LATTICE ENERGIES AND THEIR SIGNIFICANCE IN INORGANIC CHEMISTRY

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I. General Introduction and Account of the Born-Haber Cycle

This review article gives an account of the calculation of the lattice energies of ionic solids, the results of such calculations for a large number of salts and the application of these results and calculations to some problems in inorganic chemistry. No attempt has been made to deal with the many important topics, involving lattice energy calculations or calculations of a similar type, which lie outside the region of inorganic chemistry. Examples of such topics are the calculation of the surface energies of crystals, the energies of formation and of movement of point defects in ionic solids and the crystal spectra of ionic solids.

The last comprehensive review of lattice energy calculations was produced by Sherman (*114*) in 1932. Since then no extensive review of results and calculations has been undertaken, though there have been several accounts of various aspects of the subject. Pritchard (*108*) in his review of values of electron affinities has discussed a number of lattice energies. Kapustinskii (*67*) has given a brief and uncritical account of the work of the Russian school in this field. There is an excellent chapter on the calculation of the lattice energies of the alkali halides in Seitz's (*113*) book, and Partington (*103*) has given an account of some methods of calculating Madelung constants. Born and Huang (*17*) have given a very full description of the Ewald (*37*) method of obtaining these constants.

Historically the quantitative theory of ionic crystals was developed between 1918 and 1924 by Born (*14*), Born and Lande (*19, 20*), Madelung (*88*) and Haber. In particular Born devised formulae which permit the calculation of the lattice energy of an ionic crystal. The lattice energy of such a crystal may be defined as the increase in internal energy at ab-

solute zero accompanying the separation of the constituent ions to positions where they are infinitely removed from one another. In order to account for the stability of crystals known to be composed of ions it is necessary to introduce forces between the ions that are noncoulombic, for no stable equilibrium is possible in an electrostatic system of charges unless other forces are present.

The history of the development of the theory of lattice energies is largely an account of the development of the ideas about these noncoulombic forces. Though they are discussed in detail in Section II it is convenient to summarize the various expressions for the lattice energy involving these forces that have been developed and to designate them by the names that will be used for them in later sections.

(a) Born-Lande or Born Equations

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r} - \frac{N_A B}{r^n}. \tag{1}$$

Here N_A is Avogadro's number, M is the Madelung constant, z_1 and z_2 are the valencies of the ions, e is the charge on the electron, r is the distance between unlike ions, and B is a constant. If the fact that at the equilibrium distance r_0 of the ions in the crystal $(\partial U/\partial r)_{r=r_0} = 0$ is utilized then

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r_0}\left(1 - \frac{1}{n}\right). \tag{2}$$

(b) Simple Born-Mayer Equation

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r} - N_A B' e^{-r/\rho}. \tag{3}$$

Here B' is another constant and ρ has the dimensions of a length. Again if $(\partial U/\partial r)_{r=r_0} = 0$ is utilized

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r_0}(1 - \rho/r_0). \tag{4}$$

(c) Extended Born-Mayer Equation

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r} - N_A B' e^{-r/\rho} + N_A C/r^6 + \frac{9}{4} N_A h\nu_{\max}. \tag{5}$$

Here $N_A C/r^6$ and $(9/4)N_A h\nu_{\max}$ are terms introduced to allow for the induced dipole-induced dipole forces in the lattice and for the zero point energy of the lattice respectively.

(d) Huggins Treatment

This treatment is similar to the extended Born-Mayer except that adjusted crystal "basic" radii are used to obtain B' and optical data on the crystal itself to obtain C.

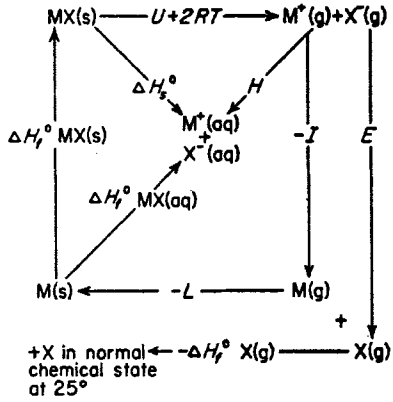
(e) Ladd and Lee's Equation

Because of the difficulty of assigning basic radii in many salts, $(\partial U/\partial r)_{r=r_0} = 0$ is used and the expression

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r_0}(1 - \rho/r_0) - N_A C/r_0^6(1 - 6\rho/r_0) - \frac{N_A D}{r_0^8}(1 - 8\rho/r_0) + \frac{9}{4}N_A h\nu_{max} \quad (6)$$

is derived.

Quite apart from its theoretical calculation, by the use of one of the expressions developed above, it is possible to relate the lattice energy of an ionic crystal to various measurable thermodynamic quantities by means of a simple Hess's law cycle. This cycle was first proposed and used by Born (*15*) and represented in its familiar graphical form by Haber (*48*). It is now usually referred to as the Born-Haber cycle. The cycle is given below for a uni-univalent salt in terms of enthalpies.



All the magnitudes refer to 25°C and 1 atm.

ΔH_f^0MX(s) is the enthalpy of formation of the crystalline salt.

ΔH_f^0MX(aq) is the enthalpy of formation of the salt in aqueous solution at unit activity.

ΔH_s^0 is the standard enthalpy of solution of the crystalline salt to unit activity.

U is the lattice energy of MX at 298.3°K (25°C).

$U + 2RT$ is the corresponding lattice enthalpy.

H is the enthalpy of hydration of the two gaseous ions to unit activity.

E is the electron affinity of the X radical.

I is the ionization potential of the metal atom.

$\Delta H_f^0X(g)$ is the standard enthalpy of formation of the X radical in the gas phase.

L is the enthalpy of sublimation of the metal M.

From this cycle the following independent relations may be derived.

(a) Between the lattice energy and the combined ion-hydration enthalpies

$$U = -H + \Delta H_s^\circ - 2RT \tag{7}$$

(b) Between the lattice energy and the electron affinity

$$\Delta H_f^0X(g) - E = U + 2RT - I - L + \Delta H_f^0MX. \tag{8}$$

The quantity $\Delta H_f^0X(g) - E$ is often called $\Delta H_f^0X^-(g)$ and the quantity $I + L$, $\Delta H_f^0M^+(g)$ as can be seen from the equation

$$MX(s) \rightarrow M^+(g) + X^-(g), \qquad \Delta H = U + 2RT \tag{9}$$

whence $U + 2RT = \Delta H_f^0M^+(g) + \Delta H_f^0X^-(g) - \Delta H_f^0MX(s)$. It must be remembered that U here is $U_{298^\circ K}$, the lattice energy at 25°C, and that this is related to the lattice energy U_0 at 0°K by

$$U_T = U_0 + \int_0^T [C_p(M^+) + C_p(X^-) - C_p(MX)] \cdot dT - 2RT. \tag{10}$$

It is usual to assume that the specific heats $C_p(M^+)$, $C_p(X^-)$ are $\frac{5}{2}$ R cal/mole in which case the relation becomes

$$U_T = U_0 + \int_0^T [3R - C_p(MX)] \cdot dT. \tag{11}$$

It must be remembered that the lattice energy given by the Born-Haber cycle is an experimental lattice energy and is not dependent upon the nature of the assumptions made about the bonding in the crystal. The classical theoretical calculations are of course dependent upon the assumption of the ionic nature of the bonding in the lattice. Because of this the Born-Haber cycle has been used mainly for three purposes.

(a) When it seems reasonable to assume that the lattice is ionic the cycle is used to calculate $\Delta H_f^0X^-(g), = \Delta H_f^0X(g) - E$, from U, and hence to calculate either E or ΔH_f^0X by the use of subsidiary data. An indirect check on the validity of the assumption of ionic nature and on the accuracy of the calculation is provided by the constancy of the value of $\Delta H_f^0X(g) - E$ from salt to salt.

(b) When the lattice may not be totally ionic the cycle is used to derive an experimental value for the lattice energy, which may then be compared with that given by the ionic theory. If the experimental lattice

energies are systematically higher than those obtained from the classical ionic theory there is probably an appreciable nonionic contribution to bonding in the crystal.

(c) If an approximate ionic structure can be assigned to an unknown or hypothetical compound then its lattice energy can be calculated and the Born-Haber cycle often used to derive a value for its enthalpy of formation.

II. The Calculation of Lattice Energies

A brief account will be given in this Section of the various methods that have been employed to calculate the lattice energies of ionic crystals, starting with a discussion of the extended classical calculation. Each term in this calculation will be discussed separately.

A. The Extended Classical Calculation

1. *The Madelung Term, U_M*

This term arises from the electrostatic interaction of the point charges with which the ions have been replaced in the theoretical consideration of the problem. The interaction energy of two point charges z_1e and z_2e, distance r_{12} apart is $z_1z_2e^2/r_{12}$. Similarly, the total electrostatic energy U_M of n such charges of magnitude z_i ($i = 1,2,3, \ldots, n$) is

$$U_M = \sum_{\text{pairs}} z_1z_2e^2/r_{ij} \tag{12}$$

in which the summation extends over all pairs of charges, each pair being considered. This may also be written in the form

$$U_M = \tfrac{1}{2} \sum_{ij}{}' z_iz_je^2/r_{ij} \tag{13}$$

where the summation is now a double sum over all charges and the superscript prime indicates that the cases $i = j$ are to be excluded. For binary crystals such as sodium chloride, sodium nitrate, and calcium fluoride, the results can always be expressed in the simple form

$$U_M = N_AM_l\frac{z^+e\,z^-e}{l} \tag{14}$$

Here U_M is the energy per mole; z^+e and z^-e are the absolute values of the charges on the positive and negative ions; l is one of the characteristic crystal dimensions; N_A is the Avogadro number and M_l is the Madelung constant, a pure number characteristic of the crystal structure and independant of the dimensions of the lattice.

The series for the Madelung constant cannot be evaluated by uncritical summation because it converges with extreme slowness. Two general methods are available for summing the Madelung series; the first is to arrange the terms so that summation takes place over electroneutral layers and the series converges sufficiently rapidly to be summed directly; the second method is to replace the point charges with a distributed charge and then use a mathematical manipulation to obtain a quickly convergent series. Both methods have been used though the first is only convenient in the case of crystals of high symmetry. Kendall (*73*) was the first worker to obtain a Madelung constant by the first method and later Evjen (*36*) evaluated the Madelung constants of NaCl, CsCl, ZnS, and $CaCO_3$ by considering the lattice to be built up of cubical or rhombohedral shells around a central ion and by summing over each in turn. However in the case of CsCl and $CaCO_3$, de Boer (*25*) and Krishnan and Roy (*75*) have pointed out that a correcting term for the residual electrical double layer has to be added because, since these crystals are body centered, the cubes and rhombohedra around the central ion are not electrically neutral but alternate in sign. The magnitude of this correcting term has been calculated by the above authors. Hojendahl (*52*) used a similar method of summation to Evjen, to obtain the Madelung constant of NaCl and of NaCl lattices distorted along a trigonal axis. By treating CsCl and $CaCO_3$ as distorted NaCl lattices he summed over neutral rhombohedral shells and avoided Evjen's difficulty. The method of summation recently described by F. C. Frank (*39*) is essentially of this type.

The first actual evaluation of a Madelung constant was made by Madelung (*88*) who used the second method. He represented an infinite row of charges with periodic repetition by a Fourier series. The potential for a point outside the row has the same periodicity as the charge distribution. By extending the above method, an expression for the potential of a plane of alternating charges may be derived. The potential for the entire crystal is found by decomposing the lattice into neutral rows of points and lattice planes and then calculating the potential due to each plane and row. Madelung's method though giving a rapidly converging series cannot be applied in many cases because of the impossibility of decomposing many lattices into neutral lines and planes.

Born (*16*) developed a method of computing the Madelung series of more general applicability. The unit cell was divided into s subcells by means of systems of equidistant planes parallel to the sides of the cell so that each ion in the unit cell was located at one of the sublattice points $(P_1/s, P_2/s, P_3/s)$ where P_1, P_2, and P_3 are integers which may assume the values 0, 1, 2, 3, . . . , s-1. For a cubic crystal the Madelung

constant is then given by

$$M_{a_0} = \frac{1}{\mu s^2} \sum_{P=0}^{s-1} Sp \cdot \Pi\,(P/s) \tag{15}$$

where μ is the number of stoichiometric molecules in the unit cell. Sp is defined by

$$Sp = \sum_{m=0}^{s-1} z_m \exp\left[\frac{2\pi i}{s}(m_1P_1 + m_2P_2 + m_3P_3)\right]. \tag{16}$$

Born called $\Pi(P/s) \equiv \Pi(P_1/s,\ P_2/s,\ P_3/s)$ the "Grundpotential." It is the potential at the origin of the unit cell of a charge distribution

$$\cos 2\pi(m_1P_1 + m_2P_2 + m_3P_3)$$

and is defined by the formula

$$\Pi(P/s) = \sum_{t=0}^{\infty}{}' \frac{\cos\,(2\pi/n)(t_1P_1 + t_2P_2 + t_3P_3)}{\sqrt{t_1^2 + t_2^2 + t_3^2}}. \tag{17}$$

The superscript prime indicates that the cases $t_1 = t_2 = t_3$ are to be excluded. The Born Grundpotential is a special case of the generalized zeta-function developed by Epstein (*33*, *34*) and Emersleben (*30*, *31*) has evaluated the zeta-function and hence the Grundpotential $\Pi(xyz)$ for a cubic lattice for all cases from $\Pi(000)$ to $\Pi(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ in steps of $\frac{1}{12}$. He used the $\Pi(xyz)$ so obtained to calculate very accurately the Madelung constants for the cubic lattice types NaCl, CsCl, ZnS, CaF_2 and Cu_2O. Relations between various grundpotentials have been shown to exist by Hund (*55*), by Emersleben (*32*) and by Sakamoto (*111*) who has summarized them and recalculated a number of Emersleben's original values.

Ewald (*37*) developed a method for evaluating the Madelung constants and other sums for crystal lattices which depends on the use of a θ-function transformation. This is probably the method of most general application though it suffers from the disadvantage that the convergence of the series obtained is less rapid than that obtained by the Emersleben method.

An account of the θ-function transformation and the evaluation of Madelung constants by this method has been given recently by Born and Huang (*17*). Bertaut (*8*, *9*) has shown that if the atoms of an ionic crystal are replaced by spherically symmetrical charge distributions, $f(r)$, which do not overlap, the Madelung constant can be expressed as a single, absolutely convergent infinite series whose terms are a function of the lattice vectors in reciprocal space. Ewald's series emerges as a

particular case of Bertaut's approach to the problem. For the case where $f(r) = a(R - r)^n$ an expression of the form

$$M_l = -\frac{Wl}{e^2} = \frac{gl}{R\mu}\sum_j z_j^2 - \frac{\pi R^2 l}{\mu V}\sum_{\mathbf{h}} |F(\mathbf{h})|^2 \cdot \phi(\mathbf{h}). \tag{18}$$

is obtained.

Here $\mathbf{M}_l$ is the Madelung constant based on l as unit distance, μ is the number of molecules in the unit cell, z_j is the charge number of atom j, V is the volume of the unit cell and h is the magnitude of the vector (h_1, h_2, h_3) in reciprocal space or the reciprocal of the spacing of the planes $(h_1h_2h_3)$. The coordinates of atom j are x_{1j}, x_{2j}, x_{3j}. The sums over j are taken over all the atoms in the unit cell. $F(\mathbf{h})$ is the Fourier transform of the Patterson function and $\phi(\mathbf{h})$ is the Fourier transform of the charge distribution $f(r)$. $F(\mathbf{h})$ is given by

$$F(\mathbf{h}) = \sum_j z_j \exp\left[2\pi i(h_1x_{1j} + h_2x_{2j} + h_3x_{3j})\right]. \tag{19}$$

Templeton (*117*) has examined the rate of convergence of Bertaut's series for various functions $f(r)$ and the errors obtained by termination after varying numbers of terms. Values of g and $\phi(\mathbf{h})$ are given in Table I for various functions $f(r)$. From Templeton's results it is clear that the assumption of a linear charge distribution gives the most rapid convergence down to an accuracy of 0.1% in the Madelung constant.

TABLE I

CHARGE DISTRIBUTIONS AND THEIR FOURIER TRANSFORMS

Atomic shape	$f(r)$, $r < R$	g	$\phi(\mathbf{h})$
Uniform	$\frac{3}{4\pi R^3}$	3/5	$\frac{18(\sin\alpha - \alpha\cos\alpha)^2}{\alpha^6}$*
Linear	$\frac{3(R-r)}{\pi R^4}$	26/35	$\frac{288(\alpha\sin\alpha - 2\cos\alpha - 2)^2}{\alpha^{10}}$
Parabolic	$\frac{15(R-r)^2}{2\pi R^5}$	25/38	$\frac{7200(\alpha\cos\alpha - 3\sin\alpha + 2\alpha)^2}{\alpha^{12}}$
Cubic	$\frac{15(R-r)^3}{\pi R^6}$	23/22	$\frac{259{,}200(\alpha^2 + \alpha\sin\alpha + 4\cos\alpha - 4)^2}{\alpha^{14}}$

* $\alpha = 2\pi\mathbf{h}R$.

If, instead of one of the simple functions given in the Table, which are equal to zero for all $r > R$, a normalized Gaussian distribution is taken, that is, $f(r) = k^3 \exp(-k^2\pi r^2)$, the Bertaut equation must be corrected to allow for the overlap of the charge distributions. In this case Bertaut

TABLE II

NUMERICAL VALUES OF THE MADELUNG CONSTANTS FOR VARIOUS CRYSTAL LATTICES

Crystal type	Space Group	M_{r_0}	M_{δ_0}	M_{a_0}	References
NaCl	$Fm3m$	1.74756	2.20178	3.49513	*30, 31, 32, 73, 88, 5, 109, 111,*
CsCl	$Pm3m$	1.76267	2.03536	2.03536	*30, 31, 6, 111*
Sphalerite	$F43m$	1.63805	2.38309	3.78293	*30, 31, 111*
Wurtzite	$C6mc$	1.64132		2.386	*47, 54, 55, 6, 111*
CaF_2	$Fm3m$	5.03878	7.33058	11.63657	*30, 31, 77, 6, 13, 111*
Cu_2O	$Pn3m$	4.44248		10.25946	*30, 31, 19, 115, 56, 111*
Rutile	$P4/mnm$		See following text		*12*
Anatase	$C4/amc$		See following text		*12*
CdI_2	$H\bar{3}1m$		See following text		*55*
β-Quartz	$H6_22$		See following text		*58*
Al_2O_3	$R\bar{3}c$		See following text		*112*
Perovskite*	Pm_3m		See following text		*22, 51, 55, 111, 114, 118*
K_2PtCl_6	Fm_3m		39.99634	63.49026	*114, 81*
$(NH_4)_3AlF_6$	Fm_3m		33.39098	53.00488	*114*
CaC_2	$I4/mmm$		See following text		*70*
Calcite	$R\bar{3}c$		See following text		*52, 36*
Aragonite	$Pmcm$		12.84724		*109*
$CaSO_4$	$Bbmm$		13.50363		*109*
$BaSO_4$	$Pnma$		13.18779		*109*
$SrSO_4$	$Pnma$		13.15651		*109*
$PbSO_4$	$Pnma$		13.16377		*109*
KN_3	$I4/mcm$		See following text		*60, 126, 127, 128*
NaN_3	$R\bar{3}m$		See following text		*52*
PtS(c/a = 1)		1.580206			*51*
PdO(c/a = 2)	$P4/nmm$				
PdO(c/a = 2)		1.604935			*111*
NbO†		1.504265			*51*
NaTl	$Fd3m$	1.513429			*51*
Cu_3VS_4		10.398386			*111*
$Ca^+(WO_4)^-$	$I4_1/a$				
(c/a = 1)		1.594364			*51*
(c/a = 2)		1.613972	1.615503		*51*
(c/a = 2)		1.633580			*51*
$A^{3+}B_3^-$‡		9.566187			*51*
BiF_3§		9.57905			*51*
ZrI_4		13.75454			*51*
YOF			See following text		*118, 51*
LaOCl	$P4/nmm$			18.75	*118*
Spinels*	$Fd3m$		See following text		*26, 27*

* Space group for the undeformed, cubic lattice given.
† NaCl-type, vacancies at 0, 0, 0 (Nb) and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ (O).
‡ Cubic. A at 0, 0, 0; B_I at $\frac{1}{2}$, $\frac{1}{2}$, 0; B_{II} at $\frac{1}{2}$, 0, $\frac{1}{2}$; B_{III} at 0, $\frac{1}{2}$, $\frac{1}{2}$.
§ Cubic face-centered, Bi at 0, 0, 0; F_I at $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$; F_{II} at $\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$; F_{III} at $\frac{1}{2}$, 0, 0.

has shown that

$$M_l = \frac{kl}{\mu}\sum_i z_j^2 - \frac{l}{2\pi V\mu}\sum_{\mathbf{h}}\frac{|F(\mathbf{h})|^2}{\mathbf{h}^2}\exp(-\pi\mathbf{h}^2/k^2) - \frac{L}{2Z}\sum_{ij}\frac{z_i z_j}{r_{ij}}\operatorname{erfc}(\sqrt{\pi}kr_{ij}). \quad (20)$$

This expression is equivalent to the double series of Ewald (*37*). The choice of the constant k is arbitrary, z_i and z_j are the charge numbers of the ions i and j and r_{ij} is the distance between them.

Recently Benson (*5*) has described a new and relatively simple formula for calculating the Madelung constants of a NaCl-type crystal and Benson and Van Zeggeran (*6*) have extended this method to CsCl-type crystals. The method appears to be capable of extension to "generalized" CsCl and NaCl type crystals.

The results of the application of these calculations to various types of crystal are discussed below. Table II summarizes the values of Madelung constants obtained for different crystal lattice types. The general formulae which have been developed to express the Madelung constants as functions of various lattice parameters and the variation of Madelung constants with crystal parameters are discussed in more detail below.

The results of Bollnow (*12*) for the Madelung constant of the rutile-type structure are expressible in the form

$$M_{r_0} = 4.816 - 4.11(0.721 - \alpha)^2 \quad (21)$$

for values of the axial ratio, $\alpha = c/a$, in the neighborhood of 0.721. For anatase the Madelung constant may be written (*12*) as

$$M_{r_0} = 4.800 - 0.707(2.620 - \alpha)^2 \quad (22)$$

where α is again the axial ratio, c/a.

For β-quartz, which has an hexagonal lattice, Hylleraas (*58*) has tabulated M_{r_0} as a function of two parameters, the axial ratio c/a and a parameter u, the distance of the oxygen ions from the hexagonal axis divided by a. His values are given in Table III.

TABLE III

VALUES OF M_{r_0} FOR THE β-QUARTZ STRUCTURE

	$c/a = 1.0$	$c/a = 1.1$	$c/a = 1.2$	$c/a = 1.414$	$c/a = 1.732$
$u = \frac{1}{12}$		4.1754			
$u = \frac{1}{4}$	4.4216	4.4275	4.4288	4.4248	4.3998
$u = \frac{5}{24}$	4.4261	4.4303	4.4317		
$u = \frac{1}{6}$	4.2209	4.2540	4.2862		

Hund (*55*) has evaluated M_{r_0} of the hexagonal cadmium iodide structure as a function of the axial ratio c/a and u, the z-coordinate of the iodide ion divided by c. The values he obtained are given in Table IV.

TABLE IV

VALUES OF M_{r_0} FOR THE CADMIUM IODIDE STRUCTURE

	$c/a = 0.815$	$c/a = 1.12$	$c/a = 1.61$	$c/a = 2.00$	$c/a = 4.00$
$u = 0$	4.55	4.63	4.64	4.64	4.64
$u = \frac{1}{16}$	4.53	4.65	4.68	4.72	4.68
$u = \frac{1}{8}$	4.58	4.72	4.74	4.73	3.87
$u = \frac{1}{4}$	4.68	4.73	4.71	3.90	−2.06

Schmaeling (*112*) has evaluated the Madelung constant of the rhombohedral corundum, Al_2O_3, structure as a function of two parameters, the approximation having been made that each aluminum atom is equidistant from six oxygen atoms. The two independent variables are $\alpha = c/a$ and $w = v/a$, where a is the diagonal of a rhombohedral face, c is one-half the length of the body diagonal, and v is the distance between adjacent aluminum atoms. The Madelung constant is then given by

$$M_{r_0} = 25.0312 - 5.930(1.312 - \alpha)^2 - 65.250(0.5454 - w)^2 + 30.70(1.312 - \alpha)(0.5454 - w). \quad (23)$$

Perovskites are compounds of the general formula ABX_3, having a cubic lattice with the atoms at the following positions: A at 0,0,0; B at ½, ½, ½; and 3X at 0, ½, ½; ½, 0, ½; ½, ½, 0. The type of perovskite with a charge of +1 on A, +2 on B, and −1 on X will be called a 1-2 type. If the charges on the cations are interchanged it is called a 2-1 type. In an analogous way one can define 1-5, 5-1, 3-3, 2-4, and 4-2 types (in which X has a charge of −2). It will be obvious that the Madelung constants of 2-4, 4-2 and the 1-2, 2-1 types merely differ by a factor of 4. Compounds do occur in which no A atoms are present but in which the B and X atoms occupy their places in the perovskite lattice. Such compounds, for example, ReO_3 and ScF_3 can be considered as 0-6 and 0-3 perovskites. The Madelung constants of the perovskites have been discussed by Sherman (*114*), by Hund (*55*), by Brauer (*22*), by Templeton (*118*), by Hoppe (*51*) and by Sakamoto (*111*). Their results are concordant and are summarized in Table V.

TABLE V

MADELUNG CONSTANTS M_{a_0} FOR DIFFERENT TYPES OF PEROVSKITE

Type	Example	Brauer	Hoppe	Templeton	Sakamoto
0-6	$ReO_3(ScF_3)$	71.616	71.6316	71.6315	
1-5	$NaTaO_3$	58.536		58.53535	
2-4	$SrTiO_3(KZnF_3)$	49.508		12.37744* (1-2)	12.377468 (1-2)
3-3	$LaAlO_3$	44.544		44.55489	
4-2	$LiBaF_3$	53.672		10.91768 (2-1)	
5-1		46.856		46.85727	
6-0		54.116			

* Sherman's value; Templeton's values are based on Sherman's value and M_{a_0} for CsCl and NaCl.

For the calcium-carbide type of lattice Kazarnovskaja (*70*) has expressed the Madelung constant, M_{b_0} as a power series in $\alpha(=c/a)$.

$$M_{b_0} = 2.2018 + 1.467(\alpha - 1)^2 - 5.919(\alpha - 1)^3 + 18.96(\alpha - 1)^4 - 24.3(\alpha - 1)^5. \quad (24)$$

For the KHF_2 structure, which is a CsCl structure compressed along a tetrad axis, Madelung constants have been calculated for a number of different values of the axial ratio c/a in the "pseudo-unit cell" (*60*, *126*, *127*). However the author (*128*) has developed a general expression,

$$M_{a_0} = 2.0354 + 0.33923(1 - \alpha^2) - 1.619(1 - \alpha^2)^2 \quad (25)$$

for the Madelung constant with the value of a_0 in the "pseudo-unit cell" containing only one molecule as the reference distance. This formula can be generalized to the simple body-centered orthorhombic lattice to give an expression,

$$M_{a_0} = 2.0354 + 0.33923[(1 - \alpha^2) + (1 - \beta^2)] + 0.3547(1 - \alpha^2)(1 - \beta^2) - 1.619[(1 - \alpha^2)^2 + (1 - \beta^2)^2] \quad (26)$$

where $\alpha = c/a$, $\beta = b/a$ and a is the largest cell side. M_{a_0} is the Madelung constant based on a.

Hojendahl (*52*) has obtained general expressions for the Madelung constants of crystals of the calcite type, which he regards as NaCl lattices compressed along one trigonal axis, and of crystals of the sodium bifluoride type, which he regards as NaCl lattices elongated along one trigonal axis. The standard distance in the crystal lattice is taken as the distance, L_0, between neighboring layers along the trigonal axis. The nearest distance between ions in the same layer is L_1. The lattice can then

be determined by one parameter $p = L_1/L_0$. The Madelung constant is given by

$$M_{L_0} = +0.3573 + 2.085\frac{1}{p^2} - 1.9185\frac{1}{p^4} + 0.7754\frac{1}{p^6} - 0.1286\frac{1}{p^8}. \quad (27)$$

The spinels are compounds of the type AB_2O_4 in which the $O^=$ ions are arranged in cubic close packing, with the A atoms occupying tetrahedral holes and B atoms octahedral holes. Verwey, de Boer, and Van Santen (*26, 27*) have calculated the Madelung constants, by the Evjen method for the various values of the parameter u given and the various charges p and q on A and B. The values $p = 3$, $q = 2\frac{1}{2}$ represents the case where A is A^{3+} and the B positions are alternately filled with 3+ and 2+ ions, for example, Fe_3O_4. The Madelung constants are given in Table VI.

TABLE VI

MADELUNG CONSTANTS, M_{a_0}, FOR THE SPINELS*

Parameter u	Charge p	Charge q	M I	M II
	4	2	138.1	138.2
0.375	2	3	128.6	128.6
	3	$2\frac{1}{2}$	130.7	130.8
	4	2	135.8	
0.380	2	3	131.4	
	3	$2\frac{1}{2}$	131.0	
	4	2	133.6	
0.385	2	3	134.0	
	3	$2\frac{1}{2}$	131.2	
	4	2	131.5	
0.390	2	3	136.5	
	3	$2\frac{1}{2}$	131.4	

* I values by Evjen method, II values by Ewald method for the ideal case (i.e. a perfectly cubic lattice) $u = 0.375$.

Yttrium oxyfluoride and several similar compounds have the fluorite type of structure with the oxygen and the fluorine distributed among the anion positions. Both Templeton (*118*) and Hoppe (*51*) have considered the Madelung constants of the crystals. There are three forms, tetragonal, rhombohedral, and cubic. Their Madelung constants are given in Table VII.

TABLE VII

THE MADELUNG CONSTANTS, M_l, OF THE YOF LATTICES

$l = (\sqrt{\tfrac{3}{4}})a_0$

Structure	M_l
Tetragonal	11.504
Rhombohedral	11.526
Cubic, with La at 0, 0, 0 O at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and F at $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$	11.71568
Cubic, with the O and the F arranged statistically	11.33725

2. The Repulsive Energy Term, $-U_R$

In order to account for the stability of ionic crystals it is necessary to introduce repulsive forces between the ions in addition to the ordinary coulombic forces. Born and Lande (*20*), in their original treatment of the problem, represented these forces as varying as the inverse nth power of the distance and treated the potential energy of the crystal as the sum of two terms, given by the expression

$$U_0 = \frac{N_A M_r z_1 z_2 e^2}{r} - \frac{N_A B}{r^n}. \tag{1}$$

Initially they tried to calculate the value of n from the Bohr model of the atom and then from the Lewis-Langmuir model. However the inapplicability of these models was soon realized and the value of n was determined empirically from the compressibility.

The constant B can be eliminated by remembering that at the equilibrium separation in the crystal, r_0, $(\partial U/\partial r) = 0$, so that

$$\left(\frac{\partial U}{\partial r}\right)_{r=r_0} = \frac{N_A M z_1 z_2 e^2}{r_0} - \frac{n N_A B}{r_0^{n+1}} = 0. \tag{27}$$

Hence

$$B = \frac{M z_1 z_2 e^2 r_0^{n-1}}{n} \tag{28}$$

and

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r_0}(1 - 1/n). \tag{2}$$

The development of wave mechanics led to the realization that ions with completed subgroups were spherically symmetrical and that, for the outermost shell the electron density fell off exponentially with distance. Unsold (*120*) and Pauling (*105*) pointed out that the application

of quantum mechanics led to an expression for the repulsive potential which involved exponential terms in r. Born and Mayer (*21*) therefore expressed the repulsive energy, u_r, between two ions in a crystal as

$$u_r = a \exp(-r/\rho) \tag{29}$$

where a and ρ were constants and r was the distance apart of the ions. They found that for the alkali halides they could adopt a constant value for $\rho (= 0.345 \times 10^{-8})$, if they determined a from the equation

$$a = b\left[1 + \frac{z_A}{n_A} + \frac{z_C}{n_C}\right] \exp\left[(r_C + r_A)/\rho\right] \tag{30}$$

where b was a constant for all the alkali halides, z_C and z_A were the valencies of the two interacting ions (equal to -1 and $+1$, respectively, for the alkali halides), n_A and n_C were the number of electrons in the outer shells of the ions and r_A and r_C were the ionic radii, as determined by Goldschmidt (*40*). Mayer and Huggins (*94*) later used the condition that at the equilibrium internuclear distance in the crystal $(\partial U/\partial r) = 0$ to determine a set of self consistent "basic radii" which when put into the equation for the lattice energy produced the equilibrium internuclear distance. By using 9 such radii they calculated the 20 lattice constants of the alkali halides to nearly the probable experimental error of their determination. Huggins (*53*) later recalculated the lattice energies of the alkali metal halides using these basic radii. The expression for the repulsive energy U_R was given by

$$U_R = bc_{++}M \exp\left[\frac{1}{\rho}(r_C + r_A - r_0)\right] + \frac{bc_{--}M'}{2} \exp\left[\frac{1}{\rho}(2r_A - k_2 r_0)\right] + \frac{bc_{++}M'}{2} \exp\left[\frac{1}{\rho}(2r_C - k_2 r_0)\right] \tag{31}$$

where b is given the value 10^{-12} ergs; c_{+-}, c_{++}, and c_{--} are the expressions $(1 + z_C/n_C + z_A/n_A)$ introduced by Pauling (*106*); M and M'

TABLE VIII

VALUES OF THE HUGGINS BASIC RADII

Ion	Basic radius 10^{-8} cm	Ion	Basic radius 10^{-8} cm
Li^+	0.475	F^-	1.110
Na^+	0.875	Cl^-	1.475
K^+	1.185	Br^-	1.600
Rb^+	1.320	I^-	1.785
Cs^+	1.455		

are the number of nearest like and unlike neighbors respectively; k_2 is the ratio of the shortest distance between like neighbors to that, r_0 between unlike neighbors and r_C and r_A are now the Huggins "basic radii." The values of Huggins basic radii are given in Table VIII. If only the coulombic and repulsive forces are considered then the lattice energy may be written as

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r} - N_A B' e^{-r/\rho} \tag{3}$$

and utilizing $(\partial U/\partial r) = 0$, B^1 can be eliminated to give an expression for U at the equilibrium distance in the crystal.

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r_0}(1 - \rho/r_0). \tag{4}$$

These two expressions are sometimes called the simple Born-Mayer expressions for the lattice energy of a crystal.

Because of the difficulty of assigning basic radii in some crystals, notably those of the halides of silver and thallium, Ladd and Lee (*76*) have extended the above expression, which eliminates B′ and hence the basic radii, to the case where other forces, that is, dispersion energy terms, are included. They obtain for the lattice energy U_0

$$U_0 = \frac{N_A M e^2}{r_0}(1 - \rho/r_0) + \frac{N_A C}{r_0^6}(1 - 6\rho/r_0) + \frac{N_A D}{r_0^8}(1 - 8\rho/r_0) - \frac{9}{4} N_A h\nu_{\max} \tag{6}$$

The values and meaning of C and D and $h\nu_{\max}$ will be discussed in the next section.

Ladd and Lee's expression leads to an interesting observation about the accuracy of the simple Born-Mayer expression. If it is used in the form

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r} - N_A B' e^{-r/\rho} \tag{3}$$

then errors are introduced by the neglect of the dispersion energy terms $N_A C/r^6$ and $N_A D/r^8$. These may be as large as 10 kcal/mole. However if the simple Born-Mayer expression is used in the form

$$U_0 = \frac{N_A M z_1 z_2 e^2}{r_0}(1 - \rho/r_0) \tag{4}$$

then the errors arise from the neglect of $(1 - 6\rho/r_0)\ N_A C/r_0^6$ and so forth. Now $\rho = 0.345$, so that for most salts, particularly those of the heavier alkali metals $(1 - 6\rho/r_0)$ is less than 0.4 so that the error has been reduced to 4 kcal/mole or less.

All the methods discussed above apply only to spherical ions, and are dependent on the assumption of spherical forces and isotropic compressibilities. When the ions are nonspherical, some assumption has to be made about the shape of their "repulsion envelopes" so that radii in different directions can be assigned. Gray and Waddington (*43*) and Waddington (*127*) have discussed this problem with relation to the nonspherical azide, N_3^-, and bifluoride, HF_2^-, ions. The calculation of the repulsive energy is also dependent upon some knowledge of the coefficient of compressibility of the crystal. It is true that for the alkali halides the assignment of basic radii enables a single value of the constant ρ to be chosen but the difficulty of calculating repulsive energies in even so similar a system as that of the alkaline earth chalcogenides and the magnitudes of the errors introduced when the compressibilities are not known has been demonstrated by Huggins and Sakamoto (*54*).

3. *The Dispersion Energy (London) Term, U_L*

London (*83*) has shown that there exists an attractive force between all molecules or ions caused by a synchronization of the oscillations of their electrons. Any two molecules or ions have an attractive energy u_L, given by

$$u_L = \frac{-3}{2r^6} \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} \alpha_1 \alpha_2 \tag{32}$$

where ϵ_1 and ϵ_2 are characteristic energies of the two molecules or ions and α_1 and α_2 are their polarizabilities. The total dispersion energy for a crystal lattice is then

$$U_L = -\frac{N_A}{r_0^6} \left[S_6 a_{12} + S_6' \frac{a_{11} + a_{22}}{2} \right] \tag{33}$$

where a_{12}, a_{11} and a_{22} are respectively the coefficients of $1/r^6$ for the positive-negative, positive-positive, and negative-negative ion pairs. S_6 and S_6' are respectively the sums over all unlike and like ions of $1/(r_i/r_0)^6$ where r_i is the distance between a given ion and the i^{th} ion in the lattice and r_0 is the shortest ion-ion distance. Such sums have been evaluated by Lennard-Jones and Ingham (*82*) and their values are given in Table IX. Born and Mayer (*21*) in the initial calculation of the dispersion energy for the alkali metal halides assumed ϵ_1 and ϵ_2 to be the ionization potentials of the free ions.

In the case of a singly charged positive ion this is the second ionization potential of the element. In the case of a negative ion it is the electron affinity. Born and Mayer (*21*) and Mayer and Helmholtz (*93*) initially used the polarizabilities of the gaseous ions calculated by Paul-

TABLE IX

COEFFICIENTS FOR THE INDUCED DIPOLE-DIPOLE AND DIPOLE-QUADRUPOLE FORCES

Lattice type	S_6	S_6'	S_8	S_8'
NaCl	6.5952	1.8067	6.1457	0.8002
CsCl	8.7088	3.5445	8.2007	2.1476
ZnS	4.354	0.762	4.104	0.253

ing (*104*). Mayer (*91*) later concluded that the values for the London dispersion energy obtained in this way were too small and that the error arose from taking polarizabilities and energies characteristic of the gaseous ions; he also pointed out that a term representing the induced dipole-induced quadrupole interactions should be included. He used the known ultraviolet absorption spectra of NaCl, KCl and KI to calculate the dispersion energy exactly and then examined the validity of various approximations. He found that to a reasonable approximation the contributions of the negative and the positive ions could be separated and that the polarizability of the positive ion from crystal to crystal was fairly constant. For the positive ion he adopted the value of α given by Pauling (*104*) and took ϵ equal to 0.75 ϵ_0 where ϵ_0 was the ionization potential of the gaseous positive ion. As a fair approximation he took ϵ for the negative ion to be 1.30 $h\nu_0$ where ν_0 is the frequency of the first sharp line in the crystal ultraviolet spectrum. α for the negative ion was found from the expression

$$\alpha = \frac{2e^2}{3}\frac{Q_{00}^2}{\epsilon} \tag{34}$$

where Q_{00}^2 was constant for any given negative ion and independent of the crystal. The values of the dispersion energy were more than doubled by using the data from the ultraviolet spectra of the crystals. The induced dipole-quadrupole energy for the crystal is given by the expression

$$U_{L'} = \frac{N_A}{r_0^8}\left[S_8 d_{12} + S_8'\frac{d_{11}+d_{22}}{2}\right]. \tag{35}$$

Here the d are the analogs of the a in the expression for the induced dipole-dipole interaction and have been discussed by Margenau (*89, 90*). S_8 and S_8' are sums of the type $1/(r_i/r_0)^8$ over all like and all unlike ions in the crystal lattice. They have been computed by Lennard-Jones and Ingham (*82*) for various lattice types and are given in Table IX. The actual value of the induced dipole-quadrupole term is about one tenth that of the induced dipole-dipole term.

4. The Zero-Point Energy Term, U_Z

The terms so far discussed all contribute to the potential energy of a spherical ion in a crystal lattice. The lattice energy at absolute zero is obtained by adding to these terms a term equal to the energy retained by the lattice at absolute zero when it is regarded as an assembly of coupled oscillators. This energy, U_Z, is the zero-point energy and is given by the Debye theory as being

$$U_Z = N_A \frac{9}{4} h\nu_{\max} \tag{36}$$

where h is Planck's constant and $\nu_{\max}$ is the Debye maximum frequency. The value of this maximum frequency may be estimated with sufficient accuracy by using infrared absorption data, assigning to $\nu_{\max}$ the frequency of the residual rays or "Reststrahlen." If the infrared data are not available Waddington (*126*) has pointed out that the relation between the absolute entropy at 298°C of the crystal, S^0_{abs}, and the Debye maximum frequency given by the expressions

$$S^0_{\text{abs}} = R[\ln f + T(d\ln f/dT)_v] \tag{37}$$

and

$$\ln f = \ln g - \frac{9}{8}\left(\frac{h\nu_{\max}}{kT}\right) - \frac{9}{\nu^3_{\max}} \int_0^{\nu_{\max}} \ln [1 - e^{-h\nu/kT}]\nu^2 \, d\nu \tag{36}$$

may be used. Here f is the partition function per molecule and g is the electronic partition function. The value of S^0_{abs} is plotted against the zero point energies of the alkali halides and the zero-point energies of other salts interpolated from their absolute entropies.

5. The Permanent Electrical Multipole Term, U_Q

The account of the term-by-term calculation of the lattice energy given above is only correct for an array of spherical ions. If nonspherical ions are present in the lattice then the initial assumption made in calculating the coulombic energy, that is, that a charged ion may be replaced by a point charge at its center, is no longer correct. However, this difficulty may be resolved if the charge distribution on the ion is known or can be calculated. Then the charge on the ion may be represented in terms of a point charge plus a permanent electrical multipole and an immediate simplification effected. The electrostatic energy can now be treated as the sum of two terms, the first, and by far the larger, being the simple Madelung energy due to the interaction of the point charges and the second being the multipole energy.

The multipole energy itself is made up of two terms, the first being

the multipole-multipole interaction energy and the second the energy of interaction of the multipole with the surrounding point charges. Of these two terms the first is very much greater than the second. In the case of symmetrical cylindrical ions, such as the azide, N_3^-, and the bifluoride, HF_2^-, ions, the multipole is in fact a quadrupole and expressions for the energy of interaction have been developed by Gray and Waddington (*43*) and by Waddington (*127*). The energy of the quadrupole-quadrupole interaction is given by

$$U_{Q-Q} = 2q^2d^4\frac{\partial^2}{\partial x_i^2}\left[\frac{1}{R^3}P_2(\cos\theta)\right] + 2q^2d^6\frac{\partial^2}{\partial x_i^2}\left[\frac{1}{R^5}P_4(\cos\theta)\right] + \quad (38)$$

Where q is the quadrupolar charge and d the length of the quadrupole, R is the distance between the two quadrupoles, θ is the angle between the line joining the centers of the quadrupoles and the axis of the first quadrupole, and x_i is the direction of the axis of the second quadrupole relative to those of the first. It is usually only necessary to compute quadrupole-quadrupole interactions for nearest and next to nearest neighbors. The quadrupole-point charge interaction energy has been summed over the whole lattice in the case of tetragonal, body-centered crystals of symmetry D_{4h} and shown to be

$$U_{Q-P} = \frac{(1.30 \pm 0.40)(1 - \alpha_3^2)qd^2e}{(a')^3}. \quad (39)$$

Here α_3 ($= c'/a'$), is the axial ratio in the pseudo-unit cell, q and d have the same signficance as before and e is the electronic charge.

B. The Kapustinskii and Templeton Calculations of the Lattice Energies of Ionic Crystals

1. Kapustinskii's Formula and the Thermochemical Radius

The method of extended calculation of lattice energies described in the previous sections is restricted to salts the crystal structures of which are exactly known. For less simple structures than those of the alkali halides the extended calculation of lattice energies becomes increasingly laborious as the symmetry decreases. If however only the first two terms in the lattice energy are considered, that is, U is taken to be $U_M - U_R$, then adopting either an inverse power law or an exponential law for the repulsive term, U may be written as either

$$U_0 = \frac{Mz_1z_2e^2N_A}{r_0}(1 - 1/n) \quad \text{or} \quad U_0 = \frac{Mz_1z_2e^2N_A}{r_0}(1 - \rho/r_0). \quad (2, 4)$$

If the number of ions in the chemical molecule is ν, the number in a

mole is $N_A\nu$. The above equations may therefore be rewritten

$$U_0 = \left(\frac{N_A\nu}{2}\right)\left(\frac{\alpha z_1 z_2 e^2}{r_0}\right)(1 - 1/n); \qquad U_0 = \left(\frac{N_A\nu}{2}\right)\left(\frac{\alpha z_1 z_2 e^2}{r_0}\right)(1 - \rho/r_0) \tag{40, 41}$$

Where $\alpha = M/(\nu/2)$. The Madelung constant, M, is proportional to the number of ions in the chemical molecule and hence α is independent of this. Although α is not identical for different lattice types, Kapustinskii (*64, 65*) found empirically that in passing from one lattice type to another the change in the constant α was proportional to the change in the interatomic distance, a result shown by Sherman (*115*) to be in agreement with the correct calculation of the Madelung constant for cuprite. Every crystal may then be considered to transform into a rock-salt lattice without change of lattice energy if the coefficients α and r_0 are simultaneously modified so as to have the values corresponding to the ions in a rock-salt lattice. U_0 can now be found either by measuring r_0 and the crystal structure and calculating M and hence α or by putting $r_0 = r_A + r_C$, the sum of the Goldschmidt ionic radii for coordination number 6, and taking $\alpha = 1.745$, its value for a rock-salt lattice. The substitutions $r_0 = r_A + r_C$ in Ångstrom units, $\rho = 0.345$ Å, $\alpha = 1.745$, and $N_A e^2 = 329.7$ kcal/Å give Kapustinskii's formula

$$U = \frac{287.2\ \nu z_1 z_2}{(r_C + r_A)}\left[1 - \frac{0.345}{(r_C + r_A)}\right] \text{kcal/mole.} \tag{42}$$

Kapustinskii's equation, of course, cannot be expected to produce values for the lattice energies as exact as those produced by extended calculation. Essentially the Kapustinskii formula ignores all contributions to the lattice energy save U_R and U_M. If the ions are nonspherical there is considerable difficulty in choosing a repulsion envelope for the ion and assigning a radius. This difficulty also arises in the extended calculation of the lattice energy but only in calculation of U_R, which is an order of magnitude less than U_M. In the Kapustinskii equation this difficulty arises in U_M as well.

Finally the most serious objection is the replacement of r_0, the interatomic distance, by $r_A + r_C$. There are many salts in which the unlike ions are not "touching," for example, NaI, where the lattice spacing is determined by $I^- - I^-$ contacts. Also, the assignment of ionic radii can only be regarded as approximate even in the alkali metal halides. In spite of these objections the Kapustinskii formula remains a useful guide to approximate lattice energies, especially in those cases where the structure is unknown. In general, as the examples discussed later will show, the values for lattice energies given by the Kapustinskii equation fall on the low side of the correct lattice energy.

One of the difficulties that arises in the use of the Kapustinskii calculation is that of assigning a value to the ionic radius of the anion when a complex salt is being considered. Yatsimirskii (*133*) has pointed out that if the reaction

$$MX(s) = M^+(g) + X^-(g) \tag{9}$$

is considered, then the enthalpy of the reaction, $U + 2RT$, is given by

$$U + 2RT = \Delta H_f^0 M^+(g) + \Delta H_f^0 X^-(g) - \Delta H_f^0 MX(s) \tag{43}$$

and if now two salts with the same anion but different cations are considered, M_1 and M_2, then

$$U_{M_1X} - U_{M_2X} = \Delta H_f^0 M_1^+(g) - \Delta H_f^0 M_2^+(g) - [\Delta H_f^0 M_1X(s) - \Delta H_f^0 M_2X(s)] \tag{44}$$

and

$$U_{M_1X} - U_{M_2X} = A\left[\frac{1}{r_{M_1^+} + r_{X^-}}\left(1 - \frac{\rho}{r_{M_1^+} + r_{X^-}}\right) - \frac{1}{r_{M_2^+} + r_{X^-}}\left(1 - \frac{\rho}{r_{M_2^+} + r_{X^-}}\right)\right] \tag{45}$$

using Kapustinskii's equation. If the enthalpies of formation of the solid salts M_1X and M_2X and $\Delta H_f^0 M_1^+(g)$ and $\Delta H_f^0 M_2^+(g)$ are known and the Goldschmidt radii of M_1 and M_2 are known, r_{X^-} can be found. The radius of X found in this way is termed by Yatsimirskii the "thermochemical radius" and it can of course be inserted into the Kapustinskii equation to give the lattice energies of the salts MX and also $\Delta H_f^0 X^-(g)$. Yatsimirskii (*133*, *134*) lists a large number of thermochemical radii and he and Kapustinskii (*68*) have also calculated a large number of thermochemical radii for tetrahedral ions and shown that they are fairly independent of the other ion in the lattice. The values they obtain for the thermochemical radii of various anions are given in Table X.

2. Templeton's Prediction of Madelung Constants

It is perhaps useful to discuss in this section the work of Templeton (*116*) on the empirical prediction of Madelung constants. He has defined a reduced Madelung constant α' by $\alpha' = 2M_{r_0}/z_1z_2\nu$ for binary lattices. Here M_{r_0} is the Madelung constant with the nearest-neighbor distance r_0 taken as the standard distance in the lattice, z_1 and z_2 are the anion and cation charge numbers and ν is the number of atoms in the chemical molecule. Templeton's reduced Madelung constant α' is just Kapustinskii's α divided by the product of the charges on the ions. Templeton has shown empirically that α' can be represented by the equation

$$\alpha' = 1.89 - 1.00/m$$

TABLE X

THE THERMOCHEMICAL RADII (Å) OF SOME COMPLEX ANIONS

Ion	NH_2^-	OH^-	NO_2^-	$HCOO^-$	CNO^-	CH_3COO^-	HCO_3^-	IO_3^-	CN^-
Radius	1.30	1.40	1.55	1.58	1.59	1.59	1.63	1.82	1.82
Ion	NO_3^-	BrO_3^-	HS^-	CNS^-	ClO_3^-	$C_6H_2(NO_2)_3O^-$	ClO_4^-	MnO_4^-	
Radius	1.89	1.91	1.95	1.95	2.00	2.23	2.36	2.40	
Ion	IO_4^-	BF_4^-	O_2^{2-}	CO_3^{2-}	SO_4^{2-}	CrO_4^{2-}			
Radius	2.49	2.28	1.80	1.85	2.30	2.40			
Ion	MoO_4^{2-}	ScO_4^{2-}	TeO_4^{2-}	BeF_4^{2-}	BO_3^{3-}	PO_4^{3-}			
Radius	2.54	2.43	2.54	2.45	1.91	2.38			
Ion	AsO_4^{3-}	SbO_4^{3-}	BiO_4^{3-}	SiO_4^{4-}					
Radius	2.48	2.60	2.68	2.4					

where m is the weighted harmonic mean of the coordination numbers, with an accuracy of better than 1% for a dozen cases of binary structures. To permit application to more complex structures, such as ternary salts, Templeton (*118*) redefined the reduced Madelung constant as $\alpha' = 2M_{r_0}/\Sigma z^2$. When the nearest neighbors of different atoms are at different distances, one can expect α' to be less than the value predicted by the above equation. The prediction will correspond more closely to α_m' defined as $\alpha_m' = \alpha' r_m/r_0$, where r_m is the harmonic mean of the distances, weighted according to their frequency of occurrence and according to the product of the charges of the ions involved.

The accuracy of the prediction for the ternary salts is less than that for the binary salts, the average deviation from the accurately calculated value being about 2% for the salts with equal distances and about 3.5% for the salts with two distances (12 cases being considered). The worst case was in error by 10%. Templeton provides a theoretical justification for his equation and points out that it will not yield accurate predictions for any structure whatever. Rather it represents approximately the largest value which is possible for a given coordination number. If a substance is a salt, it can only be stable in a structure with Madelung constants not too far below the largest one possible, since the crystal energy is determined principally by the electrostatic potential.

C. The Quantum Mechanical Prediction of Lattice Energies

An entirely different approach to the calculation of lattice energies was initiated by Hylleraas (*59*) who applied a general quantum mechanical treatment to the calculation of the lattice energy of lithium hydride. He used one-electron wave functions of the hydrogenic type with nuclear screening so that the entire computation could be performed analytically. The wave functions were

$$\psi = \exp\{-(z - \tfrac{5}{16})r/a_h\} \tag{46}$$

with $z = 1$ for hydrogen and 3 for lithium; a_h is the Bohr unit distance (0.58 Å). The chief objection to his calculation was that his approximate wave functions did not give very good binding energies for the free H^- and Li^+ states. The actual method of calculation was similar to that employed by later workers and will be discussed in connection with their calculations. His actual results were that the binding energy was 218 kcal/mole and that $a_0 = 4.42$ Å. These may be compared with empirical values of 218.5 kcal/mole and 4.084 Å.

Landshoff (*78, 79*) later calculated the lattice energies of NaCl by this general quantum mechanical method and the same method was adopted by Lowdin (*84, 85, 86*) who calculated the cohesive energies of

LiCl, NaCl, KCl, and NaF. Later Jiro Yamashita (*130, 131*) calculated the lattice energy of LiF and Benson and Wylie (*7*) also calculated the lattice energy of LiF. Recently Shoichi Kobayashi (*74*) has calculated by quantum mechanics the lattice energy of Cu_2S and Lundquist (*87*) has recalculated the lattice energy and other parameters of LiH. The basis of all these calculations is the same though Benson and Wylie's represents a simpler approach to the problem. The Hamiltonian operator for the system of N ions is written down. The total energy of the ground state of the crystal is then given by the lowest eigenvalue E of the Schrödinger equation

$$H\psi = E\psi \tag{47}$$

for the antisymmetric eigenfunctions $\psi = \psi(x_1, x_2, \ldots, x_i, \ldots, x_N)$ where x_i are the space and spin coordinates of the electron i. The solution of the equation is the lowest value of E in:

$$E = \frac{\int \psi^* \cdot H\psi \, d\tau_1, d\tau_2, \ldots, d\tau_n}{\int \psi^* \cdot \psi \, d\tau_1, d\tau_2, \ldots, d\tau_n}. \tag{48}$$

To solve this equation the one electron approximation is used. The differences in the treatments of the various authors lie in the differences in their assumptions about orthogonality in the wave functions used and in the use of either a variational or perturbation method to find the minimum energy.

It is convenient to split the energy of cohesion U up into four parts

$$U_c = U_{\text{Mad}} + U_{\text{corr}} + U_{\text{exchange}} + U_s. \tag{49}$$

The Madelung term is as in the classical theory; the U_{corr} represents a correction to the Madelung term arising from the fact that the ions are not point charges at the lattice sites but overlapping charge clouds; the term U_{exchange} is a straight exchange energy arising from the exchange of electrons on two atoms. Only the exchange terms between neighboring atoms are important. The first three terms can be considered as resulting from only pure two-body interactions. However, this is not true for the U_s term and it does include quantities which arise from the interaction of many-body forces.

Landshoff made two calculations of the lattice energy of NaCl, the first with wave functions in which the exchange of electrons within the ion was neglected, the second with Hartree-Foch wave functions in which this exchange was taken into account. He calculated the lattice energy, the lattice parameter, and the compressibility. The values he obtained are listed in Table XI and compared with the experimental ones. He treated a set of linear combinations of the wave functions of the free ions as though they were exactly orthogonalized and normalized; but in

TABLE XI

QUANTUM MECHANICAL CALCULATION OF LATTICE ENERGIES, EQUILIBRIUM DISTANCES AND COMPRESSIBILITIES

Salt	Calculation	Lattice energy (kcal/mole)	Equilibrium distance (Å)	Compressibility bar	Remarks
LiH	Hylleraas	218	4.42		Hydrogenic wave functions
	S. O. Lundquist (1954)	205			
	Experimental value	217 ± 7	4.084		
LiF	Lowdin	199.5	4.79	4.0×10^{-12}	
	Benson and Wylie	242	4.02	1.7×10^{-12}	
	Yamashita (1)	247	4.00	$1.3\text{-}1.7 \times 10^{-12}$	
	Yamashita (2)	239	4.00	1.96×10^{-12}	
	Huggins calculation	243.6	4.02 (exp) 300°K		
NaCl	Landshoff (1)	165	5.55	8.2×10^{-12}	Older Hartree wave function
	Landshoff (2)	182	5.56	4.35×10^{-12}	Hartree-Foch wave function
	Lowdin	183.2	5.54	4.5×10^{-12}	Hartree-Foch wave function
	Huggins	183.5	5.628 (exp) 300°K		
LiCl	Lowdin	187.7	5.37	4.2×10^{-12}	
	Huggins	200.2	5.144 (exp) 300°K		
KCl	Lowdin	166.9	6.17	6.0×10^{-12}	
	Huggins	167.9	6.278 (exp) 300°K		
NaF	Lowdin	205.1	4.58		
	Huggins	215.4	4.620 (exp) 300°K		
Cu_2S	Kobayashi	480	5.14		Slater's wave functions used and method of Landshoff employed
			3.95		

reality this was only true if second and third order terms were neglected. Lowdin derived a formula for a set of linear combinations of the free ion wave functions that were exactly normalized and orthogonalized and deduced values for the lattice energy, lattice parameter, and compressibility of LiF, NaF, LiCl, NaCl, KCl. His values for these quantities for sodium chloride are very close to those of Landshoff and both are in good agreement with the experimental values. His value for KCl is in good agreement but the values for NaF and LiCl are not in very good agreement with experiment, and his values of the lattice constants for LiF are a good deal out. No other calculations apart from Lowdin's have been made for NaF, LiCl and KCl but two other workers have computed the lattice energy and parameters for LiF. Yamashita assumed a wave function of the Hartree type for the $1s$ state of the Li^+ and for the $1s$ and $2s$ states of the F^- ion. For the trial function for the $2p$-electrons for the F^- ion he used Slater wave functions for the crystal with three adjustable parameters. He minimized the total energy of the crystal for various lattice distance by the use of the variational method. He initially reported the values (1) (Table XI) but later reported the values (2). He also calculated the diamagnetic susceptibility of the F^- ion in the crystal and found it to be in good agreement with the experimental measurements. His values are seen to be a good deal better than Lowdin's, probably because of the method he adopted to deduce the wave function of the F^- ion in the crystal, allowing for the effect of the crystal field on the wave functions of the free ion.

Benson and Wylie proceeded by a rather different method in calculating the lattice energy of LiF. Their assumptions are a good deal more drastic. The Li^+ ion is treated as a unit positive charge and account of the $1s$ electrons is taken only indirectly in the orthogonalization relations. All details of the inner structure of the fluorine ion were discarded and the ion was treated as a nucleus of charge $+5$, surrounded by a shell of six $2p$-electrons. The Hartree self-consistent field calculation of the radial density distribution of the two $2p$-electrons of a free fluorine ion was used. The function was suitably normalized and fitted to an analytic expression of the Slater type. A simple perturbation calculation was then carried out. The results obtained for the lattice energy, lattice constant, and compressibility are given in Table XII. The agreement obtained was fair, but it was clearly a drastic approximation to use orbitals appropriate to the free ion in the interior of the crystal. As a way of overcoming this, the outer orbitals of the fluorine ion were orthogonalized with respect to one another and made very nearly orthogonal with respect to the $1s$ orbitals of the neighboring lithium ions. The values of the lattice parameter, cohesive energy, and compressibility were de-

TABLE XII

SUMMARY OF BENSON AND WYLIE'S RESULTS FOR LiF

		Lattice parameter (Å)	Cohesive energy (kcal/mole)	Compressibility (10^{-12} bar)
(i)	Simple perturbation calculation	3.78	247.4	1.8
(ii)	Wave functions orthogonalized	5.16	188.1	4.8
(iii)	Wave functions adjusted to fit diamagnetism	4.02	242.0	1.7
(iv)	Theoretical results of Lowdin	4.79	199.5	4.0
(v)	Theoretical results of Yamashita	4.00	239	1.96
(vi)	Empirical values	4.02 (at 300°K)	243.6 (Huggins calculation)	

duced and are given in Table XII. These results show large deviations from the empirical values, larger deviations than those of the simpler treatment. It is interesting to note that these results are comparable with the more exact calculations of Lowdin, who used an essentially similar treatment. The next step of Benson and Wylie was empirical. They adjusted the wave functions of the fluorine ion to give a diamagnetic susceptibility in agreement with the experimental results. The values of the lattice energy etc. obtained in this way are given in Table XII.

It appears from the above discussion that the most satisfactory approach to the quantum mechanical calculation of lattice energies is that developed by Yamashita, in which the parameters of the outer wave functions of the ions are adjusted by a variational method to minimize the total energy of the crystal. Orthogonalization of the simple free ion wave functions seems to produce a result rather worse than that achieved by ignoring the correction. No doubt with the availability of electronic computors Yamashita's method will be extended to crystals in addition to LiF, where it may be necessary to adjust the wave functions of both the ions by a variational method, to allow for the effect of the crystal field. This will produce an exceedingly tedious calculation. Yamashita (*132*) has also used the method described above to show that the O^{2-} ion is stable in the MgO crystal, though not in the gas phase.

An example of the application of quantum mechanical calculations to more complicated systems is the calculation of the lattice energy and

lattice constant of β-Cu_2S by Kobayashi. The numerical calculation was carried out to determine the positions of the Cu^+ ions in the β-phase since this could not be determined by X-ray analysis. Slater's wave functions were used for Cu^+ and S^{2-} and the method developed by Landshoff was applied. The potential energy minimum was determined to fix the Cu^+ ions. The results of the calculation are given in Table XI.

The lattice energy of LiH has recently been recalculated by S. O. Lundquist. He has not used the old hydrogenic wave functions used by Hylleraas nor has he used the free ion orbital approach because he maintains that the deformation of the diffuse H^- ions in the field of the crystal must be considerable. The total energy was minimized with respect to the effective nuclear charge of the H^- ion.

D. The Calculation of Lattice Energies from Hydration Enthalpies

Between the lattice energy U of a crystal and the enthalpy of hydration H of the gaseous ions of the crystal to unit activity in water, there exists the relation

$$U = -H + \Delta H^\circ_s - 2RT \tag{7}$$

where S is the standard enthalpy of solution of the crystal to unit ac-

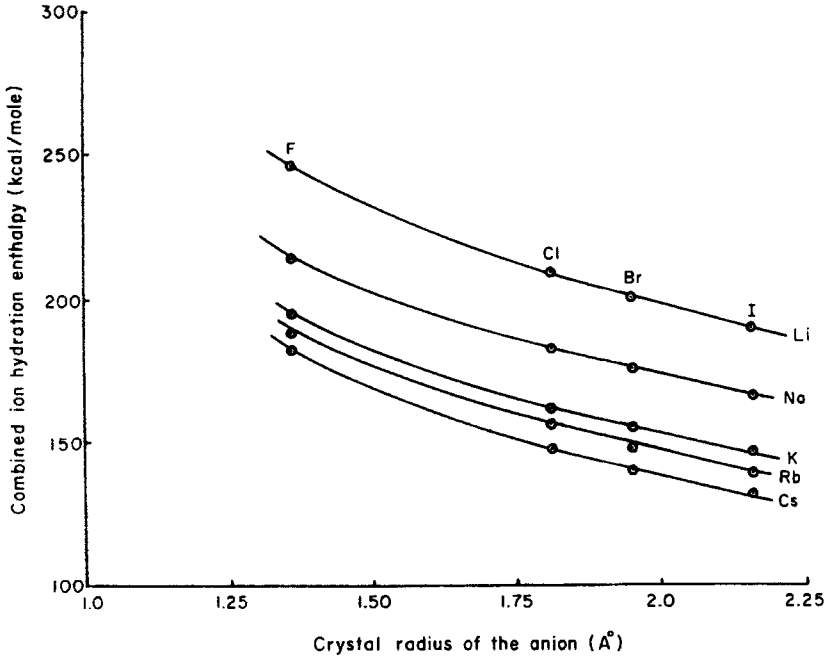


Fig. 1. Enthalpies of hydration as functions of anion radii.

tivity. The enthalpy of hydration of the ion pairs is well known for the alkali metal halides and two empirical correlations have been observed and substantiated. The first is between the enthalpy of hydration of the ion pairs and the crystal radii of the anion and cation. If the enthalpies of hydration of the alkali halides are plotted against the crystal radii of the halide ions as given by Pauling (*107*) smooth curves are obtained (Fig. 1), and thus if the ionic radius of any other anion is known it is possible to obtain from the curves by interpolation the enthalpies of hydration of the anion with the alkali metal ions.

The second empirical correlation that has been observed is between the ion pair enthalpy of hydration and the lyotropic number (Büchner, *23*, *24*). The lyotropic number was developed by Büchner as a quantitative expression of the position of the anion in the Hofmeister series. It

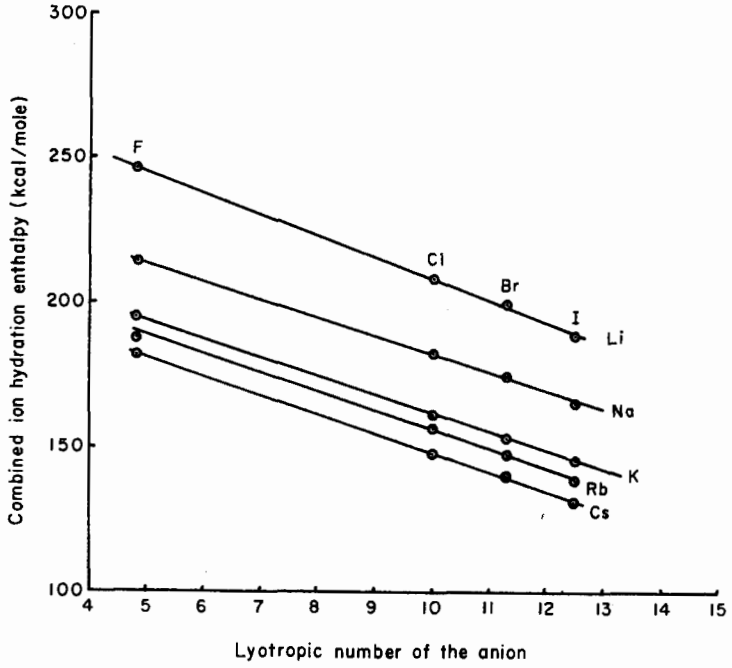


FIG. 2. Enthalpies of hydration as functions of the lyotropic numbers of the anions.

is essentially a measure of the power of an anion to bind water to itself at the expense of hydrated colloids in suspension. It is found experimentally that enthalpies of hydration of ion pairs vary linearly with the lyotropic number of the anions (see Fig. 2).

Büchner has determined the lyotropic numbers of the following

anions F^-, IO_3^-, $H_2PO_2^-$, BrO_3^-, Cl^-, NO_2^-, ClO_3^-, Br^-, NO_3^-, ClO_4^-, I^-, CNS^-, N_3^-.

If the lyotropic number of an anion is known or a crystal radius can be assigned to it, then the hydration enthalpies of its ion pairs with the alkali metal ions can be calculated and hence if the enthalpies of solution of its alkali metal salts are known their lattice energies can be found. Gray and Waddington (*43*) have used both methods to calculate the enthalpies of hydration of the alkali metal azides. The results are mutually consistent and the lattice energies derived from them are also in excellent agreement with the lattice energies found by extended calculation. Waddington (*126*) has used the Büchner lyotropic number to derive hydration heats and lattice energies for most of the anions listed above and the results obtained are found to be, in the cases where they can be checked, consistent with the thermochemical data. The individual results will be discussed in Section III.

The disadvantages and limitations of the two methods given above are the following. In the case of the crystal radius interpolation it is necessary to be consistent and use one set of crystal radii. Gray and Waddington and Waddington accepted the Pauling set. Another difficulty arises if the anion is nonspherical. If this is the case it is necessary to assign a mean radius. In the case of the azide ion the difficulty was overcome by assuming that the ion was an ellipsoid of revolution and using the change of structure and coordination number in passing from potassium to sodium azide to calculate the major and minor axes of the ellipsoid. Fortunately the curves of hydration enthalpy against anion radius are shallow ones, the sum of the hydration enthalpies changing by only about 6 kcal per 0.1 Å change in the anion radius.

Again in the case of the lyotropic number interpolation the accuracy is dependent on the accuracy of the measurement of the lyotropic number, though the sum of the hydration heats only changes slowly with lyotropic number. It must also be stressed that the lattice energies obtained in this way are not "theoretical" lattice energies in that they are not based on any model of the crystal. Rather they are empirical or experimental in that they are based on a combination of empirical hydration enthalpies and experimental enthalpies of solution.

III. Individual Values of the Lattice Energies of Alkali Metal and Alkaline Earth Salts

Before discussing the uses to which the values obtained for lattice energies can be put it seems worthwhile to give an account of the individual calculations that have been made of the lattice energies of various

alkali metal and alkaline earth salts and also to give some indication of the accuracies of the various calculations. A very large number of lattice energies can of course be computed by the use of Kapustinskii's formula (*64, 65*), and Yatsimirskii's (*133, 134*) thermochemical radii listed in Table X. These values are not in general given when they are the only values available but they are listed for comparison with the results of other workers.

A. The Alkali Metal Halides

The lattice energies of the alkali metal halides have been calculated by a large number of workers with approaches of increasing sophistication. The principal calculations by the classical ionic theory since Sherman's (*114*) review have been made by Mayer and Helmholtz (*93*), Verwey and de Boer (*125*), and by Huggins (*53*). Seitz (*113*) has also listed a series of values which differ somewhat from those given by Huggins, probably because he does not use Huggins' "basic radii" in computing the repulsion energy. More recently Ladd and Lee (*76*) have used a method to compute lattice energies which eliminates the need for basic radii and their values are included for comparison. The values of the lattice energy predicted (*66*) by the Kapustinskii equation are also included for comparison in Table XIII.

The values of Huggins are probably the most accurate lattice energies obtainable and agree with the Born-Haber cycle values to within the experimental accuracy of the cycle terms. The values given by the Kapustinskii equation will be seen to be rather low. The Born cycle values are obtained from the values of $\Delta H_f^0 M^+(g)$ and $\Delta H_f^0 MX(s)$ given by the U. S. Bureau of Standards, circular 500, and the values of $\Delta H_f^0 X^-(g)$ decided upon by Pritchard (*108*), as a result of a review of all the experimental data.

B. The Alkali Metal Hydrides

Apart from the quantum mechanical calculations of the lattice energy of LiH, due to Hylleraas (*59*) and to Lundquist (*87*), the only calculation has been made by Bichowsky and Rossini (*10*) who derived the lattice energy of LiH using a Born-Lande expression. Accurate values of the lattice energies are available from thermochemical data and Kazarnovskii (*72*) has used these values to calculate the exponent in the Born repulsion coefficient. Using a simple Born-Mayer expression, ignoring Van der Waals terms, the present author, taking $\rho = 0.345$ Å, the value found for the alkali halides, has obtained values for the lattice energies of all the alkali metal hydrides. These values are compared with the thermochemical data in Table XIV. It will be seen that the theoreti-

TABLE XIII

LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL HALIDES

Salt	Born cycle	Sherman 1932 (*114*)	Kapustinskii 1943 (*66*)	Mayer and Helmholtz 1933 (*93*)	de Boer and Verwey 1936 (*29*)	Huggins 1938 (*53*)	Seitz 1940 (*113*)	Ladd and Lee 1958 (*76*)
LiF	241.2	238.9	227.7	240.1	243.0	243.6	242.0	
LiCl	198.2	192.1	192.1	199.2	201.9	200.2	200.2	
LiBr	188.5	181.9	189.5	188.3	192.0	189.5	189.7	
LiI	175.4	169.5	170.4	174.1	178.7	176.1	176.2	
NaF	216.0	213.8	211.5	215.4	216.1	215.4	214.5	
NaCl	183.8	179.2	179.9	183.1	186.0	183.5	184.4	
NaBr	175.9	170.5	175.5	174.6	178.3	175.5	176.5	
NaI	164.5	159.6	161.0	163.9	168.9	164.3	166.1	
KF	191.5	189.2	188.5	189.7	193.5	192.5	191.8	192
KCl	166.8	163.2	162.7	165.4	168.9	167.9	167.5	165
KBr	160.7	156.6	161.3	159.3	163.4	161.3	161.7	159
KI	151.0	147.8	146.8	150.8	154.6	152.4	153.1	149
RbF	183.6	180.6	181.7	181.6	186.0	183.0	184.2	
RbCl	162.0	157.7	158.2	160.7	164.7	162.0	162.7	
RbBr	155.2	151.3	149.7	153.5	158.6	156.1	156.7	
RbI	146.5	143.0	141.0	145.3	150.3	148.0	148.4	
CsF	171.0	171.6	170.4	173.7		175.7	175.8	
CsCl	153.2	147.7	149.4	152.2		153.1	155.6	
CsBr	148.3	142.3	143.9	146.3		149.6	150.0	
CsI	140.3	134.9	134.7	139.1		142.5	142.7	

TABLE XIV

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL HYDRIDES

Salt	Quantum mechanical value	Kazarnovskii value for n	Bichowsky and Rossini	Waddington	Thermochemical value from Born cycle
LiH	218 (Hylleraas) 205 (Lundquist)	4.40	218.2	234.0	216.5
NaH		5.24		202.0	193.8
KH		5.85		177.2	170.7
RbH		6.63		168.6	164.4
CsH		6.97		162.0	156.1

cal values are too high and this is ascribed to the difference between the repulsion energies and compressibilities of the hydrides and those of the halides.

C. The Alkali Metal and Alkaline Earth Chalcogenides

The lattice energies of the alkaline earth oxides, sulfides, selenides, and tellurides have been calculated by a number of workers, though most attention has been focused on the oxides. Sherman (*114*) used the simple Born formula. Later Mayer and Maltbie (*96*) used the Born-Mayer expression for the lattice energies, calculating the London dispersion energies from the polarizabilities of the free ions. van Arkel and de Boer (*123*) also calculated the lattice energies of some of the chalcogenides. Later de Boer and Verwey (*29*) recalculated the lattice energies of the oxides, because the Mayer and Maltbie interatomic distances had been based on density measurements and differed significantly from those obtained from the X-ray data. Other calculations have been made by Fowler (*38*) and by Kapustinskii (*66*). More recently Kapustinskii and Yatsimirskii (*69*) have recalculated a large number of lattice energies and Huggins and Sakamoto (*54*) have recalculated the lattice energies of all the alkaline earth chalcogenides. They used the Huggins "basic radii" and improved expressions for the dispersion energy based on the optical properties of the crystals. Unfortunately satisfactory compressibility data were not available and so the repulsion energy term remains the major source of error in their calculation. Morris (*99*) has recently calculated the lattice energies of BaO, Li_2O, Na_2O, K_2O, Rb_2O and Cs_2O; he considers these salts to be more ionic than the alkaline earth oxides. The values obtained by the different workers are collected in Table XV.

Probably the results of Huggins and Sakamoto and of Morris represent the best available lattice energy data. Huggins and Sakamoto give values of $\Delta H_f^0O^{2-} = 221 \pm 15$, $\Delta H_f^0S^{2-} = 152 \pm 15$, $\Delta H_f^0Se^{2-} = 165 \pm 15$ and $\Delta H_f^0Te^{2-} = 145 \pm 20$ kcal/mole. Morris obtains $\Delta H_f^0O^{2-} = 211 \pm 7$ kcal/mole.

D. The Alkali Metal Hydroxides

The position with regard to the lattice energies of the alkali metal hydroxides is by no means satisfactory. At room temperature they have, with the exception of LiOH which is tetragonal, orthorhombic lattices, in which the OH^- ions are obviously not rotating. At higher temperatures they undergo a transition to cubic NaCl lattices. A number of calculations of their lattice energies have been made, not all of them based on a knowledge of the crystal structure. Born and Kornfeld (*18*)

TABLE XV

LATTICE ENERGIES (KCAL/MOLE) OF THE CHALCOGENIDES

Salt	Morris	Huggins and Sakamoto (a)	Huggins and Sakamoto (b)	Mayer and Maltbie	van Arkel and Boer; de Boer and Verwey‡	Fowler	Kapustinskii and Yatsimirskii	Zhanov (*135*)	Sherman	Kapustinskii
BeO		1026	1082		1080, 1030					
BeS		854	893					907		
BeSe		820	855							
BeTe		763	795							
MgO		907	938	939	936, 920	976	934		939	914
MgS		764	788	800	790	766	807	801	771	786
MgSe		734	757			743				
MgTe		678	699							
CaO		816	841	831	830, 825	876	845		841	
CaS		707	726	737	710	714	740		721	719
CaSe		683	701			700	704		698	684
CaTe		644	662			648				
SrO		769	792	766	784, 780	829	789		790	769
SrS		675	692	686	680	688	696		686	676
SrSe		654	671			675	664		666	644
SrTe		620	635			626				
BaO	741.3	724	746	727	740, 735	780	751		746	731
BaS		643	659	647	640	662	666		655	646
BaSe		624	639			652	638		636	617
BaTe		594	608			609				
Li_2O									695	
Li_2S									576*	
Na_2O	601.7									
Na_2S									516	
K_2O	532.8									
K_2S									565*	
Rb_2O	513.0									
Rb_2S									446*	

* Values of C. D. West (*129*).

‡ In this column when two values are given they represent upper and lower limits.

TABLE XVI

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL HYDROXIDES

Salt	Born and Kornfeld		Van Arkel and de Boer		Goubeau		Goubeau and Klemm		Kapustinskii as given by Unzhakov		Waddington		West		Hydration heat	
	U	$\Delta H_f°OH^-$	U	$\Delta H_f°OH^-$	U	$\Delta H_f°OH^-$	U	$\Delta H_f°OH^-$	U	$\Delta H_f°OH^-$	U	$\Delta H_f°OH^-$	U	$\Delta H_f°OH^-$	U	$\Delta H_f°OH^-$
LiOH	215	63.1	205	73.1	205	73.1	234	43.6	229.5	48.1					229.3	48.8
NaOH	205	41.8	166	80.8					209.0	35.8	197	50	201	46	196.1	50.7
KOH	181	42.7	145	78.7					184.0	39.7	175	49			172.7	51.0
RbOH	172	44.0	137	79.0					174.1	42.0					165.7	50.3
CsOH	158	48.1	130	76.0					165.1	41.1					156.6	49.5

calculated the lattice energies of the salts, as did van Arkel and de Boer (*123*), without a proper knowledge of the crystal structure. Later Goubeau (*41*) calculated the lattice energy of LiOH from its crystal structure; the values of the lattice energies of the other alkali metals he lists are based upon this calculation and are not direct determinations. Goubeau and Klemm (*42*) later attempted to correct Goubeau's original value for LiOH to allow for the permanent dipole moment of the OH^- ion, which is not rotating. The values for the lattice energies given by Juza (*62*) are based on fairly crude assumptions about the molecular volume of the hydroxide ion, arrived at from specific gravity measurements. West (*129*) gives a value for the lattice energy of the high temperature form of NaOH using a simple Born-Lande expression. Kapustinskii's (*65, 66*) formula has also been used to calculate a thermochemical radius of the alkali metal hydroxide ion of 1.40 Å, and inserting this into the Kapustinskii equation the lattice energies given in Table XVI are obtained. Unzhakov (*121*) quotes a slightly different set of lattice energies derived by the Kapustinskii equation. Unfortunately none of these calculations yield consistent values of $\Delta H_f^0OH^-(g) = \Delta H_f^0OH(g) - E_{OH}$ from hydroxide to hydroxide, nor values in agreement with the experimental value for E_{OH} given by Page (*102*).

The present author has used the Born-Mayer expression to calculate the lattice energies of the high temperature cubic forms of NaOH and KOH, and has also calculated the lattice energies from the hydration enthalpies obtained from interpolating on the crystal radius-hydration enthalpy plot of Fig. 1, the crystal radius of 1.47 Å found by Goubeau (*41*). The values of West, the author's Born-Mayer calculation for NaOH and KOH and the hydration enthalpy values are in good agreement with each other and lead to a value of $\Delta H_f^0OH^-(g)$ of 50 kcal/mole in good agreement with Page's experimental value for E_{OH}.

E. The Alkali Metal Hydrosulfides

The lattice energies of the high temperature forms of the alkali metal hydrosulfides were calculated by C. D. West (*129*) using a simple Born-Lande expression. Yatsimirskii (*133*) has assigned a thermochemical radius of 1.95 Å to the SH^- ion. He does not list values for the lattice energies in his paper but only the derived quantity $\Delta H_f^0SH^-(g) = 27.8$ kcal/mole. The values obtained by using his thermochemical radius in the Kapustinskii equation are given in Table XVII together with West's values for the high temperature, cubic, forms, and with the author's values using a simple Born-Mayer expression. The value of $\Delta H_f^0SH^-(g)$, obtained from each lattice energy are also listed and they are in good agreement and lead to a value of 30 kcal/mole being adopted.

TABLE XVII

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL HYDROSULFIDES

	West		Waddington		Yatsimirskii	
Salt	U	$\Delta H_f^0SH^-$	U	$\Delta H_f^0SH^-$	U	$\Delta H_f^0SH^-$
LiSH	178		181.4		183.5	
NaSH	168	33.3	168.2	33.1	172.8	28.5
KSH	155	30.1	155.3	29.8	156.5	28.6
RbSH	150	29.5	149.0	30.5	150.0	29.5
CsSH	143	28.8	139.0	32.8	144.0	27.8

F. THE ALKALINE EARTH IMIDES

The alkaline earth imides have a cubic, NaCl-type lattice and their lattice energies have been evaluated by A. P. Altshuller (*4*). Since the compressibilities were unknown he used the Born-Lande equation and adopted the value of n used by Sherman for the corresponding oxides. He did not incorporate a term to allow for the dispersion energy and found for the lattices energies of CaNH, SrNH and BaNH values of 787, 752 and 711 kcal/mole, respectively. Only the heat of formation of BaNH was available and from this a value of $\Delta H_f^0NH^-$ of 261 kcal/mole and hence a double electron affinity of -184 kcal/mole was obtained.

G. THE ALKALI METAL AMIDES

The lattice energies of the alkali metal amides were initially crudely computed by Juza (*62*), who used density measurements to calculate a molecular volume and hence a radius of 1.75 Å for the amide ion. He used this radius to obtain the lattice energy. Yatsimirskii (*133*) obtained a thermochemical radius for the amide ion of 1.30 Å. This value is widely at variance with both Juza's original value and the crystallographic value of 1.67 Å obtained by Juza and Opp (*63*). Neither Juza nor Yatsimirskii allow for the dipole moment that the amide ion possesses nor do their lattice energies produce very consistent values for $\Delta H_f^0NH_2^-$. If the value of 1.67 Å for the radius of the amide ion is used in Kapustinskii's formula the values for the lattice energies obtained are close to those given by Juza. However, the values for $\Delta H_f^0NH_2^-$ are still not consistent and the best that can be said is that the values for the lattice energies are doubtful.

H. THE ALKALI METAL CYANIDES

The lattice energies of the alkali metal cyanides, which at room temperature crystallize with the NaCl and CsCl structures, were calculated

by Sherman (*114*). Yatsimirskii (*133*) has also calculated a "thermochemical radius" of the cyanide ion of 1.82 Å and the values obtained from the Kapustinskii equation using this radius are given in Table XVIII. The present author has calculated the lattice energies of these salts, using a simple Born-Mayer expression, ignoring the dispersion energy and also using the more complicated expression of Huggins. In both ρ was taken as 0.345 Å. The values obtained by the latter method are surprisingly near those given by Sherman and are probably as good as any available. They lead to a value of $\Delta H_f^0CN^-(g) = 7$ kcal/mole. The values of Yatsimirskii are less reliable.

TABLE XVIII

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL CYANIDES

					Waddington			
	Sherman		Yatsimirskii		(i) Simple Born-Mayer		(ii) Huggins	
Salt	U	$\Delta H_f^0CN^-$	U	$\Delta H_f^0CN^-$	U	$\Delta H_f^0CN^-$	U	$\Delta H_f^0CN^-$
LiCN			192					
NaCN	169.4	+3.1	179	+12.7	174	+7.7	170.2	+3.9
KCN	154.9	+6.1	162	+13.2	158	+9.2	156.5	+7.7
RbCN	149.1	+6.3	155	+12.2	151	+8.4	150.3	+7.5
CsCN	141.3	+6.6	149	+13.3	139	+3.3	142.4	+7.7

I. THE ALKALI METAL BOROHYDRIDES

The lattice energies of the alkali metal borohydrides, which have the NaCl structure, have been calculated by Altshuller (*3*). He employed a simple Born-Lande expression and chose the values of n appropriate to the corresponding fluoride, which is isoelectronic with the borohydride. He added a dispersion energy term. The values he obtained for the lattice energy were: $NaBH_4$, 168; KBH_4, 159; $RbBH_4$, 155; $CsBH_4$, 150 kcal/mole. These values lead to a value of -23 ± 5 kcal/mole for $\Delta H_f^0BH_4^-(g)$ and hence to a value of -75 ± 5 kcal/mole for the enthalpy of the gaseous reaction

$$BH_3 + H^- = BH_4^-$$

J. THE ALKALI METAL SUPEROXIDES

The lattice energies of the alkali metal superoxides have been calculated by Evans and Uri (*35*) and by Kazarnovskii (*71*). Evans and Uri,

unlike Kazarnovskii, did not calculate accurate Madelung constants for the lattice and their values are inferior to his for that reason. The results of both calculations are given in Table XIX.

TABLE XIX

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL SUPEROXIDES

	Evans and Uri		Kazarnovskii	
Salt	U	$\Delta H_f^0O_2^-$	U	$\Delta H_f^0O_2^-$
KO_2	172.2	−17.9	168	−22.1
RbO_2	168.2	−13.2	162	−19.4
CsO_2	164.5	−7.7	156	−16.2

K. THE ALKALINE EARTH PEROXIDES

The lattice energies of the alkaline earth peroxides have been calculated by Evans and Uri (*35*) and by Vedeneev *et al.* (*124*). There is considerable discrepancy in the two sets of results but that of the Russian workers is preferred for the reasons given in Section J.

TABLE XX

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALINE EARTH PEROXIDES

	Evans and Uri		Russian workers	
Salt	U	$\Delta H_f^0O_2^{2-}$	U	$\Delta H_f^0O_2^{2-}$
CaO_2	735	+113.9		
SrO_2	698	+116.7	752.9	+171.6
BaO_2	647	+100.8	717.0	+170.8

L. THE ALKALINE EARTH ACETYLIDES

The lattice energies of the metallic carbides have been calculated by L. I. Kazarnovskaja (*70*) who obtained values of CaC_2, 813.7; SrC_2, 769.4 and BaC_2, 720.8 kcal/mole. I. Hodes (*50*) has repeated Kazarnovskaja's calculation and obtained values of $\Delta H_f^0C_2^{2-}(g)$ by means of a Born cycle. He does not give values for the lattice energies but reports a value of −245 kcal/mole for $\Delta H_f^0C_2^{2-}(g)$.

M. THE LATTICE ENERGIES OF THE ALKALI METAL AZIDES

The lattice energies of the alkali metal azides have been evaluated by Gray and Waddington (*43*), (i) by direct computation, using the

method of Huggins and allowing for the effect of the quadrupole moment of the ion, (ii) by using the equation of Kapustinskii, and (iii) by computation of hydration heats and measurement of the heats of solution. The values obtained by the different methods are given in Table XXI. The values from (i) and (iii) are in good agreement but the values from (ii) are low. An average value of $\Delta H_f^0 N_3^-(g) = 35$ kcal/mole is obtained.

TABLE XXI

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL AZIDES

Azide	Kapustinskii formula	Term-by-term calculation	Hydration heat (a) Ionic radius	Hydration heat (b) Lyotropic number
LiN_3	184		191	194
NaN_3	168.5		173	175
KN_3	153	157	155	157
RbN_3	147	150	149.5	151.5
CsN_3	140	143	143.5	145.5

N. THE ALKALI METAL BIFLUORIDES

The lattice energies of the alkali metal bifluorides have been recently computed by Waddington (*127*) by extended calculation. Values obtained are: KHF_2, 153.4; $RbHF_2$, 147.3; $CsHF_2$, 143.3 kcal/mole. They lead to a value for $\Delta H_f^0 HF_2^-(g)$ of -150 ± 5 kcal/mole.

O. THE ALKALI METAL CYANATES

Yatsimirskii (*134*) has computed a thermochemical radius of 1.59 Å for the cyanate ion and from this the lattice energies of the alkali metal cyanates may be derived by substitution in the Kapustinskii equation. However the value 1.59 Å for the radius seems to be much too low. The alkali metal cyanates have lattice parameters almost identical to the alkali metal azides and Gray and Waddington have deduced an "average radius" for the azide ion of 2.04 Å. A similar value would be expected for the cyanate ion. Adopting the value 2.04 Å, the author has (i) used it in the Kapustinskii equation to deduce lattice energies and (ii) used it in the hydration enthalpy versus crystal radii interpolation to deduce hydration enthalpies for the cyanates. Unfortunately only the lattice energies of sodium and potassium cyanates can be deduced because the enthalpies of solution of the other cyanates are unknown. The charge distribution on the cyanate ion is not known and this makes the ex-

tended calculation of cyanate lattice energies very difficult. However a preliminary calculation has been made by the author for potassium cyanate. The results obtained are summarized in Table XXII. A value of −63 kcal/mole is adopted for $\Delta H_f^0 NCO^-(g)$.

TABLE XXII

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL CYANATES

	Yatsimirskii		Kapustinskii's formula with radius of NCO^- = 2.04 Å		Hydration heat from radius of 2.04 Å		Extended calculation	
Salt	U	$\Delta H_f^0 NCO^-$	U	$\Delta H_f^0 NCO^-$	U	$\Delta H_f^0 NCO^-$	U	$\Delta H_f^0 NCO^-$
LiNCO	203		184					
NaNCO	193	−48.6	169	−71.0	176	−64.4		
KNCO	173.5	−48.1	153	−67.4	156	−64.2	158	−62.4
RbNCO	165.5		147					
CsNCO	158		140					

P. THE ALKALI METAL THIOCYANATES

The lattice energies of the alkali metal thiocyanates can be calculated from Yatsimirskii's (*133*) thermochemical radius of 1.95 Å or, in the case of NaCNS and KCNS, from the hydration enthalpies obtained from the Büchner interpolation by Waddington (*126*). The results are given in Table XXIII. There is a considerable discrepancy between them. Waddington's results lead to a value of −25.9 kcal/mole for $\Delta H_f^0 CNS^-(g)$ and Yatsimirskii's to a value of −11.5 kcal/mole.

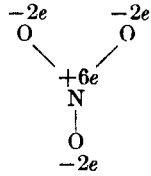
TABLE XXIII

THE LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL THIOCYANATES

Salt	Yatsimirskii U	Value from hydration heat U
LiCNS	183.5	
NaCNS	173	161
KCNS	156.5	143
RbCNS	150	
CsCNS	144	

Q. The Alkali Metal Nitrates

The only direct calculation of the lattice energy of an alkali metal nitrate was made by Topping and Chapman (*119*) in 1927. They calculated an electrostatic potential of an array of Na^+, N^{5+}, and O^{2-} ions, not including the self energy of an $N^{5+}O_3^{2-}$ group, so that this term corresponds to a Madelung energy for an array of point charges at the centers of the NO_3^- and Na^+ ions plus a multipole energy term, the multipole having the charge distribution indicated below.



This is obviously too high a charge distribution, so that the size of this term would be expected to be too large. The repulsive energy term was represented as $1/r^n$, n being taken as equal to 10; a value of 178 kcal/mole was obtained. Hojendahl (*52*) has calculated an electrostatic energy of 180 kcal/mole and using a simple Born-Lande expression the present author finds a value of 162 kcal/mole. This value is obviously too low, as no allowance has been made for the dispersion energy or for the multipole energy; these two terms together may well be of the order of 10-15 kcal/mole. Yatsimirskii (*133*) has calculated a thermochemical radius of the nitrate ion of 1.89 Å and the values obtained for the lattice energies from this value are given in Table XXIV. Waddington (*126*) has also obtained the lattice energies from the value of the hydration heats of the ion pairs obtained by the Büchner extrapolation. Yatsimirskii (*133*) gives a value of $\Delta H_f^0 NO_3^-(g) = 80$ kcal/mole while Waddington's results lead to a value of −81.4 kcal/mole.

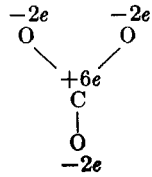
TABLE XXIV

The Lattice Energies (kcal/mole) of the Alkali Metal Nitrates

Salt	Kapustinskii formula U	Chapman and Topping U	Hydration heat value U	Hojendahl U
$LiNO_3$	187		195	
$NaNO_3$	176	178	176	162
KNO_3	160		159	
$RbNO_3$	153		155	
$CsNO_3$	148		145	

R. The Alkaline Earth and Other Metal Carbonates

The lattice energies of the carbonates of several divalent metal ions were calculated by Lennard-Jones and Dent (*80*). They calculated the lattice energy of an array of M^{2+}, C^{4+}, and O^{2-} ions, not including the self energies of the $C^{4+}O_3^{2-}$ groups. This is equivalent to calculating a Madelung energy for an array of point charges at the centers of the M^{2+} ions and the centers of the CO_3^{2-} ions plus a multipole energy, the multipoles having the distribution



This is obviously too high a charge distribution so that one would expect the total electrostatic energy to be too large. The repulsive energy was represented as $1/r^n$, n being taken equal to 10-11. However no term was included for the dispersion energy. Hojendahl (*52*) has calculated Madelung energies for a number of divalent metal carbonates with the calcite structure, and using the repulsive energy term $1/r^n$ with $n = 10$ the author has calculated the lattice energies given in Table XXV from Hojendahl's data. These are all probably too low as no permanent multipole or dispersion energy terms have been included. Kapustinskii and Yatsimirskii have calculated a thermochemical radius of 1.85 Å for the carbonate ion and the values obtained on inserting this into the Kapustinskii equation are also given in Table XXV. It will be seen from the

TABLE XXV

The Lattice Energies (kcal/mole) of the Alkaline Earth and Other Metal Carbonates

	Kapustinskii and Yatsimirskii		Lennard-Jones and Dent		Hojendahl plus repulsive term	
Salt	U	$\Delta H_f^0CO_3^{2-}$	U	$\Delta H_f^0CO_3^{2-}$	U	$\Delta H_f^0CO_3^{2-}$
$MgCO_3$	760	−67	771	−56	696	−131
$CaCO_3$	714	−37	701	−50	644	−107
$SrCO_3$	650	−64				
$BaCO_3$	625	−61				
$ZnCO_3$	746	−112	775	−83	693	−166
$CdCO_3$	700	−105	715	−90	652	−153
$MnCO_3$	728	−86	747	−67	665	−150
$FeCO_3$	746	−72	762	−66	686	−142

table that the values for $\Delta H_f^0CO_3^-(g)$ are not very consistent in any of the sets of data, nor do the sets of data agree with each other very well. The internal inconsistency may be a reflection of nonionic bonding in some of the heavy metal carbonates.

S. The Alkali Metal Borofluorides

The lattice energies of the cubic, high temperature forms of NH_4BF_4 and KBF_4 have been calculated by Altshuller (*2*). The lattice energies of KBF_4, $RbBF_4$, and $CsBF_4$ were also calculated approximately by de Boer and Van Liempt (*28*). Kapustinskii and Yatsimirskii (*68*) have calculated a thermochemical radius of 2.28 Å for the BF_4^- ion from which the lattice energies of the alkali metal salts may be found. The values obtained are given in Table XXVI. It will be seen that they are all fairly concordant and lead to a value for $\Delta H_f^0BF_4^-(g)$ of −406 kcal/mole.

TABLE XXVI

The Lattice Energies (kcal/mole) of the Alkali Metal Borofluorides

	Russian workers		de Boer and Van Liempt		Altshuller	
Salt	U	$\Delta H_f^0BF_4^-$	U	$\Delta H_f^0BF_4^-$	U	$\Delta H_f^0BF_4^-$
$LiBF_4$	167	−408				
$NaBF_4$	157	−406				
KBF_4	143	−408	148	−403	144	−407
$RbBF_4$	138	−403	135	−406		
$CsBF_4$	133	−405	129	−409		
NH_4BF_4					136	

IV. Uses of Calculations of Lattice Energies

A. $\Delta H_f^0X^-(g)$ and the Determination of Electron Affinities

The application of the Born-Haber cycle to a theoretically determined lattice energy actually gives a value for $\Delta H_f^0X^-(g)$, or $\Delta H_f^0X(g) - E$, and a knowledge of $\Delta H_f^0X(g)$ is required before a value can be assigned to the electron affinity. Alternatively, if a value of the electron affinity is available from other sources a value for the enthalpy of formation of the free radical $\Delta H_f^0X(g)$, can be obtained. However in some cases such as NO_3, O_2, NO_2, X is not a free radical but a stable molecule whose enthalpy of formation is known and then the electron affinity can be found directly. In some other cases, for example, the alkali metal halides and the alkaline earth oxides, a bond

dissociation energy is needed in addition to the lattice energy and then a value for the electron affinity can be found. The values obtained for $\Delta H_f^0X^-(g)$ from the lattice energies discussed in the preceding section are listed in Table XXVII.

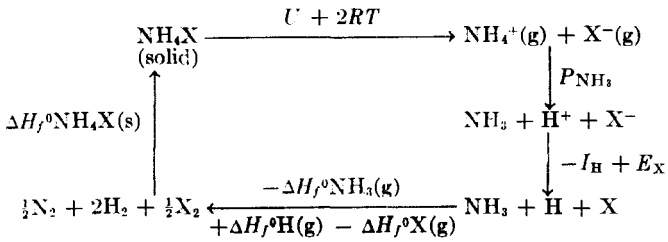
TABLE XXVII

VALUES OBTAINED FOR $\Delta H_f^0X^-(g)$ (KCAL/MOLE)

Group	Value	Group	Value	Group	Value
O^{2-}	217	NH_2^-	15	C_2^{2-}	−245
S^{2-}	152	NH^-	261	N_3^-	35
Se^{2-}	165	CN^-	7.0	HF_2^-	150
Te^{2-}	145	BH_4^-	−23	CNO^-	−63
OH^-	50	O_2^-	−19	NO_3^-	−81
SH^-	−31	O_2^{2-}	171	BF_4^-	−406

B. THE DETERMINATION OF ABSOLUTE VALUES OF PROTON AFFINITIES

The classical example of the use of lattice energies to determine proton affinities is the case of the ammonium ion. Grimm (*45*) pointed out that the following cycle could be used to obtain the proton affinity of ammonia.



The proton affinity of ammonia is therefore given by the relation

$$\begin{aligned} P_{NH_3} &= -(U + 2RT) + I_H - E_X + \Delta H_f^0NH_3(g) + \Delta H_f^0H(g) \\ &\quad + \Delta H_f^0X(g) - \Delta H_f^0NH_4X(s) \\ &= -(U + 2RT) + \Delta H_f^0H^+(g) + \Delta H_f^0NH_3(g) + \Delta H_f^0X^-(g) \\ &\quad - \Delta H_f^0NH_4X \end{aligned}$$

where I_H is the ionization potential of the hydrogen atom.

Values for the lattice energies of the ammonium halides were originally calculated by Grimm (*45*); later van Arkel and de Boer (*122*) gave a value of 148 kcal/mole for the lattice energy of NH_4Cl. Probably not too much reliance can be placed on these values. Bleick (*11*)

using the extended Born-Mayer method, calculated the lattice energies of all the ammonium halides. His values together with the resulting proton affinities are given in Table XXVIII. The actual value obtained, 209 kcal/mole, differs by about 3 kcal/mole from that given by Bleick because more recent thermochemical data have been employed. It will be seen that there is a discrepancy in the lattice energy of ammonium fluoride, which has the wurtzite structure (4:4 coordination); the reason is that the actual lattice energy of NH_4F contains an appreciable energy term due to hydrogen bonding.

TABLE XXVIII

THE LATTICE ENERGIES (KCAL/MOLE) OF THE AMMONIUM HALIDES AND THE PROTON AFFINITY OF AMMONIA

Salt	NH_4F	NH_4Cl	NH_4Br	NH_4I
U_0^0	175.2	161.6	154.0	145.5
$-(U + 2RT)$	−176.4	−162.8	−155.2	−146.7
$-\Delta H_f^0 NH_4X(s)$	+111.6	+75.38	+64.61	+48.3
$\Delta H_f^0 H^+(g)$	367.08	367.08	367.08	367.08
$\Delta H_f^0 X^-(g)$	−64.8	−59.2	−54.9	−49.1
$\Delta H_f^0 NH_3(g)$	−11.04	−11.04	−11.04	−11.04
P_{NH_3}	227.6	209.4	210.5	208.5

The method outlined above is capable of extension to a number of groups though no very wide use has been made of it. Sherman (*114*) calculated the proton affinity of water by assuming that the lattice energy of hydroxonium perchlorate ($H_3O^+ClO_4^-$) was the same as that of $NH_4^+ClO_4^-$ since the unit cells of the two solids are isomorphous and very nearly the same size. He obtained a value of 182 kcal/mole. The proton affinities of the methylamines could be obtained by this method if their lattice energies were known. Certainly approximate values could be obtained by the use of the Kapustinskii equation.

TABLE XXIX

PROTON AFFINITIES (KCAL/MOLE)

Group	NH_3	NH_2^-	NH^{2-}
Proton affinity	209	393	613
Group	H_2O	OH^-	O^{2-}
Proton affinity	182	375	554
Group		SH^-	S^{2-}
Proton affinity		342	550

The lattice energies of the alkali metal hydroxides, the alkali metal amides, the alkaline earth chacogenides and the alkaline earth imides, give values for $\Delta H_f^0OH^-(g)$ etc. and so enable the proton affinities of these groups to be calculated. The values obtained are given in Table XXIX.

C. The Absolute Enthalpies of Formation of Complex Ions

In aqueous solution the factors which affect the enthalpy of formation of a complex ion are complicated by the presence of an effect caused by a change in the enthalpy of solvation. If we consider the reaction

$$BF_3(aq) + F^-(aq) \rightarrow BF_4^-(aq)$$

we see that a fluoride ion has lost its solvation sheath and that a borofluoride ion has been solvated. In the similar reaction in the gas phase

$$BF_3(g) + F^-(g) \rightarrow BF_4^-(g)$$

there are no solvation effects and the only effects are due (1) to a change of hydridization of the original bonds and (2) to the formation of a new bond. The calculated lattice energies of the alkali metal salts enable values for $\Delta H_f^0F^-(g)$ and $\Delta H_f^0BF_4^-(g)$ to be assigned and hence the enthalpy of the reaction can be calculated. So far there are data available for only a few complex ions, for example, HF_2^-, BH_4^-, BF_4^-, and the values for their enthalpies of formation are given in Table XXX.

TABLE XXX

The Enthalpies of Formation of Some Complex Ions

Complex ion	Reaction	Enthalpy (kcal/mole)
BF_4^-	$BF_3 + F^- \rightarrow BF_4^-$	−76
BH_4^-	$BH_3 + H^- \rightarrow BH_4^-$	−75
HF_2^-	$HF + F^- \rightarrow HF_2^-$	−58

D. Lattice Energies and Nonionic Contributions to Bonding in Crystal Lattices

Sherman (*114*) and other workers have compared crystal energies obtained by the Born-Haber cycle from experimental thermochemical data with theoretical values calculated assuming strict ionic character. The differences obtained have been used to indicate deviations from strict heteropolarity. Sherman (*114*) in his review gives results for 50 crystals, the computations being made with the Born-Lande equation.

Later workers have used the Born-Mayer equation and the extended Mayer-Huggins method, allowing for the Van der Waals and zero-point energies. The computations made and their comparison with thermochemical data, utilizing the most recent data, either from the *U. S. Bureau of Standards Circular* 500 or from later sources, will be considered below.

1. The Halides of Univalent Metals (Other than the Alkali Metals)

After Sherman (*114*), the lattice energies of the argentous, the thallous and the cuprous halides were recalculated by Mayer (*92*) and by Mayer and Levy (*95*). Later Altshuller (*1*) and Morris and Ahrens (*100*) corrected the earlier experimental values for the lattice energies, using new values for the heats of sublimation of the metals. Ladd and Lee (*76*) have recently recalculated the lattice energies of the silver and thallous halides by a method avoiding the use of the Huggins basic radii, which are difficult to fix for these salts. The values obtained, together with the best values for the thermochemical lattice energies are given in Table XXXI.

It will readily be seen that the deviations between the theoretical

TABLE XXXI

LATTICE ENERGIES (KCAL/MOLE) OF SOME UNIVALENT HALIDES

Salt	Sherman	Mayer; Mayer and Levy	Ladd and Lee	Cycle values: Morris and Ahrens	Cycle values: Ladd and Lee
AgF	207.9	219	220	231	228
AgCl	187.3	203	199	219	216
AgBr	181.3	197	195	217	214
AgI	175.9	190	186	214	211
TlF				198	
TlCl	159.3	167	164	176	175
TlBr	154.9	164	159	173	172
TlI	148.4	159	152	168	166
CuF					
CuCl	206.1	216		234	
CuBr	197.7	208		232	
CuI	187.7	199		229	
AuF					
AuCl				249	
AuBr				249	
AuI				251	

and experimental lattice energies for the halides of a given metal are least in the fluoride and increase through the chloride and bromide and are greatest in the iodide, in accordance with the increasing polarizability and decreasing electronegativity of the halide. Again for the metal salts of a given halide the deviations increase in passing from the thallous through the argentous to the cuprous salts. This is, as Morris and Ahrens point out, in the order of increasing ionization potential and decreasing radius of the ion. It is interesting to note that aurous iodide, the only aurous halide whose structure has been reported, has a lattice consisting of chains of —Au—I—Au—I—Au—.

2. The Halides of the Divalent Metals

Sherman (*114*) originally presented a good deal of data on the theoretical and thermochemical lattice energies of the divalent metal halides, the calculations being made with the Born-Lande equation. Morris (*98*) has extended the theoretical calculation, again using the Born-Lande equation and has recalculated the thermochemical data. McClure and Holmes (*97*) have also recalculated the thermochemical data for the lattice energies of the transition metals. The results of these calculations are given in Table XXXII.

Before these results are discussed however the occurrence of a new energy term in those crystals in which the metal ion has an unfilled d shell must be considered. Under the influence of the electrostatic field of the neighboring negative ions the otherwise degenerate orbitals of the metal ion are split; the nature of the splitting depends on the symmetry of the crystal field. This splitting produces a stabilization energy. For an account of the theory and references to earlier work the reader is referred to the review articles by Orgel (*101*) and Griffith and Orgel (*44*). Orgel (*101*) pointed out that if the thermochemical lattice energies of the divalent transition metal halides were plotted against their atomic number a minimum occurred at the manganous salt, which has the d^5 configuration. Recently Hush and Pryce (*57*) have repeated the Orgel plot and drawn a smooth curve through the values of the lattice energies of the calcium, manganous, and zinc salts. Here the metal ions have the configurations $3d^0$, $3d^5$, $3d^{10}$, so that in these salts the crystal field stabilization energy is zero. The difference between points on this smooth curve and the actual thermochemical values of the lattice energies gives, to a first approximation, the crystal field stabilization energies. More refined calculations carried out on the oxides of the transition metals suggest that the approximation yields values which are rather low (*57*). The variation of thermochemical lattice energy with atomic number is

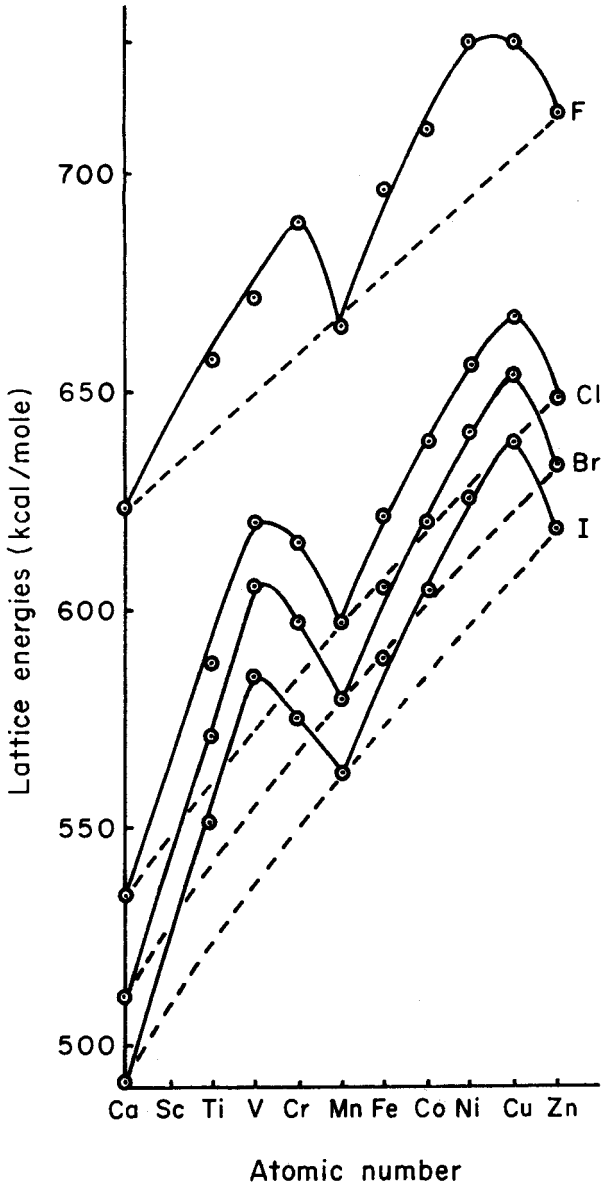


FIG. 3. Crystal field stabilization of dihalides of first row transition metals.

shown in Fig. 3 and the values of the crystal field stabilization energy are given in Table XXXII.

It will be seen from Table XXXII, that after allowing for the crystal field stabilization energy, there is very little discrepancy in the case of

TABLE XXXII

LATTICE ENERGIES (KCAL/MOLE) OF DIVALENT HALIDES

Salt	Structure	Ionization potential ev.	Sherman	Δ	Morris	Δ	Born-Haber cycle	Crystal field stabilization energy
MgF_2	Rutile	15.03	696.8	−1.8	684	+11	695	0
CaF_2	Fluorite	11.87	617.7	+6	622	+2	624	0
TiF_2							657 ± 15‡	17^{++}
VF_2							671.5 ± 20‡	23^{++}
CrF_2							688 ± 3	30^{++}
MnF_2	Rutile	15.64	656.3	+6	662	0	662	0
FeF_2	Rutile	16.18	657.7		681	+15	696	21.8
CoF_2	Rutile	17.05			688	+20	708	24.8
NiF_2	Rutile	18.15	697.1	+31	694	+34	728	35.0
CuF_2	Rutile	20.29	689.6	+37	627	+100	727	27.0^{++}
ZnF_2	Rutile	17.96			688	+22	710	0
BaF_2	Fluorite	10.00	556.4	+10	561	+5	566	0
SrF_2	Fluorite	10.03	587.5	0	592	−4	588	0
PbF_2	Fluorite	15.03	580.7	+14	584	+11	595	0
CdF_2	Fluorite	16.90	628.7	+33	634	+28	662	0
HgF_2	Fluorite	18.751			626	+29	655	0
$SrCl_2$	Fluorite	11.03	493.6	+12	496	+10	506	0
$MgBr_2$	CdI_2	15.03			513	+62	575	0
$MnBr_2$	CdI_2	15.64			522	+61	583	0
$FeBr_2$	CdI_2	16.18			530	+77	607	16^{++}
$CoBr_2$	CdI_2	17.05			536	+88	624	20^{++}
MgI_2	CdI_2	13.57			486	+62	548	
CaI_2	CdI_2	11.87			455	+37	492	0
TiI_2	CdI_2	13.57			486	+62	548	30.6
MnI_2	CdI_2	15.64			481	+82	563	0
FeI_2	CdI_2	16.18			493	+96	589	14.8
CoI_2	CdI_2	17.05			502	+103	605	26.5
PbI_2	CdI_2	15.03	461	+49	460	+50	510	0
CdI_2	CdI_2	16.90	477	+99	477	+99	576	0

Δ Represents the difference between the Born-Haber cycle and the calculated values of the lattice energy.

* There seems to be some doubt as to the structure of CuF_2, which perhaps explains the large discrepancy between Morris' and Sherman's values.

++ These values of the crystal field stabilization energy have been calculated by the author, the rest are from the paper by Hush and Pryce (*15*).

‡ Estimate only.

the fluorides between the calculated lattice energies and those obtained from the Born-Haber cycle. This indicates that the fluorides are predominantly ionic. The small discrepancies which arise in the case of CdF_2 and HgF_2 are probably no larger than could be accounted for by a London dispersion term, which has been neglected in the simple calculation. Practically no data are available for the chlorides but by the time the bromides have been reached the discrepancies are large and cannot be explained by the crystal field stabilization energies, which are too small. The discrepancies are even larger in the case of the iodides. Within a given series of halide salts the size of the deviation increases with increase in the ionization potential of the metal ion, as was pointed out by Morris (*98*).

3. The Chalcogenides of the Monovalent Metals (Other than the Alkali Metals)

A few lattice energies of these compounds have been calculated by Sherman (*114*) and his values together with the values given by the Born-Haber cycle are given in Table XXXIII. It will be seen that the

TABLE XXXIII

THE LATTICE ENERGIES (KCAL/MOLE) OF SOME CHALCOGENIDES OF MONOVALENT METALS

Salt	Structure	*I*	Sherman	Δ	Cycle
Ag_2O	Cuprite	7.574	585	+129.1	714.1
Cu_2O	Cuprite	7.724	682	+95.7	777.7
Cu_2S	Fluorite	7.724	612	+61	672.7
Cu_2Se	Fluorite	7.724	599	+94.3	693.3

differences between the thermochemical and the calculated values are very large, so that these crystals cannot be considered to be primarily ionic.

4. The Chalcogenides of the Divalent Metals

The lattice energies of the chalcogenides of the alkaline earth metals and beryllium have already been discussed in Section I and it was noted that even in these compounds there appeared to be a non-ionic contribution in the sulfides, selenides, and tellurides. Values for the lattice energies of other chalcogenides are given in Table XXXIV, being taken from Sherman (*114*) and from Hare and Brewer (*49*) for some oxides. The size of the crystal field stabilization energy, given under (i) as a first approximation and under (ii) as the value obtained by a more

TABLE XXXIV

LATTICE ENERGIES (KCAL/MOLE) OF SOME DIVALENT METAL CHALCOGENIDES

Salt	Structure	I (ev)	Sherman	Δ	Hare and Brewer (i)	Δ	Hare and Brewer (ii)	Δ	Cycle	Crystal field stabilization (i)	Crystal field stabilization (ii)
CaO	NaCl	11.87			846.7	−18.9	833	−4.8	828.2	0	
TiO	NaCl	13.57			959.1	−31.3	916	+11.8	927.8	62.5	74.1
VO	NaCl	14.71			990.1	−54.0	940	−3.9	936.1	55.2	63.9
MnO	NaCl	15.64	912	−0.6	915.9	−3.5	890	+21.4	911.4	0	
FeO	NaCl	16.18	944	−6.4	937.6	0	907	+30.6	937.6	13.1	13.6
CoO	NaCl	17.05	950	+4.1	957.6	−3.5	917	+37.1	954.1	18.9	20.3
NiO	NaCl	18.15			974.4	−0.2	934	+40.2	974.2	26.2	29.1
ZnO	Wurtzite	17.96	977	−12.6					964.4	0	
CdO	NaCl	16.90	867	+37.2					904.2	0	
HgO											
PbO											
ZnS	Sphalerite	17.96	819	+45.5					864.5	0	
ZnS	Wurtzite	17.96	816	+45.3					861.3	0	
CdS	Wurtzite	16.90	770	+42.7					812.7	0	
HgS	Sphalerite	18.75	774	+79.5					853.5	0	
PbS	NaCl	15.03	705	+35.4					740.4	0	
MnS	NaCl	15.64	788	+13.3					801.3	0	
ZnSe	Sphalerite	17.96	790	+73.1					863.1	0	
CdSe	Sphalerite	16.90	745	+73.3					808.3	0	
HgSe	Sphalerite	18.75	749	+117.9					866.9	0	
MnSe	NaCl	15.64	762	+27.6					789.6	0	

refined treatment, as calculated by Hush and Pryce (*57*) is also given in Table XXXIV.

It will be readily seen from the table that the values for the oxides given by the simple Born-Lande [Hare and Brewer (i)] and the simple Born-Mayer [Hare and Brewer (ii)] expressions show quite large divergences, as much as 50 kcal/mole. The differences between these values and the cycle values in no way parallel the crystal field stabilization energy and it is quite evident that the accuracy of these simple calculations is probably less than the size of the crystal field stabilization term. All that can be said is that, within the accuracy of the calculations there appears to be no evidence for any appreciable nonionic character in bonding. It is interesting to compare this with the case of the fluorides of the same elements discussed in the previous section where the same appears to hold true. The values for a few sulfides and selenides are also given in Table XXXIV and it will be seen that here the differences between the calculated and the thermochemical values increase in size in passing from sulfide to selenide and in passing from zinc through cadmium to mercury, as would be expected from considerations of decreasing electronegativity in the anions and increasing ionization potential in the cations.

5. The Oxides of Some Trivalent Metals

Sherman (*114*) has calculated the lattice energies of Al_2O_3 and Cr_2O_3. No other calculations appear to have been made. In Table XXXV the calculated values are compared with those obtained thermochemically.

TABLE XXXV

THE LATTICE ENERGIES (KCAL/MOLE) OF OXIDES OF THE TRIVALENT METALS

Salt	Structure	*I*	Sherman	Δ	Cycle
Al_2O_3	Corundum	1307.4	3708	−45	3663
Cr_2O_3	Corundum	1310	3655	−113	3542

It will be seen that in both cases the calculated values are higher than the thermochemical ones and that the differences are relatively small. This indicates the essentially ionic nature of these compounds.

6. The Oxides of the Tetravalent Metals

Sherman (*114*) has calculated the lattice energies of SnO_2 and PbO_2. These calculated values, together with the thermochemical values are given in Table XXXVI. The calculated value for SnO_2 is very close to

TABLE XXXVI

THE LATTICE ENERGIES (KCAL/MOLE) OF THE OXIDES OF THE TETRAVALENT METALS

Salt	Structure	I	Sherman	Δ	Cycle
SnO_2	Rutile	2143	2734	−19	2715
PbO_2	Rutile	2264	2620	+153	2763

the thermochemical value, while for PbO_2 the difference between the two is about 6%. In view of the uncertainty of the calculation this cannot be taken as very definite evidence of nonionic character.

E. THE DETERMINATION OF THE STABILITY OF HYPOTHETICAL COMPOUNDS

In 1923 Grimm and Herzfeld (*46*) calculated the lattice energies of a whole series of hypothetical compounds. From these lattice energies they obtained, by the use of the Born-Haber cycle, the enthalpies of formation of the compounds. To obtain the lattice energies of some of the hypothetical compounds they used the Born-Lande equation. For some of the other compounds they assumed their lattice energies to be equal to those of neighboring stable compounds in the periodic table, for example

$$U_{NeCl} = U_{NaCl},\ U_{NaCl_2} = U_{MgCl_2},\ U_{MgCl} = U_{NaCl},\ U_{AlCl_2} = U_{MgCl_2}.$$

Now from the Born-Haber cycle

$$U_{M'X_n} + (n+1)RT = \Delta H_f{}^0M'^{n+}(g) + n\Delta H_f{}^0X^-(g) - \Delta H_f{}^0M'X_n(s) \quad (50)$$

$$U_{M''X_n} + (n+1)RT = \Delta H_f{}^0M''^{n+}(g) + n\Delta H_f{}^0X^-(g) - \Delta H_f{}^0M''X_n(s) \quad (51)$$

and so, if $U_{M'X_n} = U_{M''X_n}$

$$\Delta H_f{}^0M'X_n(s) - \Delta H_f{}^0M''X_n(s) = \Delta H_f{}^0M'^{n+}(g) - \Delta H_f{}^0M''^{n+}(g) \quad (52)$$

or

$$\Delta H_f{}^0M'X_n(s) = \Delta H_f{}^0M'^{n+}(g) - \Delta H_f{}^0M''^{n+}(g) + \Delta H_f{}^0M''X_n(s). \quad (53)$$

The assumptions inherent in this are (i) that the lattices considered, both real and hypothetical, are totally ionic, or if not that the nonionic contribution is the same in each, and (ii) that the lattices have the same energy, that is that the ions M′ and M″ have the same radius. Neither of these assumptions can be expected to be completely true, for example Na^+, Ne^+ and Mg^+ are not isoelectronic, but the deviations resulting from the assumptions should be small. Though the results of Grimm and Herzfeld need recalculating, because of the change in the values of

the thermochemical quantities employed, their underlying conclusions remain unchanged. They calculated by the method outlined above the enthalpies of formation of the hypothetical monohalides and corresponding chalcogenides of the inert gases and of the alkaline earth metals, and of the dihalides and corresponding chalcogenides of the alkali metals and of aluminum as well as of other compounds. The results given in Table XXXVII follow their treatment, except that more modern thermochemical data are used. In Table XXXVII the monohalides are also considered.

TABLE XXXVII

ENTHALPIES OF FORMATION (KCAL/MOLE) OF MONOHALIDES AND OXIDES OF THE INERT GASES AND THE ALKALINE EARTH METALS

	Salt				
M	MF	MCl	MBr	MI	M_2O
He	255	+303	+316	+336	+660
Ne	+208	+246	+258	+275	+589
A	+100	+130	+141	+156	+382
Kr	+68	+97	+107	+121	+320
Xe	+39	+62	+72	+85	+316
Be	−14	+34	+48	+67	+122
Mg	−68	−30	−18	−1	+36
Ca	−69	−38	−28	−13	+44
Sr	−78	−49	−39	−24	+28
Ba	−73	−50	−41	−27	+31
Zn		−44	−37	−28	−63
Cd	−58	−40	−33	−24	−26
Hg		−48	−44	−39	
Ga*	−68	−45	−32	−13	
In*	−72	−41	−27	−13	
Al	−94	−45	−30	−11	

* The values for Ga and In are based on an assigned ionic radius.

It will be seen from this table that the monohalides of the inert gases all would be unstable to decomposition into their elements and so obviously could not exist in an ionic lattice. However this is not so for the other monohalides all of which, with the exception of BeCl, BeBr, and BeI, are stable with respect to decomposition to the elements. In these compounds the question arises as to their stability with regard to their disproportionation. In the case of the alkaline earths, zinc and cadmium, the disproportionation reaction is

$$2\,MCl \rightarrow M + MCl_2.$$

In the case of Hg, the transition $2HgX \rightarrow Hg_2X_2$ must be considered and in the case of indium and gallium the disproportionation to the trihalide will be considered. It is interesting to note in passing that the value $\Delta H_f^0 InCl = 41$ kcal/mole is quite close to the thermochemical value quoted in the U. S. Bureau of Standards, circular 500. The enthalpies of disproportionation are given in Table XXXVIII. The conclusions that

TABLE XXXVIII

ENTHALPIES OF DISPROPORTIONATION (KCAL/MOLE) OF THE MONOHALIDES

	Salt			
M	MF	Cl	Br	I
		(1) $2MX \rightarrow M + MX_2$		
Mg	−148	−93	−88	−84
Ca	−152	−114	−105	−102
Sr	−134	−100	−93	
Ba	−140	−106	−98	−92
Zn		−11	−4	+6
Cd	−49	−13	−9	+4
		(2) $2HgX \rightarrow Hg_2X_2$		
Hg		−7	−5	+10
		(3) $3MX \rightarrow 2M + MX_3$		
Ga		+10	+6	−12
In		−5	−16	−16
Al	−29	−31	−36	−42

can be drawn from the table are very interesting. As would be expected, it appears that no monohalide of the alkaline earth metals is stable to disproportionation. However, when the monohalides of zinc and cadmium are considered, the enthalpies of disproportionation are much smaller and in fact positive values are obtained for iodides. However, the accuracy of the calculation does not permit a firm conclusion to be drawn and, for exact statements about equilibria, free energies are required. With both gallium and indium the enthalpies of disproportionation of the monohalides are small and in some cases positive. These are of course just the elements in which unipositive states, of low stability, do appear to occur. The experimental evidence is fairly strong for indium but weaker for gallium. The low enthalpies of disproportionation of the aluminum halides are interesting.

Grimm and Herzfeld also pointed out the instability of the hypothetical dihalides of the alkali metals. The values of the enthalpies of

formation of these compounds together with those of some other compounds of divalent states is given in Table XXXIX.

TABLE XXXIX

THE ENTHALPIES OF FORMATION (KCAL/MOLE) OF SOME HYPOTHETICAL DIHALIDES AND THE CORRESPONDING OXIDES

	Salt				
M	MF_2	MCl_2	MBr_2	MI_2	MO
Li		+1061	+1095	+1133	+1037
Na	+403	+513	+533	+580	+522
K	+104	+204	233	+267	+243
Rb	+39	+131	+158		+188
Cs	−30	+51	+76	+113	+123
Al	−185	−65	−35	+2	−55
Cu	−127	−52	−34	−5	−37
Ag	−49	+23	+40	+67	+55

It will be seen from the table that all the dihalides of the alkali metals with the exception of CsF_2, are actually unstable to their formation from the elements. CsF_2 is of course unstable to disproportionation, the enthalpy of the reaction

$$CsF_2 = CsF + \tfrac{1}{2}F_2$$

being −96.9 kcal/mole. All the hypothetical aluminum dihalides are markedly unstable to the disproportionation reaction

$$3\,AlX_2 = 2\,AlX_3 + Al.$$

The well-known thermochemical values for the cupric halides are included for comparison with the values for the hypothetical argentic halides, which are seen, with the exception of AgF_2, to be unstable with respect to their elements. The value for AgO is rather surprising in view of the stability of this compound. This is obviously an example of the approach breaking down because of the assumptions (i) and (ii) above not being fulfilled. AgO is probably not mainly ionic and is not isomorphous with CdO. AgF_2 is seen to be not only stable with respect to its elements but also thermochemically neutral with respect to disproportionation. ΔH for

$$AgF_2 = AgF + \tfrac{1}{2}F_2$$

is approximately zero.

F. Lattice Energies and the Effect of Fluorides and Oxides on the Oxidation State of Metal Salts

It is a well-known truism of inorganic chemistry that most metals show their highest oxidation states in their oxides or fluorides. A consideration of the lattice energies of these compounds and the Born-Haber cycle will reveal why this is the case. Consider a halide MX_n, then

$$U + (n + 1)RT = \Delta H_f^0 M^{n+}(g) + n\Delta H_f^0 X^-(g) - \Delta H_f^0 MX_n(s)$$

or rewriting the expression

$$\Delta H_f^0 MX_n(s) = \Delta H_f^0 M^{n+}(g) + n\Delta H_f^0 X^-(g) - U - (n + 1)RT.$$

If the compound is to be formed the reaction has to be exothermic so that, neglecting the small term $(n + 1)RT$, if $\Delta H_f^0 MX_n(s)$ is to be < 0 then

$$U > \Delta H_f^0 M^{n+}(g) + n\Delta H_f^0 X^-(g). \tag{54}$$

For all the halogens the term $\Delta H_f^0 X^-(g) = \Delta H_f^0 X - E$ is not very different from -60 kcal/mole so that the factor determining n from halide to halide will be U. The quantity U is always higher for the fluorides than for the chlorides; it will be seen from Fig. 3 that the lattice energies of the transition metal difluorides are all about 60 kcal/mole greater than those of the corresponding dichlorides.

A similar argument may be applied to the oxides. Consider the compound $MO_{n/2}$; then

$$\Delta H_f^0 MO_{n/2} = \Delta H_f^0 M^{n+}(g) + \frac{n}{2}\Delta H_f^0 O^{2-}(g) - U \tag{55}$$

so that if the compound is to be exothermic

$$U > \Delta H_f^0 M^{n+}(g) + \frac{n}{2}\Delta H_f^0 O^{2-}(g). \tag{56}$$

Here the lattice energy U is usually greater than that for the corresponding fluoride, for example $U_{MgO} = 938$ kcal/mole, $U_{MgF_2} = 695$ kcal/mole, because of the double charge on the oxide ion. However this is offset by the value of $\Delta H_f^0 O^{2-}(g)$, which is $+217$ kcal/mole, as compared to approximately -64 kcal/mole for $\Delta H_f^0 F^-(g)$.

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