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CRYSTAL ENERGIES FOR SOME TRANSITION METAL OXIDES

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UCRL-3138
Chemistry Distribution

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Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

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September 1955

Printed for the U.S. Atomic Energy Commission

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ABSTRACT

The lattice energies of some transition metal oxides have been calculated using the Born-Haber cycle and compared with theoretical values.

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INTRODUCTION

Ionic crystal energies can be expressed in terms of a relatively simple theory because of the importance of the well-understood Coulomb forces in the over-all interionic interactions. The alkali halides have received a great deal of attention, and the agreement obtained between theory and experiment is excellent. On the other hand, very little has been done with the transition metal oxides; consequently some of the necessary data for a complete theoretical treatment of these compounds is lacking. The purpose of this paper is to review briefly the simple theory of Born and two other more complete theories, calculate the lattice energies of several bivalent mono-oxides from these theories, and then compare these calculated energies to the experimental energies found from using the Born-Haber thermochemical cycle.

CALCULATION OF THEORETICAL LATTICE ENERGIES

The Born Theory of Ionic Crystals[4]

The lattice energy of an ionic crystal is the energy change involved in bringing the constituent ions (infinitely separated initially) to their respective positions in the crystal lattice. At large ionic separations the only significant force in operation between ions is the Coulomb interaction. At shorter ionic separations the outer electron shells begin to overlap and this gives rise to a repulsive force. At the equilibrium distance (i.e., in the stable crystal lattice) this repulsive force just balances the Coulombic attraction between unlike ions. Assuming for this case that the repulsive force is proportional to r^{-n} we have for the potential between ions

$$V_{1,2} = -\frac{e^2 z_1 z_2}{r_{1,2}} + \frac{b}{r_{1,2}^n}, \tag{1}$$

where e is the electronic charge, z is ionic charge, r is the ionic separation between ions 1 and 2, b and n are constants. The potential energy per unit cell can be written

$$V = -\frac{e^2 z^2 A}{r} + \frac{B}{r^n}, \tag{2}$$

where A is the Madelung constant depending only on the structure of the crystal.

Differentiating Eq. (2) with respect to r and equating to zero (since at equilibrium $dv/dr = 0$ at $r = r_o$),

$$\frac{dV}{dr} = \frac{e^2 z^2 A}{r_o^2} - \frac{B}{r_o^{n+1}} = 0 \quad . \tag{3}$$

Solving for B,

$$B = \frac{e^2 z^2 A r_o^{n-1}}{n} \quad . \tag{4}$$

Substituting this in Eq. (2) and expressing the potential for a crystal in equilibrium,

$$V = -\frac{e^2 z^2 A}{r_o} \left(1 - \frac{1}{n}\right) \tag{5}$$

The lattice energy per mole is

$$U_o = -N_oV = \frac{e^2 z^2 AN_o}{r_o}\left(1 - \frac{1}{n}\right). \qquad (6)$$

This equation was originally derived by Born and Lande.[2]

In evaluating the lattice energies the following constants were used:

$e = 4.80223 \times 10^{-10}$ e.s.u. = electronic charge,

$z = 2$ = charge on each ion,

$A_a = 3.495115$ = Madelung's constant for NaCl type crystal,

$N_o = 6.0238 \times 10^{23}$ = Avogadro's number,

$n = 8$ = repulsive factor.[7]

Substitution of these constants into the equation and converting into kcal gives

$$U_o = \frac{4061.6}{a_o} \text{ kcal}, \qquad (7)$$

where a_o is the length of the edge of the cubic unit of crystal structure in angstroms.[8]

Table I

Calculated Lattice Energies from Born Equation

Crystal	a_o	U_o (calculated)	U* Born-Haber Cycle	$U - U_o$
CaO	4.797	846.7	858	11
TiO	4.235	959.1	957	-2
VO	4.10	990.1	966	-24
MnO	4.4345	915.9	941	25
FeO	4.332	937.6	967	29
CoO	4.24	957.9	984	26
NiO	4.1684	974.4	1,003.8	29

*Electron affinity of $O + 2e = O^{--}$ taken as -187.6 kcal (See Table III and Fig. 1).

More Refined Methods

(1) Using Repulsive Energy as an Exponential Law

In deriving Eq. (6) it was assumed that the repulsive energy was proportional to r^{-n}. Quantum mechanics has shown that the repulsion due to the interpenetration of electronic clouds follows an exponential law of the form $be^{-r/\rho}$. Substituting this into Eq. (2) for B/r^n one obtains

$$V = -\frac{e^2 z^2 A}{r} + b\, e^{-r/\rho} \quad . \qquad (8)$$

Differentiating and equating to zero as before leads to the equation

$$b\, e^{-r_o/\rho} = \frac{e^2 z^2 A \rho}{r_o^2} \quad . \qquad (9)$$

Substituting this into Eq. (8) and multiplying by $-N_o$, one obtains for the lattice energy

$$U_o = \frac{e^2 z^2 A N}{r_o} \left(1 - \frac{\rho}{r_o}\right) \quad . \qquad (10)$$

Using the same constants as before with the additional constant $\rho = 0.345$,[1] Eq. (10) becomes

$$U_o = \frac{2320}{r_o} \left(1 - \frac{0.345}{r_o}\right) \quad . \qquad (11)$$

Table II

Calculated Lattice Energies from Eq. (11)

Crystal	r_o	$1 - 0.345/r_o$	U_o	U* Born-Haber Cycle	$U - U_o$
CaO	2.39	0.856	833	858	25
TiO	2.12	0.837	916	957	41
VO	2.05	0.832	940	966	26
MnO	2.20	0.843	890	941	51
FeO	2.15	0.840	907	967	60
CoO	2.12	0.837	917	984	67
NiO	2.08	0.834	934	1,004	70

*Electron affinity of $O + 2e = O^{--}$ taken as -187.6 kcal (See Fig. 2).

(2) Including van der Waals' Forces and Zero-Point Energy

A more accurate theory of lattice energies would take into account van der Waals' forces and zero-point vibrational energy in addition to the Coulombic and repulsive energies treated above. However, the calculation of van der Waals' forces (London forces) requires the polarizabilities of the ions involved, and for the most part these are not available for the +2 ions of the transition series. Another difficulty arises when these additional terms are added, and that is in the calculation of the repulsive energy, since differentiating and equating to zero no longer produces a

simple expression. It is necessary to take the second derivative and relate it to the compressibility, another physical property that is difficult to obtain, for the transition metal oxides. The data are readily available for CaO, so a calculation of the lattice energy of CaO will be made which includes a term for the van der Waals' force and another term for the zero-point energy. The potential energy for CaO per ion pair is given by the expression

$$V = -\frac{A\,z^2\,e^2}{r} - \frac{C}{r^6} + 6\,b\,e^{-r/\rho} \quad . \tag{12}$$

Each term in Eq. (10) will be evaluated separately.

First term: This is just the electrostatic potential between ions in a crystal lattice. The value of r for CaO = 2.40 when $A_r = 1.747$;

$$\frac{A\,z^2\,e^2}{r} = 67.2 \times 10^{-12} \text{ ergs} = 966 \text{ kcal/mole.}$$

Second term: The constant C is subdivided[3] into $6.595\,c_{+-} + 1.807\,(c_{++} + c_{--})/2$ where c_{+-}, c_{++}, c_{--} are obtained from London's Equation, $C_{A_1B_1} = \frac{3}{2}\,\alpha_A\,\alpha_B\left(\frac{I_A\,I_B}{I_A+I_B}\right)$, α is polarizability, and I is ionization potential.

For Ca^{++}, $\alpha_A = 0.4725 \times 10^{-24}$ cc^5,

$I_A = 81.5 \times 10^{-12}$ ergs.

For O^{--}, $\alpha_B = 3.92 \times 10^{-24}$ cc^5,

$I_B = 8.0 \times 10^{-12}$ ergs .

So that $c_{+-} = 20.21 \times 10^{-60}$ erg cm, $c_{++} = 13.65 \times 10^{-60}$ erg cm, $c_{--} = 92.1 \times 10^{-60}$ erg cm, $C = 228.8 \times 10^{-60}$ erg cm.

$$\frac{C}{r^6} = 1.197 \times 10^{-12} \text{ ergs} = 17.2 \text{ kcal/mole}$$

Third term: Differentiating and equating to zero, one obtains from Eq. (12)

$$\frac{d\,V}{d\,r} = \frac{A\,z^2\,e^2}{r^2} + \frac{6\,C}{r^7} - \frac{6\,b}{\rho}\,e^{-r/\rho} = 0 \quad . \tag{13}$$

Taking the second derivative and relating to compressibility

$$\frac{d^2V}{d\,r^2} = -\frac{2\,A\,z^2\,e^2}{r^3} - \frac{42\,C}{r^8} + \frac{6\,b}{\rho^2}\,e^{-r/\rho} = \frac{18\,A}{\beta}\,. \qquad (14)$$

This gives two equations to evaluate b and ρ. Rearranging and combining:

$$\rho = \frac{\left[\frac{A\,e^2}{r^2} + \frac{6\,C}{r^7}\right]}{\left[\frac{18r}{\beta} + \frac{2Ae^2}{r^3} + \frac{42C}{r^8}\right]}, \qquad (15)$$

and

$$6\,b\,e^{-r/\rho} = \rho\left(\frac{A\,e^2}{r^2} + \frac{6\,C}{r^7}\right). \qquad (16)$$

β for CaO $\cong 0.75 \times 10^{-12}$ cm^2/dyne. After straightforward calculating it is found that $\rho = 0.346 \times 10^{-8}$ cm, which is in good agreement with Kapustinsky's[1] value.

$$6\,b\,e^{-r/} = 8.65 \times 10^{-12} \text{ ergs} = 124.2 \text{ kcal/mole}.$$

The remaining factor to be calculated is the zero-point vibrational energy, which is equal to $9/8\ R\Theta_o$ where Θ_o = Debye temperature. From low-temperature heat-capacity curves Θ_o is calculated to be roughly 550°.[6]

$$9/8\ R\Theta_o = 9/8 \times 1.987 \times 550 = 1.2 \text{ kcal/mole}.$$

Total lattice energy for CaO:

Term	Value (kcal/mole)
Electrostatic $\frac{A\,z^2\,e^2\,N_o}{r}$	966
van der Waals' C/r^6	17.2
Repulsive $-66\,e^{-r/\rho}$	-124.2
Zero-Pt. Vt. $-9/8\ R\Theta_o$	- 1.2
	U = 857.8 kcal/mole

This value would agree with the experimental value computed from the Born-Haber cycle if an electron affinity of oxygen of -187.6 kcal were accepted. There is no direct measurement of this quantity.

EXPERIMENTAL LATTICE ENERGIES

Born-Haber Cycle[4]

In order to relate the lattice energy of an ionic crystal to known thermochemical quantities Born and Haber devised their famous cycle, which is similar to the one following (shown for a bivalent oxide):

$$\begin{array}{ccccc}
M^{++}_{(g)} & + & O^{=}_{(g)} & \longrightarrow & M\,O_{(s)} \\
\uparrow I & & \uparrow -E & & \downarrow +Q \\
M_{(g)} & + & O_{(g)} & \xleftarrow{S+D} & M_{(s)} + 1/2\ O_{2(g)}.
\end{array}$$

Equation	ΔH
$M^{++}_{(g)} + O^{=}_{(g)} = MO_{(s)}$	$-U$ = -lattice energy
$MO_{(s)} = M_{(s)} + 1/2\ O_{2(g)}$	$+Q$ = +heat of formation
$M_{(s)} = M_{(g)}$	S = heat of sublimation
$1/2\ O_{2(g)} = O_{(g)}$	D = heat of dissociation
$M_{(g)} = M^{++}_{(g)} + 2e^{-}$	I = ionization energy
$O_{(g)} + 2e = O^{=}_{(g)}$	$-E$ = -electron affinity

Since this is a closed cycle the net energy change is zero and

$$U = Q + S + D + I - E. \tag{17}$$

In Table III, E = -187.6 kcal derived from the CaO calculations above has been assumed.

Data and Calculations

Table III

Summary of Data and Calculations (all values are in kcal/mole)

Crystal	Q	S	D	I	U + E	U
CaO	150.65	42.3	59.55	417.65	670.2	857.8
TiO	123.9	113.2	59.55	473.16	769.8	957.4
VO	99.5	122.7	59.55	496.34	778.1	965.7
MnO	92.05	66.73	59.55	535.06	753.4	941.0
FeO	63.8	97.9	59.55	558.31	779.6	967.2
CoO	57.1	102.0	59.55	577.45	796.1	983.7
NiO	57.3	101.75	59.55	597.58	816.2	1,003.8

The heats of formation of the oxides are from Coughlin.[9] The heats of sublimation are from Brewer.[10] The value of $D(O_2)$ is from Brix and Herzberg.[11] The I values are from Moore.[12] Where necessary, all values have been converted to 298.15°K. Thus the experimental values of U given in Table III are for 298°K. Whereas the theoretical values from Eqs. (7) and (11) do not include the increase in heat content due to vibrational excitation upon heating from 0°K to 298°K. However, the total increase in heat content for TiO, for example, upon heating from 0°K to 298°K is only 1.475 kcal, of which some is associated with the thermal expansion and stretching of bonds. Thus the lattice constants at 298°K were used in Eqs.(7) and (11) and all results compared at 298°K without correction for vibrational contribution other than the zero-point contribution in the CaO calculation.

DISCUSSION OF RESULTS

In Fig. 1 is plotted the difference between the experimental and the calculated lattice energies (using Eq. (7)) against increasing atomic number of the metal ion. It was expected that the energy difference would be positive for TiO and VO, coming to a minimum at MnO, and going through another maximum for the others as has been found for the aqueous ions and other compounds of these elements.[13] The answer could be in the choice of the repulsive factor n or perhaps in the lattice constant a_o for VO and TiO. The lattice constants could be in error due to nitrogen or carbon impurities or non-stoichiometric compositions. The crystal energy is considerably changed by a small change in n. If n is given values of 8 for CaO, 7 for TiO, 6 for VO, 8 for MnO, 8 for FeO, 7.5 for CoO, and 8 for NiO, the entire picture is changed to one that is reasonable; n has been related to compressibility[3] by the equation $(n - 1) = Kr^4/\beta$ where K is a constant, including the electronic charge and Madelung's constant, et cetera, r is interionic distance and β is compressibility. In calculating lattice energies from Eq. (7), n was taken as 8 for all the oxides as suggested by Sherman.[7] Substituting known values for r and approximating β one obtains a set of values for n that appear to be quite reasonable with those previously given empirically (i.e., there is a minimum for the n value of VO and a maximum value for CaO).

Fig. 2 shows the difference between experimental and calculated lattice energies using Eq. (11) with the repulsive term as an exponential. The general form of the graph is much more reasonable, but the large deviations found with the heavier transition metals are not as good. This is probably because these heavier oxides are not so ionic as the lighter oxides.

It appears that no simple theory gives a precise explanation of the variation of heats of formation of the transition metal oxides. It would be valuable to obtain spectral data for the splitting of the electronic levels of the transition metal ions in the oxide crystal fields and then by difference obtain some values for the repulsive contributions to the lattice energy.

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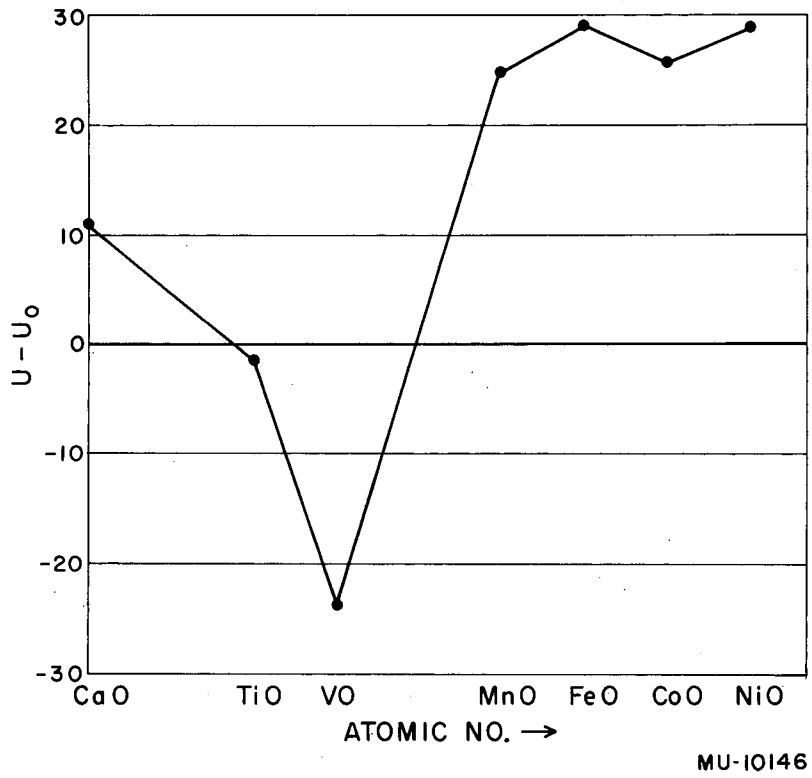

Figure 1. Differences in lattice energies in kcals found experimentally and calculated from Eq. (7) with repulsive force $\alpha\ 1/r^n$.

$$U_o = \frac{A\ N\ z^2\ e^2}{r}\ (1 - 1/n);\quad n = 8$$

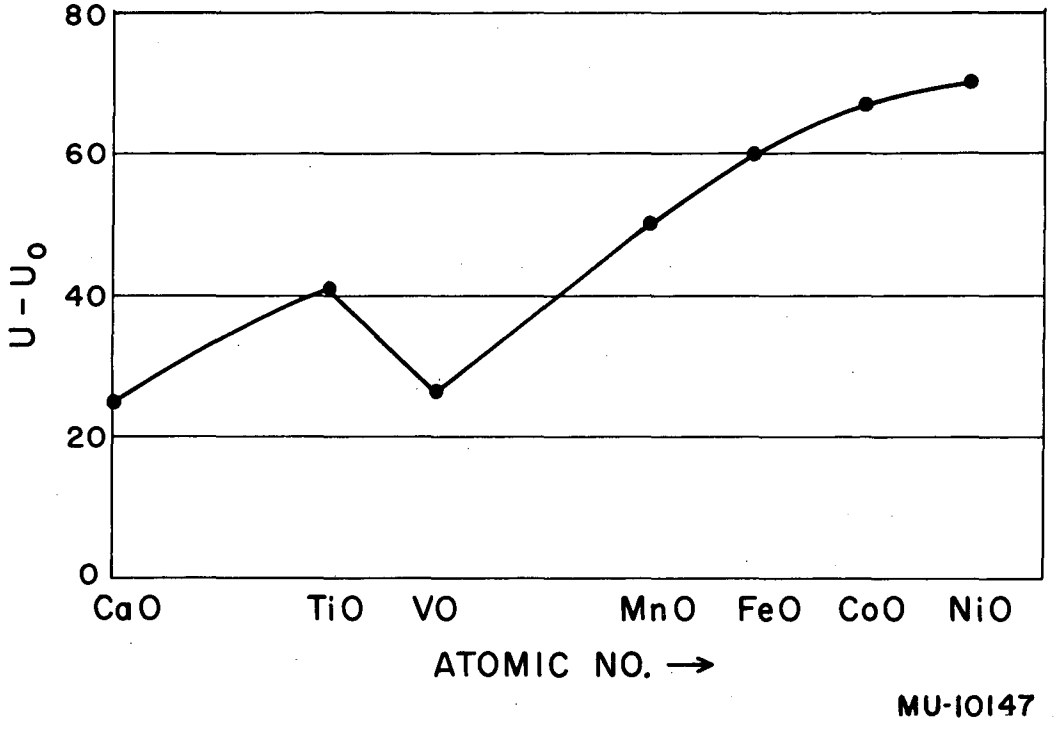

Figure 2. Differences in lattice energy in kcals found experimentally and calculated by Eq. (11) with repulsive force $\alpha\ e^{-r/e}$.

$$U_o = \frac{A\ N_o\ z^2\ e^2}{r_o} \quad (1 - \rho/r_o)$$