CRYSTAL ENERGIES OF IONIC COMPOUNDS AND THERMOCHEMICAL APPLICATIONS

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I. INTRODUCTION

It was found by W. H. Bragg and W. L. Bragg (176) in 1913 that the sodium chloride crystal is built up not of discrete molecules but of either atoms or ions, inasmuch as each sodium atom or ion is immediately surrounded by six chlorines equidistant from it, and each chlorine by six sodiums. Further investigations showed that sodium chloride is not unique in this respect; it was found that in many other inorganic crystals the stoichiometric molecule is not the fundamental constituent of the crystal, each atom instead being surrounded symmetrically by other atoms in such a way that no finite aggregates are present. Many of these structures are described later in this paper.

Shortly after the early work on the determination of the structure of crystals had been carried out, it was assumed that these crystals are composed of ions rather than neutral atoms, but no very good proof of this was given. Debye and Scherrer tried to show the existence of ions in the lithium fluoride crystal from a study of the intensity of reflection of x-rays, but their proof was subsequently shown to be invalid. Only within the last four years has a satisfactory proof of the existence of ions in crystals based on intensity of reflection of x-rays been carried out (180, 181). A quantitative theory of ionic crystals was developed between 1918 and 1924 by Madelung, Haber, and especially Born (174). In particular, Born derived formulas which permit the calculation of the energy of formation of an ionic crystal from separated ions. Thermochemical considerations involving this energy have aided greatly in facilitating the understanding of many crystal properties. Moreover, verification of the quantitative results obtained from the Born theory affords the best substantiation of the hypothesis that many crystals are built up of ions.

Many investigators, notably Grimm (178) and his coworkers, have made comprehensive studies of the energy relations of crystals which, however, have in general not been very accurate because of lack of necessary data. Within recent years a great amount of thermochemical data has been published which can be used in conjunction with crystal energies to obtain important thermal quantities, the values of which have hitherto not been known or have been known only with low accuracy. It is the purpose of this paper to present the fundamental ideas of the Born theory and its thermochemical applications, to tabulate values of Madelung constants and other quantities used in this treatment, to summarize the most recent thermochemical data appropriate for calculations involving crystal energies (heats of sublimation, heats of dissociation, ionization potentials, etc.), to obtain values of the electron affinity of electronegative atoms and other thermochemical quantities with the aid of the Born cycle, and to draw conclusions relative to the types of bonds in a number of crystals.

II. THE LATTICE ENERGY OF IONIC CRYSTALS

Our concept of an ideal crystal is based upon the fundamental idea that the crystal may be built up by the repetition of unit atomic groupings. In order to discuss the properties of a crystal it is convenient to select some portion that will be representative of the indefinitely extended whole. For this purpose a parallelepiped is chosen from which the entire crystal may be built by repetition along the coördinate axes; this parallelepiped is called the unit cell.

The lattice energy of an ionic crystal may be defined as the energy change in the process of bringing the ions infinitely separated from one another to the positions they occupy in the crystal. In order to account for the stability of crystals assumed to be composed of ions, it is necessary to introduce forces between the ions which are not Coulomb forces, for it is known that no stable equilibrium is possible in an electrostatic system of charges producing fields for which the Laplace equation holds. Born and Landé assumed that in addition to the Coulomb forces between the ions there are intrinsic repulsive forces which change rapidly with the distance. The idea that molecules in a solid are held in equilibrium by an attractive force and a more rapidly changing repelling force was suggested as early as 1785 by Boscovitch. The potential expression

$$\phi = -\frac{a}{r^m} + \frac{b}{r^n}, \quad a, b > 0; n > m \tag{1}$$

has been used by several investigators, notably Grüneisen (11) and Mie (26). Born and Landé (4, 5) considered a crystal to be composed of ions and put $m = 1$ and $a = A\epsilon^2$ in the above potential expression.

For the potential of a system consisting of two ions at a distance r apart we write

$$\phi = -\frac{z_1 z_2 \epsilon^2}{r} + \frac{b}{r^n} \tag{2}$$

Here z_1 and z_2 are the valences of the ions, ϵ is the unit of electrical charge (4.770 E.S.U.[2]) and b and n are constants. Figure 1 shows the form of this function. This potential function is to be regarded as a first approximation only. Since the forces between the ions are considered to be central forces which vary as inverse powers of the distance, the potential may be expanded

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[2] Throughout this article values of the physical and chemical constants will be taken from the paper by Birge (2).

into a power series in $1/r$. In equation 2 only the minimum number of terms are retained. The van der Waals' attractive forces are neglected, since they are small compared to the electrostatic forces. The forces due to polarization are small compared to the electrostatic and repulsive forces and their inclusion would constitute an approximation of the second order. Moreover the crystals with which we shall be most concerned possess a high degree of symmetry; hence the induced dipole moments of the ions are self-compensating. To just what extent it is justifiable to assume that the forces between the ions are purely central will be discussed later.

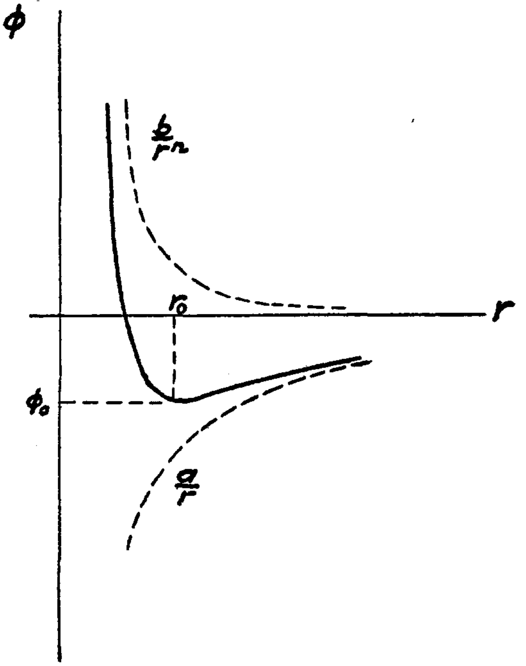

FIG. 1. CRYSTAL ENERGY AS A FUNCTION OF INTERIONIC DISTANCE

$$\phi = -\frac{a}{r} + \frac{b}{r^n}$$

In accordance with equation 2 we may write for the energy per unit cell

$$\Phi = -\frac{\alpha^2\epsilon^2\mu A}{r} + \frac{B}{r^n} \qquad (3)$$

where α is the largest common factor in the valences of all the ions,
μ is the number of stoichiometric molecules in the unit cell,
A is a constant depending only on the structure of the crystal; (it can be calculated from electrostatics and is known as the Madelung constant), and
n is a constant which can be determined from the compressibility of the crystal.

The constant B can be determined from the condition for equilibrium in the crystal $\frac{\mathrm{d}\Phi}{\mathrm{d}r} = 0$, when r has the value R_0, a characteristic equilibrium distance. From equation 3,

$$\left(\frac{\mathrm{d}\Phi}{\mathrm{d}r}\right)_{r = R_0} = \frac{\alpha^2\epsilon^2\mu A}{R_0^2} - \frac{nB}{R_0^{n+1}} = 0 \tag{4}$$

Hence,

$$B = \frac{\alpha^2\epsilon^2\mu A R_0^{n-1}}{n} \tag{5}$$

Substituting this value for B in equation 3,

$$\Phi = -\frac{\alpha^2\epsilon^2\mu A}{r} + \frac{\alpha^2\epsilon^2\mu A R_0^{n-1}}{nr^n} \tag{6}$$

For a crystal in equilibrium

$$\Phi_0 = -\frac{\alpha^2\epsilon^2\mu A}{R_0} + \frac{\alpha^2\epsilon^2\mu A R_0^{n-1}}{nR_0^n} = -\frac{\alpha^2\epsilon^2\mu A}{R_0}\left(1 - \frac{1}{n}\right) \tag{7}$$

$$= \Phi_0^{(1)} + \Phi_0^{(n)}$$

where

$$\Phi_0^{(1)} = -\frac{\alpha^2\epsilon^2\mu A}{R_0} \tag{8}$$

is the potential due to the Coulomb forces, and

$$\Phi_0^{(n)} = \frac{\alpha^2\epsilon^2\mu A}{nR_0} \tag{9}$$

is the potential due to the intrinsic repulsive forces.

R_0 may be determined from x-ray data or from the density of the crystal.

The lattice energy per mole is

$$U_0 = -\frac{N\Phi_0}{\mu} \tag{10}$$

where N is Avogadro's number.

By introducing 7 in 10,

$$U_0 = \frac{\alpha^2\epsilon^2 NA}{R_0}\left(1 - \frac{1}{n}\right) \tag{11}$$

In general it will be found convenient to choose for R_0 the cube root of the molecular volume.

$$R_0 = \delta_0 \tag{12}$$

For binary compounds the smallest anion-cation distance will often be found useful for a value of R_0.

In the treatment which follows, the distance $R_0 = \delta_0$ will be used for convenience, although it is to be remembered that any characteristic equilibrium distance may be used, provided the corresponding value of the Madelung constant is employed. Values of the Madelung constant are proportional to the corresponding equilibrium distances, that is,

$$\frac{A_{R_0}}{R_0} = \frac{A_{\delta_0}}{\delta_0} \tag{13}$$

Substituting 12 in 11,

$$U_0 = \frac{\alpha^2\epsilon^2 NA_{\delta_0}}{\delta_0}\left(1 - \frac{1}{n}\right) \tag{14}$$

Introducing numerical values for the constants N and ϵ, we have

$$\frac{N\epsilon^2}{1\text{ Å.}} = 329.7 \text{ kilogram-calories} \tag{15}$$

Hence,

$$U_0 - \frac{329.7\ \alpha^2 A_{\delta_0}}{\delta_0}\left(1 - \frac{1}{n}\right) \text{ kilogram-calories per mole} \tag{16}$$

where δ_0 is expressed in Ångström units.

When δ_0 is determined from the observed value of the density, equation 16 may be transformed into a more useful form by introducing the relation between density and molecular volume.

$$U_0 = 279.0\,\alpha^2 \left(\frac{\rho}{M}\right)^{\frac{1}{3}} A_{\delta_0} \left(1 - \frac{1}{n}\right) \tag{17}$$

in which ρ is the density expressed in grams per cubic centimeter and M is the gram-molecular weight.

1. The Coulomb energy of ionic crystals

In order to calculate the Madelung constant from electrostatics, we shall consider an idealized crystal in which the ions are to be regarded as spherically symmetrical and at rest in their equilibrium positions. Even at the absolute zero of temperature the ions in any actual crystal possess zero-point energy, which, however, is negligible compared to total energy. The energy of a mole of crystal will be evaluated by determining the ratio of the energy of a crystal to the number of moles of that crystal as the number of moles becomes indefinitely large. This mode of evaluation neglects the energy due to the surface forces, for in any actual crystal the total energy depends upon the amount of surface and the particular planes which form the faces. This energy may also be neglected in a first approximation. Calculations have been made of the surface energy of sodium chloride; they will be discussed later.

The electrostatic energy may be written as

$$\Phi_0^{(1)} = -\frac{\epsilon^2}{2} \sum_{s=1}^{\gamma}{}' \sum_{t=1}^{\infty}{}' \frac{z_s z_t}{r_{st}} \tag{18}$$

Here z_s and z_t are the valences of the s'th and t'th ion respectively, and r_{st} is the distance between them. The primes on the summation signs signify that the terms for which $r = 0$, that is, for $s = t$, shall be omitted from the summation. γ is the number of ions in a unit cell. The factor $\frac{1}{2}$ arises from the fact that in the double summation each pair of ions is counted twice.

We write

$$\Phi_0^{(1)} = -\frac{\epsilon^2}{2}\sum_s z_s\xi_s \tag{19}$$

where $\epsilon\xi_s$ is the potential of the s'th ion, ξ_s being given by the equation

$$\xi_s = \sum_t{}' \frac{z_t}{r_{st}} = \frac{2\,\alpha A_s}{\delta_0} \tag{20}$$

From equation 7,

$$\frac{1}{\mu}\sum_{s=1}^{\gamma} A_s z_s = \alpha A_s \tag{21}$$

The series for ξ_s given by equation 20 converges with extreme slowness. Despite this and the fact that the Madelung constant for sodium chloride had been calculated by Madelung and later by Ewald, Kendall (15), in discussing Ghosh's theory of strong electrolytes, carried out the direct summation to obtain a roughly correct value of the Madelung constant of sodium chloride, showing that the direct method can be used.

The evaluation of the Coulomb energy of a crystal was first made by Madelung (24), although unknown to him a method of solution had previously been given by Riemann and Appell (1). P. P. Ewald (10) found a rapidly converging series which is applicable to the problem. Modifications of this method have been worked out by Born (3) and Emersleben (9), which considerably simplify the calculation for any crystal of the cubic type. Kornfeld (16) has applied Ewald's method to the evaluation of the energies of dipole and quadrupole lattices.

1. Madelung's method. Madelung first considered an infinite row of charges with periodic repetition of pattern after a length *a*. The electric density along the row may be represented by a Fourier series. The potential for a point outside the row may be represented by a corresponding Fourier series having the same period as the electric density. The potential must satisfy Laplace's equation and must vanish at infinity. These conditions are sufficient to determine the expression for the potential. For an electrically neutral row of alternating charges the potential at a point (r, x) proves to be

$$V(r,x) = \frac{8\,\epsilon^2}{a} \sum_{l\,=\,1,3,5\ldots}^{\infty} K_0\left(\frac{2\,\pi l r}{a}\right) \cos\frac{2\,\pi l x}{a} \tag{22}$$

Here K_0 is the Hankel function tabulated by Jahnke and Emde (14) as

$$\tfrac{1}{2}\,i\pi H_0^{(1)}(iz)$$

The series is rapidly convergent, only a few terms being necessary to attain good accuracy.

Equation 22 is not valid as r approaches the value zero. The potential at a charge in a neutral row of charges is

$$V(0,0) = -\frac{4\,\epsilon^2}{a}\left(\frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \ldots\ldots\ldots (-1)^{n+1}\cdot\frac{1}{n} + \ldots\right) \tag{23}$$

The charge at the origin must be omitted, for otherwise the potential would be infinite.

By extending the above method, an expression for the potential of a plane of charges may be derived. For an infinitely extending neutral rectangular plane lattice consisting of alternating charges as in a sodium chloride layer, the potential at a height z above the plane is

$$V(z,xy) = \frac{16\,\epsilon^2}{ab} \sum_{l\,=\,1,3..}^{\infty} \sum_{m\,=\,1,3..}^{\infty} \frac{e^{-2\pi z\sqrt{\frac{l^2}{a^2}+\frac{m^2}{b^2}}}}{\sqrt{\frac{l^2}{a^2}+\frac{m^2}{b^2}}} \cos\frac{2\,\pi l x}{a} \cos\frac{2\,\pi m y}{b} \tag{24}$$

The potential of the entire crystal is obtained by decomposing the lattice into neutral point series and lattice planes and then calculating the potential due to each plane and row.

2. Ewald's method. By means of the identity

$$\frac{1}{r} = \int_0^{\infty} e^{-rx}\,dx \quad (r \neq 0) \tag{25}$$

the potential given by equation 20 may be expressed as an integral. The integrand can be represented as a theta function of three variables. If a transformation formula is applied to this theta function a Fourier representation of the potential is obtained. By introducing an arbitrary constant, η, the integral expressing the potential may be separated into two terms by means of the relation.

$$\int^{\infty} y\mathrm{d}x = \int_0^{\eta} y\mathrm{d}x + \int_{\eta}^{\infty} y\mathrm{d}x \tag{26}$$

By applying the transformation formula for the theta function to the first integral, Ewald obtained two series which are suitable for numerical calculation.

The potential ξ_s in equation 20 is given by the following equations

$$\xi_s = \xi_s^{(1)} + \xi_s^{(2)} \tag{27}$$

where

$$\xi_s^{(1)} = \frac{1}{\pi\mu\delta_0^3} \sum_{hkl}{}' S_{hkl}\, d_{hkl}^2\, e^{-\frac{\pi^2\delta_0^2}{\eta^2 d_{hkl}^2}} - \frac{2\, z_s \eta}{\delta_0 \sqrt{\pi}} \tag{28}$$

and

$$\xi_s^{(2)} = \frac{1}{\delta_0} \sum_{t}{}' z_t \frac{\left[1 - \Omega\left(\frac{\eta R_t}{\delta_0}\right)\right]}{R_t/\delta_0} \tag{29}$$

The value of the arbitrary constant η determines the rapidity of convergence of each series.

S_{hkl} is defined by the relation

$$S_{hkl} = \sum_{j=1}^{\gamma} z_j\, e^{-2\pi i(hx_j + ky_j + lz_j)} \tag{30}$$

where x_j y_j z_j are the coördinates of the j'th ion relative to the s'th ion.

hkl are the Miller indices of a plane, d_{hkl} being the interplanar distance for this set of planes.

The accent on the summation sign in equation 28 signifies that the term for which $(hkl) = (000)$ is to be omitted.

R_t is the distance from the t'th ion to the s'th ion.

The function $\Omega\left(\frac{\eta R_t}{\delta_0}\right)$ is defined by the probability integral

$$\Omega\left(\frac{\eta R_t}{\delta_0}\right) = \int_0^{\frac{\eta R_t}{\delta_0}} e^{-x^2}\,dx \qquad (31)$$

In actual computation a value of η is chosen that will make the two series equally rapidly convergent. In this case each series is itself rapidly convergent, only a few terms being needed to give high accuracy. A valuable feature of Ewald's method is that an independent check on the numerical result may be obtained by carrying through the computation a second time using a different value of η.

3. Born's method. By dividing the unit cell into n sub-cells by means of three systems of equidistant planes parallel to the sides of the cell, any given ion distribution may be approximated by considering each ion to be located at one of these sub-lattice points. The position of an ion is given by the coördinates $\frac{P_1}{n}\ \frac{P_2}{n}\ \frac{P_3}{n}$, where P_1, P_2, P_3 are integers which may assume the values $0, 1, 2, \ldots n-1$.

For a cubic crystal the energy of a unit cell is given by the equation

$$\Phi_0^{(1)} = -\frac{\epsilon^2}{\mu n^3 a_0}\sum_{P=0}^{n-1} S_P\,\Pi\left(\frac{P}{n}\right) \qquad (32)$$

where a_0 is the length of a cube edge of the unit cell.

S_P is defined by the equation

$$S_P = \sum_{m=0}^{n-1} z_m\, e^{\frac{2\pi i}{n}(m_1P_1 + m_2P_2 + m_3P_3)} \qquad (33)$$

Born designates

$$\Pi\left(\frac{P}{n}\right) \equiv \Pi\left(\frac{P_1}{n}\frac{P_2}{n}\frac{P_3}{n}\right)$$

as the "Grundpotential". It is the potential at the origin of a charge distribution

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

The Grundpotential is defined by the formula

$$\Pi\left(\frac{P}{n}\right) = {\sum_{t=0}^{\infty}}' \frac{\cos \frac{2\pi}{n}(t_1P_1 + t_2P_2 + t_3P_3)}{\sqrt{t_1^2 + t_2^2 + t_3^2}} \tag{34}$$

The accent on the summation sign signifies that the term for which $t_1 = t_2 = t_3 = 0$ is to be omitted.

By means of the Ewald formulas the Grundpotential may be separated into two terms

$$\Pi = \Pi^{(1)} + \Pi^{(2)} \tag{35}$$

where

$$\Pi^{(1)}(z) = \frac{1}{\pi}\sum_{k}\frac{e^{-\frac{\pi^2}{\eta^2}R^2_{k-z}}}{R^2_{k-z}} - \frac{2\eta}{\sqrt{\pi}} \tag{36}$$

and

$$\Pi^{(2)}(z) = \sum_{m=1}^{\infty}\frac{1 - \Omega(\eta\sqrt{m})}{\sqrt{m}}\sum_{k^2=m}\cos 2\pi(k_1z_1 + k_2z_2 + k_2z_3) \tag{37}$$

In equation 36,

$$R^2_{k-z} = (k_1 - z_1)^2 + (k_2 - z_2)^2 + (k_3 - z_3)^2 \tag{38}$$

By means of these formulas Emersleben has calculated a table of Grundpotentials for $n = 12$.

The energy of a unit cell as given by equation 32 may be calculated with great simplicity, since only a small number of terms are involved in the summation.

4. Madelung constants. Of the three methods just described for evaluating the Madelung constant, Ewald's method is the only one of general applicability. Although the series given by equations 22, 23, and 24 converge rapidly, Madelung's method cannot be applied in many cases because of the impossibility of decomposing the lattice into neutral point series and lattice planes. Moreover, the method has the disadvantage that it is easy to omit through oversight the potential due to a row of charges, as was done by Landé (17) in the calculation of the Madelung constant of fluorite. An evaluation of the Madelung constant by the use of the Born Grundpotential is by far the most convenient. Unfortunately, however, the numerical table of Grundpotentials calculated by Emersleben can be applied only to cubic crystals in which the parameters determining the ionic positions are integral multiples of one-twelfth of the length of a cube edge.

In the sodium chloride structure, the first for which the Madelung constant was evaluated (by Madelung himself), the positions of the ions are completely determined by the symmetry requirements of the structure. In general, however, this is not the case; the positions of the ions depend on one or more parameters, and the Madelung constant must be evaluated as a function of these parameters. For more than one parameter the calculations become very laborious.

Table 1 gives the Madelung constants which have been evaluated. Here r_0 is the smallest anion-cation distance, δ_0 is the cube root of the molecular volume, and a_0 is the edge of the unit cube. The maximum values of the Madelung constants are given for those structures where they have been evaluated as a function of one or more parameters. These structures will now be considered individually.

(1) Rutile and anatase. Bollnow (37) has calculated by the Ewald method the Madelung constants for the rutile and anatase structures as functions of parameters which determine the cation-anion distance.

Figure 2 and figure 3, taken from "Strukturbericht" (177), show the structures. The lattice is tetragonal in each case. Each structure is determined by two parameters—the axial ratio and a parameter which fixes the position of the oxygen ions. By assuming in each case that the oxygen ions are coördinated about the titanium ions so that the titanium-oxygen distance is constant, relations between the two parameters are given by the geometry of the structures. This assumption is in agreement with the experimentally measured values of the parameters. Thus one independent parameter becomes sufficient to determine each structure.

TABLE 1

Madelung constants

STRUCTURE	A_{r_0}	A_{δ_0}	A_{a_0}	REFERENCE
NaCl	1.747558	2.201785	3.495115	(40, 44, 47)
CsCl	1.762670	2.035356	2.035356	(40)
Sphalerite	1.63806	2.38309	3.78292	(40)
Wurtzite	1.641	2.386		(41, 42)
Fluorite	5.03878	7.33058	11.63656	(38, 40, 45)
Cuprite	4.11552	6.54364	9.50438	(4)
Rutile	4.816	7.70		(37)
Anatase	4.800	8.04		(37)
CdI_2	4.71	6.21		(42)
β-Quartz	4.4394	9.5915		(43)
Corundum	25.0312	45.825		(48)
Perovskite		12.37744*	12.37744*	
K_2PtCl_6		39.99636†	63.49026†	(46)
$(NH_4)_3AlF_6$		33.39098‡	53.00488‡	

* These values have been computed by the author.

† The values given are those computed by the author; they are in agreement with the results of Lennard-Jones and Dent (46). The Pt-Cl distance is taken as 0.25 times the length of a cube edge.

‡ Unpublished calculations of F. J. Ewing.

The results of Bollnow for the Madelung constant of rutile may be expressed as a power series in $0.721 - \alpha$ for values of α in this neighborhood, α being the axial ratio. The equation is[3]

$$A_{r_0} = 4.816 - 4.11(0.721 - \alpha)^2 \tag{39}$$

The maximum occurs for $\alpha = 0.721$. The average observed values for a number of crystals is only 0.67.

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[3] These equations have been calculated by Pauling (29).

For anatase the equation expressing the Madelung constant as a function of the axial ratio is the following:[3]

$$A_{r_0} = 4.800 - 0.709(2.620 - \alpha)^2 \tag{40}$$

The maximum value of A_{r_0} occurs for $\alpha = 2.620$, the observed value being 2.51.

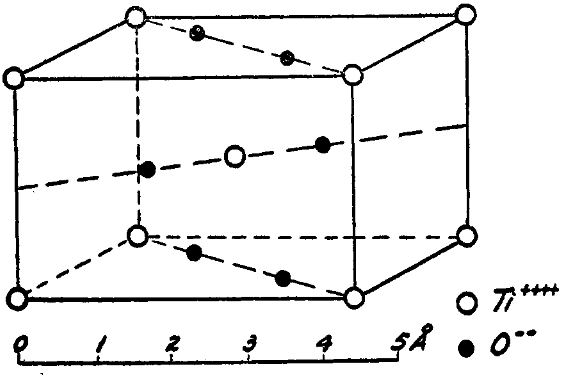

Fig. 2. Rutile

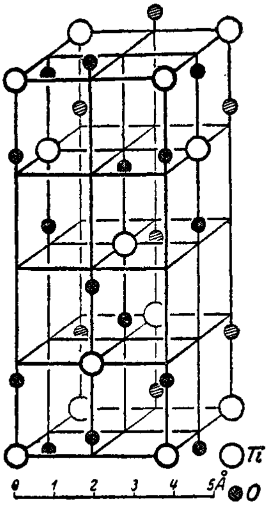

Fig. 3. Anatase

Since Bollnow has not taken into consideration the repulsive forces, this being physically equivalent to considering the ions as rigid particles, it is not to be expected that there will be close agreement between the calculated and observed axial ratios. By considering in detail the repulsive forces Pauling (29) and also Lennard-Jones and Dent (19) have obtained satisfactory agreement with experiment, and have accounted for the observed variation in axial ratio for different crystals with the rutile structure.

(2) β-Quartz. Hylleraas (43) determined the Madelung constant of the hexagonal crystal β-quartz as a function of two parameters by a procedure similar to that used by Bollnow for anatase and rutile.

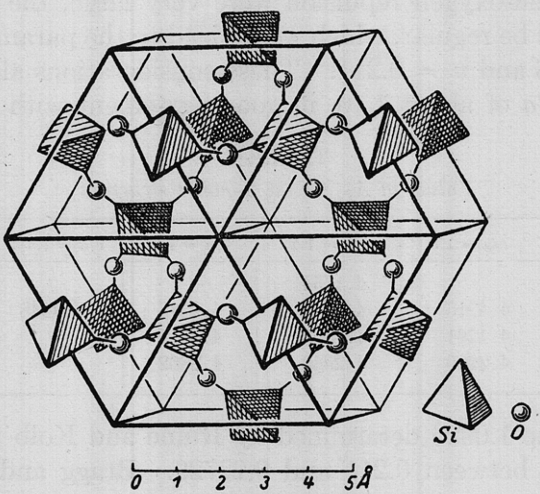

FIG. 4. β-QUARTZ

Figure 4, taken from "Strukturbericht" (177), shows the lattice of β-quartz. The unit cell contains three molecules. The structure is completely specified by three parameters—the axial ratio c/a, the silicon-oxygen distance, and a parameter which determines the position of the oxygen ions. By considering β-quartz to be an ideally coördinated structure with constant silicon-oxygen distance, the number of independent parameters is reduced to two. For convenience Hylleraas chose the axial ratio c/a, and the parameter u determining the distance of the oxygen ions from the hexagonal axis. Table 2 gives the values of A_{r_0}.

The maximum value of A_{r_0} is 4.4445, the corresponding values of c/a and u being 1.117 and 0.22729 respectively. By assuming the compressibility of β-quartz to be not greatly different from that of α-quartz, the compressibility data yield a value of $n = 8$.

Hylleraas repeated the preceding calculations, taking the oxygen-oxygen repulsive forces into account and using the value $n = 8$, and found that the minimum of the potential energy occurs at $c/a = 1.0978$ and $u = 0.216$, the value of A_{r_0} being 4.4394. If the oxygen-oxygen repulsion were very large, the SiO_4 tetrahedra would be regular, which would lead to the parameter values $c/a = 1.098$ and $u = 0.211$. These considerations all indicate a value for c/a of about 1.10, in good agreement with the experimental value 1.0926 determined by Rinne and Kolb (30), and a value for u between 0.211 and 0.22729. Bragg and Gibbs (7) have made x-ray measurements leading to $u = 0.208$, with limits of 0.187 and 0.219, while Wyckoff (36) reports 0.197 ± 0.004. If Wyckoff's value is accurate, some other factor must be taken into account to explain the drop below 0.211. It is probable that this factor is a tendency to form bonds with some shared-electron-pair character. The angle between the two bonds formed by an oxygen atom is 155.5° for $u = 0.211$, whereas electron-pair bonds would tend to make the angle 109.5° with each other. The angle is decreased by decreasing u, so that this effect would lead to a change of u in the desired direction.

TABLE 2

Values of A_{r_0} for the β-quartz structure

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

(3) Cadmium iodide. Hund (42) has evaluated the Madelung constant of cadmium iodide as a function of two parameters which determine the structure.

Figure 5, taken from "Strukturbericht" (177), shows the hexagonal lattice. Hund chooses for the two parameters the axial ratio, c/a, and the z coördinate of the iodide ion, u. Table 3 gives the values of A_{r_0}.

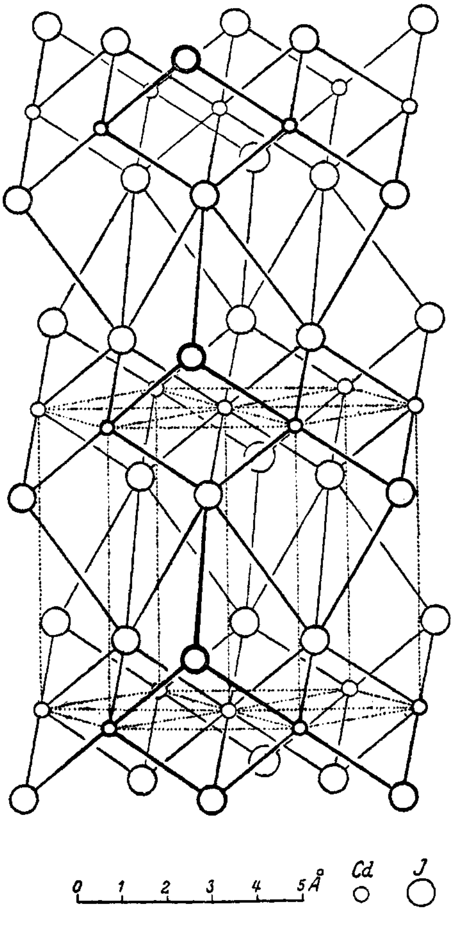

Fig. 5. Cadmium Iodide

The maximum value of A, 4.74, lies at $c/a = 1.61$ and $u = 1/8$, approximately. The values observed for cadmium iodide and other crystals with this structure are $c/a = 1.61$ and $u = 1/4$, the difference in the value of u probably being due to the effect of the repulsive potential of the ions and to a tendency to form bonds with some covalent character or for the cations to polarize the anions. Hund in his paper attempted to take the effect of polarization of the iodide ions upon the energy into account.

(4) Corundum. Schmaeling (48) has evaluated the Madelung constant of corundum as a function of two variables. Figure 6, reproduced from the paper by Pauling and Hendricks (182), shows the structure.

The unit of structure is a rhombohedron containing two molecules of Al_2O_3. At each vertex and at the center of the rhombohedron there is a molecule of Al_2O_3 so arranged that the three oxygen ions form an equilateral triangle in a plane normal to the line joining the two aluminum ions and midway between them. Thus each aluminum ion is surrounded by six oxygen ions at the corners of an irregular octahedron, three of the oxygen ions being closer to a given aluminum ion than the remaining three. Each oxygen ion is surrounded by four aluminum ions at the corners of an irregular tetrahedron, two of the aluminum ions being closer to a given oxygen than the remaining two. Table 4 gives the experimental values of the ionic distances for corundum and the isomorphous crystal hematite.

TABLE 3

Values of A_{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
1/16	4.53	4.65	4.68	4.72	4.68
1/8	4.58	4.72	4.74	4.73	3.87
1/4	4.68	4.73	4.71	3.90	−2.06

The structure is completely determined by four independent parameters which may be chosen as follows:

a = the diagonal of a rhombohedral face,
c = one-half the length of a body diagonal,
v = the distance between two adjacent aluminum ions, and
r_1 = the radius of a circle circumscribed about an equilateral triangle containing three adjacent oxygen ions.

From these, three dimensionless variables may be derived:—

$$\gamma = \frac{c}{a};\ \omega = \frac{v}{a};\ \mu = \frac{r_1}{a}$$

It is impractical to carry out the calculation of the lattice energy as a function of these three independent variables. The actual crystals may be roughly approximated by the ideal case in which

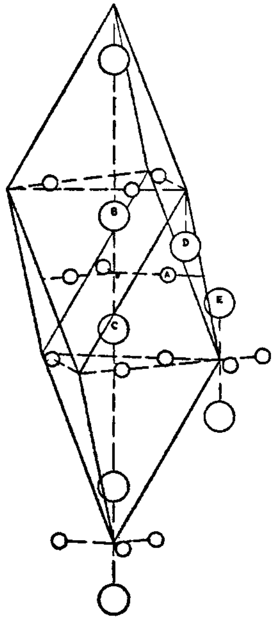

FIG. 6. CORUNDUM

each aluminum ion is equidistant from six oxygen ions. This approximation reduces the number of independent variables to two. Equation 41 expresses the Madelung constant as a function of γ and ω.

$$A_{r_0} = 25.0312 - 5.930(1.312 - \gamma)^2 - 65.250(0.5454 - \omega)^2 + 30.70(1.312 - \gamma)(0.5454 - \omega) \tag{41}$$

The maximum value of A_{r_0} is 25.0312, corresponding to γ =

1.312 and $\omega = 0.5454$. Table 5 compares these results with experiment.

The deviation of approximately 5 per cent in the calculated and observed parameters is not surprising, in view of the assumptions which were made in order to carry out the calculations. The values in table 4 show that in reality corundum and hematite deviate considerably from the ideal coördinated structure. The percentage deviation in the calculated and observed parameters is due in part to this idealization and in part to the fact that the repulsive forces were not considered.

TABLE 4

Ionic distances for corundum and hematite

	r'	r''	MEAN	PERCENTAGE DEVIATION
Al_2O_3	1.990 ±0.020	1.845 ±0.015	1.906	4.4
Fe_2O_3	2.060 ±0.035	1.985 ±0.025	2.02	2.0

TABLE 5

Values of γ, ω, and μ for corundum and hematite

	CORUNDUM			HEMATITE		
	Calculated	Observed	Percentage deviation	Calculated	Observed	Percentage deviation
γ	1.312	1.366	4.0	1.312	1.366	4.0
ω	0.5454	0.575 ±0.006	5.1	0.545	0.575 ±0.006	5.1
μ	0.286	0.303 ±0.003	5.6	0.286	0.292 ±0.007	0.2

The value of the Madelung constant included in table 1 is the maximum for the ideal structure.

2. The repulsive energy of ionic crystals

It has already been pointed out that in order to account for the stability of ionic crystals it is necessary to introduce repulsive forces in addition to the ordinary Coulomb forces. In the Born equation for the crystal energy (equation 3) the first term, which gives the energy due to the Coulomb forces, follows directly from Coulomb's law. On the other hand the analytical form of the repulsive potential is purely empirical. It has previously been shown that for any given crystal the two constants which occur in the repulsive potential of equation 3 can be evaluated from the observed interionic distance and the compressibility. This method of evaluation is necessary as long as there is lack of knowledge concerning the repulsive forces. However, it has the disadvantage that two principal properties of the crystal must be experimentally determined in order to calculate other properties; hence that calculations can be carried out only for actually existent crystals. A more satisfactory treatment would be one in which the two constants are determined independently of any crystal property so that the repulsive energy could be evaluated by a procedure analogous to the methods given for determining the Coulomb energy.

After setting up the expression for the potential energy, Born and Landé (6) sought to evaluate the repulsive exponent by considering the interaction of the ions on the basis of the Bohr atomic model in which the electrons are supposed to revolve about the nucleus in plane orbits. This treatment led to the value of $n = 5$ for all ions, which is in disagreement with compressibility data. Born and Landé attributed this disagreement to the fact that the electrons are not revolving in plane orbits but are spatially distributed about the nucleus. Born then calculated the repulsive exponent by considering the interaction of the ions on the basis of the Lewis-Langmuir model in which the electrons of the completed outer shell are arranged at the corners of a cube. This led to a value of $n = 9$ for all ions except those with the helium structure, for which $n = 5$. This model has formed the basis of very extensive studies in which the attempt was made to correlate physical properties of substances with the size of the hypothetical cubes estimated from experimental data. However, the idea that repulsive forces of ions arise from the interaction of quadripole and higher moments is no longer valid. Unsöld (34) has pointed out that according to quantum mechanics ions with completed sub-groups are spherically symmetrical. The repulsive forces arise mainly from the mutual interpenetration of the ions and the resultant repulsion of the nuclei.

1. Repulsive exponents derived from compressibilities. The relation between the repulsive exponent n and the compressibility can be derived from the following considerations.

In accordance with equations 7 and 10 we may write for the molal energy of a crystal

$$- U = - \frac{\alpha^2\epsilon^2 NA}{r} + \frac{\alpha^2\epsilon^2 NA{\delta_0}^{n-1}}{nr^n} \tag{42}$$

The condition

$$\left(\frac{\mathrm{d}U}{\mathrm{d}r}\right)_{r=\delta_0} = 0 \tag{43}$$

is satisfied. From equation 42

$$\left(\frac{\mathrm{d}^2U}{\mathrm{d}r^2}\right)_{r=\delta_0} = - \frac{\alpha^2\delta^2 AN(n-1)}{\delta_0^3} \tag{44}$$

The compressibility is defined by the equation

$$\chi = - \frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}P} \tag{45}$$

where P is the pressure and v is the molal volume.
Hence

$$\frac{1}{\chi} = - v\frac{\mathrm{d}P}{\mathrm{d}v} \tag{46}$$

The pressure applied to the crystal is related to the total energy, E, of the crystal by the thermodynamic equation

$$P = T\left(\frac{\partial P}{\partial T}\right)_v + \left(\frac{\partial E}{\partial v}\right)_T \tag{47}$$

At 0°K. the term $T\dfrac{\partial P}{\partial T}$ equals 0, and equation 47 becomes

$$P = \frac{\mathrm{d}U}{\mathrm{d}v} = \frac{\mathrm{d}U}{\mathrm{d}r}\cdot\frac{\mathrm{d}r}{\mathrm{d}v} \tag{48}$$

since the total energy at 0°K. is entirely potential (except for zero-point energy which is negligible in comparison with U).

Differentiating 48

$$\frac{\mathrm{d}P}{\mathrm{d}v} = \frac{\mathrm{d}^2U}{\mathrm{d}v^2} = \frac{\mathrm{d}^2U}{\mathrm{d}r^2}\left(\frac{\mathrm{d}r}{\mathrm{d}v}\right)^2 + \frac{\mathrm{d}^2r}{\mathrm{d}v^2}\cdot\frac{\mathrm{d}U}{\mathrm{d}r} \tag{49}$$

When the crystal is in equilibrium with the applied pressure, equation 49 becomes

$$\frac{\mathrm{d}P}{\mathrm{d}v} = \left[\frac{\mathrm{d}^2U}{\mathrm{d}r^2}\left(\frac{\mathrm{d}r}{\mathrm{d}v}\right)^2\right]_{r\,=\,\delta_0} \tag{50}$$

Substituting this value of $\mathrm{d}P/\mathrm{d}v$ in 46,

$$\frac{1}{\chi} = -v\left[\frac{\mathrm{d}^2U}{\mathrm{d}r^2}\left(\frac{\mathrm{d}r}{\mathrm{d}v}\right)^2\right]_{r\,=\,\delta_0} \tag{51}$$

The molal volume v is

$$v = Nr^3 \tag{52}$$

Differentiating with respect to r,

$$\frac{\mathrm{d}v}{\mathrm{d}r} = 3\,Nr^2 \tag{53}$$

hence,

$$\left(\frac{\mathrm{d}r}{\mathrm{d}v}\right)^2_{r\,=\,\delta_0} = \frac{1}{9\,N^2\delta_0} \tag{54}$$

By substituting 44 and 54 in 51

$$\frac{1}{\chi} = N\delta_0^3\cdot\frac{\alpha^2\epsilon^2AN(n-1)}{\delta_0^3}\cdot\frac{1}{9\,N^2\delta_0^4} = \frac{\alpha^2\epsilon^2A}{9\,\delta_0^4}\,(n-1) \tag{55}$$

Finally,

$$n = 1 + \frac{9\,\delta_0^4}{\alpha^2\epsilon^2A\chi} \tag{56}$$

Slater (32) measured the compressibilities of eleven alkali halides up to pressures of 12,000 atmospheres, and at two different temperatures. By extrapolation he obtained the values of the compressibilities at zero pressure and 0°K. Column 2 of table 6 gives the values of n calculated from equation 56.

Lennard-Jones (18) has determined the force fields of the inert gases from the observed equations of state and viscosity values. By assuming that the repulsive exponent for an ion is the same as for the inert gas of the same electronic configuration, he prepared a table of n values for different ion pairs. Column 3 of table 6 gives the results for the sodium halides.

In calculating ionic radii in crystals Pauling derived an expression for the dependence of radius on valence of the ion; this expression involves the repulsive exponent n. Pauling has chosen values of n in accordance with table 7. Averages of these values for the two ions concerned are given in the fourth column of table 6.

In calculating the crystal energy by the Born equation (equation 11) n is involved as the factor $(1 - 1/n)$ In many crystals n is approximately equal to nine, so that a change of n by one unit changes the crystal energy by approximately 1.5 per cent. Since this is approximately the error inherent in the Born theory, it is not significant for the purposes of evaluating crystal energies to know n more precisely than this. The procedure which Pauling has used affords a simple means of determining the repulsive exponent for any ion-pair; since these values are in agreement with the results of experiment, they will be used in all calculations of crystal energies throughout this paper.

TABLE 6

Repulsive exponents for alkali halides

	n(Slater)	n(Lennard-Jones)	n(Pauling)
LiF	5.9		6.0
LiCl	8.0		7.0
LiBr	8.7		7.5
NaCl	9.1	9.0	8.0
NaBr	9.5	9.0	8.5
NaI		10.0	9.5

A more general expression than the Born equation for the crystal energy is the following:

$$\Phi = -\frac{A\epsilon^2}{r} + \frac{b_{11}B_{11}}{r^{n_{11}}} + \frac{b_{12}B_{12}}{r^{n_{12}}} + \frac{b_{22}B_{22}}{r^{n_{22}}} \qquad (57)$$

The subscripts 11, 12, and 22 refer to cation-cation, anion-cation, and anion-anion interaction respectively. The numerators of the three repulsive terms have each been divided into two factors, in analogy with the Coulomb term. b_{11}, b_{12}, and b_{22} (analogous to ϵ^2) denote the force constants between the ions. B_{11}, B_{12}, and B_{22} (analogous to the Madelung constant) depend only upon the value of n and the type of structure. For the sodium chloride structure, B_{11} is given by the relation

$$B_{11}(n_{11}) = \sum_{\substack{l_1+l_2+l_3 \\ \text{even}}}' \frac{1}{(l_1 + l_2 + l_3)^{\frac{n_{11}}{2}}} \tag{58}$$

l_1, l_2, and l_3 are integers. The accent on the summation sign signifies that the term for which $l_1 = l_2 = l_3 = 0$ is to be omitted.

TABLE 7

Values of the repulsive exponent, n

ION TYPE	n
He	5
Ne	7
Ar, Cu^+	9
Kr, Ag^+	10
Xe, Au^+	12

At first Born assumed that all ions repel each other in the same way, but later he concluded from experimental values of the coefficients of elasticity of sodium and potassium chlorides that like ions exert a characteristic attraction about one-half as great as the intrinsic repulsion of unlike ions. In other words, b_2B_2 in equation 57 was taken as $-\frac{1}{2}b_{11}B_{11} = -\frac{1}{2}b_{22}B_{22}$. This result was accepted and used for all types of crystals in the treatment of residual rays, heats of sublimation of crystals, the relative stabilities of different crystal structures, and other properties of crystals. Born's result is incorrect. It is improbable that the constants in equation 75 are ever negative. Moreover Pauling has shown that the relative magnitude of the repulsive forces between unlike ions and those between like ions varies with the "sizes" of the ions. In simple cases the forces between two atoms or ions may be calculated by means of quantum mechanics (27). In the case of ions each having several electrons the calculations are very complicated. Using a simple atomic model capable of treatment by the perturbation methods of quantum mechanics, Pauling (29) has derived an expression showing the dependence of the repulsive energy upon the relative sizes and valences of the ions. The constants b_{11}, b_{12}, and b_{22} are given by the relations[4]

$$b_{11} = \beta_{11}(r_+ + r_+)^{n_{11}-1} B_0 \qquad (59)$$

$$b_{12} = \beta_{12}(r_+ + r_-)^{n_{12}-1} B_0 \qquad (60)$$

$$b_{22} = \beta_{22}(r_- + r_-)^{n_{22}-1} B_0 \qquad (61)$$

r_+ and r_- are "standard radii" characteristics of the sizes of the ions, β_{11}, β_{12}, and β_{22} are factors which depend upon the valences of the ions, and B_0 is a constant for all ions.

Lennard-Jones and Dent (20) have evaluated the force constants for ions by a procedure which is fundamentally similar to that used by Pauling. They have employed a relation between the relative sizes of atoms and ions (obtained by Wasastjerna from refractive indices of crystals and salts) and the corresponding force constants. Values of these force constants were tabulated by them (20).

In evaluating the constants B_{11}, B_{12}, and B_{22} Lennard-Jones considered an infinitely large crystal and took for the limits of summation in equation 58 $l_1 + l_2 + l_3 = 2$ to $l_1 + l_2 + l_3 = \infty$. This procedure is not justified theoretically, for it assumes that the repulsion is given by the same law of force for all distances and that the repulsive force between two ions is independent of the presence of intervening ions. Pauling has carried out the summations only over the immediately neighboring ions. For values of n of the order of magnitude of nine, the series given by equation 58 converges so rapidly that it is relatively unimportant which value of B is used. Lennard-Jones and Ingham (22) have calculated values of B appropriate to simple, face-centered, and body-centered cubic lattices for values of n from 4 to 30.

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[4] In Pauling's paper these equations are misprinted, the factors $(r_\pm + r_\pm)^{n-1}$ being given as $(r_\pm + r_\pm)^n$.

Pauling has applied his treatment in the discussion of a number of crystal properties. In particular he has shown the importance of the relative sizes of ions in causing deviations from additivity of interionic distances of alkali halides and in affecting many other crystal properties.

By using the force constants and repulsive exponents in conjunction with the proper crystal potential constants Lennard-Jones (19, 21), Chapman (8), Topping (33), and others have evaluated the crystal energy as a function of the interionic distance and a parameter which determines the structure. For the crystals which have been considered—carbonates and nitrates of the calcite structure, crystals of the rutile structure, etc.—it is found that the interionic distances determined by x-rays correspond closely to the minimum energy.

3. Criticism of the Born treatment

The Born expression for the repulsive potential can be considered only as a rough approximation, the two constants B and n being so chosen that first and second derivatives at $r = r_0$ are given correctly. It was indeed pointed out by Unsöld (35) and Pauling (28) that the quantum mechanics leads to a complicated expression for the repulsive potential which involves exponential terms in r. It cannot be expected, then, that the Born expression will give correctly the repulsive potential itself or its third and higher derivatives. This has been verified by Slater's measurements of the alkali halides. If the Born expression were correct, the quantities

$$1 - \frac{9\,\delta_0^4}{13.94\,\epsilon^2\chi_0} \quad \text{and} \quad \frac{3\,\psi_0}{\chi_0} - 10$$

should both be equal to the repulsive exponent for a sodium chloride type crystal (ψ_0 is the pressure coefficient of compressibility and χ_0 the compressibility, both extrapolated to 0°K.). The values of these quantities found by Slater, given in table 8, are not in general identical for a given substance. Some crystals show large differences which make the Born treatment necessarily inaccurate for them.

Hildebrand (12) has considered the thermodynamic limitations of the Born equation. The constants B and n in the repulsive energy term should be evaluated from the lattice constant at 0°K. and the compressibility at 0°K. and zero pressure. If the compressibility at ordinary temperatures is used, the value of the repulsive exponent thus calculated will be too small because the thermal pressure will have been omitted. By applying a thermodynamic equation of state, Hildebrand has given a method of evaluating the energy of a crystal from its elastic constants at room temperature, thus avoiding the uncertain extrapolation of the compressibility to 0°K. The repulsive exponents of six alkali halides thus calculated lie between 11 and 12, and the values found for the crystal energies at room temperature are 1 to 2 per cent higher than those ordinarily calculated.

TABLE 8

Quantities derived from compressibilities at 0°K.

CRYSTAL	$1 - \frac{9\,\delta_0^4}{13.94\,\epsilon^2\chi_0}$	$\frac{3\,\psi_0}{\chi_0} - 10$
LiF	5.9	14.3
LiCl	8.0	11.9
LiBr	8.7	12.8
NaCl	9.1	9.8
NaBr	9.5	9.5
KF	7.9	8.9
KCl	9.7	6.5
KBr	10.0	7.1
KI	10.5	6.8
RbBr	10.0	6.2
RbI	11.0	6.8

These considerations show that values of the crystal energy calculated with the use of the Born repulsive potential expression can hardly be trusted to be more accurate in general than to within 25 per cent of the contribution of the repulsive potential to the energy; that is, to within 2 or 3 per cent of the crystal energy itself. It will be found later that this conclusion is substantiated by thermochemical considerations involving calculated crystal energies. The fact that crystal energies can not be calculated with greater accuracy does not, however, prevent their use in many interesting and important considerations.

4. The surface energy and edge energy of sodium chloride

In calculating the crystal energy, the energy due to the surface forces and edge forces in any actual crystal was neglected. It is of interest to consider the magnitude of these energies. Lennard-Jones and Taylor (23) have calculated the surface energies and edge energies for several crystals. For the (001) plane in sodium chloride the surface energy amounts to 96 ergs per square centimeter and the edge energy to 3.97×10^{-6} ergs per centimeter. The crystal energy of sodium chloride (table 17) is 179,200 calories per mole, so that for one mole of crystal in the form of a cube bounded by (001), (010), and (100) planes, the surface and edge energies are entirely negligible compared to the crystal energy. If, however, one mole of sodium chloride consists of a large number of minute crystals, the surface and edge energies may become appreciable in comparison to the crystal energy. A simple calculation shows that for crystals of sodium chloride in the form of cubes bounded by (100), (010), and (001) planes the sum of surface and edge energies is less than one per cent of the crystal energy when the length of a cube edge is greater than 27 Å., and is less than one-tenth of one per cent when the length of a cube edge is greater than 220 Å.

III. THE BORN-HABER THERMOCHEMICAL CYCLE

Unfortunately the lattice energy is not a directly measurable quantity. Born (175) and Haber (179) devised a thermochemical cycle by means of which the crystal energy can be related to measurable thermal data. This cycle is shown below[5]

$$\begin{tikzcd}
{[MX]} \arrow[r, "U"] & (M^+) + (X^-) \arrow[d, "-I+E"] \\
{[M]} + \frac{1}{2} X_2 \arrow[u, "-Q"'] & (M) + (X) \arrow[l, "-S-D"']
\end{tikzcd}$$

---

[5] In accordance with the customary chemical practice brackets are used to designate crystalline substances while parentheses denote substances in the gaseous state.

(For convenience a binary uni-univalent crystal is used as an example in this discussion, although it is to be remembered that the treatment is valid for any other type of crystal provided that appropriate modifications are made.)

This diagram represents the following cycle:

1. The crystal is dispersed into gaseous ions.
2. The ions are converted into monatomic (neutral) gases.
3. The elements as monatomic gases are converted to their standard states at 25°C. and one atmosphere pressure.
4. The elements in their standard states are combined to form the crystal.

The symbols are defined by the following thermochemical equations:

$[MX] = (M^+) + (X^-)$	$\Delta H_{298} = U$, crystal energy
$[MX] = M + \frac{1}{2} X_2$	$\Delta H_{298} = Q$, chemical heat of formation
$[M] = (M)$	$\Delta H_{298} = S$, heat of sublimation
$\frac{1}{2} X_2 = (X)$	$\Delta H_{298} = D$, heat of dissociation
$(M) = (M^+) + (E^-)$	$\Delta H_{0°K.} = I$, ionization potential
$(X^-) = (X)\ (E^-)$	$\Delta H_{0°K.} = E$, electron affinity

The changes in heat content[6] must add up to zero; hence,

$$U = Q + S + I + D - E \tag{62}$$

The cycle given by equation 62 is to be regarded as isothermal at 25°C. If the heat capacity of the metallic ion is assumed to be the same as that of the gaseous metal, then the change of ionization potential with temperature will depend only upon the heat capacity of the electrons. If a corresponding assumption be made concerning the heat capacities of the electronegative atom and ion, then the change of electron affinity with temperature will similarly depend only upon the heat capacity of the electrons. Since the electron affinity and ionization potential enter into the thermochemical cycle with opposite sign, the error introduced by neglecting the thermal energy of the electrons in

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[6] For the definition of heat content and other chemical terms used in this paper the reader is referred to Lewis and Randall: Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill Book Co., New York. The nomenclature of this book will be followed throughout this paper.

the process of ionization of the metal will just cancel that introduced by neglecting the thermal energy of the electrons in the process of removing an electron from the electronegative atom.

The Born-Haber cycle can be applied to the calculation of any one thermal quantity when all the others are known. Many applications of this kind have been made. Within recent years many new thermal data have been published and those which are appropriate to the Born-Haber cycle have been collected and are tabulated in this paper.

1. Chemical heats of formation of compounds

The chemical heat of formation of a compound at 25°C. is the change in heat content which occurs when the compound is formed from the elements in their standard states at 25°C. The heats of formation of many inorganic salts are well known. The values to be used in thermochemical calculations have not been collected separately but are given in appropriate tables. Unless otherwise specified, the values given are those tabulated in the International Critical Tables, Volume V, or in Landolt-Börnstein, 5th edition, 1st or 2nd Ergänzungsband.

2. Heats of sublimation of metals

The molal heat of sublimation of a metal at the temperature T will be defined as the change in heat content which occurs when one gram-atom of the metal in the crystalline state which is most stable at this temperature is converted to monatomic vapor. With the exception of those of the alkali metals and the V-b and VI-b groups of the periodic table all metallic vapors can be considered to be monatomic at all temperatures. If the heat of vaporization of a metal is known at the temperature T_v and the heat of fusion at the melting point T_F, then the heat of sublimation at 298.2°K.[7] can be calculated by means of the equation

$$\Delta H_s = \Delta H_v + \Delta H_F + \int_{298}^{T_F} (c_p)_s \mathrm{d}T + \int_{T_F}^{T_v} (c_p)_l \mathrm{d}T - \int_{298}^{T_v} (c_p)_g \mathrm{d}T \quad (63)$$

---

[7] For convenience 25°C. will hereafter be written as 298°K., although the more precise value 298.2°K. will be used in calculations which warrant this accuracy.

$(c_p)_s$, $(c_p)_l$, and $(c_p)_g$ refer to the atomic heat capacities of crystal, liquid, and vapor, respectively. If the metal has several allotropic modifications between 25°C. and the melting point, the term

$$\int_{298}^{T_F} (c_p)_s \mathrm{d}T$$

must be replaced by the expression

$$\int_{298}^{T_1} (c_p)_{s_1} \mathrm{d}T + \int_{T_1}^{T_2} (c_p)_{s_2} \mathrm{d}T + \ldots \int_{T_{n-1}}^{T_F} (c_p)_{s_n} \mathrm{d}T + \Delta H_{12} + \Delta H_{23} + \ldots \Delta H_{n-1,n}$$

where the modification s_1 is stable between 298°K. and T_1, s_2 between T_1 and T_2, etc., and ΔH_{12} is the heat of transition at the temperature T_1 between s_1 and s_2, etc.

The heat of vaporization is the largest of the energy quantities occurring in equation 63; it comprises about 80 to 95 per cent of the heat of sublimation, and should therefore be known with the greatest percentage accuracy, but unfortunately this is almost never the case. For some metals the error in the value of the heat of vaporization is greater than the value of the terms involving the heat capacities. For this reason no cognizance will be taken of the various allotropic forms of a metal, except for iron, cobalt, nickel, etc., for which the heats and temperatures of transition are well known.

1. Heats of vaporization. Reliable calorimetric determinations of heats of vaporization of metals are available only for mercury and cadmium (50). For all other metals it is necessary to calculate the heat of vaporization from other data. There are two important methods available, one of which depends upon the use of the Clausius-Clapeyron equation, the other upon the use of the Sackur-Tetrode equation and the third law of thermodynamics.

In its exact form the Clausius-Clapeyron equation may be written

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H}{T \Delta v} \tag{64}$$

where P denotes the vapor pressure of the liquid or solid, ΔH the heat of vaporization or sublimation, and ΔV the change in volume which occurs when the liquid or solid is converted to vapor. It is to be noted that the evaluation of ΔH based on the Clausius-Clapeyron equation alone requires vapor pressure to be known at least for two different temperatures. If the vapor pressure is known for only one temperature, e.g., the normal boiling point, it is possible to evaluate ΔH by means of the Sackur-Tetrode equation and the third law of thermodynamics.

When a solid or liquid is in equilibrium with its vapor, we may write

$$\Delta F = 0 = \Delta H - T\Delta S \tag{65}$$

Here ΔS is the change in entropy when one mole of solid or liquid at the temperature T is converted to vapor. If the condensed phase is a liquid,

$$\Delta H_v = T\Delta S = T(S_v - S_l) \tag{66}$$

The entropy of a perfect monatomic vapor can be calculated by means of the Sackur-Tetrode equation:

$$\begin{aligned} S_v &= R\ln T + \frac{3}{2}R\ln W - R\ln P_{\text{atm}} + R\ln Q - 2.2985 \qquad (67) \\ &= 11.4351 \log T + 6.861 \log W - 4.574 \log P_{\text{mm}} + 4.574 \log Q + 10.8780 \end{aligned}$$

Here W is the atomic weight of the element, and
Q is the quantum weight of the normal state;

$$Q = 2j + 1 \tag{68}$$

where j is the total angular-momentum quantum number.

The entropy of a liquid at the temperature T may be obtained from the following equation:

$$S_1 = \int_0^{T_F} (c_p)_s \frac{\mathrm{d}T}{T} + \frac{\Delta H_F}{T_F} + \int_{T_F}^{T} (c_p)_s \frac{\mathrm{d}T}{T} \tag{69}$$

When the necessary data are available, equations 65, 66, and 68 permit the evaluation of the heat of vaporization. Unfortunately only meagre data exist for the heat capacities of liquid metals, and in some cases only approximate values are known for the heat capacities of solid metals. Particularly at high temperatures, the heat of sublimation of a metal calculated by these equations will be in considerable error unless accurate heat capacity data are employed.

In addition to the two rigorous methods just described for determining the heat of vaporization, there exist several empirical rules by means of which the heat of vaporization can be calculated. The best known is Trouton's rule, which states that the entropy of vaporization at the normal boiling point is the same for all substances. Actually the entropy of vaporization increases with the boiling point. Hildebrand (52) has restated the rule so as to eliminate this trend. Hildebrand's rule may be stated as follows: the entropy of vaporization of all non-associating liquids is the same at the temperatures at which the liquids give the same vapor concentrations. In applying this rule to metals, the author has used mercury, zinc, or cadmium as reference substances, since their vapor pressures have been well investigated.

The high chemical activities of most metals and the high temperatures necessary to obtain appreciable vapor pressures make accurate measurements difficult, and unless great precautions are taken in experimental procedure, the vapor pressures may not even be of the correct order of magnitude.[8] It is therefore not surprising to find poor agreement in many cases between the results of different investigators.

2. Heats of fusion. Calorimetric values of the heats of fusion are known for most metals. In many cases there is disagreement in the data of several investigators for a given metal. This is to be expected, since the high melting points of many metals and the ease of oxidation of the low melting metals make it difficult to obtain accurate results. There are several methods of estimating the heat of fusion non-calorimetrically, e.g., by the time of crystallization of the melt. The results obtained are

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[8] For a critical discussion of the sources of error involved in vapor pressure measurements, compare A. Smith and A. W. C. Menzies (56).

usually of a low order of accuracy, but they afford an estimation of a value for the heat of fusion when no other data are available.

3. Heat capacities of metals in the gaseous, liquid, and crystalline states. Since almost no measurements have been made on the heat capacities of metallic vapors, the kinetic theory value $(c_p)_g = 5/2\,R$ will be used for a monatomic vapor at all temperatures. The heat capacities of a few metals in the liquid state have been measured. Individual results for a given metal differ greatly, and with the exception of mercury no really reliable values are known. While it is not essential to have highly accurate heat capacity data for the purpose of calculating the heat of sublimation at 298°K. when it is known at some other temperature, it is important for the calculation of the entropy of a liquid. In many cases the uncertainty in the value for the heat of vaporization calculated by means of equation 66 is due almost entirely to the error in the value of the heat capacity of the liquid.

4. The heat of sublimation of copper as an example. As an illustration of the way in which the data were employed to obtain the heat of sublimation, copper will be considered in detail. The thermal data are summarized below.

Melting point: 1083°C.

Heat capacity of the liquid: 7.8 calories per degree, this being the average value between the melting point and 1450°C. Umino (57).

Heat capacity of the solid:

$$c_p = 5.77 + 2.859\cdot10^{-3}t - 4.826\cdot10^{-7}t^{2*} \tag{70}$$

$$= 4.96 + 3.114\cdot10^{-3}T - 4.826\cdot10^{-7}T^2$$

* t denotes °C.

These equations, valid in the temperature range 0°C. to the melting point, have been derived from the data of Umino (57) on the heat evolved when a sample of copper is cooled from various temperatures to 0°C.

$$c_p = 5.78 + 2.017\cdot10^{-3}t - 8.255\cdot10^{-7}t^2 \tag{71}$$

$$= 5.17 + 2.468\cdot10^{-3}T - 8.255\cdot10^{-7}T^2$$

These equations, valid in the temperature range −25°C. to 730°C., have been derived from the tabulated values at different temperatures of Eastman, Williams, and Young (49).

$$c_p = 8.254 - \frac{946}{t + 373} = 8.254 - \frac{946}{T + 100} \tag{72}$$

This equation, valid from room temperature to the melting point, has been obtained by Maydel (55) from experimental data alone.

Heat of fusion: 2670 ± 270 calories per mole. Harteck (51).
3175 calories per mole. Umino (57).
2650 calories per mole. International Critical Tables, Vol. II. This value has been derived from the results of Glaser (2650 calories), Richards (2740 calories), and Wüst, Menthen, and Durrer (2610 calories).

Heat of vaporization: 73.0 ± 2.2 kilogram-calories per mole at the melting point. Harteck (51).
65.9 kilogram-calories per mole at 2200°K., from the vapor pressure equation given in International Critical Tables, Vol. III.
75.98 kilogram-calories per mole at 2110°K.; vapor pressure measurements of Fischer and Grieger.[9]

Heat of sublimation: 82.2 kilogram-calories per mole at 298°K. Jones, Langmuir and MacKay (53).

Entropy of the solid at 25°C.: 8.03 calories per degree. International Critical Tables, Vol. III.
8.1 calories per mole. Landolt-

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[9] Unpublished data.

Börnstein Tables, 5th edition.

From these data the heat of sublimation of copper may be calculated as follows:

Change in heat content when 1 mole of solid copper is heated from 25°C. to 725°C.

4730 calories, from heat capacity equation of Umino.

4470 calories, from equation of Eastman, Williams, and Young.

4820 calories, from equation of Maydel.

4670 calories, *average*.

Change in heat content when 1 mole of solid copper is heated from 725°C. to 1083°C.

2840 calories, from equation of Umino.

2690 calories, from equation of Maydel.

The *average* is 2770 calories. Hence the change in heat content when one mole of solid copper is heated from 25°C. to 1083°C. (the melting point) is $4670 + 2770 = 7440$ calories.

Change in entropy when one mole of solid copper is heated from 298°K. to 1000°K.

7.967 calories per degree, from equation of Umino.

7.612 calories per degree, from equation of Eastman, Williams, and Young.

8.158 calories per degree, from equation of Maydel.

The *average* value is 7.912 calories per degree.

Change in entropy when one mole of solid copper is heated from 1000°K. to 1356°K.

2.417 calories per degree, from equation of Umino.

2.285 calories per degree, from equation of Maydel.

The *average* value is 2.351. Hence the change in entropy when one mole of solid copper is heated from 25°C. to the melting point is $7.912 + 2.351 = 10.26$ calories per degree.

The value for the heat of fusion given by Harteck is the mean of the most reliable published data. Umino's result is not very trustworthy, because of the small size of sample used and the errors inherent in the experimental procedure. The value given by the International Critical Tables agrees well with that of Harteck. A mean value of 2.70 kilogram-calories will be adopted for the heat of fusion.

The value for the heat of vaporization given by Harteck is derived from his own vapor pressure measurements as well as those of several other investigators.

The vapor pressure equation given by the International Critical Tables includes the data of many investigators. From this equation 65.9 kilogram-calories is the value of the heat of vaporization at 2200°K. Taking 5/2 R for the heat capacity of the vapor and 8.3 calories per degree as the average value of the heat capacity of the liquid from the melting point to 2200°K., the heat of vaporization at the melting point is $65.9 + 2.5 = 68.4$ kilogram-calories.

The value for the heat of vaporization given by Fischer and Grieger is derived from their vapor pressure measurements in the temperature region 2167° to 2707°K. Using the same heat capacity values of liquid and vapor as in the previous case, the heat of vaporization at the melting point is $75.98 + 3.43 = 79.41$ kilogram-calories.

Using 5/2 R for the heat capacity of the vapor and the results obtained for the change in heat content when the solid is heated from 25°C. to the melting point, the heat of sublimation from the data of Jones, Langmuir, and McKay is $82.2 - 2.2 = 80.0$ kilogram-calories at the melting point. Subtracting 2.70 kilogram-colories for the heat of fusion, the heat of vaporization is 77.3 kilogram-calories.

The entropy of solid copper at the melting point is $8.05 + 10.26 = 18.31$ calories per degree. The entropy change in fusion is $2700/1356 = 1.99$ calories per degree, so that the entropy of the liquid at the melting point is $18.31 + 1.99 = 20.30$ calories per degree. The entropy of the liquid at 2490°K. is $20.30 + 8.3 \ln \frac{2490}{1356} = 25.34$ calories per degree. Taking the vapor pressure of the liquid as 105.2 mm. at 2490°K. (from the measurements of Fischer and Grieger), the entropy of the vapor at this temperature and pressure, calculated from the Sackur-Tetrode equation, is 54.21 calories per degree. The entropy change in vaporization at 2490°K. is therefore 28.87 calories per degree. The heat of vaporization is 28.87·2490 = 71.9 kilogram-calories at 2490°K. and 71.9 + 3.8 = 75.7 kilogram-calories at the melting point.

Using as a reference the vapor pressure equation for zinc determined by Maier (54) from a critical review of the data, and taking 105.2 mm. as the vapor pressure at 2490°K., Hildebrand's rule yields 74.69 kilogram-calories for the heat of vaporization at this temperature and 78.5 kilogram-calories at the melting point. If 1.16×10^{-3} mm. be used for the vapor pressure at 1420°K. (from the measurements of Harteck), then Hildebrand's rule yields 76.5 kilogram-calories for the heat of vaporization at this temperature and 76.7 kilogram-calories at the melting point.

TABLE 9

Molal heat of vaporization of copper at the melting point

ΔH	AUTHOR	METHOD
kg-cal.		
73.0 ±2.2	Harteck	Vapor pressure data
79.41	Fischer and Grieger	Vapor pressure data
77.3	Jones, Langmuir, and McKay	Vapor pressure data derived from measurements of the rate of evaporation of the solid
68.4	International Critical Tables	Vapor pressure data
75.7		Entropy data and the Sackur-Tetrode equation
78.5		Hildebrand's rule (vapor pressure datum of Fischer and Greiger at 2490°K.)
76.7		Hildebrand's rule (vapor pressure datum of Harteck at 1420°K.)

Table 9 summarizes the various values for the heat of vaporization.

The values of Harteck and of Fischer and Grieger should be given most weight. Although the results derived from the data of Jones, Langmuir, and McKay and from entropy considerations agree well with the others, they are not reliable, the former because the measurements are not made under equilibrium conditions, the latter because of the uncertainty in the heat capacity of liquid copper. The results obtained with the aid of Hildebrand's rule serve as a useful check upon the other values. The value obtained from the International Critical Tables is doubtless in error, and will be given no weight. A weighted mean of 77.0 kilogram-calories will be adopted. The heat of sublimation at the melting point is therefore 79.7 kilogram-calories and at 25°C. it is 81.9 kilogram-calories.

The procedure used in evaluating the heat of sublimation of copper has been employed for the other metals. For many metals such as sodium, potassium, cadmium, and mercury, the data are much more extensive and reliable than for copper; in other cases the data are very meagre and unreliable. In general, the higher the melting and boiling points of a particular metal, the less reliable will be the heat of sublimation. For many metals the heat capacity of the liquid has not been determined. In these cases an estimated value of 7.5 was used, this being approximately the mean for many metals. The results of Maydel, in which the heat capacity is expressed as a function of the temperature by means of the equation of an equilateral hyperbola, have been found to be most useful, particularly when other data were lacking. In evaluating the heat of vaporization, results of vapor pressure measurements were usually given most weight. Whenever the vapor pressure of a given metal at various temperatures was measured by two or more investigators, the heat of vaporization was calculated from the results of each investigator and the heats of vaporization then averaged. A more satisfactory procedure would be to plot the vapor pressures obtained by each investigator on a single log p versus $1/T$ diagram and then to determine the value of ΔH from the best curve through all the points. The difference in the value of the heat of sublimation obtained by these two methods of evaluation is almost always smaller than the probable error in the measurements, so the simpler procedure is justified.

Where reliable heat capacity data are available, the value of the heat of vaporization determined from entropy values has been given full weight. Usually, however, the heat capacity data of liquid metals are very unreliable; hence the heat of vaporization determined by this method is not considered to be accurate.

Where reliable vapor pressure data are available, it is found that the value of the heat of vaporization determined from them agrees well with the value determined from Hildebrand's rule by a comparison with mercury, zinc, or cadmium. For this reason the author has used Hildebrand's rule extensively to differentiate between widely discordant vapor pressure data for a given metal.

5. *Tabulation of thermal data.* Table 10 summarizes the data obtained for the metals.[10] Column 2 gives the melting points, column 3 the heats of fusion, and column 4 the heats of vaporization at the melting point. The value of the heat of sublimation in column 5 is obtained by adding the values for the heat of vaporization and of fusion in columns 3 and 4. The heat of sublimation at 25°C. is given in column 6. Values for the change in heat content when one mole of metal is heated from 0°K., to 25°C. taken from Landolt-Börnstein, 5th edition, 2nd Ergänzungsband, are given in column 7. These results enable the heat of sublimation at 0°K. to be determined, values of which are given in column 8. Column 9 gives the values of the entropy of the solid at 25°C. All data are expressed in kilogram-calories per mole.

3. *Ionization potentials of the elements*

The ionization potential of an atom is usually defined as the energy required to remove an electron from the atom. This definition is ambiguous, for in an atom containing many electrons there will obviously be many ionization potentials corresponding to the removal of the various electrons. The ionization potential corresponding to the removal of the most loosely bound electron from the atom in its normal state to form an ion in its lowest energy state will be referred to in this paper as the first ionization potential. Similarly the ionization potential corresponding to the removal of the most loosely bound electron from the univalent ion to form a bivalent ion in its lowest energy state will be referred

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[10] Because of the very large number of data which have been employed in evaluating the quantities given in this table, references to original papers have been omitted. In most cases they are given in Landolt-Börnstein, 5th edition, 1st and 2nd Ergänzungsbände. An effort was made to consider all data published prior to October, 1931.

TABLE 10

Thermal data for metals

METAL	MELTING POINT	ΔH_F	ΔH_v(m.p.)	ΔH_s(m.p.)	ΔH_s (298°K.)	H_s	ΔH_s(0°K.)	S°_{298}
	°*K.*							
Aluminum	932	2.35	52	54	55	1.057	55	6.62
Antimony	903	4.5	43	48	49			12.4
Arsenic	1090*	5.60	23.2	28.8	30.4			8.4
Barium	931	1.40	46.0	47.4	49.1			(13.7)
Beryllium	1558	3.2						2.1
Bismuth	544	2.65	49	52	52			13.95
Cadmium	595	1.50	25.25	26.75	27.21	1.492	27.22	12.34
Calcium	1083	3.14	42.6	45.7	47.5	1.379	47.4	9.95
Cesium	299	0.513	18.60	19.11	19.11			13.6
Chromium	1870	3.65	67.0	70.7	75.9			5.5
Cobalt	1762	3.95	77.5	81.5	85.9			6.8
Copper	1356	2.70	77.0	79.7	81.9	1.181	81.6	8.05
Gold	1336	3.15	85	88	91	1.449	91	11.40
Iron	1803	3.68	76.5	80.2	93.8			6.49
Lead	600	1.20	46.0	47.2	47.4	1.645	47.6	15.59
Lithium	459	0.115	38.0	38.1	38.3			7.6
Magnesium	923	1.70	33.6	35.3	36.5	1.235	36.3	8.1
Manganese	1530	3.56	65.0	68.6	74.2			7.3
Mercury	234.4	0.555	14.710	15.265	15.22	2.242	15.362	18.28
Molybdenum	2895	8.38	140	148	155	1.088	155	6.83
Nickel	1725	4.25	77.0	81.3	85.0			7.24
Palladium	1822.4	3.65	110	114	118			8.9
Platinum	2046.7	6.26	116	121	125	1.380	125	9.98
Potassium	336.8	0.570	21.00	21.57	21.65	1.693	21.86	15.20
Rubidium	311	0.553	19.35	19.90	19.92			(12.3)
Selenium	490	1.30	10.7†	12.0†	13.4†			(12.1)
Silicon	1688	3.71	79	83	85	0.750	84	4.35
Silver	1234	2.60	63	66	67	1.365	67	10.04
Sodium	371.1	0.630	25.21	25.84	26.00	1.548	26.07	12.04
Strontium	1025	1.4	36.2	37.6	39.7			(12.4)
Tellurium	725	0.93	14‡	15‡	16‡			(13.5)
Thallium	575	1.47	43.1§	44.6	45.6	1.610	45.7	14.9
Tin	505	1.66	75	77	78	1.540	78	12.5
Tungsten	3655	11.2	186	197	210	1.220	210	8.1
Zinc	692	1.74	29.10	30.84	31.59	1.347	31.46	9.94

* Vapor pressure 35.8 atmospheres.

† To give 0.5 moles of Se_2 vapor.

‡ To give 0.5 moles of Te_2 vapor.

§ Derived from the unpublished vapor pressure measurements of Fischer and Grieger.

to as the second ionization potential, and so on for the higher ionization potentials. Obviously the energy required to remove n electrons from a normal atom will be the sum of the first n ionization potentials.

1. Tabulation of ionization potentials. Ionization potentials can be obtained with great accuracy from spectroscopic data. They can also be obtained, but usually less accurately, from electron-collision experiments.[11] Many spectroscopic determinations of ionization potentials have been published recently. All the available values, expressed in volts, are collected in table 11, which will be used extensively in the thermochemical calculations given in the following sections. Where references are not given, the values have been taken from Landolt-Börnstein, 5th edition, 2nd Ergänzungsband. Much less extensive tables of ionization potentials have been published by Noyes and Beckman (112), Rabinowitch and Thilo (119), and Russell (126).

2. Theoretical values of ionization potentials. Recently ionization potentials for helium and helium-like ions have been calculated theoretically by Hylleraas (88) with the use of the quantum mechanics. Table 12 shows that there is complete agreement between these values and the experimental ones.

Milne (109) has derived an approximate theoretical equation for the total energy of binding of all the electrons in an atom as a function of the atomic number by the use of the Thomas-Fermi (128) treatment, in which the electrons in an atom are assumed to behave as a completely degenerate gas obeying the Fermi-Dirac statistics. Milne's equation is

$$\Sigma I = 17\ N^{7/3} \text{ volts} \tag{73}$$

N being the atomic number and ΣI being the total energy of binding of the electrons, that is, the sum of the successive ionization potentials. The constant 17 is not considered to be accurate since it occurs as the difference of two large numbers. The ionization

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[11] For a detailed systematic account of the earlier developments, compare "Critical Potentials," by Compton and Mohler, Bulletin of the National Research Council; also the monograph, "Anregung von Quantensprüngen durch Stösse," by J. Frank and P. Jordan, Springer, Berlin (1926).

TABLE 11

Ionization potentials of the elements

ELEMENT	ATOMIC NUMBER	I	II	III	IV	V	VI	VII	VIII	REFERENCES
H..........	1	13.530								I (60)
He.........	2	24.4764	54.142							I (114), II (60)
Li..........	3	5.368	75.282	121.86						II (76)
Be.........	4	9.2810	18.14	153.10	216.86					I (116), III (78)
B..........	5	8.33	23.98	37.75	258.1	338				IV (75)
C..........	6	11.217	24.28	47.7	64.190	389.9	487			I (85, 115), III (63), IV (77), V (75)
N..........	7	14.48	29.47	47.17	(73.5)	97.428	(546.7)	663		I (67), V (77), VI (99)
O..........	8	13.550	34.93	54.88	77.0	109.19	137.482	(733)	866	I (86), VI (77), VII (99)
F..........	9	18.6	34.6	(58.02)	(84.88)	(113.0)	(152.9)	184.0	(945.8)	I (99), II (74), III (99), IV (99) V (99), VI (99), VII (99), VIII (99)
Ne.........	10	21.47	40.77	63.2						I (62), II (62), III (62, 68)
Na.........	11	5.116	47.0							I (119), II (81)
Mg.........	12	7.61	14.97	80						III (101)
Al..........	13	5.96	18.75	28.32	(122)					
Si..........	14	8.12	16.27	33.30	44.95	(169)				I (80), III (64)
P..........	15	11.1	19.81	30.04	51.1	64.74				IV (64)
S...........	16	10.31	23.30	34.9	47.08	(67)	87.67			III (89)
Cl..........	17	12.96	23.70	39.7	47.4	67.7	(88.7)	113.7		I (91), II (110, 111), III (117), IV (117) V (117), VI (117), VII (117)
A..........	18	15.69	27.80	40.7	170					I (62, 69), II (62, 69, 72), III (68), IV (62)
K..........	19	4.321	31.7	46.5						
Ca.........	20	6.09	11.82	50.8						

Sc..........	21	6.57	12.80	24.64	(72.2)					
Ti..........	22	6.80	13.60	27.6	44.66	(95.7)				
V..........	23	6.76	14.7	29.6	48.3	68.64	(122)			III (130), IV (129)
Cr..........	24	6.73	16.6	(31)	(50.4)	(72.8)				I (66), V (129)
Mn..........	25	7.40	15.70	(32)	(52)	(75.7)				
Fe..........	26	7.83	16.5							
Co..........	27	7.81	17.3							I (65)
Ni..........	28	7.606	18.13							I (127)
Cu..........	29	7.69	20.2							
Zn..........	30	9.35	17.89							
Ga..........	31	5.97	18.9	30.58	63.9					
Ge..........	32	8.09	15.86	31.97	45.50	(90)				I (122), II (82)
As..........	33	9.96		28.19	49.9	62.4				I (105), III (121)
Se..........	34	9.70			42.74	72.8	81.4			IV (124), V (124), VI (119)
Br..........	35	11.80	(19.1)	(25.7)						I (92), II (70), III (70)
Kr..........	36	13.940	(26.4)	(31.23)						I (106), II (90), III (58, 71)
Rb..........	37	4.159	(16)	27.3						I (119), III (98)
Sr..........	38	5.67	10.98							
Y..........	39	6.5	12.3	20.6						I (108), II (108), III (108)
Zr..........	40	6.92	13.97	24.00	33.83					I (94), II (93, 95), III (95)
Mo..........	42	7.35								
Ru..........	44	(7.5)								
Rh..........	45	(7.7)								
Pd..........	46	(9.0)	(19.8)							I (119)
Ag..........	47	7.53	17.1	34						I (61), III (83)
Cd..........	48	8.95	16.84	(32)						
In..........	49	5.76	18.81	27.91	(53)					II (96), III (125)
Sn..........	50	7.37	14.52	30.49	40.57					IV (125)
Sb..........	51	8.35	(18.8)	24.7	43.91	55.4				II (73)
Te..........	52	(8.7)			37.7	59.95	72.0			I (126), IV (122), VI (123)

TABLE 11—*Concluded*

ELEMENT	ATOMIC NUMBER	I	II	III	IV	V	VI	VII	VIII	REFERENCES
I..........	53	10.44								I (79)
Xe..........	54	12.078	21.1	(28.51)						I (84, 107), II (87), III (71)
Cs..........	55	3.877	23.4							I (119), II (97)
Ba..........	56	5.19	9.95							
La..........	57	5.5	(12.5)							
Ce..........	58	(6.91)			(26.0)					IV (59)
Pr..........	59	(5.76)								
Nd..........	60	(6.31)								
Sm..........	62	(6.55)								
Gd..........	64	(6.65)								
Tb..........	65	(6.74)								
Dy..........	66	(6.82)								
Yb..........	70	(7.06)								
W..........	74	8.1								I (126)
Re..........	75	7.85								I (104)
Pt..........	78	8.9								I (100)
Au..........	79	9.19								
Hg..........	80	10.39	18.672							II (113)
Tl..........	81	6.08	20.30	29.7						III (102)
Pb..........	82	7.39	14.97	31.91	43.93					
Bi..........	83	7.25	25.4							II (103)
Rn..........	86	10.689								I (120)
Ra..........	88	(5.4)	10.2							

potentials of the first eight elements can be used to test the validity of Milne's equation. In table 13 the constant in Milne's equation is calculated for these elements. The second column gives the sum of the successive ionization potentials for each element, and the third column the values of $N^{7/3}$. In the fourth column the ratios $\Sigma I/N^{7/3}$ are given; these should be equal to the constant in Milne's equation. Except in the case of hydrogen, the values are remarkably constant. The pronounced deviation shown by hydrogen is not surprising, since the treatment given by Thomas and Fermi should hold only for atoms containing many electrons. The values of the constant should therefore approach an asymptotic value as the atomic number increases, as it seems to be doing.

TABLE 12

Theoretical and experimental values of ionization potentials

SUBSTANCE	I (theoretical)	I (experimental)
He	24.469	24.4672
Li^+	75.278	75.282 ±0.012
Be^{++}	153.149	153.10 ±0.1
B^{+++}	258.09	258.1 ±0.2
C^{++++}	390.12	389.9 ±0.4

4. Heats of formation at 25°C. of monatomic gases of the electronegative elements

In applications of the Born-Haber cycle it is desired to know the heat of formation of the monatomic gas of the electronegative element from the standard state at 25°C. Many of the electronegative elements exist as diatomic gases at room temperature so that the heats of dissociation are desired. For elements such as iodine, bromine, sulfur, etc., which are not diatomic gases at room temperature, the heat of vaporization or sublimation as well as the heat of dissociation must be taken into account.

The heat of dissociation of a diatomic gas can be determined by either chemical or spectroscopic methods. In many cases the spectroscopic values are the more accurate and are employed in future considerations in this paper. Hylleraas (142) has calculated the heat of dissociation of hydrogen by the perturbation methods of quantum mechanics, obtaining 4.37 ± 0.12 volt-electrons as compared with the best experimental value 4.465 ± 0.04 volt-electrons (147). Since the experimental value is the more reliable, it will be adopted in our calculations.

1. Tabulation of Data. Table 14 summarizes the data, all quantities being expressed in kilogram-calories per gram-atom. In the ΔH_0 column the heats of dissociation at 0°K. of the diatomic gases are tabulated. With the exception of that for iodine, the values are taken from the compilation by Sponer (149). In the V, S, and D columns the following quantities are tabulated: the heat of vaporization at 25°C. of bromine to form diatomic gas; the heat of sublimation at 25°C. of the element to form diatomic gas; and the heat of formation at 25°C. of the monatomic gas. The last quantity is obtained by adding the heat of vaporization or sublimation to the heat of dissociation. The heat of dissociation at 25°C. is obtained from the value at 0°K. by adding the term $\int_0^{298} \Delta c_p dT$, where Δc_p denotes the difference in the heat capacity between one gram-atom of the monatomic gas and one-half mole of the diatomic gas. For hydrogen and iodine the values of the integrals given by Giauque (137, 138) have been used; in all other cases the kinetic theory values of the heat capacities of the gases are employed, so that the heat of dissociation at 25°C. is 3/4 RT = 0.444 kilogram-calorie

TABLE 13

The constant in Milne's equation, calculated for the first eight elements

ELEMENT	ΣI	$N^{7/3}$	$\Sigma I/N^{7/3}$
	volts		
H	13.530	1	13.530
He	78.6184	5.040	15.600
Li	202.510	12.980	15.602
Be	397.381	25.398	15.646
B	666.16	42.749	15.583
C	1024.287	65.416	15.658
N	1471.748	93.734	15.701
O	2026.032	128	15.828

larger than at 0°K. The heats of sublimation of selenium and tellurium are taken from table 10.

In applications of the Born-Haber cycle the heat of formation of the monatomic gas from the standard state at 25°C. will be denoted by D and for convenience will be referred to as "the heat of dissociation," although it is only for elements which exist as diatomic gases at room temperature that D actually represents the heat of dissociation.

5. *Electron affinities of the electronegative elements*

In order to obtain the crystal energy from experimental data to be compared with the theoretical value, Born devised the thermochemical cycle to which frequent reference has been made. The electron affinity of the electro-negative element is one of the thermal quantities which enter into the cycle. Except for hydrogen, the electron affinities are unknown or are known with low accuracy, although many attempts have been made to determine them spectroscopically. Soon after the formulation of the Born theory, Frank (155) believed he found in the emission spectrum of iodine vapor a continuous band which could be attributed to the process of formation of iodide ion from an atom and a free electron. If this were the true origin of the band, then the energy corresponding to the edge on the long wave length side would be

TABLE 14

Heats of formation at 25°C. of monatomic gases of electronegative elements

ELEMENT	ΔH_0	V	S	D	REFERENCES
	kg-cals.	*kg-cals.*	*kg-cals.*	*kg-cals.*	
Hydrogen	51.47 ±0.46			51.94	(147)
Fluorine	31.65 ±0.3			32.2	(150)
Chlorine	28.43 ±0.09			28.87	(135, 145)
Bromine	22.61 ±0.09	3.83		26.88	(134, 139, 143)
Iodine	17.694 ±0.023		7.439	25.413	(133, 138)
Oxygen	58.7 ±0.1			59.2	(136, 140)
Sulfur	51.3 ±0.1		14.84	66.6	(141 143, 146)
Selenium	41.5		13.4	55	(148)
Tellurium	34.5		16	51	(148)
Nitrogen	103.7 ±3.0			104.3	(132, 144)

just the electron affinity of iodine. However, later experiments showed that this band has a different origin. Many other investigators believed they had found electron-affinity spectra, but Oldenberg (160) has pointed out that all these bands have a different origin. Recently von Angerer and Müller (151) reported that they had actually located these bands in the spectra of the alkali halide vapors, but unfortunately their conclusions are not free from objections and therefore their results too cannot be considered to be reliable.

1. The electron affinity of hydrogen. Many attempts have been made to calculate the electron affinity of hydrogen by the application of the Born cycle to the alkali hydrides (158, 159, 161). The values of the electron affinity calculated in this way were always unreliable because of the uncertainty in the crystal energies involved, arising from lack of knowledge of the lattice constants and compressibilities of the alkali hydride crystals.

Hylleraas (156, 157) recently devised a method of calculating the electron affinity of hydrogen by means of the quantum mechanics, obtaining the value 16.3 kilogram-calories. Using this same method of calculation, Bethe (154) obtained 17 ± 1 kilogram-calories, and Starodubrovski (162) 16.40 ± 0.03 kilogram-calories.

2. Electron affinities of free radicals. Bent (152, 153) has recently determined the electron affinities of several gaseous triarylmethyl compounds. The free energy of the reaction whereby sodium is added to the free radical to give the ion in ether solution was determined. These results were then combined with free energy values of other reactions (some of which were estimated) to obtain electron affinities. Table 15 gives the results. These results are interesting in comparison with the electron affinities of the halogens and CN, tabulated in tables 17 and 19.

3. Tabulation of electron affinity values. The first application of the Born cycle that we shall make will be the calculation of the electron affinities of several elements, given in the next section. For convenience the values obtained are given in table 16, together with those for hydrogen and triphenylmethyl.

The relative values for the electron affinities of the halogens are in accord with their known chemical properties. The value of the electron affinity of the CN molecule is in agreement with the known similarities in the chemical properties of cyanides and halides. The negative values for oxygen, sulfur, and selenium are not surprising, for it is to be remembered that the process considered is the formation of bivalent ions, which involves the binding of two electrons to the atom.

TABLE 15

Electron affinities of gaseous triarylmethyl radicals at 0°K.

SUBSTANCE	E
	kg-cals. per mole
Triphenylmethyl	59 ± 5
Diphenylbiphenylmethyl	60
Diphenyl-α-naphthylmethyl	60
Phenyl-α-naphythylbiphenylmethyl	60

TABLE 16

Electron affinities of electronegative atoms and molecules

SUBSTANCE	E	REFERENCE
	kg-cals. per mole	
H	16.40 ± 0.03	(162)
F	98.5	Table 17
Cl	92.5	Table 17
Br	87.1	Table 17
I	79.2	Table 17
CN	74.1	Table 19
$C(C_6H_5)_3$	59 ± 5	(152)
O	−168	Table 18
S	−79.4	Table 18
Se	−97	Table 18

IV. APPLICATIONS OF THE BORN-HABER THERMOCHEMICAL CYCLE

1. *Electron affinities of the halogens*

We shall first apply the Born-Haber cycle to the evaluation of the electron affinities of the halogens. Although the cycle may be applied to any halide to determine the electron affinity of the corresponding halogen, we shall use only the alkali halides, since they correspond most closely to the "pure ionic" type of crystal. All the alkali halides except cesium chloride, cesium bromide, and cesium iodide have the sodium chloride structure, these three crystals having the cesium chloride structure. Table 17 gives the necessary data and the electron affinity calculated by application of the cycle to each crystal. Column 2 contains values of the lattice constant, a_0, taken from "Strukturbericht."[12] Values of n, the repulsive exponent in the Born potential expression, have been obtained in accordance with table 7, as previously described, and are given in column 3. Values of U_0, the crystal energy, cal-

TABLE 17

Electron affinities of the halogens calculated from the Born-Haber cycle

CRYSTAL	a_0	n	U_0	U	Q	I	S	D	E
LiF............	4.02	6.0	238.9	240.1	144.7	123.8	38.3	32.2	98.9
NaF...........	4.619	7.0	213.8	215.0	136.6	118.0	26.0	32.2	97.8
KF............	5.33	8.0	189.2	190.4	134.5	99.6	21.7	32.2	97.6
RbF...........	5.63	8.5	180.6	181.8	132.8	95.9	19.9	32.2	99.0
CsF............	6.008	9.5	171.6	172.8	131.5	89.4	19.1	32.2	99.4
								mean =	98.5
LiCl...........	5.143	7.0	192.1	193.3	97.5	123.8	38.3	28.9	95.2
NaCl..........	5.628	8.0	179.2	180.4	98.2	118.0	26.0	28.9	90.7
KCl...........	6.277	9.0	163.2	164.4	104.9	99.6	21.7	28.9	90.7
RbCl..........	6.54	9.5	157.7	158.9	104.9	95.9	19.9	28.9	90.7
CsCl...........	4.110	10.5	147.7	148.9	106.6	89.4	19.1	28.9	95.1
								mean =	92.5
LiBr...........	5.490	7.5	181.9	183.1	83.7	123.8	38.3	26.9	89.6
NaBr..........	5.962	8.5	170.5	171.7	86.3	118.0	26.0	26.9	85.6
KBr...........	6.586	9.5	156.6	157.8	94.2	99.6	21.7	26.9	84.6
RbBr..........	6.854	10.0	151.3	152.5	96.1	95.9	19.9	26.9	86.3
CsBr..........	4.287	11.0	142.3	143.5	97.5	89.4	19.1	26.9	89.4
								mean =	87.1
LiI............	6.000	8.5	169.5	170.7	65.0	123.8	38.3	25.4	81.8
NaI...........	6.462	9.5	159.6	160.8	69.5	118.0	26.0	25.4	78.1
KI.............	7.052	10.5	147.8	149.0	78.9	99.6	21.7	25.4	76.6
RbI...........	7.325	11.0	143.0	144.2	80.8	95.9	19.9	25.4	77.8
CsI............	4.56	12.0	134.9	136.1	83.9	89.4	19.1	25.4	81.7
								mean =	79.2

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[12] Ewald, P. P., and Hermann, C.: Strukturbericht (177). Values of all lattice constants used in this paper will be taken from this book, unless otherwise specified.

culated in each case from a_0, n, and the appropriate Madelung constant by means of equation 11, are given in column 4. Column 5 gives the changes in heat content when the crystal is formed out of dispersed ions. These are obtained in each case by adding to the crystal energy the energy due to the pressure-volume products.[13] Column 6 gives the values of the chemical heats of formation, column 7 the values of the first ionization potential of the alkali metals, obtained from table 11 by multiplying the value in volts by 23.054, column 8 the heats of sublimation of the metals, and column 9 the value of the heat of dissociation of the halogen. Finally, in the last column of the table is given the value of the electron affinity of the halogen, obtained by the addition of the quantities in the preceding five columns.

It is seen that the values for fluorine are consistent to better than 2 per cent, although the absolute error may be greater than this. Since the electron affinity is obtained by the addition of several quantities, the absolute rather than the percentage errors of these quantities determine the error in the value of the electron affinity. The crystal energy varies inversely with the lattice constant, so that a small error in the value of the lattice constant produces a fairly large absolute error in the crystal energy. For chlorine, bromine, and iodine, it is seen that the electron affinity as determined from the lithium and cesium salts is about 4 per cent higher than when determined from the sodium, potassium, and rubidium salts. This disagreement is probably due mainly to the error in the crystal energies, either the crystal energies of the lithium and cesium salts being approximately 2 per cent too low, or those of the sodium, potassium, and rubidium salts approximately 2 per cent too high. From the Born cycle alone it is not possible to say which of these two possibilities is correct, so that there is an uncertainty in the value of all these crystal energies of at least 2 per cent. The crystal energies of lithium chloride, lithium bromide, and lithium iodide may be in error because of some

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[13] Neglecting the volume of the crystal compared to the volume of the dispersed ions, and considering the perfect gas equation of state to be valid for each type of ion, the energy due to the pressure-volume products is nRT, where n denotes the number of moles of ions necessary to form one mole of crystal.

unknown effect of the small values of the radius ratios of these salts. Since cesium chloride, cesium bromide, and cesium iodide have the cesium chloride structure, the disagreement in the values of the electron affinities calculated from these salts compared to the values calculated from other salts may be due to this cause. Pauling (169) has indeed pointed out that on the basis of the Born equation equilibrium between the cesium chloride and the sodium chloride structure should occur when the ratio of the anion-cation distance in cesium chloride to that in sodium chloride is 1.009, whereas equilibrium actually occurs for values of this ratio differing from this by 2 to 4 per cent, which shows that the values of crystal energies of sodium chloride and cesium chloride structures calculated by the Born equation are inaccurate to this extent.

The values obtained in this paper for the electron affinities of the halogens do not differ greatly from those given originally by Born or from those of later investigators.

2. Electron affinities of oxygen, sulfur, and selenium. The data on the alkaline earth oxides, sulfides, and selenides, all of which have the sodium chloride structure, have been employed to calculate the electron affinities of oxygen, sulfur, and selenium. Table 18 summarizes the results. In column 7 the sum of the first and second ionization potentials, giving the energy required to remove two electrons from the metal, is recorded. The beryllium salts were omitted because of lack of data which would permit an evaluation of the heat of sublimation, and the tellurides because of lack of data concerning the chemical heats of formation of these salts.

For oxygen, sulfur, and selenium the electron affinity is the energy at 0°K. required to remove two electrons from the gaseous ion. The negative values signify that the formation of the ion from the atom and electrons is an endothermic process. This is seen not to be surprising when the process is considered in steps. The first electron may attach itself to the neutral atom with the evolution of energy, but in order to attach a second electron to the univalent negative ion, work must be done against the electrostatic forces of repulsion of the negative ion and the electron. The individual values of the electron affinities for a given atom differ considerably from one another, leading to large probable errors in the mean values. Except for the heat of dissociation of Se_2 vapor, the thermal data are fairly reliable, so that the disagreement in the electron affinities may be attributed mainly to the error in the values of the crystal energies. Since the oxides, sulfides, and selenides of the alkaline earth metals are composed of divalent ions, the crystal energy is approximately four times as large as for an alkali halide with the same lattice constant, and so the absolute error in the crystal energy is approximately four times as great as in the case of the alkali halides.

TABLE 18

Electron affinities of oxygen, sulfur, and selenium

CRYSTAL	a_0	n	U_0	U	Q	I	S	D	E
MgO..........	4.208	7.0	938.9	940.1	146	520.6	36.5	59.2	−178
CaO..........	4.802	8.0	840.9	842.1	151.7	412.9	47.5	59.2	−171
SrO...........	5.15	8.5	789.7	790.9	141	383.8	39.7	59.2	−167
BaO..........	5.53	9.5	745.8	747.0	133	349.0	49.1	59.2	−157
								mean =	−168
MgS..........	5.190	8.0	777.1	778.3	82.2	520.6	36.5	66.6	−72.4
CaS..........	5.686	9.0	720.6	721.8	114	412.9	47.5	66.6	−80.8
SrS...........	6.01	9.5	686.2	687.4	113	383.8	39.7	66.6	−84.3
BaS...........	6.37	10.5	654.7	655.9	111	349.0	49.1	66.6	−80.2
								mean =	−79.4
CaSe.........	5.912	9.5	697.6	698.8	88.4	412.9	47.5	55	−95
SrSe..........	6.23	10.0	665.9	667.1	90.1	383.8	39.7	55	−99
BaSe..........	6.59	11.0	635.9	637.1	88.2	349.0	49.1	55	−96
								mean =	−97

3. *The electron affinity of gaseous CN*

The electron affinity of gaseous CN can be obtained from the data on sodium cyanide and potassium cyanide crystals. Wyckoff (172) has pointed out that according to Pauling's theory of the rotation of molecules in crystals (170) the CN^- ions in alkali cyanides are probably rotating and therefore behave as spherically symmetrical ions. Sodium cyanide, potassium cyanide, and rubidium cyanide have the sodium chloride structure, while cesium cyanide has the cesium chloride structure. Table 19 gives the pertinent data for these crystals.

The heat of dissociation of cyanogen into CN gas is just the energy of the C-C bond; the value used is an unpublished one calculated by Pauling. The lattice constants have been determined by Natta and Passerini (168). The lack of information on the heats of formation of rubidium cyanide and of cesium cyanide prevents the calculation of the electron affinity of CN from these two salts.

The agreement in the values for the electron affinity of CN obtained from sodium cyanide and potassium cyanide is evidence in favor of the assumption that the CN^- ions in these crystals are rotating.

TABLE 19

The electron affinity of gaseous CN

CRYSTAL	a_0	n	U_0	U	S	I	Q*	D	E
NaCN.............	5.83	7.0	169.4	170.6	26.0	118.0	58.3	43.8	75.5
KCN..............	6.51	8.0	154.9	156.1	21.7	99.6	63.6	43.8	72.6
RbCN.............	6.82	8.5	149.1	150.3	19.9	95.9		43.8	
CsCN.............	4.25	9.5	141.3	142.5	19.1	89.4		43.8	

* ΔH_{298} for the reaction $[MCN] = [M] + \frac{1}{2}(C_2N_2)$.

4. The proton affinity of ammonia

It was pointed out by Grimm (164) that the crystal energies of the ammonium halides and the electron affinities of the halogens provide a method of calculating the proton affinity of ammonia, that is, the energy change for the reaction

$$(NH_4^+) = (NH_3) + (H^+)$$

The cycle used in the calculation is shown below.[14]

$$\begin{tikzcd}
& {[NH_4X]} \arrow[r, "U"] & NH_4^+ + X^- \arrow[dr, "P_{NH_3}"] & \\
\frac{1}{2} N_2 + 2 H_2 + \frac{1}{2} X_2 \arrow[ur, "-Q_{NH_4X}"] & & & NH_3 + H^+ + X^- \arrow[dl, "-I_H + E_X"] \\
& & NH_3 + H + X \arrow[ull, "-D_H - D_X"', "Q_{NH_3}"] &
\end{tikzcd}$$

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[14] X denotes any halogen. All substances except the NH_4X compounds are gases.

The proton affinity of ammonia at 0°K. is given by the relation

$$P_{NH_3} = U + Q_{NH_4X} - Q_{NH_3} + D_H + I_H + D_X - E_X - \frac{5}{2}RT$$

in which the symbols have the following significance:

U = lattice energy of an ammonium halide,
Q_{NH_4X} = chemical heat of formation of an ammonium halide,
Q_{NH_3} = chemical heat of formation of ammonia,
D_H = heat of dissociation of hydrogen,

TABLE 20

Crystal energies of the ammonium halides

CRYSTAL	STRUCTURE	a_0	r_0	n	U_0	U
NH_4F	Wurtzite		2.63	7.0	176.3	177.5
NH_4Cl	CsCl	3.86		8.0	152.1	153.3
NH_4Br	CsCl	4.05		8.5	146.2	147.4
NH_4I	NaCl	7.24		9.5	142.4	143.6

TABLE 21

Proton affinity of ammonia

	NH_4F	NH_4Cl	NH_4Br	NH_4I
U	177.5	153.3	147.4	143.6
Q_{NH_4X}	111.9	75.1	64.7	48.6
Q_{NH_3}	10.9	10.9	10.9	10.9
D_H	52.0	52.0	52.0	52.0
I_H	311.9	311.9	311.9	311.9
D_X	32.2	28.2	26.9	25.4
E_X	98.5	92.5	87.1	79.2
$\frac{5}{2}RT$	1.5	1.5	1.5	1.5
P_{NH_3}	221.0	209.0	208.6	202.7

I_H = ionization potential of hydrogen,
D_X = heat of dissociation of a halogen molecule,
E_X = electron affinity of a halogen, and
P_{NH_3} = proton affinity of ammonia.

Table 20 gives the crystal energies of the ammonium halides, and table 21 the thermal data required. The mean of the values of the proton affinity of ammonia from ammonium chloride, ammonium bromide, and ammonium iodide is 206.8 kilogram-calories.

It is interesting to discuss the differences in the values of the proton affinity calculated from the various ammonium halides. The agreement to within 0.2 per cent of the values from ammonium chloride and ammonium bromide is of course accidental, but it does indicate the consistency of the data. The lower value calculated from ammonium iodide is consistent with the discrepancy of the electron affinities calculated from the cesium and sodium chloride type of crystals. The high value of the proton affinity from ammonium fluoride is surprising, but may be explained in the following way. Pauling has pointed out in his lectures that the unexpected occurrence of the wurtzite structure for ammonium fluoride is probably due to the formation of hydrogen bonds. The formation of these bonds (non-rotating ammonium ion) causes the crystal energy to be different from the value given in the table and hence causes a corresponding difference in the value obtained for the proton affinity.

5. *Crystal energies of binary compounds of the halogens, oxygen, etc.*

The electron affinities of the halogens, obtained from the alkali halides, and of oxygen, sulfur, and selenium, obtained from the alkaline earth salts, will now be employed in conjunction with other thermal data to calculate the crystal energies for all binary salts for which data are available, and a comparison will be made of the values obtained with those calculated from the Born equation. Tables 22 and 23 summarize the results for the halides and for the oxides. sulfides, and selenides.

In fifteen of the fifty crystals, the observed and calculated values of the crystal energy agree to within 2 per cent. This agreement supports but does not prove the assignment of an extreme ionic structure to these crystals. On the other hand pronounced disagreement between theoretical and experimental values does indicate that the salt is not composed purely of spherically symmetrical ions, but that the bonds probably have to some extent the character of electron-pair bonds. This would be expected to cause $\Delta = U_{\text{exp}} - U_{\text{theor}}$ to be positive, in agreement with the

TABLE 22

Application of the Born-Haber cycle to halide crystals

CRYSTAL	STRUCTURE	a_0	r_0	δ_0	n	U_0	Q	I	S	$E-D$	U_{Exp}	U_{Theor}	Δ
AgF	NaCl	4.92			8.5	206.7	48.7	173.6	67	66.3	223.0	207.9	15.1
MgF_2	Rutile		1.96		7.0	695.0	264.3	520.6	36.5	132.6	688.8	696.8	−8.0
CaF_2	Fluorite	5.451			8.0	615.9	289.4	412.9	47.5	132.6	617.2	617.7	−0.5
SrF_2	Fluorite	5.78			8.5	585.7	289.3	383.8	39.7	132.6	580.2	587.5	−7.3
BaF_2	Fluorite	6.19			9.5	554.6	281.6	349.0	49.1	132.6	547.1	556.4	−9.3
MnF_2	Rutile			3.39	8.0	654.5	170.9	532.5	74.2	132.6	645.0	656.3	−11.3
FeF_2	Rutile		2.12		8.0	655.9	154.2	560.9	93.8	132.6	676.3	657.7	18.6
CuF_2	Rutile		2.01		8.0	691.8	160.7	578.9	81.9	132.6	692.9	689.6	−4.7
NiF_2	Rutile		2.00		8.0	695.3	187.8	593.3	85.0	132.6	733.5	697.1	36.4
CdF_2	Fluorite	5.40			8.5	626.9	172.5	594.6	27.2	132.6	661.9	628.7	33.0
PbF_2	Fluorite	5.93			9.5	578.9	159.4	515.5	47.4	132.6	589.7	580.7	9.0
CuCl	Sphalerite	5.41			9.0	204.9	32.5	177.3	81.9	63.6	228.1	206.1	22.0
AgCl	NaCl	5.54			9.5	186.1	30.3	173.6	67	63.6	207.3	187.3	20.0
TlCl	CsCl	3.84			10.5	158.1	48.7	140.2	45.6	63.6	170.9	159.3	11.6
$SrCl_2$	Fluorite	6.98			9.5	491.8	197.7	383.8	39.7	127.2	494.0	493.6	0.4
CuBr	Sphalerite	5.68			9.5	196.5	24.6	177.3	81.9	60.2	223.6	197.7	25.9
AgBr	NaCl	5.76			10.0	180.1	23.9	173.6	67	60.2	204.3	181.3	23.0
TlBr	CsCl	3.97			11.0	153.7	41.0	140.2	45.6	60.2	166.6	154.9	11.7
CuI	Sphalerite	6.05			10.5	186.5	15.8	177.3	81.9	53.8	221.2	187.7	33.5
AgI					11.0	174.7	15.1	173.6	67	53.8	201.9	175.9	26.0
TlI	CsCl	4.18			12.0	147.2	30.1	140.2	45.6	53.8	162.1	148.4	13.7
CdI_2	Cadmium iodide		2.99		11.0	475.2	48.9	594.6	27.2	107.6	563.1	477.0	86.1
PbI_2	Cadmium iodide		3.12		12.0	459.1	41.8	515.5	47.4	107.6	497.1	460.9	36.2

TABLE 23

Application of the Born-Haber cycle to oxides, sulfides, and selenides

CRYSTAL	STRUCTURE	a_0	r_0	δ_0	n	U_0	Q	I	S	$E - D$	U_{Exp}	U_{Theor}	Δ
Li_2O	Fluorite	4.61			6.0	693.5	142	247.6	76.6	−227	693	695	−2
Cu_2O	Cuprite	4.26			8.0	680.6	39.9	354.6	163.8	−227	786	682	104
Ag_2O	Cuprite	4.74			8.5	583.3	7.0	347.2	134	−227	715	585	130
MnO	NaCl	4.43			8.0	910.4	96.5	560.9	74.2	−227	959	912	47
FeO	NaCl	4.28			8.0	942.3	64.3	578.9	93.8	−227	964	944	20
CoO	NaCl	4.25			8.0	949.0	57.5	593.3	85.9	−227	964	950	14
NiO	NaCl	4.172			8.0	966.7	58.9	594.6	85.0	−227	966	968	−2
ZnO	Wurtzite		1.94		8.0	976.1	83.1	628.0	31.6	−227	970	977	−7
CdO	NaCl	4.70			8.5	865.3	62.3	594.6	27.2	−227	911	867	44
SnO_2	Rutile			3.28	8.5	2732	137.4	2143	78	−454	2813	2734	79
PbO_2	Rutile			3.27	9.5	2618	66.0	2264	47.4	−454	2832	2620	212
Al_2O_3	Corundum			3.50	7.0	3705	380.8	2445.2	110	−682	3618	3708	−90
Cr_2O_3	Corundum			3.62	8.0	3652	288.9	2505.0	151.8	−682	3627	3655	−28
Na_2S	Fluorite	6.53			8.0	514.1	89.8	236.1	52.0	−146	524	516	8
Cu_2S	Fluorite	5.59			9.0	610.1	19.0	354.6	163.8	−146	683	612	71
MnS	NaCl	5.21			9.0	786.4	59.7	560.9	74.2	−146	841	788	53
ZnS	Wurtzite		2.36		9.0	815.1	45.9	628.0	31.6	−146	852	816	36
ZnS	Sphalerite	5.42			9.0	818.2	45.9	628.0	31.6	−146	852	819	33
CdS	Wurtzite		2.52		9.5	768.4	33.9	594.6	27.2	−146	802	770	32
HgS	Sphalerite	5.84			10.5	772.9	10.9	669.9	14.7	−146	842	774	68
PbS	NaCl	5.93			10.5	703.3	22.9	515.5	47.4	−146	732	705	28
MnSe	NaCl	5.45			10.0	761.2	23.9	560.9	74.2	−152	811	762	49
ZnSe	Sphalerite	5.66			9.5	788.7	33.5	628.0	31.6	−152	845	790	55
CdSe	Sphalerite	6.04			10.0	743.4	17	594.6	27.2	−152	791	745	46
HgSe	Sphalerite	6.068			11.0	747.4	4.1	699.9	14.7	−152	841	749	92
PbSe	NaCl	6.14			11.0	682.5	12	515.5	47.4	−152	727	684	43
Cu_2Se	Fluorite	5.749			9.5	597.1	7.4	354.6	163.8	−152	678	599	79

results given in the table. (The large negative value found for aluminum oxide is not significant, since the crystal energy was calculated by using the Madelung constant for the ideally coördinated structure whereas the actual structure departs considerably from it.) Most of the fluorides and oxides seem to have an ionic structure, the fluorides of silver, nickel, and cadmium and the oxides of copper, silver, cadmium, lead, and tin being pronounced exceptions. On the other hand, sodium sulfide alone of the sulfides and selenides can be considered as ionic. Of the halogens other than the fluorides, only $SrCl_2$ can be of the extreme ionic type. The deviations shown in the series AgF, AgCl, AgBr, AgI and CuCl, CuBr, and CuI increase in the order given, indicating that the ion-forming tendency of the halogens falls off in the same way as the electron affinity. The thallous halides and the iodides of cadmium and lead are also seen not to be extreme ionic crystals.

The general conclusion which can be drawn from the evidence provided by crystal energy considerations is that the halides, oxides, and sulfides of the alkali and alkaline earth metals and many fluorides and oxides of other metals are probably essentially ionic, whereas the sulfides, selenides, chlorides, bromides, and iodides of eighteen-shell atoms are not essentially ionic.

6. *Crystal energies of compounds with the perovskite structure*

As an example of the application of the Born-Haber cycle to complex crystals, the energies of several crystals having the perovskite structure have been calculated.[15] Table 24 contains the calculated crystal energies, and table 25 the crystal energies obtained by means of the cycle, according to the following equation:[16]

$$U_{\mathrm{exp}} = Q_{\mathrm{MX}} + Q_{\mathrm{NX_2}} + I_{\mathrm{M}} + S_{\mathrm{M}} + I_{\mathrm{N}} + S_{\mathrm{N}} + 3\,D_{\mathrm{X}} - 3\,E_{\mathrm{X}} \qquad (74)$$

Heats of formation of these compounds are not known; we have assumed tentatively that the heat of formation of $KMgF_3$ is the sum of the heats of formation of KF and MgF_2, and similarly for

---

[15] The cubic unit of the perovskite structure contains one molecule, $KMgF_3$, say, with K^+ at 0, 0, 0; Mg^{++} at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; 3 F^- at $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$.

[16] The subscripts M and N denote univalent and divalent metals respectively.

the other compounds. For $KMgF_3$ the theoretical crystal energy is greater than the experimental value. This difference may, however, be just the heat of formation from KF and MgF_2. The difference of more than 10 per cent in the theoretical and experimental values of the crystal energy of $CsHgCl_3$ indicates that this compound is not strongly ionic, for it is very improbable that the heat of formation from CsCl and $HgCl_2$ has a large negative value. The excellent agreement between the theoretical and experimental values of the crystal energy of $CaSnO_3$ is probably accidental.

TABLE 24

Theoretical crystal energies of several compounds of the perovskite structure

CRYSTAL	a_0	n	U_0	U
$KMgF_3$	4.00	7.5	884.2	886.6
$KNiF_3$	4.008	8.0	890.9	893.3
$KZnF_3$	4.05	8.0	881.7	884.1
$CsCdCl_3$	5.20	10.0	706.3	708.7
$CsHgCl_3$	5.44	11.0	681.2	683.6
$CaSnO_3$	3.92	8.0	3643.6	3646.0

TABLE 25

Experimental crystal energies of several compounds of perovskite structure

	$KMgF_3$	$KNiF_3$	$KZnF_3$	$CsCdCl_3$	$CsHgCl_3$	$CaSnO_3$
Q_{MX}	134.5	134.5	134.5	106.6	106.6	151.7
Q_{NX_2}	264.3	187.8	192.7	92.2	53.4	137.4
I_M	99.6	99.6	99.6	89.4	89.4	412.9
S_M	21.7	21.7	21.7	19.1	19.1	47.5
$3D_X$	99.3	99.3	99.3	86.7	86.7	177.6
$3E_X$	298.2	298.2	298.2	277.5	277.5	−504
I_N	520.6	593.3	628.0	594.6	669.9	2143
S_N	36.5	85.0	31.6	27.2	14.7	78
U_{exp}	878.3	923.0	909.2	738.3	762.3	3652
U_{theor}	886.6	893	884	709	684	3646
Δ	−8.3	30	25	29	78	6

7. *Heats of solution of alkali ions and of halide ions*

In order to test the correctness of the Born equation for calculating crystal energies, Fajans and Schwartz (163) calculated values for the differences in the heats of solution of alkali ions and of halide ions by combining the value of the crystal energy of a salt with the value for its heat of solution. The sum of the crystal energy and the heat of solution of a given salt is equal to the sum of the heats of solution of anion and cation, as can be seen from the following thermochemical equations:

$$
\begin{aligned}
&[\mathrm{MX}] && = (\mathrm{M}^+) + (\mathrm{X}^-) && ;\ \Delta H = U_{\mathrm{MX}} \\
&[\mathrm{MX}] + \mathrm{n\ H_2O} && = \mathrm{M}^+(\mathrm{aq}) + \mathrm{X}^-(\mathrm{aq}) && ;\ \Delta H = -\,L_{\mathrm{MX}} \\
&\mathrm{M}^+(\mathrm{aq}) + \mathrm{X}^-(\mathrm{aq}) && = (\mathrm{M}^+) + (\mathrm{X}^-) + \mathrm{n\ H_2O}; && \Delta H = W_{\mathrm{M}^+} + W_{\mathrm{X}^-}
\end{aligned}
$$

The third equation is obtained by subtracting the second from the first, so that

$$W_{\mathrm{M}^+} + W_{\mathrm{X}^-} = U_{\mathrm{MX}} + L_{\mathrm{MX}} \tag{75}$$

W is the heat of solution of an ion while L is the heat of solution of a salt. From the above relation between W, U, and L, we obtain the following expressions for the difference in the heats of solution of two cations M and N or two anions X and Y.

$$(W_{\mathrm{M}^+} + W_{\mathrm{X}^-}) - (W_{\mathrm{N}^+} + W_{\mathrm{X}^-}) = W_{\mathrm{M}^+} - W_{\mathrm{N}^+} = (U_{\mathrm{MX}} + L_{\mathrm{MX}}) - (U_{\mathrm{NX}} + L_{\mathrm{NX}}) \tag{76}$$

$$W_{\mathrm{X}^-} - W_{\mathrm{Y}^-} = (U_{\mathrm{MX}} + L_{\mathrm{MX}}) - (U_{\mathrm{MY}} + L_{\mathrm{MY}}) \tag{77}$$

Thus for two binary salts having a common anion the difference in the value of $U + L$ for each salt is equal to the difference in the heats of solution of the cations, and similarly for two binary salts having a common cation $W_{\mathrm{M}^+} - W_{\mathrm{N}^+}$ should be independent of the common ion of the two salts, so that for the case of the alkali halides four independent values of $W_{\mathrm{M}^+} - W_{\mathrm{N}^+}$ can be obtained, one corresponding to each of the four halogens, and five independent values of $W_{\mathrm{X}^-} - W_{\mathrm{Y}^-}$. The crystal energies which Fajans employed in these calculations were obtained by using the value 9 for the repulsive exponent n for all crystals, and the values of $W_{\mathrm{M}^+} - W_{\mathrm{N}^+}$ and $W_{\mathrm{X}^-} - W_{\mathrm{Y}^-}$ showed pronounced trends. Fajans' calculations have been repeated using the crystal energies obtained in the previous sections of this paper. Table 26 gives Fajans' values for the heats of solution of the alkali halides at infinite dilution, and table 27 the values of $W_1 - W_2$ at infinite dilution. The figures in light print in each row give the value of $U_{MX} + L_{MX}$ for the salt whose anion is indicated at the head of the column and whose cation is given at the left of the row. The figures in heavy type give the values of the differences in the heats of solution of various pairs of ions. The consistency in the results is much better than that obtained by Fajans. There are, however, certain discrepancies. Thus the value of $W_{F^-} - W_{Cl^-}$ obtained from cesium fluoride and cesium chloride is higher than those calculated from the other salts. These discrepancies are probably to be attributed to errors in the crystal energies. They could be made to disappear, for example, by increasing the crystal energies of cesium chloride, cesium bromide and cesium iodide by 3.5 kilogram-calories per mole and the energies of lithium chloride, lithium bromide, and lithium iodide by 2.0 kilogram-calories

TABLE 26

Heats of solution of the alkali halides

	F	Cl	Br	I
Li	−1.0	8.8	11.7	14.8
Na	−0.6	−0.9	0.1	1.8
K	4.2	−4.1	−4.8	−4.9
Rb	5.8	−4.5	−6.0	−6.5
Cs	8.4	−4.7	−6.7	−8.2

TABLE 27

Differences in heats of hydration between alkali ions and between halide ions

	F	$W_{F^-} - W_{Cl^-}$	Cl	$W_{Cl^-} - W_{Br^-}$	Br	$W_{Br^-} - W_{I^-}$	I
Li	239.1	**37.0**	202.1	**7.3**	194.8	**9.3**	185.5
$W_{Li^+} - W_{Na^+}$	**24.7**		**22.8**		**23.6**		**22.9**
Na	214.4	**35.1**	179.3	**8.1**	171.2	**8.6**	162.6
$W_{Na^+} - W_{K^+}$	**19.8**		**19.0**		**18.2**		**18.5**
K	194.6	**34.3**	160.3	**7.3**	153.0	**8.9**	144.1
$W_{K^+} - W_{Rb^+}$	**7.0**		**5.9**		**6.5**		**6.4**
Rb	187.6	**33.2**	154.4	**7.9**	146.5	**8.8**	137.7
$W_{Rb^+} - W_{Cs^+}$	**6.4**		**10.2**		**9.7**		**9.8**
Cs	181.2	**37.0**	144.2	**7.4**	136.8	**8.9**	127.9

per mole. If this correction were made, the values of $W_{M^+} - W_{N^+}$ and $W_{X^-} - W_{Y^-}$ would be consistent and would remain consistent as long as all the crystal energies were then in error by the same amount. Thus there is an uncertainty in the values of all crystal energies, this uncertainty being of the same magnitude and direction as was found from the discrepancies in the electron affinities of the halogens and in the proton affinity of ammonia.

If the absolute value of the heat of solution of one alkali ion or one halide ion were known, then the results obtained would permit an evaluation of the heats of solution of all the other ions. Webb (171) has attempted to calculate the absolute heat of solution of an ion, but his results are not sufficiently reliable for this purpose.

TABLE 28

Crystal energies of the alkali hydrides

CRYSTAL	Q	I	S	D	E	U	U_0
LiH	21.6*	123.8	38.3	51.9	16.4	219.2	218.0
NaH	12.8†	118.0	26.0	51.9	16.4	192.3	191.1
KH	12‡	99.6	21.7	51.9	16.4	168.8	167.6
RbH	12‡	95.9	19.9	51.9	16.4	163.3	162.1
CsH	12‡	89.4	19.1	51.9	16.4	156.0	154.8

* Landolt-Börnstein Tables, 1st Ergänzungsband.

† Hagen and Sieverts (165).

‡ Unpublished measurements of A. Monossohn used by Kasarnowsky (167).

8. *Compressibilities of the alkali halides*

The electron affinity of hydrogen being known with considerable certainty, the Born-Haber cycle may be employed to evaluate the crystal energies of the alkali hydrides, all of which have the sodium chloride structure. The Born equation for the crystal energy may be used to evaluate the repulsive exponent for each hydride, and by means of equation 56 the compressibilities may then be calculated. Kasarnowsky (167) has carried out such calculations. He measured the densities of the hydrides (166) and calculated the lattice constants from them. Recently, however, Zintl and Harder (173) have measured the lattice constants directly by x-rays and it was thought desirable to repeat the calculations, using these latest values of the lattice constants and the thermal data of this article. Table 28 summarizes the data used. The crystal energies in the last column of the table are obtained by combining the quantities tabulated in the previous columns.

Table 29 gives the values of the repulsive exponents and compressibilities calculated from the crystal energies and the lattice constants. The relation between n and compressibility is given by the following equation

TABLE 29

Compressibilities of the alkali hydrides

CRYSTAL	U_0	a_0	n	χ
				sq. cm. per dyne
LiH	218.0	4.084	4.40	2.32×10^{-12}
NaH	191.1	4.880	5.24	3.78×10^{-12}
KH	167.6	5.700	5.85	6.16×10^{-12}
RbH	162.1	6.037	6.63	6.67×10^{-12}
CsH	154.8	6.376	6.97	7.83×10^{-12}

$$\chi = \frac{2.829 \cdot 10^{-13}\, a^4}{n - 1} \tag{78}$$

No experimental determinations of the compressibilities have been made, and so a check upon these calculated values is not available. Comparison between calculated and observed values would afford a direct test of the essential correctness of the Born equation for the crystal energy.

V. CRYSTAL ENERGIES OBTAINED INDEPENDENTLY OF THE BORN THEORY

In the preceding pages the Born theory of ionic crystals has been presented. Several attempts have been made to determine crystal energies independently of the Born theory; these will now be discussed.

1. Quantum mechanical treatment of lithium hydride

Recently Hylleraas (13) has treated the many electron problem of the lithium hydride lattice with the aid of the quantum mechanics. Without the introduction of any empirical data, the lattice energy of lithium hydride was calculated to be 219 kilogram-calories per mole and the lattice constant 4.42 Å. The value of the energy determined from the Born cycle (table 17) is 218 kilogram-calories and the experimental value of the lattice constant is 4.084 Å. (173). The agreement in the values of the energy is seen to be excellent, providing a remarkable substantiation of the quantum mechanical treatment. The theoretical and experimental lattice constants differ by more than 8 per cent, but Hylleraas pointed out that the use of more accurate eigenfunctions would doubtless give a more accurate value of the lattice constant without appreciably changing the energy.

Hylleraas has thus demonstrated the possibility of giving a fundamental theoretical treatment of the structure of crystals, but unfortunately it is impractical to apply the treatment to crystals containing eight- and eighteen-shell ions because of the great complexity of the calculations.

2. Slater's treatment of the alkali halides

Slater (32) has evaluated the crystal energies of a number of alkali halides directly from his measurements of the compressibility and its pressure coefficient, both extrapolated to 0°K. He expressed the crystal energy at 0°K. as a Taylor's series in r in the region near $r = r_0$, the experimental data giving the values of the first, second, and third derivatives. Extrapolating to large values of r, he showed that his series approached the value resulting from the Coulomb energy alone, and then combined it with the Coulomb expression to obtain values of the crystal energies. Table 30 gives his results. The crystal energies calculated from the Born formula (table 17) are included for comparison.

The crystal energies determined with the aid of the Born equation were calculated by using lattice constants determined at room temperatures, so that these energies represent the crystal energies at room temperatures, while the values of Slater are for 0°K. The difference in crystal energy between two temperatures depends upon the heat capacity of the crystal and its ions. For the alkali halides this amounts to approximately 2 kilogram-calories between 0°K. and 25°C. so that the Born values should be increased by this amount in order to compare with those of Slater. Slater estimates a probable error of 5 kilogram-calories in his results; hence the two sets of values may be said to be in rough agreement.

TABLE 30

Crystal energies determined from compressibility data and from the Born formula

SUBSTANCE	U (Slater)	U (Born)
LiF	231	239
KF	182	189
LiCl	189	192
NaCl	178	179
KCl	164	163
LiBr	180	182
NaBr	169	171
KBr	157	157
RbBr	152	151
KI	148	148
RbI	147	143

3. *Direct thermochemical determination of the crystal energies of potassium iodide and cesium iodide*

Mayer (25) has recently determined directly the energy of ionic dissociation of potassium iodide and cesium iodide vapors. If these energies are added to the corresponding energies of sublimation, the crystal energies are obtained directly. The method is not of general applicability because the ionic dissociation of most salt vapors is too small to be measurable except at extremely high temperatures. Mayer reports 148.6 ± 4 kilogram-calories and 131 kilogram-calories for the crystal energies at 18°C. of potassium iodide and cesium iodide. The values determined from the Born formula (table 17) are 147.8 and 135 kilogram-calories, respectively. This provides a remarkable check of the Born formula and hence a substantiation of the quantities, such as electron affinities, derived with its use.

VI. ACKNOWLEDGMENTS

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Notes added July 20, 1932: Since the submission of this article for publication, two important papers dealing with crystal energies have appeared.

Throughout this article the Born treatment of ionic crystals has been employed, in which the crystal energy is expressed by the two parameter equation

$$\Phi(r) = -\frac{A\epsilon^2}{r} + \frac{B}{r^n}$$

Recently Born and Mayer (Z. Physik **75**, 1 (1932)) have obtained a new expression for the crystal energy in which the inverse n'th power repulsive term is replaced by an exponential term (such as is suggested by quantum mechanics) and in addition, the energy due to the van der Waals' attractive forces and the zero-point energy are taken into account. London (Z. physik. Chem. **11B**, 222 (1930)) has shown that the van der Waals' potential may be represented by an inverse sixth power term. Just as in the original, this new formula for the crystal energy contains two parameters, to be determined from the properties of the crystal.

Mayer and Helmholz (Z. Physik **75**, 19 (1932)) have applied the revised theory to the calculation of the lattice energies of the alkali halides and have employed the values obtained in various thermochemical calculations, the results of which indicate their essential correctness. Table 31 shows the comparison between the electron affinities obtained by using the crystal energies calculated by Mayer and Helmholz (with the aid of the new theory, and by the author (on the basis of the old theory).

The discrepancies vary from 0.8 kilogram-calorie for fluorine to 4.2 kilogram-calories for chlorine. Since the more refined treatment of the crystal lattice doubtless leads to more trustworthy crystal energy values, the electron affinities calculated from them are consequently more reliable than those given in this paper, and may be considered to be correct within 3 kilogram-calories.

TABLE 31

Electron affinities of the halogens

HALOGEN	MAYER AND HELMHOLZ	SHERMAN
	kg-cals.	*kg-cals.*
F	97.7	98.5
Cl	88.3	92.5
Br	83.2	87.1
I	75.5	79.2

The proton affinity of water vapor

At the suggestion of Dr. G. H. Cady, I have calculated an approximate value for the proton affinity of water vapor by assuming the crystal energies of the isomorphous crystals NH_4ClO_4 and H_3OClO_4—($HClO_4 \cdot H_2O$)—to be the same. [X-ray oscillation photographs obtained by M. Volmer (Ann. **440**, 200 (1924)) for each of these crystals show almost identical spacings and relative intensities of reflection, corresponding at most to a small difference in the crystal energies if the Madelung constants are the same.] Applying the Born thermochemical cycle to each of these crystals, the proton affinity of water vapor, which is the heat evolved in the reaction

$$H_2O\ (g) + H^+\ (g) = H_3O^+\ (g)$$

can be calculated by means of the thermochemical equation

$$P_{H_2O} = P_{NH_3} + Q_{NH_3} - Q_{H_2O} + Q_{H_3OClO_4} - Q_{NH_4ClO_4}$$

P_{NH_3}, the proton affinity of ammonia, has been previously calculated and found to be 206.8 kilogram-calories. The values of Q, the chemical heats of formation of the various compounds, are taken from International Critical Tables, Volume V. The value of P_{H_2O} is thus calculated to be

$$\begin{aligned} P_{H_2O} &= 206.8 + 10.9 - 57.8 + 100.4 - 78.3 \\ &= 182 \text{ kilogram-calories.} \end{aligned}$$

This value seems reasonable in comparison with the proton affinity of ammonia.

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