Heat of Formation of O$^-$

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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$^-$,$\Delta H_f^o$(O$^-$), is calculated to be 197±5 kcal/mole. Using the largest value of $\Delta H_f^o$(O$^-$), 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 $\Delta H_f^o$(O$^-$) 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. In the case of the alkali halides (MX), the heat of formation is readily calculable because the relevant electron affinities (X$^-$+$e^-$→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$^2-$+$2e^-$→O$^-$) has not been available. Huggins and Sakamoto and Morris have calculated the heat of formation of the O$^-$ ion [$\Delta H_f^o$(O$^-$)] 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–Mayer approach) or individually evaluating the repulsion parameter from bulk modulus data (Born–Mayer approach). Previously, Huggins and Sakamoto used a Huggins–Mayer form for the repulsion energy and a resulting equation for the lattice energy of the form:

$$W_L = -\frac{A_{R_T^2}}{R} - \frac{C_R}{R^6} - \frac{D_R}{R^8} + c_{+} + c_{-} M \exp \left[ \frac{(R_A+R_B-R)}{\rho} \right]$$

$$+ \frac{1}{2} M' \left( c_{-} \exp \left( \frac{(2R_B-k_2R)}{\rho} \right) + c_{+} \exp \left( \frac{(2R_A-k_2R)}{\rho} \right) \right),$$

(1)

where $A_{R_T^2}$ 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, $c_{+}$, $c_{-}$, $c_{+}$, and $c_{-}$ 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 $\rho$ is a repulsion constant.

The heat of formation of O$^-$ is obtained from

$$\Delta H_f^o(O^-) = \Delta H_f^o(\text{cation}) - (W_L - 5RT).$$

(2)

In the absence of good bulk moduli for the oxides, except for MgO, they were not able to directly calculate an appropriate repulsion parameter, $\rho$, 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 $\Delta H_f^o(\text{O}^-) = 221±15$ kcal/mole. All of the uncertainty was ascribed to uncertainty in $\rho$. The various oxides gave different values for $\Delta H_f^o(\text{O}^-)$ and it was assumed that the largest was the true value. The lower values of $\Delta H_f^o(\text{O}^-)$ calculated by Huggins and Sakamoto for BeO, CaO, SrO, and BaO were largely accounted for by covalent bonding effects. Morris 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.

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MgO, CaO, and ZnO. 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 treatment 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 of \( \Delta H_f^\circ(O^{2-}) \).

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

\[
W_L = -\frac{A_{eq}^2}{R} \left( \frac{1}{R} - \frac{\rho}{R} \right) - \frac{3V\alpha K}{R} \frac{W_{\text{vib}}}{C_v} - \frac{C_r}{R^6} \left( \frac{1}{R} - \frac{6\rho}{R} \right) - \frac{D_r}{R^8} \left( \frac{1}{R} - \frac{8\rho}{R} \right) + W_{\text{vib}},
\]

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

\[
\frac{R}{\rho} = \left[ \frac{9V\alpha K + 2A_{eq}^2}{R} + 42 \frac{C_r}{R^6} + 72 \frac{D_r}{R^8} \right] \left/ \left[ \frac{A_{eq}^2}{R} + \frac{6C_r}{R^6} + \frac{8D_r}{R^8} - 3V\alpha K \frac{W_{\text{vib}}}{C_v} \right] \right.
\]

where

\[
F = 1 - \frac{W_{\text{vib}}}{C_v} \left[ \frac{1}{K} \frac{\partial K}{\partial T} \right] + \frac{\alpha}{K} \left( \frac{\partial K}{\partial P} \right)_T - \frac{\beta}{K} \left( \frac{\partial K}{\partial T} \right)_P + \frac{\alpha}{C_v^2} \left[ T \frac{\partial C_v}{\partial T} - \frac{W_{\text{vib}}}{C_v} \left( \frac{\partial C_v}{\partial T} \right)_P \right],
\]

and \( K \) is the isothermal bulk modulus, \( \rho \) is the repulsive parameter, \( V \) is the molecular volume, \( \alpha \) is the thermal expansivity, \( W_{\text{vib}} \) 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. \( W_{\text{vib}}, C_v, \) 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, \( C_r \) and \( D_r \) were taken from Huggins and Sakamoto 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 \( W_{\text{vib}} \) 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

\[
W_L = -\frac{A_{eq}^2}{R} \left[ 1 - \frac{\rho}{R} \right],
\]

where

\[
R/\rho = \left[ 9V\alpha K + 2A_{eq}^2 \right] + 2,
\]

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.

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

\[
-4.8 \text{ kcal/mole for BeO}, \quad -9.8 \text{ kcal/mole for CaO}, \quad \text{and} \quad -25.4 \text{ kcal/mole for ZnO}.
\]

These relative degrees of covalency are not as we would predict from a table of electronegativities such as that of Pauling (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 \( \Delta H_f^\circ(O^{2-}) = 197 \pm 5 \text{ kcal/mole} \). 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

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2. N. Soga, J. Geophys. Res. 73, 5353 (1968).
### Table I. Thermal, elastic, and structural data used to calculate lattice energies.

<table>
<thead>
<tr>
<th></th>
<th>Ω (°K)</th>
<th>10Ων (°K)⁻¹</th>
<th>Cv cal/mole °K⁻¹</th>
<th>W_vib cal/mole</th>
<th>(∂Cv/∂T)_v cal/mole °K⁻² (°K)²⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>1274</td>
<td>17.7</td>
<td>5.52</td>
<td>0.071</td>
<td>0.023</td>
</tr>
<tr>
<td>MgO</td>
<td>941</td>
<td>31.5</td>
<td>7.58</td>
<td>0.164</td>
<td>0.021</td>
</tr>
<tr>
<td>CaO</td>
<td>654</td>
<td>28.1</td>
<td>9.49</td>
<td>0.327</td>
<td>0.014</td>
</tr>
<tr>
<td>ZnO</td>
<td>410</td>
<td>15.0</td>
<td>10.85</td>
<td>0.572</td>
<td>0.006</td>
</tr>
</tbody>
</table>

**A. Thermal data**

<table>
<thead>
<tr>
<th></th>
<th>K_T (Mb)</th>
<th>(∂K_T/∂P)_T (10⁻³ Mb⁻¹)</th>
<th>(∂K_T/∂T)_T (10⁻³ Mb⁻² °K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>2.157</td>
<td>5.5</td>
<td>-0.17</td>
</tr>
<tr>
<td>MgO</td>
<td>1.599</td>
<td>4.52</td>
<td>-0.24</td>
</tr>
<tr>
<td>CaO</td>
<td>1.049</td>
<td>5.26</td>
<td>-0.18</td>
</tr>
<tr>
<td>ZnO</td>
<td>1.389</td>
<td>4.8</td>
<td>-0.15</td>
</tr>
</tbody>
</table>

**B. Elastic data**

<table>
<thead>
<tr>
<th>Structure</th>
<th>V (Å³)</th>
<th>R (Å)</th>
<th>A_V (10⁻⁶ erg·cm⁻³)</th>
<th>D_H (10⁻⁶ erg·cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>13.77</td>
<td>2.3968</td>
<td>84.8</td>
<td>39.8</td>
</tr>
<tr>
<td>MgO</td>
<td>18.67</td>
<td>2.6529</td>
<td>188</td>
<td>107.9</td>
</tr>
<tr>
<td>CaO</td>
<td>27.83</td>
<td>3.0304</td>
<td>540</td>
<td>526.9</td>
</tr>
<tr>
<td>ZnO</td>
<td>23.74</td>
<td>1.8740</td>
<td>245.8</td>
<td>187.6</td>
</tr>
</tbody>
</table>

**C. Structural data**

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### Table II. Lattice energy terms.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Coulombic (kcal/mole)</th>
<th>Repulsion (kcal/mole)</th>
<th>Thermal (kcal/mole)</th>
<th>van der Waals (kcal/mole)</th>
<th>Lattice energy total (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>-1317.31</td>
<td>263.77</td>
<td>-0.16</td>
<td>1.62</td>
<td>-1052.1</td>
</tr>
<tr>
<td>MgO</td>
<td>-1102.80</td>
<td>197.27</td>
<td>-0.20</td>
<td>0.84</td>
<td>-904.9</td>
</tr>
<tr>
<td>CaO</td>
<td>-965.41</td>
<td>160.37</td>
<td>-0.06</td>
<td>0.32</td>
<td>-804.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>-1109.88</td>
<td>187.58</td>
<td>-0.19</td>
<td>0.31</td>
<td>-922.2</td>
</tr>
</tbody>
</table>

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### Table III. ΔH_f^°(O^°) at 298K calculated from data for four oxides.

<table>
<thead>
<tr>
<th></th>
<th>ΔH_f^°(oxide, crystal) (kcal/mole)</th>
<th>ΔH_f^°(cations, ideal gas) (kcal/mole)</th>
<th>(W_vib - 5RT) c</th>
<th>Total (kcal/mole)</th>
<th>ΔH_f^° (Huggins and Sakamoto)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>-143.1</td>
<td>714.4</td>
<td>-1055.0</td>
<td>197.5</td>
<td>228</td>
</tr>
<tr>
<td>MgO</td>
<td>-143.8</td>
<td>561.8</td>
<td>-907.9</td>
<td>202.3</td>
<td>237</td>
</tr>
<tr>
<td>CaO</td>
<td>-151.8</td>
<td>463.6</td>
<td>-807.7</td>
<td>192.5</td>
<td>233</td>
</tr>
<tr>
<td>ZnO</td>
<td>-83.3</td>
<td>664.9</td>
<td>-925.1</td>
<td>176.9</td>
<td>208</td>
</tr>
</tbody>
</table>

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W_ν from Table II. SRT = 2.96 kcal/mole at 298K.

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(see for example, Hafner and Raymond\textsuperscript{11}) but they
could account for some of the differences between
\(\Delta H_p^o(\text{O}^{2-})\) derived for the several oxides.

The value of Huggins and Sakamoto\textsuperscript{3} for \(\Delta H_p^o(\text{O}^{2-})\)
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
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.

\textbf{ACKNOWLEDGMENTS}

We have profited from discussion of these calculations
with D. L. Anderson and W. B. Kamb. This research
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\textbf{Kerr Constant and Optical Anisotropy of Polymeric Chains}

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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.

\textbf{I. INTRODUCTION}

The optical anisotropy \(\langle(\Delta\gamma)^2\rangle\),\textsuperscript{1} the molar Kerr
constant \(K_m\),\textsuperscript{2} and the optical anisotropy of Kuhn's
random link \(\Delta\Gamma\) (an equivalent to the stress-optical
coefficient)\textsuperscript{3,4} are given, respectively, by

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

\begin{equation}
K_m = \frac{2\pi N_A}{45kT}\left[3 \langle uu^\alpha y u\rangle - \langle Tr(u^2\gamma)\rangle\left( kT \right)^{-1}\right]
+ \left[3 \text{Tr}(\gamma y\gamma') - \langle(\text{Tr}\gamma)(\text{Tr}\gamma')\rangle\right] ,
\end{equation}

and

\begin{equation}
\Delta\Gamma = \frac{1}{2} (r^2)^{-1} (3 \langle rr^\alpha r\rangle - \langle Tr(r^2\gamma)\rangle) ,
\end{equation}

where \(\gamma\) and \(\gamma'\), respectively, are the optical and static
polarizability tensors of a polymer chain; \(r\) and \(u\),
respectively, are the end-to-end and dipole-moment
vectors with \(r = \mid r\mid\) and \(u = u\); \(N_A\) 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

\textsuperscript{1} K. Nagai, J. Chem. Phys. 47, 4690 (1967).

following rearrangement is made:

\begin{equation}
3 \langle uu^\alpha y u\rangle - \langle Tr(u^2\gamma)\rangle = 3 \text{Tr}(\gamma uu^\alpha u) - \langle(Tr\gamma)(Tr uu^\alpha u)\rangle ,
\end{equation}

\begin{equation}
3 \langle rr^\alpha r\rangle - \langle Tr(r^2\gamma)\rangle = 3 \text{Tr}(\gamma rr^\alpha r) - \langle(Tr\gamma)(Tr rr^\alpha r)\rangle .
\end{equation}

We note that \(rr^\alpha r\) and \(uu^\alpha u\) are a kind of tensors, i.e.,
dyadic tensors.

In a previous paper\textsuperscript{1} 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-

\textsuperscript{1} K. Nagai, J. Chem. Phys. 47, 4690 (1967).