1102.80	197.27	-0.20	0.84	-904.9
CaO	-965.41	160.37	-0.06	0.32	-804.8
ZnO	-1109.88	187.58	-0.19	0.31	-922.2

^a $-A_R q^2/R$.^b $A_R q^2 \rho/R^2$.^c $-[3V\alpha K/(R/\rho)] (W_{\text{vib}}/C_V)$.^d $-(C_R/R^6) [1 - (6\rho/R)] - (D_R/R^8) [1 - (8\rho/R)]$.TABLE III. $\Delta H_f^\circ(\text{O}^{2-})$ at 298°K calculated from data for four oxides.

	ΔH_f° (oxide, crystal) ^a (kcal/mole)	ΔH_f° (cation, ideal gas) ^b (kcal/mole)	$(W_L - 5RT)^c$ (kcal/mole)	Total (kcal/mole)	ΔH_f° (Huggins and Sakamoto)	
					$\rho = 0.333$	$\rho = 0.40$
BeO	-143.1	714.4	-1055.0	197.5	228	172
MgO	-143.8	561.8	-907.9	202.3	237	206
CaO	-151.8	463.6	-807.7	192.5	233	208
ZnO	-83.3	664.9	-925.1	176.9

^a R. A. Robie and D. R. Waldbaum, Bull. Geol. Surv. **1968** 1259.^b F. D. Rossini, D. R. Wagman, W. H. Evans, S. Levine, and I. Jaffe,

Natl. Bur. Std. (U. S.) Circ. 500 (1952).

^c W_L from Table II. $5RT = 2.96$ kcal/mole at 298°K.

(see for example, Hafner and Raymond¹¹) but they could account for some of the differences between $\Delta H_f^\circ(\text{O}^{2-})$ derived for the several oxides.

The value of Huggins and Sakamoto³ for $\Delta H_f^\circ(\text{O}^{2-})$ is about 25 kcal/mole greater than our comparable value. Most of this discrepancy (15 kcal/mole) is due to their choice of repulsive parameter. But, even taking their values for the repulsive parameter, a difference of 10 kcal/mole remains. This difference must arise from their use of a Huggins-Mayer-type equation for the

¹¹ S. Hafner and M. Raymond, *J. Chem. Phys.* **49**, 3570 (1968).

lattice energy [Eq. (1)] whereas we have used a Born-Mayer-type equation [Eq. (3)]. The latter appears to us to be more suitable for use with the present data because the repulsion parameter can now be explicitly calculated from accurate bulk modulus data.

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Kerr Constant and Optical Anisotropy of Polymeric Chains

KAZUO NAGAI

Government Industrial Research Institute, Osaka, Midorigaoka 1, Ikeda, Osaka, Japan

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Theories of the Kerr constant K_m and the optical anisotropy $\langle(\Delta\gamma)^2\rangle$ of polymer molecules are developed on the basis of the additivity principle of bond polarizabilities and the rotational-isomeric-state approximation for rotations about skeletal bonds. Expressions are derived for both (i) polymer chains of finite length but of an arbitrary sequence of bonds and (ii) stereo-regular (or multirepeat) polymers of infinite length. The close similarity between K_m and $\langle(\Delta\gamma)^2\rangle$, and of them with the optical anisotropy $\Delta\Gamma$ of Kuhn's random link, is pointed out.

I. INTRODUCTION

The optical anisotropy $\langle(\Delta\gamma)^2\rangle$,¹ the molar Kerr constant K_m ,² and the optical anisotropy of Kuhn's random link $\Delta\Gamma$ (an equivalent to the stress-optical coefficient)^{2,3} are given, respectively, by

$$\langle(\Delta\gamma)^2\rangle = \frac{1}{2}[3 \text{Tr}\langle\gamma^2\rangle - \langle(\text{Tr}\gamma)^2\rangle], \quad (1)$$

$$K_m = (2\pi N_A/45kT) (3\langle\mathbf{u}^{\text{tr}}\gamma\mathbf{u}\rangle - \text{Tr}\langle\mathbf{u}^2\gamma\rangle) (kT)^{-1} \\ + [3 \text{Tr}\langle\gamma\gamma'\rangle - \langle(\text{Tr}\gamma)(\text{Tr}\gamma')\rangle], \quad (2)$$

and

$$\Delta\Gamma = \frac{1}{2}\langle r^2\rangle^{-1} (3\langle\mathbf{r}^{\text{tr}}\gamma\mathbf{r}\rangle - \text{Tr}\langle r^2\gamma\rangle), \quad (3)$$

where γ and γ' , respectively, are the optical and static polarizability tensors of a polymer chain; \mathbf{r} and \mathbf{u} , respectively, are the end-to-end and dipole-moment vectors with $r = |\mathbf{r}|$ and $u = |\mathbf{u}|$; N_A is the Avogadro number, k is the Boltzmann constant, T is the absolute temperature; Tr and the superscript tr, respectively, denote the trace and transpose of a tensor; and the averages refer to those on a polymer chain in the unperturbed state. As seen, these three quantities are very similar. The similarity would be closest when the

following rearrangement is made:

$$3\langle\mathbf{u}^{\text{tr}}\gamma\mathbf{u}\rangle - \text{Tr}\langle\mathbf{u}^2\gamma\rangle \equiv 3 \text{Tr}(\gamma\mathbf{u}\mathbf{u}^{\text{tr}}) \\ - \langle(\text{Tr}\gamma)(\text{Tr}\mathbf{u}\mathbf{u}^{\text{tr}})\rangle, \quad (4)$$

$$3\langle\mathbf{r}^{\text{tr}}\gamma\mathbf{r}\rangle - \text{Tr}\langle r^2\gamma\rangle \equiv 3 \text{Tr}(\gamma\mathbf{r}\mathbf{r}^{\text{tr}}) - \langle(\text{Tr}\gamma)(\text{Tr}\mathbf{r}\mathbf{r}^{\text{tr}})\rangle. \quad (5)$$

We note that $\mathbf{r}\mathbf{r}^{\text{tr}}$ and $\mathbf{u}\mathbf{u}^{\text{tr}}$ are a kind of tensors, i.e., dyadic tensors.

In a previous paper⁴ we have derived two types of expression for $\Delta\Gamma$: (i) one for polymer chains of finite length but of an arbitrary sequence of bonds and (ii) the other for stereo-regular polymers of infinite length. Stereo-irregular polymers can be treated only through the former expression, while stereo-regular polymers can be handled more effectively through the latter expression. Both expressions were derived on the basis of the following two assumptions: the additivity principle of bond polarizabilities and the rotational-isomeric-state approximation for rotations about skeletal bonds.

In this paper we derive two types of expressions, (i) and (ii) above, for $\langle(\Delta\gamma)^2\rangle$ and K_m , based on the same assumptions as in the case of $\Delta\Gamma$. Flory and his co-

¹ K. Nagai, *J. Chem. Phys.* **47**, 4690 (1967).

² K. Nagai and T. Ishikawa, *J. Chem. Phys.* **43**, 4508 (1965).

³ K. Nagai, *J. Chem. Phys.* **40**, 2818 (1964).

⁴ K. Nagai, *J. Chem. Phys.* **47**, 2052 (1967).