

LATTICE ENERGY OF IONIC CRYSTALS

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THE lattice energies of ionic crystals play a considerable role in diverse chemical processes, and an extensive survey could be made of the achievements in various directions by many researchers in this field. The present Review, however, pursues a much narrower aim: to summarise chiefly some investigations carried out by the Reviewer and his colleagues in developing various methods of evaluating lattice energies as well as analysing and generalising the results obtained by these methods.

Crystal lattice energy and its calculation by means of ionic charges and radii

The concept of crystal lattice energy, U , which, as is known, equals the heat of dissociation of one mole of solid into its structural components, became widespread after Max Born¹ first proposed the following equation for the energy of the lattice of ionic crystals:

$$U = A \frac{Ne^2\eta_1\eta_2}{r} \left(1 - \frac{1}{m}\right) \quad . \quad . \quad . \quad . \quad (1)$$

where η_1 , η_2 and e are the ionic and electronic charges, N is Avogadro's constant, r is the inter-ionic distance, m is the electronic shells repulsion exponent, and A is the structural coefficient (Madelung constant). Considering the quantum-mechanical character of the repulsion forces acting between the electronic shells of ions, Born and Joseph Mayer² later improved equation (1) as follows:

$$U = A \frac{Ne^2\eta_1\eta_2}{r} \left(1 - \frac{\rho}{r}\right) \quad . \quad . \quad . \quad . \quad (2)$$

introducing in it the constant, ρ , which characterises these forces and which for most crystals may be regarded as practically constant and having the value 0.345.

For all the significance of this achievement, which is an advance in the theory of solids, the sphere of the calculations is somewhat limited by inadequate knowledge of the structure and parameters of crystals, permitting the application of equations (1) and (2) only to solids previously investigated by X-rays for the establishment of r and A . In general chemistry and also in geochemistry, however, it was desirable to extend the sphere of the calculations of U by some simpler method than the use of equations (1) and (2), but without any essential loss of accuracy.

¹ M. Born, *Verhandl. deut. phys. Ges.*, 1918, **20**, 202; 1919, **21**, 13.

² M. Born and J. Mayer, *Z. Physik*, 1932, **75**, 1.

For the solution of this problem the Reviewer³ used his empirically found parallelism connecting the differences between A and the Madelung constant for crystals of the rock-salt type, and the differences between r and the sum of the ionic radii of the given crystal when referred to the co-ordination number 6. This makes it possible to reconstruct imaginatively, so to speak, an "iso-energetic" rebinding of a crystal of any given type into a rock-salt lattice structure, which can be easily computed since, thanks to V. Goldschmidt, the ionic radii (τ_C and τ_A) are well known for most elements.

The aforesaid permits the following transformation of equation (1). The number of ions per mole of a crystal equals the product of Avogadro's constant and the number of ions in the molecule, $N\Sigma n$. Let us rewrite eqn. (1) so as to separate in the right-hand part of the equation the work of removing one ion (cation or anion) from the lattice, and then multiply and divide this part by $\frac{1}{3}N\Sigma n$. We denote the structural coefficient referred to one ion, $\alpha = A/(\Sigma n/2)$,

$$\text{or} \quad U = \frac{\Sigma n}{2} \cdot \alpha \cdot \frac{Ne^2 \eta_1 \eta_2}{r} \left(1 - \frac{1}{m} \right)$$

Since the changes of α are equal to the changes in the interionic distances, it is obvious that we obtain the same value for U by calculating it with the aid of r derived by X-ray measurements and the structural factor corresponding to the given lattice, and by taking the Goldschmidt ionic radii referred to the co-ordination number 6 (instead of $r = \tau_C + \tau_A$) together with the structural coefficient of rock-salt type lattices, $\alpha = 1.745$. In the above equation m varies little around the mean value of 9, and the adoption of this average value little affects the accuracy of the U calculations. Since $Ne^2 = 329.7$ kcal. per Å, we, as a result, obtain equation (3) in which the numerical factors are grouped in one coefficient of proportionality

$$U = 256.1 \Sigma n \eta_1 \eta_2 / (\tau_C + \tau_A) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This permits us to calculate the energy of any type of lattice with the aid of charges and radii, *i.e.*, with the aid of well-known magnitudes.

A defect of this formula is that it is associated with antiquated concepts of the character of repulsion forces. We therefore, later, similarly transformed the quantum-mechanical equation (2) for lattice energy. This equation which has been described, for example, by Partington⁴ yields

$$U = 287.2 \Sigma n \frac{\eta_1 \eta_2}{\tau_C + \tau_A} \left(1 - \frac{0.345}{\tau_C + \tau_A} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where 287.2 is the numerical factor summing all constants. Such is the general expression. It is in accord with modern concepts of the nature of the solid state and at the same time permits evaluation in advance of the lattice energies of any ionic crystals not yet investigated by X-ray measurements, *i.e.*, with r and the structural factors A still unknown experimentally.

³ A. Kapustinskii, *Z. phys. Chem.*, 1933, **22**, B, 257.

⁴ J. R. Partington, "An Advanced Treatise on Physical Chemistry", Vol. III, Longmans, London, 1952, p. 383; A. Kapustinskii, *Acta Physicochim.*, 1943, **18**, No. 5, 370.

Yet it is approximately as accurate as Born and Mayer's equation and therefore opens up some wider prospects for extending the evaluation of lattice energy to various scientific investigations.

“Thermal” (“thermochemical”) ionic radii

As we shall show in greater detail later, to verify the accuracy of equations (3) and (4) we have compared the results of calculations with experimental results (with the so-called “experimental” evaluations of lattice energy) obtained by summing the thermochemical values already known from the Born-Haber cycle.

In the Goldschmidt system, when such data were available and the radius of one of the ions was lacking, it was possible to “reverse” the calculation and thus, by using eqn. (3) or (4), obtain from the thermal data the radius of a simple or complex ion.⁵ At the Reviewer's suggestion such values have been named “thermal” or “thermochemical” ionic radii. As an example we may cite the calculation for a tin ion, Sn^{2+} , lacking from the Goldschmidt table.⁶ Computed in three separate ways, namely, from “experimental” energies of stannous sulphide, oxide, and chloride lattices, this calculation produces identical results fluctuating within the error range generally accepted in evaluating radii, namely, $\tau_{\text{Sn}^{2+}} = 1.04 \pm 0.02 \text{ \AA}$.

Our above-mentioned investigation, which was noted by Goldschmidt,⁶ has permitted the number of known geometric characteristics of ions in the crystallochemistry of inorganic compounds, to be increased by means of the Born-Haber cycle from purely energetic magnitudes. The entropy of aqueous ions was later added to them.⁷

This method is helpful to a certain extent also in finding the dimensions of more complex ions or radicals which may be assumed to have spherical symmetry. Thus, for example, the Reviewer and K. B. Yatsimirsky,⁸ proceeding from equation (4), have calculated the thermochemical radii of a large number of tetrahedral ions. We have found that they all obey the additivity principle and only for a few combinations of relatively large anions with small cations are there small deviations; these are explained by the peculiar “intrusion effect” due to the fact that in this kind of structure the small outer cation is capable of penetrating into the “cavities” between the ions comprising the large anion, owing to which the distances between the particles diminish.* Table I gives the dimensions of some ions.

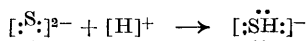
⁵ A. Kapustinskii, *Z. Krist.*, 1933, **86**, A, 359.

⁶ V. M. Goldschmidt, “Kristallochemie”, Handwörterbuch der Naturwissenschaften, 2nd edn., Vol. 5, Jena, 1934 (Russian translation, Leningrad, 1937, p. 25).

⁷ A. Kapustinskii, *Doklady Akad. Nauk S.S.S.R.*, 1941, **30**, 625.

⁸ A. Kapustinskii and K. Yatsimirsky, *Zhur. obshchei Khim.*, 1949, **19**, 2191.

* The “intrusion effect” can be observed not only in complex ions but also in simple ones, which reduces the formally binary system to a monolithic spherical form. Such, for example, is the nearly spherical hydrogen sulphide ion, HS^- , formed by placing a negligibly small proton in the electronic environment of a large anion, S^{2-}



which agrees well with the insignificant polarity (0.65×10^{-18}) of such a system (cf. A. Kapustinskii, I. Makolkin, and L. Krishtalik, *Zhur. fiz. Khim.*, 1947, **21**, 126).

TABLE 1. "Thermochemical" radii of tetrahedral ions in Å

Ion	ClO_4^-	MnO_4^-	BF_4^-	SO_4^{2-}	CrO_4^{2-}	MoO_4^{2-}	BeF_4^{2-}
Radius	2.36	2.40	2.28	2.30	2.40	2.54	2.45
Ion	IO_4^-	SeO_4^{2-}	TeO_4^{2-}	PO_4^{3-}	AsO_4^{3-}	SbO_4^{3-}	BiO_4^{3-}
Radius	2.49	2.43	2.54	2.38	2.48	2.60	2.68

Strictly speaking, the later examples belong to complex compounds. Typical examples of complex ions will be treated in the following section.

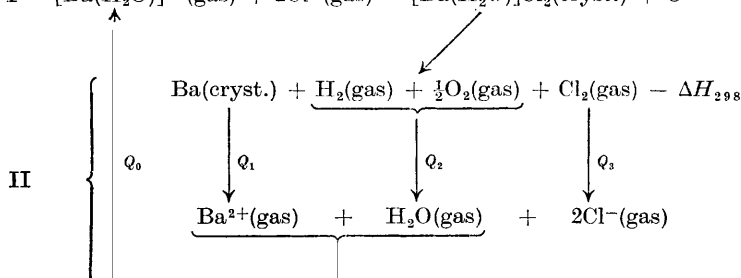
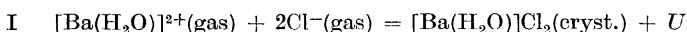
The energetics of complex compounds

While some complex radicals, especially those of octahedral configuration, may be considered as spheres whose dimensions are directly and fully determined by their radii, there are a good many ions whose structure is far from spherical. In all cases, however, one may speak of effective ionic radii as spherical particles which can equivalently, *i.e.*, without changing the energy of the lattice as a whole, replace in the solid an ion of any configuration.¹⁰ Such effective thermochemical radii can, evidently, be found in the same way, *i.e.*, from the Born-Haber cycle in combination with the crystal-lattice energy equation (4). They are constant and additive magnitudes to such an extent that it is clearly manifest even for such ions which in fact are very far from being spherical.

A good example of this is the complex compound formed by two particles of approximately equal size, such as an ion of barium and a molecule of water, which may be illustrated by crystalline monohydrates of various barium salts. Eley and Evans's⁹ investigation permits us to calculate the thermal effect of the process:



From the cycle:



it follows that the sum of this thermal effect (Q_0) and the already known thermal effects of the separate stages (Q_1 , Q_2 , Q_3 , and ΔH_{298} of part II of the

⁹ D. Eley and M. Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093.

cycle equals the thermal effect of part I, *i.e.*, the energy of the lattice U of barium chloride monohydrate taken here as a concrete example. We can, therefore, by deriving the latter magnitude from the cycle and using equation (4), proceed to evaluate the effective ion radius $\tau_{[\text{Ba}(\text{H}_2\text{O})]^{2+}}$ from various monohydrates containing anions of already known dimensions (see Table 2).

TABLE 2. "Thermochemical" radius in Å

Compound . .	$[\text{Ba}(\text{H}_2\text{O})]\text{Cl}_2$	$[\text{Ba}(\text{H}_2\text{O})]\text{Br}_2$	$[\text{Ba}(\text{H}_2\text{O})]\text{I}_2$
Radius . . .	1.62	1.61	1.60
Compound . .	$[\text{Ba}(\text{H}_2\text{O})](\text{NO}_3)_2$	$[\text{Ba}(\text{H}_2\text{O})](\text{CN})_2$	$[\text{Ba}(\text{H}_2\text{O})](\text{ClO}_3)_2$
Radius . . .	1.60	1.60	1.61

The average magnitude of $\tau_{[\text{Ba}(\text{H}_2\text{O})]^{2+}} = 1.6 \pm 0.01$ Å.

Here additivity is manifestly not less, at any rate, than in the determination of the dimensions of simple ions with the aid of lattice parameters determined by X-ray measurements.

In the last three compounds in Table 2 the anions are also complex radicals. Yatsimirskii,¹⁰ in his book (which is the first monograph on the thermochemistry of complex compounds), has not only computed the thermochemical radii for 36 complex anions and 67 complex cations and shown their constancy and additivity, but has based the theoretical part of his monograph mainly on various applications of eqn. (4). This has enabled him to extend the energy characteristics of ions quite widely in the chemistry of complex compounds, establish many hitherto unknown binding energies of gaseous addenda to the complexing agent (heat of hydration, entropies of complex ions in the solution, and alkyl affinities), calculate the heat of solution and solubility of salts and the thermal stability of complex compounds, and, lastly, outline some theoretical principles of the use of complex compounds in chemical analysis.

Lattice energy and chemical analysis

It is fascinating for a chemist to see the realisation, even if only in part, of chemical syntheses predicted on the basis of crystallochemistry, confirmed by the production of new, theoretically suggested compounds.

Since for condensed states the entropy factor is negligible and the free-energy changes, which determine the trend of the chemical reaction, closely approach thermal effects, the apparent problem is to find the free-energy changes, if they are known, by means of "thermochemical" radii and eqn. (4). The negativity of the thermal effect ($Q = -\Delta F$) thus found indicates that the synthesis cannot occur, while a positive effect shows that

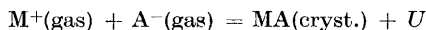
¹⁰ K. B. Yatsimirskii, "Thermochemistry of Complex Compounds", ed. A. F. Kapustinskii, U.S.S.R. Academy of Sciences, Moscow, 1951.

the planned reaction for obtaining the substance under consideration can be accomplished, and the more positive the effect, the more probable is its corresponding reaction. Following this preliminary theoretical prediction a number of hitherto unknown compounds have been synthesised¹¹ such as, for example, $[\text{Mg}(\text{CO}, \text{N}_2\text{H}_4)_6][\text{SnCl}_6]$, $[\text{Ca}(\text{CO}, \text{N}_2\text{H}_4)_6][\text{SnCl}_6]$, and $[\text{Co}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2][\text{PbCl}_6]$.

Crystallochemical electronegativity of simple and complex ions

The fairly long-known concept of electronegativity as the tendency of atoms in the molecule to attract electrons first received a strictly quantitative expression in the covalent-bond theory, which Science owes to Pauling.¹² He also used it to calculate heats of formation. Unfortunately, these calculations are rather rough and, for all compounds not containing nitrogen and oxygen, even contradict the facts of the existence of endothermic compounds.

Theoretically it would be preferable to take as a basis, not the common standard of thermochemistry (the physical state of reagents at 25°C and 1 atm.), but the state of gaseous ions (reagents) and crystals (products) under equal thermodynamic conditions. The exothermic heat of reaction under such conditions is the energy of the crystal lattice:



If the charge of the ion is η then its potential $V = \eta/\tau$ and ion energy $W = \eta^2/2\tau$.

For the initial state of the system (reagents) the energy equals the total energy of the ions:

$$H_1 = W_{\text{cation}} + W_{\text{anion}} = \eta^2/2\tau_{\text{C}} + \eta^2/2\tau_{\text{A}}$$

Such additivity does not take place in crystal lattices, for which, in accordance with Mulliken's¹³ quantum-mechanical investigation, it may be assumed that the energy of the ions in the lattice is proportional to the geometrical mean of the ionic potentials, η being the proportionality factor:

$$H_2 = \eta\sqrt{(V_{\text{C}}V_{\text{A}})} = \sqrt{[(\eta^2/\tau_{\text{C}})(\eta^2/\tau_{\text{A}})]}$$

The quantity showing the potential and characterising the energy of the electron attraction to the ion being described by R (this energy increases with the increase of the ion charge and decreases with the increase of the ion radius):

$$R_{\text{C}}^2 = \eta^2/2\tau_{\text{C}} \quad \text{and} \quad R_{\text{A}}^2 = \eta^2/2\tau_{\text{A}}$$

Then:

$$U = H_1 - H_2$$

$$U = R_{\text{C}}^2 + R_{\text{A}}^2 - \sqrt{(4R_{\text{C}}^2R_{\text{A}}^2)} = (R_{\text{C}} - R_{\text{A}})^2$$

¹¹ K. Yatsimirskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1948, 263; A. Kapustinskii and V. Vaver, *ibid.*, 1951, 631.

¹² L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, 1940.

¹³ R. Mulliken, *J. Chem. Phys.*, 1934, **11**, 782.

or, finally, passing from one bond, for which the conclusion has been drawn, to the summation, Σ , of all the bonds :

$$U = \Sigma(R_C - R_A)^2 \quad . \quad . \quad . \quad . \quad (5)$$

Here the magnitudes R characterise the energy of the electron attraction to the ion in the crystal lattice, and, therefore, in contrast to Pauling's electronegativities, may be called "crystallochemical electronegativities". It is most convenient to compute their values directly from experimental data, *i.e.*, from the lattice "experimental" energies, the fluoride ion being assumed to have $R = 1$. Then with equation (5) it is not difficult to obtain the corresponding data for the other ions (thus, for chlorine, $R = 2.1$; sulphur, 0.4; oxygen, 1.8, etc.).

To what extent these values are really additive may be judged from the example of zinc compounds (Table 3).

TABLE 3. *Crystallochemical electronegativity of zinc ion*
(*kcal./mole at 25°C*)

Compound	ZnO	ZnS	ZnF ₂	ZnCl ₂
Lattice "experimental" energy U	970	852	672	630
R for Zn ²⁺	20.2	20.2	19.3	19.9

Despite the wide range of the lattice-energy changes, R for Zn²⁺ remains constant within 3% (mean 20.0 ± 0.2). The R thus found for various other ions are given in Table 4.

TABLE 4. *Ion crystallochemical electronegativity (kcal./mole at 25°C)*
(For the fluoride ion R is assumed to be unity)

H ⁻ 1.8						
Li ⁺ 16.5	Be ²⁺ 21.2	B ³⁺ 24.2	C ⁴⁺ 30.2	O ²⁻ - 1.8	F ⁻ 1.0	Fe ²⁺ 19.9
Na ⁺ 15.6	Mg ²⁺ 19.7	Al ³⁺ 23.0	Si ⁴⁺ 26.2	S ²⁻ - 0.4	Cl ⁻ 2.1	Co ²⁺ 20.0
K ⁺ 14.8	Ca ²⁺ 18.6	Sc ³⁺ 21.3	Ti ⁴⁺ 25.0	Se ²⁻ - 0.1	Br ⁻ 2.3	Ni ²⁺ 20.1
	Cu ⁺ 17.5					
	Cu ²⁺ 19.6	Zn ²⁺ 20.0	Ga ³⁺ 22.8	Cr ³⁺ 22.5	I ⁻ 2.7	
Rb ⁺ 14.5	Sr ²⁺ 18.1					Mn ⁴⁺ 26.1
	Ag ⁺ 16.8	Cd ²⁺ 19.0	In ³⁺ 22.2	Sn ⁴⁺ 24.2		Mn ²⁺ 19.8
Cs ⁺ 14.1	Ba ²⁺ 17.6	La ³⁺ 20.1		Pb ⁴⁺ 24.8	Tl ³⁺ 15.2	Pb ²⁺ 18.0

These new physicochemical constants,¹⁴ which permit an approximate evaluation of crystal lattice energy, like the other constants, appear to obey the Mendeleev Periodic Law (Fig. 1).

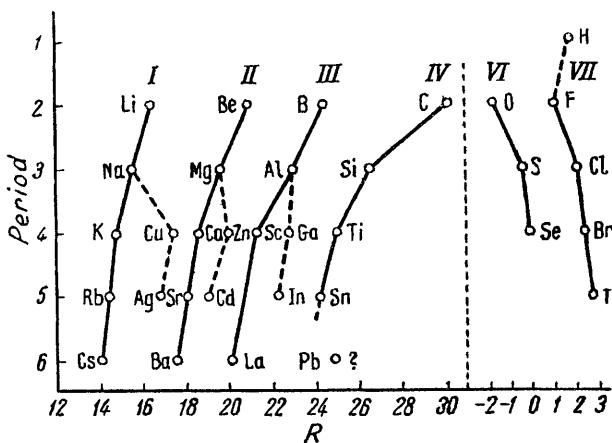


FIG. 1

The Mendeleev Periodic System and ion crystallochemical electronegativity. Lines connect elements of like groups (and subgroups).

As the Reviewer and Yakushevskii¹⁵ have shown, R has similarly been calculated for 79 complex ions, and not only has the possibility of considering the complex ion in the lattice as a sphere been confirmed, but it has also been demonstrated that the influences of various neutral addenda, such as the molecules of water and ammonia, on the crystallochemical electronegativity of a central ion in a complex compound, are practically equal.

Lattice energy and the thermochemical logarithmic rule

In Fig. 1 it has already been shown that crystal-lattice energy manifests periodicity in accordance with the Mendeleev system. Let us examine this matter in somewhat greater detail.

The approximate dependence, established earlier,¹⁶ between the heat of formation of chemical compounds (calculated for the equivalent weight) and the place of elements in the Mendeleev system, determined by the atomic number, the so-called thermochemical logarithmic rule, in the mathematical expression, indicates that there is a linear dependence between the heats of formation and the logarithmic atomic number in the series of similar compounds (halides, oxides, etc.) in both the groups and periods of the Mendeleev system. This approximate concordance is observed for ions and atoms having analogous electronic shells. The above-mentioned rule, which basically shows the connection between thermochemistry and

¹⁴ A. Kapustinskii, *Doklady Akad. Nauk S.S.S.R.*, 1949, **3**, 467; 1949, **4**, 663.

¹⁵ A. Kapustinskii and B. Yakushevskii, *Izvest. Sekt. Platinny drug. blagorod. Metall.*, 1952, 152.

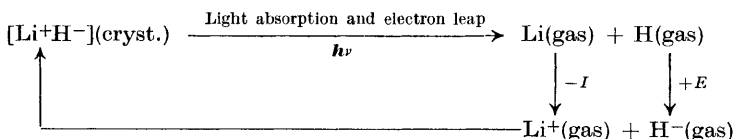
¹⁶ A. Kapustinskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1948, 568, 581.

the Mendeleev periodic system and was recently discussed in Long's¹⁷ excellent review, extends also to lattice crystal energy. This is only natural since the latter is a most simple kind of thermochemical constant referred to the physical standard state, ionic gas-crystal, uniform for all ionic crystals. A detailed exposition of this question is given by the Reviewer in an article soon to appear.*

Isotopy and crystallochemistry

The thermochemistry of isotopes still receives insufficient attention. We therefore would like to recall here our work, jointly with Shamovskii and Bayushkina,¹⁸ dealing with this subject. In it, the elementary photochemical process in the ionic crystal is treated as corresponding to the direct "leap" of the electron in the lattice from anion to cation, with the formation of neutral atoms. In this case, from the cycle which may be called "photochemical", it is easy to obtain an expression for the maximum absorption band $h\nu$ from which

$$h\nu = E - I + U \quad . \quad . \quad . \quad (6)$$



where E is electron affinity, I is ionisation energy, and U is lattice energy. In accordance with the example chosen to illustrate the cycle, lithium hydride was used in the investigation. Subliming this substance in a high vacuum on a quartz plate and determining spectrophotometrically the maximum absorption of the crystals in the ultraviolet part of the spectrum, and then performing the same experiments with lithium deuteride, we obtained results permitting us, with the aid of equation (6), to calculate U for lithium compounds with light and heavy hydrogen isotopes :

$$U_{\text{LiH}} = 219.2 \text{ kcal./mole} \quad \text{and} \quad U_{\text{LiD}} = 220.8 \text{ kcal./mole} \quad . \quad (7)$$

These values appeared to be in agreement with theoretical lattice-energy calculations carried out by Zintl and Hardner¹⁹ with the aid of X-ray measurements. Substitution in the lithium hydride crystal of the light hydrogen isotope, protium, by the heavy isotope, deuterium, increases the crystal lattice energy by 0.5%.

¹⁷ L. H. Long, *Quart. Rev.*, 1953, **7**, 134.

¹⁸ A. Kapustinskii, L. Shamovskii, and K. Bayushkina, *Acta Physicochim.*, 1937, **6**, 799.

¹⁹ E. Zintl and A. Hardner, *Z. phys. Chem.*, 1935, **28**, B, 478, 493.

* A. F. Kapustinskii, "Ionic Crystals Lattice Energy and the Thermochemical Logarithmic Rule", Transactions of Mendeleev Institute of Chemical Technology, Moscow.

Errors in lattice-energy calculations and possibility of their greater accuracy

It is known that the more complete expression for lattice energy

$$U = A \frac{Ne^2 \eta_1 \eta_2}{r} \left(1 - \frac{\rho}{r} \right) + \frac{c}{r^6} + \varepsilon_0 \quad . \quad . \quad . \quad (8)$$

contains additional terms, namely, the zero-point energy, ε_0 , and the van der Waals forces, c/r^6 , with the constant c computed by the London method (a good exposition of this question is given by Glasstone²⁰). Comparison, however, with experimental data obtained by the Born-Haber cycle indicates that for purely ionic crystals the second and the third term have little significance and, therefore, attention should be directed chiefly to the possibility of increasing the accuracy of the first term as playing the main role in the general balance of crystal energy.

Since the crystal lattice energy equations considered in this Review [which are reduced to taking account precisely of the first term of eqn. (8)] have found certain currency in investigations of general chemistry and geochemistry it is important to have a clear idea regarding the accuracy of these expressions.

Though the last question seems a simple, elementary one, it is, unfortunately, not always possible to get a satisfactory answer to it, as direct experimental determinations, subject to comparison with theoretically computed energies, have been carried out only very rarely, and the accuracy of the values in the Born-Haber cycle has usually been unknown. Nevertheless, the Reviewer and Weselowsky²¹ had in 1933 verified equation (3) on then accessible thermochemical material and showed that the accuracy of equation (3) is of approximately the same order as that of eqn. (1). Later, the Reviewer⁵ had similarly verified the accuracy of the improved equation (4) which was already based on the quantum-mechanical concepts of the nature of repulsion forces.

In Fig. 2, the points on the co-ordinates $U/\Sigma n \eta_1 \eta_2$ and $1/(\tau_C + \tau_A)$ represent experimental data for metal halides, oxides, and chalcogenides; the curve corresponds to equation (4), the accuracy of which is of the order of 2—3%. It will be noted that in most cases the ionic radii themselves are known with the same accuracy.

Gradually, with the progress of experimental thermochemistry, the accuracy of various magnitudes in the Born-Haber cycle has increased, and so has the number of direct experimental determinations of U . Rossini and Wagman together with Evans, Levine, and Jaffe of the National Bureau of Standards, U.S.A., have carried out a critical selection²² of the more reliable thermochemical constants, though still not supplied, as a rule,

²⁰ S. Glasstone, "Textbook of Physical Chemistry", Macmillan, New York, 1946.

²¹ A. Kapustinskii and B. Veselovskii, *Z. phys. Chem.*, 1933, **22**, B, 261.

²² F. Rossini, D. Wagman, W. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", Circular of the National Bureau of Standards, No. 500, Washington, D.C., 1952.

with an accuracy limit. This work partially includes, besides results of previous works by Mayer, and Helmholtz,²³ more recent results of direct determinations of lattice energies by Saha, Srivastava, and Tandon.²⁴

As for the ionic radii values in equations (3) and (4) no essential changes and improvements have been made in them in the past period.

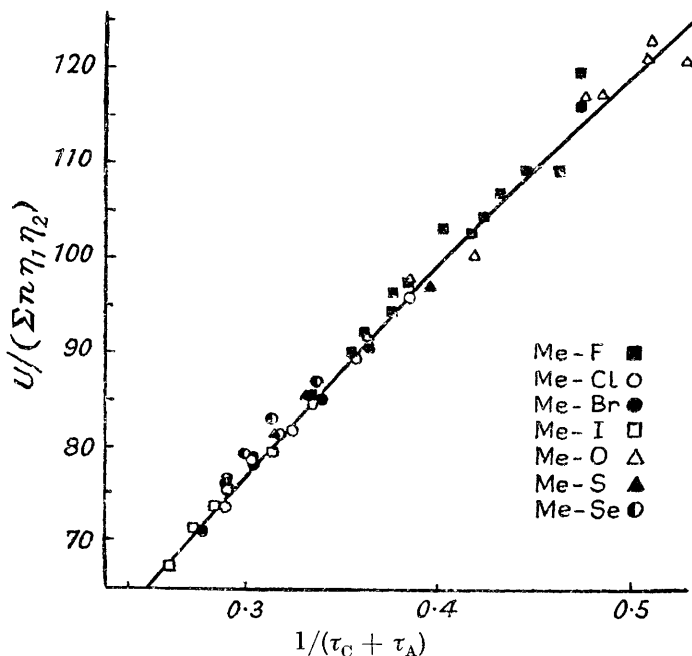


FIG. 2

Comparison of "experimental" lattice energies (points) with those (curve) calculated by means of equation 4.

The Reviewer and Yatsimirskii have this year used new thermochemical data for a reverification of equation (4). The work has been published in the *Zhurnal obshchei Khimii*. As an object for investigation we took halides of Groups I and II of the Mendeleev system. All of them, though they crystallise with different structures, are typical ionic compounds, and there are for all of them thermochemical data giving a clear idea of the accuracy of the measurements. At the same time, since the ions under consideration belong to the noble-gas type, the Goldschmidt ion radii used were not subject to doubt. If in equation (4) the accuracy of the value of the experimentally obtained coefficient for $\rho = 0.30$ is increased, one may reach the

²³ J. Mayer, *Z. Physik*, 1930, **61**, 798; L. Helmholtz and J. Mayer, *J. Chem. Phys.*, 1934, **2**, 245.

²⁴ M. Saha and A. Tandon, *Proc. Nat. Inst. Sci., India*, 1937, **3**, 288; B. Srivastava, *ibid.*, 1938, **4**, 365; A. Tandon, *Indian J. Phys.*, 1937, **11**, 99; *idem*, *Proc. Nat. Inst. Sci., India*, 1937, **7**, 102.

conclusion that this formula continues true with the same accuracy for the experimental thermochemical material.

When necessary this accuracy may even be increased by the introduction of the empirically found dependence of ρ on the sum of ionic radii :

$$\rho = 0.345 - 0.00435(\tau_C + \tau_A)^2 \quad . \quad . \quad . \quad (9)$$

When the crystal lattice energy (4) is substituted into our equation we obtain the following particular form of this expression :

$$U = 287.2 \Sigma n \frac{\eta_{11}^{1/2}}{\tau_C + \tau_A} \left[1 - \frac{0.345}{\tau_C + \tau_A} + 0.00453(\tau_C + \tau_A) \right] \quad . \quad . \quad (10)$$

In this case, a comparison of calculated results with experimental data shows that the errors are distributed statistically and that the quadratic mean deviation for salts of the MX type is 0.8 kcal. (*i.e.*, about 0.5%) and for salts of the MX₂ type 5.2 kcal. (*i.e.*, about 1%). This more accurate expression is unfortunately more cumbersome.

There is hardly any sense in any further improvement of the expression for lattice energy by means of ionic radii until the values of the ionic radii themselves are known with greater accuracy. Whether this will be possible is hard to say. Thorough investigation of ionic radii from all aspects is needed. An account of such a theoretical investigation by the Reviewer will be found in the first issue of the new *Zhurnal neorganicheskoi Khimii* which began to appear in the U.S.S.R. in 1956.

Electron affinity of oxygen, sulphur, and selenium

The more accurate thermochemical data already mentioned above have, in their turn, enabled us to obtain greater accuracy for some of the values which play an essential part in general chemistry. Thus, in combination with Pritchard's²⁵ critically selected data on the heats of formation of gaseous atoms of oxygen, sulphur, and selenium, one can find the values of electron affinity with precise limits of possible errors (Table 5).

TABLE 5. *Electron affinity (kcal. at 25°)*

$O_{\text{gas}} + 2e = O^{2-}_{\text{gas}}$	$\Delta H_{298} = 172 \pm 5$
$S_{\text{gas}} + 2e = S^{2-}_{\text{gas}}$	$\Delta H_{298} = 100 \pm 2$
$Se_{\text{gas}} + 2e = Se^{2-}_{\text{gas}}$	$\Delta H_{298} = 117 \pm 2$

²⁵ H. Pritchard, *Chem. Rev.*, 1933, **52**, 529.