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ON THE FORCES ACTING BETWEEN ATOMS AND IONS AND THE PHYSICAL PROPERTIES OF MATTER IN BULK

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CONTENTS

1. Introduction

We consider a system, consisting of two atoms or ions, situated at a given distance, R, from each other. Such a system is characterized by a certain potential energy $F(R)$, denoting the work required to decrease the interval between the two atoms or ions from ∞ to R. The question of this potential energy has been the subject of numerous theoretical investigations, commencing with Heitler's and London's well-known papers (Heitler and London 1927; London 1928 *a*, *b*) on the reciprocal action of two atoms of hydrogen. On the other hand, we possess no further empirical knowledge concerning this potential energy F. The present paper is an attempt to analyse, by the aid of accessible experimental data, the question of the dependence of energy on the interatomic distance for atoms and ions with closed shells.

Attempts have been made to find reasonable expressions for the forces acting between the ions in crystal lattices, by the aid of values experimentally determined for density, elastic constants and compressibility of crystals. However, these attempts have not been very successful, this being due to the fact that the above-mentioned properties are determined by the first and second derivatives of the potential function for a single value $R = R_0$ (WASASTJERNA 1935 *d*), whereas the general course of the function $F(R)$ remains unknown. A potential energy of the rather arbitrarily chosen form bR^{-n}, where b and n are two constants, has generally been added to the potential energy of the electrostatic force. Later investigations by LENNARD-JONES and TAYLOR (1925) and the present author (WASASTJERNA 1932 *d*) are definitely in favour of the conception that the potential energy of the repulsive force can be represented by an inverse power law only over a very small range of R, and outside this range the character of the function must be modified. A few years ago BORN and MAYER (1932) also, in an interesting paper on compressibility, replaced the inverse power by an exponential function. Its introduction was suggested by the exponential falling off of the wave function at large distances, and SLATER's and KIRKWOOD's calculations of the repulsive force between two helium atoms. The present author has shown (WASASTJERNA 1932 *d*) that an exponential falling off of the repulsive force can be deduced from experimental facts. If one desires empirically to attain a more thorough knowledge of the mutual potential energy of atoms and ions, the problem must, however, be attacked on a much broader front than hitherto has been the case.

2. THE GENERAL PROPERTIES OF THE POTENTIAL FUNCTIONS

We consider a lattice, consisting of an equal number of positive ions i and negative ions k. The potential energy of a gram-molecule may be denoted as $\Phi^{(ik)}(R)$. The electrostatic contribution to the potential energy of the lattice is indicated by the expression $-Ncz^2e^2R^{-1}$, where N is AVOGADRO's number, c is MADELUNG's constant, which depends on the structure of the lattice, z the ionic charge, expressed in elementary units, and e the charge of an electron. R is the distance between nearest neighbours in the lattice. At equilibrium $R = R_0$. As the product cz^2 often occurs later, we write $cz^2 = C$. The electrostatic contribution to the potential energy of the lattice is thus given by the expression $-NCe^2R^{-1}$. We define a function $\chi^{(ik)}(R)$ by subtracting from the potential energy $\Phi^{(ik)}(R)$ the electrostatic potential energy according to formula

$$\Phi^{(ik)}(R) = -\frac{NCe^2}{R} + \chi^{(ik)}(R). \tag{2·1}$$

We call the function $\chi^{(ik)}(R)$ the total potential energy of the repulsive force. We shall show that the forces corresponding to the potential energy $\chi^{(ik)}(R)$ act only between immediate neighbours in the lattice, or at least that such forces between other ions are negligible. As all these neighbours are assumed to be geometrically equivalent, our assertion implies that the potential energy $\chi^{(ik)}(R)$ may be written

$$\chi^{(ik)}(R) = Nq\phi^{(ik,\,q)}(R), \tag{2·2}$$

where ϕ denotes the mutual potential energy of the repulsive force between two neighbouring ions with opposite charges. The function ϕ may depend both on the ion pair (i, k) and on the co-ordination number $q =$ the number of the nearest neighbours. In previous papers (Wasastjerna 1935 *b*, *c*) the present author has shown that density, compressibility, elastic constants and the frequencies and amplitudes of the infra-red vibrations depend solely on the derivatives $\phi'(R_0)$ and $\phi''(R_0)$, provided that ϕ has the physical significance of mutual potential energy of two neighbours with opposite charges and that the repulsive forces act only between nearest neighbours in the lattice. This makes it possible to calculate the elastic constants, also the frequencies and amplitudes of the vibrations from density and compressibility, without knowledge of the analytical form of function $\phi(R)$. Calculated and observed values of these quantities show good agreement. Further, it was shown (Wasastjerna 1935 *d*) that if the sums appearing in the theory of lattices are extended over the whole of the lattice instead of over the nearest neighbours only, an attractive force between geometrically equivalent ions must be added to obtain agreement between calculated and observed data for the elastic constants and the characteristic frequencies of the infra-red vibrations. Such an attractive force can hardly be accepted (Lennard-Jones and Taylor 1925); we can therefore conclude that the repulsive forces act only between nearest neighbours in the lattice, or at least that such forces between other ions are negligible.

It seems to be evident that the attractive force, acting between geometrically equivalent ions, which has earlier (Born and Brody 1922; Born and Bormann 1920; Heckmann 1924) been deduced from density and elastic properties, is only apparent (Wasastjerna 1935 *d*). About one-third of this attraction appears in consequence of the sums appearing in the lattice theory, having been extended over the whole of the lattice, instead of over the nearest neighbours only. The remaining two-thirds of the assumed attraction appear as a consequence of the values for the coefficient of compressibility and the elastic constants, determined at room temperature, having been used in formulae, which, according to their derivation, are strictly valid at the absolute zero point only.

Further, the potential energy of two neighbouring ions is practically independent of q. This can be shown as follows: If ϕ is independent of q, equation (2·2) becomes

$$\chi^{(ik)}(R) = Nq\phi^{(ik)}(R). \tag{2·3}$$

Within a limited range of R, $\phi^{(ik)}(R)$ can be replaced by a function fairly arbitrarily chosen as to form, e.g. bR^{-n}, where b and n are two parameters. These parameters may be calculated for instance from the density and compressibility. The condition of equilibrium is

$$\frac{\partial \Phi^{(ik)}(R)}{\partial R} = \frac{NCe^2}{R^2} + Nq\frac{\partial \phi^{(ik)}(R)}{\partial R} = 0, \tag{2·4}$$

and leads to a range of equilibrium values of R_0 according to the values of C and the co-ordination number q, that is

$$R_0^{(ik)} = R_0^{(ik)}(C, q). \tag{2·5}$$

After b and n have been determined for a given instance (C_0, q_0), we find that, according to (2·5), the interatomic interval R_0 can be calculated for other cases $(C \neq C_0, q \neq q_0)$. ZACHARIASSEN (1931) has shown that formula (2·5), derived from the condition of equilibrium (2·4), correctly represents the empirically known dependence of the atomic interval on the lattice structure (C, q). The simple additivity expressed by formula (2·3) can thus be regarded as assured, at least when looked upon as an expression for a permissible approximation.

From (2·4) the value of the interatomic distance R_0 is given by

$$\frac{1}{e^2}(R_0^{(ik)})^2\left(\frac{\partial\phi^{(ik)}(R)}{\partial R}\right)_{R=R_0{}^{(ik)}} = -\frac{C}{q}. \tag{2·6}$$

Experience shows that the lattice interval $R_0^{(ik)}$ is equal to the sum of two constants $r_0^{(i)}(C, q)$ and $r_0^{(k)}(C, q)$, characteristic of the two ions i and q. These constants are usually called "ionic radii" for short. The ionic radii, however, depend on the lattice type, thus on C and q. This question has been investigated by GOLDSCHMIDT (1932), who found that the relative alterations of the interatomic distance $R_0^{(ik)}$ at the transition from one lattice type A to another one B, are practically identical. These two empirical laws may be summarized in the formula

$$R_0^{(ik)} = (\rho^{(i)} + \rho^{(k)})\, g(C, q), \tag{2·7}$$

where $\rho^{(i)}$ and $\rho^{(k)}$ are two constants, characteristic of the ions in question, and g a function, which depends only on C and q. Let

$$x^{(ik)} = \frac{R^{(ik)}}{\rho^{(i)} + \rho^{(k)}}, \tag{2·8}$$

then

$$x_0^{(ik)} = \frac{R_0^{(ik)}}{\rho^{(i)} + \rho^{(k)}} = g(C, q), \tag{2·9}$$

independent of (i, k). Also combining (2·6) and (2·7)

$$\frac{\rho^{(i)} + \rho^{(k)}}{e^2}\left(\frac{\partial\phi^{(ik)}}{\partial x}\right)_{x=x_0{}^{(ik)}} = -\frac{C}{qg^2(C, q)}, \tag{2·10}$$

independent of (i, k). But $x_0^{(ik)}$ is independent of (i, k) by (2·9), so for all (i, k) we can write

$$\frac{\rho^{(i)} + \rho^{(k)}}{e^2}\frac{\partial\phi^{(ik)}}{\partial x} = f_1'(x), \tag{2·11}$$

where $f_1'(x)$ is the same function for all (i, k). Thus

$$\frac{\rho^{(i)} + \rho^{(k)}}{e^2}\phi^{(ik)}(R) = f_1(x) + \lambda_1^{(ik)} = f_1\left(\frac{R}{\rho^{(i)} + \rho^{(k)}}\right) + \lambda_1^{(ik)} \tag{2·12}$$

and

$$\phi^{(ik)}(R) = \frac{e^2}{\rho^{(i)} + \rho^{(k)}}\{f_1(x) + \lambda_1^{(ik)}\} = \frac{e^2}{\rho^{(i)} + \rho^{(k)}}\left\{f_1\left(\frac{R}{\rho^{(i)} + \rho^{(k)}}\right) + \lambda_1^{(ik)}\right\}. \tag{2·13}$$

As the arguments which lead to formula (2·11) apply only to the range of x covered by the ionic lattices, an integration constant λ_1 must be introduced in (2·12) and (2·13). The significance of this constant will be explained later.

Function $\phi^{(ik)}(R)$ has the physical significance of the potential energy arising from the reciprocal action of the electronic systems of the two ions i and k. The general form of expression (2·13) is of decisive importance to the problems we investigate. The potential energy of the lattice can be written

$$\Phi^{(ik)} = \frac{Ne^2}{\rho^{(i)}+\rho^{(k)}}\left\{-\frac{C}{x}+q(f_1(x)+\lambda_1^{(ik)})\right\}. \tag{2·14}$$

The condition of equilibrium $\quad \dfrac{\partial}{\partial R}\Phi^{(ik)}(R) = 0$

leads to an interatomic distance $R_0 = (\rho^{(i)}+\rho^{(k)})\,x_0$, which is given by

$$f_1'(x_0) = -\frac{C}{qx_0^2}. \tag{2·15}$$

It has been shown empirically (Wasastjerna 1932*c*) that a simple relation exists between the atomic and ionic refractivities and the apparent radii for all atoms and ions of rare gas type. As the refractivity depends on the radial charge density (Kirkwood 1932; Wasastjerna 1932*a*)

$$D = 4\pi r^2 \Sigma\,\psi^2,$$

where r is the distance from the centre of the atom and where Schrödinger's characteristic functions have been denoted by ψ, also the repulsive force

$$\phi'(R_0) = \left(\frac{\partial\phi^{(ik)}(R)}{\partial R}\right)_{R=R_0} = \frac{e^2}{(\rho^{(i)}+\rho^{(k)})^2}f_1'(x_0)$$

must thus depend on the radial charge densities $D^{(i)}$ and $D^{(k)}$. Seeing that the parameters $\rho^{(i)}$ and $\rho^{(k)}$ contained in function $\phi'(R_0)$ are independent of each other and characterize the two ions i and k, the possibility that the function f_1' has the same general form for all atoms and ions of rare gas type is only conceivable if the electron distribution can be satisfactorily expressed by a general analytical function containing only one parameter dependent on the structure of the atom or ion under consideration, which parameter must have the character of a length

$$D^{(i)}(r) = D(\rho_0^{(i)}, r). \tag{2·16}$$

As the relation expressed in (2·16) can only appear in the outermost, analogously built, parts of the atoms and ions under consideration, we may draw the further conclusion that both the refractivity and the repulsive force are determined by the radial density in the outermost electronic shells of the atoms and ions.

Thomas (1927), Fermi (1928) and Hartree (1928) have developed methods of calculating the distribution of electrons in atoms with non-Coulomb central fields. Hartree's method, which has become generally known as the method of the self-consistent field, has proved applicable and has led to extremely valuable results. The electron distribution D in the outermost shell, as calculated according to Hartree, can be approximately expressed in a form compatible with condition (2·16) (Wasastjerna 1932 *b*):

$$D^{(i)}(r) = \frac{1}{\rho_0^{(i)}} B(\xi), \tag{2·17}$$

where $\xi = r/\rho_0^{(i)}$ and where $\rho_0^{(i)} = \left(\int rD^{(i)}\,dr \Big/ \int D^{(i)}\,dr\right)$.

Further, any theory of polarizability (Kirkwood 1932; Wasastjerna 1932 *a*, *c*) seems to give a refractivity I, which is nearly proportional to ρ_0^4. We may thus write

$$I = \gamma\rho_0^4, \tag{2·18}$$

where the proportionality factor γ has the character of a reciprocal length. The numerical value of γ can be determined by calculating for different ions the values ρ_0, which inserted into (2·17) give electron distribution curves, which should as near as possible agree with the corresponding curves calculated by Hartree, and by then comparing these values ρ_0 with the refractivities I for the same ions. Good agreement with Hartree's curves is obtained (Wasastjerna 1932 *b*) with a numerical value $\gamma = 10$, when I is expressed in cm.^{3} and ρ_0 in Ångström units. The same numerical value for γ has been theoretically derived (Wasastjerna 1932 *c*), but the approximations made were so crude that a direct comparison with Hartree's curves undoubtedly constitutes a more reliable basis for determining γ than the theoretical calculation. It should be added that the numerical value of γ is not actually very relevant, as only the relative values of ρ are of interest in equations (2·7)–(2·14), so long as the functions g, f_1', f_2' are considered as unknown. That the values ρ in (2·13) may be replaced by the values ρ_0 as calculated according to (2·18) can thus be checked by the condition (cf. equations (2·7)–(2·9))

$$\frac{R_0^{(ik)}}{\rho_0^{(i)} + \rho_0^{(k)}} = x_0, \tag{2·19}$$

where x_0 is a constant, which depends solely on C and q.

The arguments, which lead to formula (2·13), apply only to the range of x covered by the ionic lattices. At great interatomic distances the potential energy arising from the reciprocal action of the atoms becomes negative and corresponds to van der Waals' force. As is well known (Eisenschitz and London 1930) the potential energy of this attractive force has the form $\phi_2^{(00)} = -\beta R^{-6}$, where β is a constant. If we confine ourselves to the rare gases we may write (London 1931) $\beta \propto \alpha^2 E_j$, where α is the electric polarizability and E_j the ionization energy. As $\alpha \propto I$ and $I \propto \rho_0^4$ according to

(2·18) we may write $\beta \propto \rho_0^8 E_j$. Further, in Table III it is shown that $E_j \propto \rho_0^{-1}$. The potential energy $\phi_2^{(00)}$ can thus be represented by a function

$$\phi_2^{(00)}(R) = \frac{e^2 \rho_0}{2a_0^2} f_2(x), \tag{2·20}$$

where $x = \dfrac{R}{\rho_0^{(i)} + \rho_0^{(k)}} = \dfrac{R}{2\rho_0}$ and where a_0 is a general constant which has the character of a length. This constant is arbitrarily given the value $0{\cdot}529 \times 10^{-8}$ cm., which is equal to the radius of the first Bohr orbit for hydrogen. The quantities e and a_0 are introduced in order to give the expression the correct dimension. The factor 2 is written in the denominator for other formal reasons (cf. formulae (2·21)–(2·22)).

Summarizing results, we may say that, according to (2·13) and (2·20), the forces acting between two rare gas atoms can be expressed by a formula

$$\frac{\partial \phi_1^{(00)}}{\partial R} = \frac{1}{2\rho_0} \frac{\partial \phi_1}{\partial x} = \frac{e^2}{(2\rho_0)^2} f_1'(x), \quad x < x_1 \tag{2·21}$$

for small values of x and by a formula

$$\frac{\partial \phi_2^{(00)}}{\partial R} = \frac{1}{2\rho_0} \frac{\partial \phi_2}{\partial x} = \frac{e^2}{(2a_0)^2} f_2'(x), \quad x > x_2 \tag{2·22}$$

for large values of x. Between these two ranges of x values there is a gap, where the form of function ϕ' is unknown. Anticipating the results of the numerical calculations given in the following sections we may state that both f_1' and f_2' pass through several orders of magnitude, when $x = \dfrac{R_0}{2\rho_0}$ is increased in proportion 2/1. Functions ϕ_1' and ϕ_2' are thus very closely related to one another, both being chiefly dependent on x. By interpolation we can therefore undoubtedly fill up the gap with a function

$$\frac{\partial}{\partial R} \phi^{(00)}(R) = e^2 \left(\frac{f_1'(x)}{(2\rho_0)^2} + \frac{f_2'(x)}{(2a_0)^2} \right), \tag{2·23}$$

however artificial this function may be. As (2·21) must change continually into (2·23) at the limit $x = x_1$, and (2·23) must pass continually over into (2·22) at the limit $x = x_2$, we may conclude that function $f_1'(x)$ in (2·23) completely predominates at the limit $x = x_1$, where $f_2'(x)$ can be neglected as compared with $f_1'(x)$, while the importance of $f_1'(x)$ continually diminishes when x rises and gradually vanishes at the limit $x = x_2$, where formula (2·23) passes into (2·22). For small values of x, where $f_2'(x)$ can be neglected, the constant λ in $\phi_1^{(00)}$ (cf. (2·13)) is thus equal to the expression

$$\left(\frac{\rho_0}{a_0}\right)^2 f_2(x) = \left(\frac{\rho_0}{a_0}\right)^2 f_2(x_1)$$

in the integrated formula

$$\phi^{(00)}(R) = \frac{e^2}{2\rho_0}\left(f_1(x) + \left(\frac{\rho_0}{a_0}\right)^2 f_2(x)\right). \tag{2·24}$$

Consequently, the potential energy of the forces acting between two rare gas atoms can be expressed by (2·24) for all values of x.

For ions of rare gas type the constant β in equation $\phi_2^{(ik)} = -\beta R^{-6}$ may be regarded as unknown. Formula (2·24) is thus replaced by a formula

$$\phi^{(ik)}(R) = \frac{e^2}{\rho_0^{(i)} + \rho_0^{(k)}}\left(f_1(x) + u^{(ik)} f_2(x)\right), \tag{2·25}$$

where $u^{(ik)}$ depends on the ion pair (i, k). From (2·13) we know, however, that $f_2'(x)$ gradually vanishes for small values of x.

It should be stressed that only function $\phi(R)$ has physical significance, from which it follows that no extrapolation of an asymptotic analytical expression $f_2(x)$ into the range $x < x_1$ should be made. It is doubtful if it can be physically justified to take VAN DER WAALS' forces into account when calculating, for example, the compressibilities of ionic crystals.

Some important circumstances should be discussed before we pass on to numerical calculations. In deducing the ionic refractivities originally indicated by the present author (WASASTJERNA 1922) it was as a first approximation assumed that the refractivities of salts can be calculated additively, without reference to the disturbances resulting from the influence of the ions upon one another or upon the molecules of the solvent. W. L. BRAGG (1924), in an interesting paper on the effect of atomic arrangement on refractive index, and FAJANS, JOOS and various collaborators (1924) discuss the alteration in refractivity of an ion in the presence of other neighbouring ions, from which it is evident that the refractivity I cannot be regarded as an absolute ionic constant, but tends to a certain limit when the ions are dispersed. FAJANS and his collaborators have tried to estimate these disturbances. Certain objections may be raised against every method by which the numerical values of the ionic refractivities have hitherto been derived (FOWLER 1929). The most reliable values are probably the means of the values recently given by FAJANS (1934) as lower and upper limits. These mean values are collected in Table I.

TABLE I. ATOMIC AND IONIC REFRACTIVITIES (CM.^{3})

O^{--} = 7·1	F^- = 2·4	Ne = 1·0	Na^+ = 0·50	Mg^{++} = 0·30
S^{--} = 23·0	Cl^- = 9·0	A = 4·2	K^+ = 2·3	Ca^{++} = 1·5
Se^{--} = 29·0	Br^- = 12·6	Kr = 6·4	Rb^+ = 3·9	Sr^{++} = 2·7
Te^{--} = 40·9	I^- = 19·1	X = 10·4	Cs^+ = 6·6	Ba^{++} = 4·9

In accordance with formula (2·18) and Table I we arrive at the following values (Table II) for the quantities ρ_0 (ρ_0 is expressed in cm.):

TABLE II. VALUES OF $\rho_0 \times 10^8$

$O^{--} = 0{\cdot}91_8$
$S^{--} = 1{\cdot}23_1$
$Se^{--} = 1{\cdot}30_5$
$Te^{--} = 1{\cdot}42_2$
$F^{-} = 0{\cdot}70_0$
$Cl^{-} = 0{\cdot}97_4$
$Br^{-} = 1{\cdot}05_9$
$I^{-} = 1{\cdot}17_6$
$Ne = 0{\cdot}56_2$
$A = 0{\cdot}80_5$
$Kr = 0{\cdot}89_4$
$X = 1{\cdot}01_0$
$Na^{+} = 0{\cdot}47_3$
$K^{+} = 0{\cdot}69_3$
$Rb^{+} = 0{\cdot}79_0$
$Cs^{+} = 0{\cdot}90_1$
$Mg^{++} = 0{\cdot}41_6$
$Ca^{++} = 0{\cdot}62_2$
$Sr^{++} = 0{\cdot}72_1$
$Ba^{++} = 0{\cdot}83_7$

Table III shows that $E_j \propto \rho_0^{-1}$ for rare gases, a result which was anticipated in deducing formula (2·20). V denotes the ionization potential in volts, E_j the corresponding energy in ergs.

TABLE III

	V	$E_j \times 10^{11}$	$\rho_0 \times 10^8$	$E_j \rho_0 \times 10^{19}$
Ne	23·5	3·74	0·562	2·10
A	15·5	2·46	0·805	1·98
Kr	13·9	2·21	0·894	1·98
X	12·2	1·94	1·010	1·96

3. THE FORCES BETWEEN ATOMS

(*a*) *In homopolar lattices.* LONDON (1931) has shown that the VAN DER WAALS energy of an assembly of atoms or centres is obtained by adding together the mutual potential energies of every pair of atoms. According to (2·2) the function f_1, on the contrary, falls so rapidly with increasing x that only the nearest neighbours need be taken into consideration when calculating lattice energies. The potential energy Φ of the lattice is thus obtained by adding together the energies (2·24), the summation in regard to f_1 being extended only over the nearest neighbours, whereas in regard to f_2 it covers the lattice as a whole. The distance between the nearest neighbours is, as before, denoted by R, while the distance between a given atom and any other atom n in the lattice is denoted by R_n. The quotients x and x_n correspond to R and R_n.

The rare gases form face-centred cubic lattices with $q = 12$. As further the VAN DER WAALS energy decreases with the inverse sixth power of R_n, we write $f_2(x_n) = -\nu x_n^{-6}$, where ν is an unknown constant. The lattice energy is thus given by the formula

$$\Phi = \frac{N}{2}\left(q\frac{e^2}{2\rho_0}f_1(x) + \sum_n \frac{e^2\rho_0}{2a_0^2}f_2(x_n)\right) = \frac{N}{2}\left(q\frac{e^2}{2\rho_0}f_1(x) - p\frac{e^2\rho_0}{2a_0^2}\nu x^{-6}\right), \tag{3·1}$$

where the value of the quantity $p = \sum_n \left(\frac{R}{R_n}\right)^6 = 14{\cdot}45$ arising through the summation is obtained from the tables calculated by JONES and INGHAM (1925). The condition of equilibrium $\Phi'(x_0) = 0$ leads to equations

$$f_1'(x_0) = -\frac{6p\nu}{q}\frac{\rho_0^2}{a_0^2 x_0^7}, \tag{3·2}$$

$$\ln(-f_1'(x_0)) = \text{const.} + \ln\left(\frac{\rho_0^2}{a_0^2 x_0^7}\right). \tag{3·3}$$

From Table IV it appears that $\ln(-f_1'(x))$ is a linear function of x. Then it follows that $f_1'(x)$ can be represented by an exponential function $\exp(a-bx)$, where $b=5{\cdot}7$, and further, according to (3·2), that

$$f_1(x_0) = -\frac{1}{b} f_1'(x_0) = \frac{6pv}{qb}\,\frac{\rho_0^2}{a_0^2 x_0^7}. \tag{3·4}$$

TABLE IV

	$R_0 \times 10^8$	$\rho_0 \times 10^8$	x_0	$\ln(\rho_0^2/a_0^2 x_0^7)$	$8{\cdot}45-5{\cdot}7x$
Ne	3·04	0·56	2·71	−6·9	−7·0
A	3·84	0·80	2·40	−5·3	−5·2
Kr	4·20	0·89	2·36	−5·0	−5·0
X	4·60	1·01	2·28	−4·5	−4·5

If this value for $f_1(x_0)$ be entered in equation (3·1), we arrive at

$$-\Phi = \frac{Ne^2 pv\rho_0}{4a_0^2 x_0^6}\left(1-\frac{6}{bx_0}\right). \tag{3·5}$$

According to F. BORN (1922) the heat of sublimation $(-\Phi)$ for argon is 1835 cal. or $7{\cdot}68\times10^{10}$ ergs. If, further, the values $N=6{\cdot}06\times10^{23}$, $e=4{\cdot}77\times10^{-10}$, $a_0=0{\cdot}529\times10^{-8}$, $\rho_0=0{\cdot}80\times10^{-8}$, $x_0=2{\cdot}40$, $p=14{\cdot}45$ and $b=5{\cdot}7$ be entered in equation (3·5), we obtain $v=0{\cdot}18$. Equation (3·4) and Table IV give

$$\ln f_1(x) = \ln 6pv - \ln qb + 8{\cdot}45 - 5{\cdot}7x = 7{\cdot}0 - 5{\cdot}7x, \tag{3·6}$$

$$\left\{\begin{aligned} f_1(x) &= 1100\exp(-5{\cdot}7x), &(3{\cdot}7)\\ f_2(x) &= -0{\cdot}18x^{-6}. &(3{\cdot}8)\end{aligned}\right.$$

The simple calculations carried through in this section show how the general considerations in § 2 enable us to deduce, from the fragmentary data concerning the potential functions of the forces between individual atoms, general functions f_1 and f_2, common to all rare gas atoms, which make it possible to determine the course of the potential function $\phi(R)$ with a fair degree of accuracy. Within the interval $2{\cdot}3<x<2{\cdot}7$ the potential energy of the forces between two rare gas atoms can be written (cf. (2·24))

$$\phi(R) = \frac{e^2}{2\rho_0}\left\{1100\exp(-5{\cdot}7x) - 0{\cdot}18\left(\frac{\rho_0}{a_0}\right)^2 x^{-6}\right\}. \tag{3·9}$$

As the first term for $x>2{\cdot}7$ falls extremely rapidly towards zero, the equation (3·9) is probably applicable to all values $x>2{\cdot}3$. On the contrary, whether an extrapolation to values $x<2{\cdot}3$ is permissible or not must be carefully examined.

(*b*) *In gases.* According to the kinetic theory of gases (JEANS 1925) formula

$$\phi(\overline{R}_0) = kT \tag{3·10}$$

holds good. $\overline{R}_0$ is the mean distance at the impact of the atoms, k is BOLTZMANN's constant and T the absolute temperature. From formulae (2·24) and (3·10) it follows that

$$f_1(x_0) = \frac{2\rho_0 kT}{e^2} - \left(\frac{\rho_0}{a_0}\right)^2 f_2(x_0), \tag{3·11}$$

where $x_0 = (\overline{R}_0/\rho_0)$. In this connexion the question concerning the interatomic distance $\overline{R}_0$ presented by the kinetic theory of gases requires further discussion. When, like SUTHERLAND (1893) and CHAPMAN (1911, 1916, 1917), we take into account the deviations from rectilinear trajectories, the atoms are regarded as incompressible spheres, and the whole apparent displacement of the interatomic distance at the moment of impact, occurring in connexion with a variation of temperature, is explained as produced by such deviations. Since, however, $\overline{R}_0$ is in reality a function of temperature, SUTHERLAND's correction does not give us a correct interatomic distance, and the atomic radius calculated according to SUTHERLAND has thus hardly any simple physical significance. In view of this it is more correct, in calculating $\overline{R}_0$, to employ the uncorrected value of $\overline{R}_0$ according to the kinetic theory or the corresponding uncorrected value, calculated by the help of measurements of viscosity. These points were stressed by the writer (WASASTJERNA 1923) already in 1923; the $\overline{R}_0$ values, given in Table V, have since been used in several papers (WASASTJERNA 1923, 1932*c*, *d*). These values are, however, very uncertain, which makes any further calculations unreliable. It must be clearly realized that the calculations based on these figures do not prove the truth of any theory, but rather only indicate that theory and facts, as far as we can judge at present, are not conflicting.

TABLE V

	$R_0 \times 10^8$	$\rho_0 \times 10^8$	x_0
Ne	2·48	0·56	2·21
A	3·14	0·80	1·96
Kr	3·52	0·89	1·98
X	4·00	1·01	1·98

As the calculated values of x_0 for A, Kr and X are almost identical we deal with these three gases as a single group and thus take into consideration the two points

$$x_0 = 2·21, \qquad \rho_0 = 0·56 \times 10^{-8},$$

$$x_0 = 1·97, \qquad \rho_0 = 0·90 \times 10^{-8}.$$

We enter the values $k = 1·371 \times 10^{-16}$ and $T = 273$ in formula (3·11) and assume as an experiment that $f_2(x)$ can be represented by expression (3·8). From Table VI it appears that the values for $f_1(x)$ calculated in this manner according to (3·11) agree with formula (3·7), and that the expression (3·9) thus seems applicable also within the range $2·0 < x < 2·3$.

TABLE VI

x_0	$\dfrac{2\rho_0 kT}{e^2}$	$-\left(\dfrac{\rho_0}{a_0}\right)^2 f_2(x)$	$\ln f_1(x)$ from (3·11)	$\ln f_1(x)$ from (3·7)
2·21	0·0018	0·0017	−5·65	−5·6
1·97	0·0030	0·0089	−4·4	−4·2

The interval under consideration, $2{\cdot}0 < x < 2{\cdot}7$, is actually very large, as may be seen from the fact that $\ln f_1(x)$ within this interval falls from $-4{\cdot}2$ to $-8{\cdot}4$. Fig. 1 illustrates the course of the functions

$$\ln\left|\frac{2\rho_0}{e^2}\frac{\partial\phi}{\partial x}\right| = \ln\left|f_1'(x) + \left(\frac{\rho_0}{a_0}\right)^2 f_2'(x)\right|. \qquad (3{\cdot}12)$$

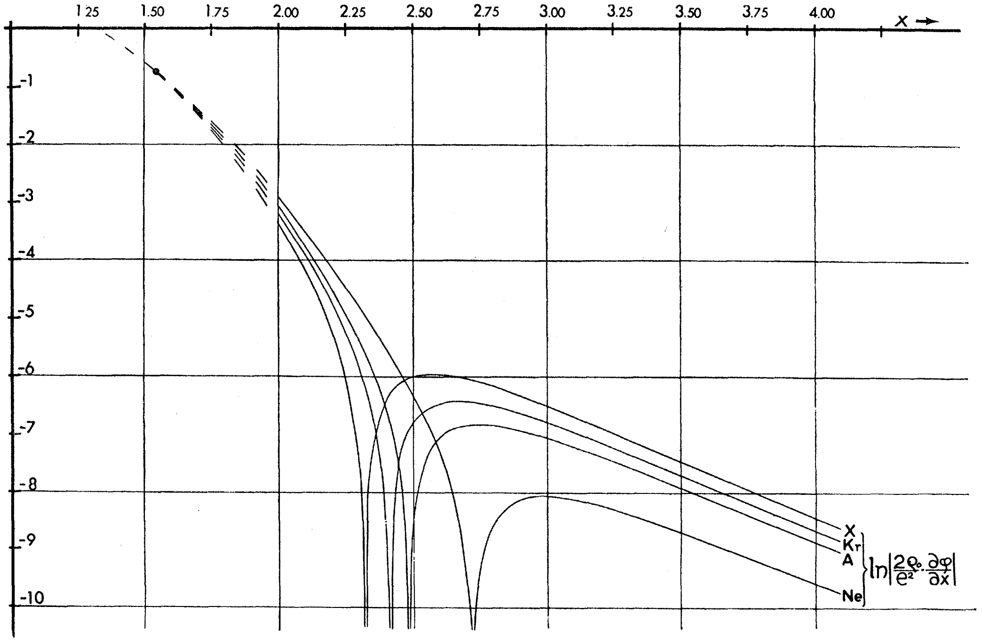

FIG. 1

The left branches of the curves correspond to repulsive, and the right hand ones to attractive forces. For small values of x the curves approach each other asymptotically, as f_2' gradually vanishes as compared with f_1'. The curves are parallel for large values of x, as the VAN DER WAALS forces differ from each other only in respect of multiplicative constants.

4. THE FORCES BETWEEN IONS

(*a*) *In bivalent lattices.* The salts formed by the positive ions Mg, Ca, Sr, Ba and the corresponding negative ions O, S, Se, Te crystallize in face-centred cubic lattices ($q = 6$) with the exception of MgTe, which forms a lattice with $q = 4$. The experimentally determined interatomic distance R_0 ($q = 4$) $= 2{\cdot}76$ for MgTe is therefore, according to Goldschmidt (1932), divided by 0·94, whereby a calculated interatomic distance R_0 $(q=6)=2{\cdot}94$ is obtained in an imagined, face-centred lattice comparable with the other salts. From Table VII it will be seen that x_0 takes practically speaking the same value, $1{\cdot}56 \pm 0{\cdot}03$, for all salts in question.

Table VII

Salt	$R_0 \times 10^8$	$(\rho_0^{(i)}+\rho_0^{(k)}) \times 10^8$	x_0 $(T=291^\circ)$
MgO	2·10	1·33	1·58
MgS	2·60	1·65	1·58
MgSe	2·73	1·72	1·59
(MgTe)	(2·94)	1·84	(1·60)
CaO	2·40	1·54	1·56
CaS	2·84	1·85	1·54
CaSe	2·96	1·93	1·53
CaTe	3·17	2·04	1·55
SrO	2·58	1·64	1·57
SrS	3·01	1·95	1·54
SrSe	3·12	2·03	1·54
SrTe	3·33	2·14	1·56
BaO	2·97	1·76	1·57
BaS	3·19	2·07	1·54
BaSe	3·30	2·14	1·54
BaTe	3·50	2·26	1·55

For bivalent ions the values of ρ_0, given in Table II, thus meet condition (2·19). From this it follows that the derivative of the second term in formula (2·25), which should disappear for small values of x, can be neglected for $x=1{\cdot}56$, and that formula (2·14) is applicable for bivalent lattices. However, the condition of equilibrium $\Phi'(R_0)=0$ is strictly valid only at the absolute zero point. Taking into consideration the approximately known mean expansion of the salts, we lower the value 1·56 found at room temperature to $x_0=1{\cdot}54$ at the absolute zero point. The condition of equilibrium and (2·14) give us for $x_0=1{\cdot}54$

$$\left.\begin{aligned} f_1'(x_0) &= -\frac{C}{qx_0^2} = -\frac{cz^2}{qx_0^2} = -\frac{1{\cdot}75\times 2^2}{6\times(1{\cdot}54)^2} = -0{\cdot}49,\\ \ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\,\frac{\partial\phi}{\partial x}\right| &= \ln(-f_1'(x_0)) = -0{\cdot}7. \end{aligned}\right\} \tag{4·1}$$

On the other hand, for the same point $x_0=1{\cdot}54$, we calculate according to (3·6)

$$\ln(-f_1'(x_0)) = \ln 5{\cdot}7 + 7{\cdot}0 - 5{\cdot}7x_0 = -0{\cdot}0_4.$$

The expressions (3·7) and (3·8) previously found for f_1 and f_2 are thus no more applicable for $x<2{\cdot}0$. It is, however, meaningless to construct analytical expressions for the functions f_1 and f_2 for the interval $1{\cdot}5<x<2{\cdot}0$ as the necessary values for the functions

$$\ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\,\frac{\partial\phi}{\partial x}\right|$$

are easily obtained by means of graphic interpolation.

(*b*) *In monovalent lattices.* The salts formed by the positive ions Na, K, Rb, Cs and the corresponding negative ions F, Cl, Br, I crystallize in face-centred cubic lattices, with the exception of CsCl, CsBr and CsI which crystallize in space-centred lattices. Table VIII gives the interatomic distances R_0 at the absolute zero point (estimated according to data for densities and coefficients of expansion, given in LANDOLT-BÖRNSTEIN's Tables), the values of $(\rho_0^{(i)}+\rho_0^{(k)})$, according to Table II, and finally the quotients x_0 at the absolute zero point. Seeing that for univalent lattices x_0 is calculated by the aid of very certain data, the systematic scattering of the values of x_0 is undoubtedly real and corresponds to the scattering of the curves

$$\ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\frac{\partial\phi}{\partial x}\right|$$

in the neighbourhood of $x = 1\cdot 9$ (cf. fig. 2). This interpretation is definitely supported by the results of the calculations carried through in § 5. Yet, within the limits of experimental errors, chlorides, bromides and iodides of the same metal obtain the same value x_0.

TABLE VIII

Salt	$R_0 \times 10^8$	$(\rho_0^{(i)}+\rho_0^{(k)}) \times 10^8$	x_0
NaF	2·298	1·173	1·959
NaCl	2·789	1·447	1·927
NaBr	2·950	1·532	1·926
NaI	3·190	1·649	1·935
KF	2·651	1·393	1·903
KCl	3·113	1·667	1·867
KBr	3·261	1·752	1·861
KI	3·486	1·869	1·865
RbF	2·794	1·490	1·875
RbCl	3·258	1·764	1·847
RbBr	3·408	1·849	1·843
RbI	3·628	1·966	1·845
CsF	2·975	1·601	1·858
CsCl	3·524	1·875	1·879
CsBr	3·674	1·960	1·874
CsI	3·901	2·077	1·878

Formula (2·13) thus represents a fairly crude approximation for univalent lattices, and in more exact calculations it must be replaced by formula (2·25). The potential energy Φ of the lattice is obtained by the electrostatic energies and the functions $u_n f_2(x_n)$ being added over the lattice as a whole, but $f_1(x_n)$ only over the nearest neighbours (cf. § 3*a*). We write

$$s = \frac{\sum_n u_n f_2(x_n)}{q f_2(x)}, \quad \phi_s(x) = \frac{e^2}{\rho_0^{(i)}+\rho_0^{(k)}}\left(f_1(x)+s f_2(x)\right).$$

The potential energy of the lattice receives the form

$$\Phi = \frac{Ne^2}{\rho_0^{(i)}+\rho_0^{(k)}}\left\{-\frac{C}{x}+q f_1(x)+\sum_n u_n f_2(x_n)\right\} = N\left\{\frac{-Ce^2}{(\rho_0^{(i)}+\rho_0^{(k)})\,x}+q\phi_s(x)\right\}. \qquad (4\cdot 2)$$

However, within the range under consideration the functions $f_1(x)$ and $f_2(x)$ are unknown, as is also the case with the constants s. On the other hand, the functions

$$\ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\,\frac{\partial\phi_s}{\partial x}\right| = \ln|f_1'(x)+sf_2'(x)|$$

can be calculated according to formulae (3·7)–(3·8) *for given values of* s and $x \geqslant 2{\cdot}0$. As further, according to § 4*a*, all these functions independent of s, meet asymptotically in the point

$$x = 1{\cdot}54,\quad \ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\,\frac{\partial\phi}{\partial x}\right| = -0{\cdot}7$$

a graphic interpolation is fairly plain. Fig. 2 illustrates the curves

$$\ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\,\frac{\partial\phi_s}{\partial x}\right|,$$

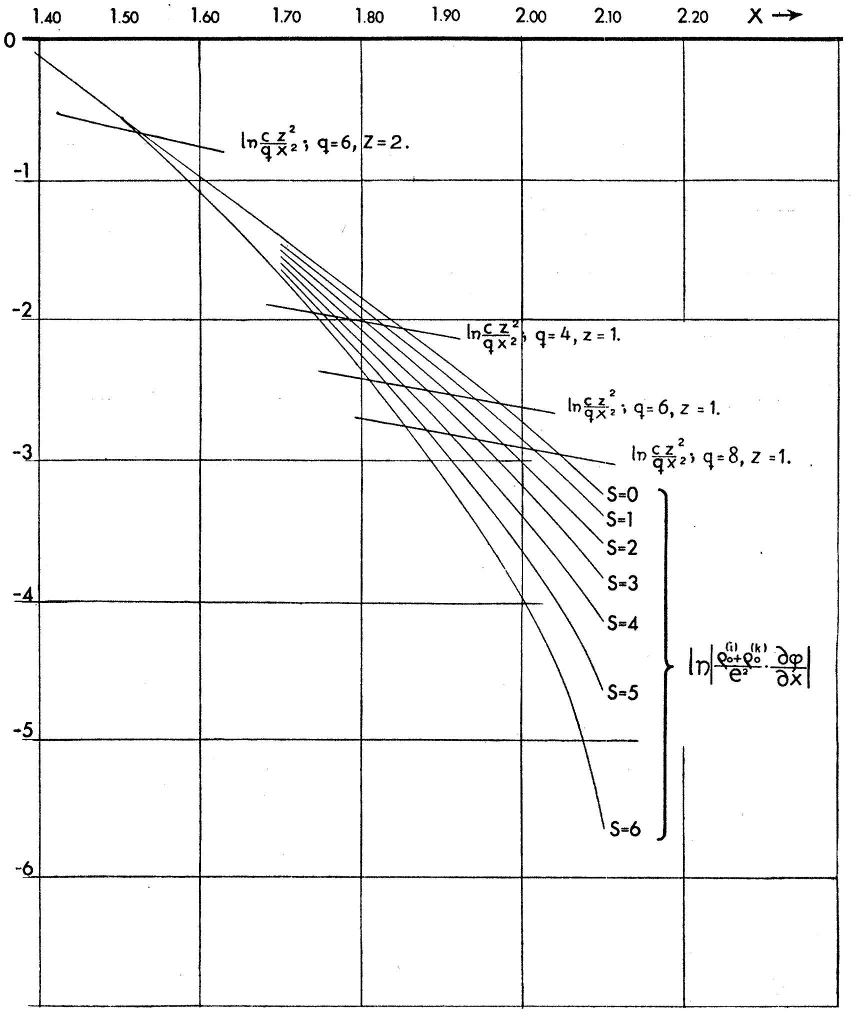

FIG. 2

corresponding to the values $s = 0, 1, 2, \ldots, 6$. The curves are drawn so that they gradually join with the curves calculated according to (3·7)–(3·8) for $x > 2$. The condition of equilibrium is

$$\Phi'(x_0) = N\left\{\frac{Ce^2}{(\rho_0^{(i)}+\rho_0^{(k)})\,x_0^2} + q\phi_s'(x_0)\right\} = 0, \tag{4·3}$$

whence it follows that

$$\ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\frac{\partial\phi_s}{\partial x}\right|_{x=x_0} = \ln\frac{C}{qx_0^2}. \tag{4·4}$$

According to (4·4) the different values of $x_0(s, q)$ thus correspond to the points at which the curves $\ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\frac{\partial\phi_s}{\partial x}\right|$ cut the curves $\ln\frac{C}{qx^2}$. Within the range under consideration the last-mentioned curves appear as straight lines. By drawing the curves on a large scale, the values of $x_0(s, q)$, corresponding to different values of (s, q), will be graphically obtained and from the slope of the curves we arrive at the values for the quantity

$$\mu(x_0) = \left(\frac{\partial}{\partial x}\ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\frac{\partial\phi_s}{\partial x}\right|\right)_{x=x_0} = \frac{\phi''(x_0)}{\phi'(x_0)}. \tag{4·5}$$

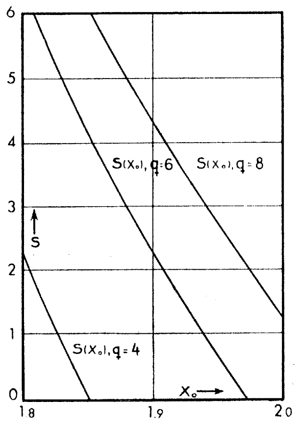

FIG. 3

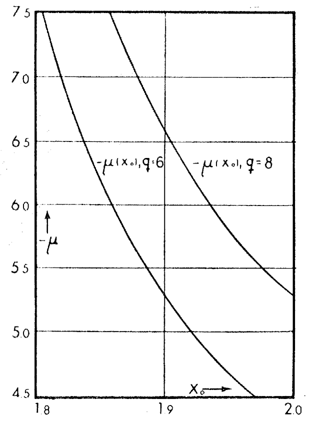

FIG. 4

Figs. 3 and 4 illustrate the connexion thus found between the quantities s, q, x_0, $\mu(x_0)$. The curve $\mu(x_0)$, $q = 4$, which falls outside the diagram is of no interest, as corresponding lattices do not exist. The curves obtained by graphic interpolation are naturally to some extent uncertain. Particular exactitude is thus not claimed for the numerical results, based on these curves.

TABLE IX

Salt	x_0	q	s	$-\mu(x_0)$
NaF	1·959	6	0·4	4·6
NaCl, NaBr, NaI	1·929	6	1·3	4·9
KF	1·903	6	2·2	5·2
KCl, KBr, KI	1·864	6	3·6	5·9
RbF	1·875	6	3·2	5·7
RbCl, RbBr, RbI	1·845	6	4·4	6·3
CsF	1·858	6	3·8	6·0
CsCl, CsBr, CsI	1·877	8	5·1	7·1

5. Some theoretical calculations of the physical properties of certain crystals

(*a*) *The compressibilities of crystals.* According to Hildebrand (1931) the energy E of a crystal can be represented as the sum of a pure function of volume and a pure function of temperature. Hence

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{1}{3V} R_0 \Phi'(R_0), \tag{5·1}$$

$$\left(\frac{\partial^2 E}{\partial V^2}\right)_T = \frac{1}{9V^2}\left(R_0^2 \Phi''(R_0) - 2R_0 \Phi'(R_0)\right), \tag{5·2}$$

where V is the volume of a gram-molecule. The thermodynamic equation

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \tag{5·3}$$

gives for $P=0$

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V = -T\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{T}{\kappa V}\left(\frac{\partial V}{\partial T}\right)_P, \tag{5·4}$$

$$\left(\frac{\partial^2 E}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right)_T + T\frac{\partial^2 P}{(\partial T)_V\,(\partial V)_T} = \frac{1}{\kappa V}\left[1 + \frac{T}{\kappa}\left(\frac{\partial \kappa}{\partial T}\right)_V\right], \tag{5·5}$$

where κ is the coefficient of compressibility, which as previously shown by the writer (Wasastjerna 1935 *a*) at least in the first approximation is only indirectly dependent on temperature through the expansion caused by temperature. In equation (5·5) we can thus write $\left(\frac{\partial \kappa}{\partial T}\right)_V = 0$. Formulae (5·1), (5·2), (5·4), (5·5) and (4·2) give us the equations

$$3\frac{T}{\kappa}\left(\frac{\partial V}{\partial T}\right)_P = R_0 \Phi'(R_0) = x_0 \Phi'(x_0) = N\left[\frac{Ce^2}{(\rho_0^{(i)}+\rho_0^{(k)})\,x_0} + q x_0 \phi_s'(x_0)\right], \tag{5·6}$$

$$\frac{9V}{\kappa} + 6\frac{T}{\kappa}\left(\frac{\partial V}{\partial T}\right)_P = R_0^2 \Phi''(R_0) = x_0^2 \Phi''(x_0) = N\left[\frac{-2Ce^2}{(\rho_0^{(i)}+\rho_0^{(k)})\,x_0} + q x_0^2 \phi_s''(x_0)\right]. \tag{5·7}$$

From these equations κ is given by

$$\kappa = -\frac{9V(\rho_0^{(i)}+\rho_0^{(k)})\,x_0}{NCe^2\left(x_0\dfrac{\phi_s''(x_0)}{\phi_s'(x_0)}+2\right)}\left[1-\left(\frac{x_0\dfrac{\phi_s''(x_0)}{\phi_s'(x_0)}-2}{3}\right)\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right], \tag{5·8}$$

where $V = 2NR_0^3$ for a cubic face-centred lattice and $V = \frac{8N}{3\sqrt{3}}R_0^3$ for a space-centred lattice. For practical reasons we introduce the symbol

$$\vartheta(x_0) = -\frac{R_0 \phi_s''(R_0)}{\phi_s'(R_0)} - 2 = -\frac{x_0 \phi_s''(x_0)}{\phi_s'(x_0)} - 2 = -x_0 \mu(x_0) - 2, \tag{5·9}$$

as expression (5·9) very often occurs in this section. We arrive at the following formulae for the two types of lattices A (NaCl) and B (CsCl):

$$(\kappa_T)_A = \frac{18R_0^4}{Ce^2\vartheta}\left(1+\frac{\vartheta+4}{3}\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right), \tag{5·10}$$

$$(\kappa_T)_B = \frac{(24/\sqrt{3})\,R_0^4}{Ce^2\vartheta}\left(1+\frac{\vartheta+4}{3}\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right), \tag{5·11}$$

where R_0, ϑ and $\frac{1}{V}\frac{\partial V}{\partial T}$ refer to temperature T. As $\frac{\phi_s''(x_0)}{\phi_s'(x_0)}$ is practically independent of temperature, we obtain

$$\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial T}\right)_P = \left(1-\frac{2}{3\vartheta}+\frac{\vartheta+4}{3+(\vartheta+4)\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P}\right)\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{5·12}$$

In order to calculate $\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial P}\right)_T$ we make use of the identity

$$\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial T}\right)_V = \frac{1}{\kappa}\left[\left(\frac{\partial \kappa}{\partial T}\right)_P + \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial \kappa}{\partial P}\right)_T\right] = \frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial T}\right)_P + \frac{1}{\kappa}\left[\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial P}\right)_T\right]\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]. \tag{5·13}$$

As already mentioned $\left(\frac{\partial \kappa}{\partial T}\right)_V = 0$. Consequently

$$\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial P}\right)_T = -\kappa\left(1-\frac{2}{3\vartheta}+\frac{\vartheta+4}{3+(\vartheta+4)\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P}\right). \tag{5·14}$$

The agreement between observed and calculated values (Table X) is very satisfactory. The experimental investigations concerning $\frac{\partial \kappa}{\partial T}$ and $\frac{\partial \kappa}{\partial P}$ are rather difficult, and the observed values may therefore be impaired by considerable errors.

(*b*) *The elastic constants.* We confine ourselves to cubic face-centred lattices. The number of independent elastic constants in crystals of this type is reduced to two. These moduli are usually denoted by c_{11} and c_{12} (cf. e.g. *Handbuch der Physik*, 2nd ed., **24**, 631 (1933)). For instance the compressibility is given in terms of c_{11} and c_{12} by

$$\frac{1}{\kappa} = \tfrac{1}{3}(c_{11}+2c_{12}). \tag{5·15}$$

At the absolute zero point c_{11} and c_{12} are given by (Wasastjerna 1935*e*)

$$c_{11} = \frac{S_0e^2}{6R_0^4}\left[\vartheta+3-3\frac{S_1}{S_0}\right], \tag{5·16}$$

$$c_{12} = \frac{S_0e^2}{4R_0^4}\left[\frac{S_1}{S_0}-1\right], \tag{5·17}$$

where S_0 and S_1 are two constants, the values of which are $S_0 = 1{\cdot}747$ and $S_1 = 3{\cdot}226$. From (5·15)–(5·17) we obtain

$$c_{11} = \frac{1}{\kappa}\left[3 - \frac{9}{\vartheta}\left(\frac{S_1}{S_0} - 1\right)\right], \tag{5·18}$$

$$c_{12} = \frac{1}{2\kappa}\left[\frac{9}{\vartheta}\left(\frac{S_1}{S_0} - 1\right)\right]. \tag{5·19}$$

TABLE X

Salt	$(R_0 \times 10^8)_T$*	$\vartheta = -x_0\mu - 2$ (Table IX)	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \times 10^5$†	$\kappa \times 10^{12}$ barye^{-1} Theor. (5·10), (5·11)	$\kappa \times 10^{12}$ barye^{-1} Exp.‡	$\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial T}\right)_P \times 10^4$ Theor. (5·12)	$\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial T}\right)_P \times 10^4$ Exp.§,‡	$-\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial P}\right)_T \times 10^{11}$ Theor. (5·14)	$-\frac{1}{\kappa}\left(\frac{\partial \kappa}{\partial P}\right)_T \times 10^{11}$ Exp.‡
NaF	2·312	7·01	9·8	2·0	2·1	4	.	1	2
NaCl	2·812	7·45	10·0	4·2	4·3	4	7	2	2
NaBr	2·978	7·45	11·9	5·4	5·1	5	8	2	3
NaI	3·225	7·45	13·5	7·6	7·1	6	.	3	4
KF	2·669	7·90	10·0	3·2	3·3	4	1(?)	1	2
KCl	3·137	9·00	10·1	5·5	5·6	5	5	3	3
KBr	3·290	9·00	11·0	6·7	6·7	5	6	3	3
KI	3·522	9·00	12·5	9·0	8·5	6	6	4	4
RbF	2·815	8·69	9·5	3·7	4·1	4	.	2	.
RbCl	3·284	9·62	9·85	6·2	6·6	5	8	3	.
RbBr	3·437	9·62	10·4	7·5	7·9	5	.	4	3
RbI	3·664	9·62	11·9	9·7	9·6	6	.	5	4
CsF	3·005	9·15	9·5	4·5	4·2	5	10(?)	2	3
CsCl	3·562	11·33	13·65	5·9	5·9	7	9	3	3
CsBr	3·714	11·33	13·9	7·0	7·1	7	9	4	4
CsI	3·946	11·33	14·6	9·0	8·6	7	7	5	5

* BORN and MAYER 1932.
‡ BRIDGMAN 1932.
† HENGLEIN 1925, BAXTER and HAWKINS 1916.
§ "International Critical Tables."

The theory is, however, strictly valid only at the absolute zero point and formulae (5·18) and (5·19) do not correctly account for the temperature variation of the elastic moduli, as studied by DURAND (1936) and ROSE (1936). In Table XI the theoretical values are calculated from (5·18), (5·19) and (5·10); the experimental values are observed by BRIDGMAN (1929).

TABLE XI

Salt	$c_{11} \times 10^{-11}$ dyn. cm.$^{-2}$ Theoretical	$c_{11} \times 10^{-11}$ dyn. cm.$^{-2}$ Experimental	$c_{12} \times 10^{-11}$ dyn. cm.$^{-2}$ Theoretical	$c_{12} \times 10^{-11}$ dyn. cm.$^{-2}$ Experimental
NaCl	4·7	4·9	1·2	1·3
NaBr	3·7	3·3	0·9	1·3
KCl	3·9	3·7	0·8	0·8
KBr	3·2	3·3	0·6	0·6
KI	2·4	2·7	0·5	0·4

For NaCl VOIGT (1910) has obtained the experimental value $c_{11} = 4{\cdot}7 \times 10^{11}$.

(*c*) *The proper frequencies of the vibrations in crystals.* The proper frequency ν_0 can be calculated according to the formula (Wasastjerna 1935 *c*, *e*)

$$\nu_0^2 = \frac{S_0 e^2}{12\pi^2 R_0^3}\left(\vartheta - \frac{2\pi}{S_0}\right)\left(\frac{1}{m_1}+\frac{1}{m_2}\right), \tag{5·20}$$

where m_1 and m_2 are the masses of the two ions. Barnes and Czerny (1931) have shown that in infra-red the position of the absorption maximum strictly coincides with the proper frequency, provided that the crystal layers are sufficiently thin. Table XII contains the proper wave lengths $\lambda_0 = c/\nu_0$, calculated according to (5·20), as well as the wave lengths for the absorption maxima for a number of alkali halides of the rock salt type, observed by Barnes (1932).

Table XII

Salt	$\lambda_0 \times 10^4$ (calc.)	$\lambda_0 \times 10^4$ (obs.)	Salt	$\lambda_0 \times 10^4$ (calc.)	$\lambda_0 \times 10^4$ (obs.)
NaF	40·4	40·6	KBr	86·5	88·3
NaCl	58·9	61·0	KI	102·0	102·0
NaBr	72·5	74·7	RbCl	79·7	84·8
NaI	85·1	85·5	RbBr	109·4	114·0
KCl	67·9	70·7	RbI	133·7	129·5

(*d*) *The amplitudes of the thermal vibrations.* If $\overline{u_n^2}$ is the mean of the squares of the total displacements of an atom, we have for a crystal of the rock salt type

$$\overline{u_n^2} = 3\overline{u_{nx}^2}, \tag{5·21}$$

where $\overline{u_{nx}^2}$ is the mean of the squares of the displacements, in any arbitrary direction x, of ions of the type n from their mean positions. For values of the temperature sufficiently high we may write (Waller 1925; Waller and James 1927)

$$\overline{u_{nx}^2} = \alpha_n + \beta_n T. \tag{5·22}$$

If zero-point energy having Planck's value be assumed, α_n is equal to zero. The following mean value

$$\frac{\overline{u^2}}{3T} = \overline{\beta} = \frac{\Sigma m_n \beta_n}{\Sigma m_n},$$

where m_n is the mass of an atom of the type n, can be calculated from the potential of repulsion. The following formula is approximately true (Wasastjerna 1935 *e*)

$$\overline{\beta} = \frac{kR_0^3}{3\pi^2 S_0 e^2}\left\{\left[\frac{2\sqrt[3]{(3\pi^2)}}{\frac{S_1}{S_0}-1}\right]\left[\frac{4\vartheta^2 + 24\vartheta\left(\frac{S_1}{S_0}-1\right) - 90\left(\frac{S_1}{S_0}-1\right)^2}{4\vartheta^2 - 6\vartheta\left(\frac{S_1}{S_0}-1\right) - 45\left(\frac{S_1}{S_0}-1\right)^2}\right]^2 + \left[\frac{9\pi^2 m_1 m_2}{(m_1+m_2)^2\left(\vartheta - \frac{2\pi}{S_0}\right)}\right]\right\}, \tag{5·23}$$

where k is Boltzmann's constant. Table XIII contains the values for $\overline{\beta}$ and $\sqrt{\overline{u^2}}$, calculated according to formula (5·23).

The constant $\overline{\beta}$ can be determined experimentally by a quantitative study of the reflexions of X-rays. Waller and James (1927) thus find for NaCl $\overline{\beta}=5{\cdot}8\times10^{-21}$, while James and Brindley (1928) have obtained the value $\overline{\beta}=7{\cdot}2\times10^{-21}$ for KCl.

Table XIII

Salt	$\overline{\beta}\times10^{21}$	$\sqrt{\overline{u^2}}\times10^8$	Salt	$\overline{\beta}\times10^{21}$	$\sqrt{\overline{u^2}}\times10^8$
NaF	3·11	0·165	KI	7·95	0·264
NaCl	5·14	0·212	RbF	4·08	0·189
NaBr	5·63	0·222	RbCl	6·32	0·236
NaI	6·74	0·243	RbBr	7·53	0·257
KF	4·06	0·188	RbI	9·00	0·281
KCl	6·06	0·231	CsF	4·52	0·199
KBr	6·78	0·244			

All the values for $\overline{\beta}$ and $\sqrt{\overline{u^2}}$ given in Table XIII are assuredly too low, this being due to the deduction of formula (5·23) in certain respects being based on a theory, which is strictly valid only at the absolute zero point. On the other hand, the *relative* values for different salts are probably very nearly correct. By the aid of an experimental value for $\sqrt{\overline{u^2}}$, e.g. for NaCl, we can thus, in accordance with Table XIII, calculate $\sqrt{\overline{u^2}}$ for the remainder of the salts in question. This table is therefore of a certain interest as regards the quantitative X-ray study of alkali halides.

(*e*) *The energy of a crystal.* According to (4·2) the potential energy of the lattice is given by

$$\Phi=-\frac{NCe^2}{R}\left(1-\frac{qR}{Ce^2}\phi_s(x)\right), \tag{5·24}$$

where

$$\frac{R}{e^2}\phi_s(x)=x\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\phi_s(x)=x(f_1(x)+sf_2(x)). \tag{5·25}$$

The numerical values of (5·25) can be calculated from (3·7) and (3·8) for $x=a=2$. For $x_0<2$ upper and lower limits can be calculated as follows: Within the range under consideration, (x_0, a), function $\ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\frac{\partial\phi_s}{\partial x}\right|$ lies between two straight lines drawn through the point

$$x_0,\ \ln\left|\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\phi_s'(x_0)\right|$$

with the derivatives $\mu(a)$ and $\mu(x_0)$. Hence

$$-\frac{\phi_s'(x_0)}{\mu_s(a)}\Big[\exp\{(a-x_0)\,\mu_s(a)\}-1\Big]<\phi_s(x_0)-\phi_s(a)<-\frac{\phi_s'(x_0)}{\mu_s(x_0)}\Big[\exp\{(a-x_0)\,\mu_s(x_0)\}-1\Big]. \tag{5·26}$$

From the condition of equilibrium (4·3) it follows that (5·26) can be written

$$\frac{1}{x_0\,\mu_s(a)}\Big[\exp\{(a-x_0)\,\mu_s(a)\}-1\Big]<\frac{qR_0}{Ce^2}\Big[\phi_s(x_0)-\phi_s(a)\Big]$$
$$<\frac{1}{x_0\,\mu_s(x_0)}\Big[\exp\{(a-x_0)\,\mu_s(x_0)\}-1\Big], \tag{5·27}$$

where $\phi_s(a)$ and $\mu_s(a)$ can be calculated according to (5·25) and (3·7), (3·8), and where x_0 and $\mu_s(x_0)$ are obtained from figs. 3, 4. Necessary data for univalent lattices are collocated in Table XIV. For bivalent lattices a corresponding calculation is of less interest, as the s values for these salts are unknown. We can only state that for bivalent face-centred lattices $x_0 \sim 1{\cdot}54$, $\mu(x_0) \sim 4{\cdot}0$. We propose to assume $s<6$, from which it follows that

$$\frac{qR_0}{Ce^2}\phi_s(x_0) = 0{\cdot}12 \pm 0{\cdot}03. \tag{5·28}$$

Table XIV

	$x_0(s)$		$\mu_s(x_0)$		$\frac{qR_0}{Ce^2}\phi_s(x_0)$	
s	$(q=6)$	$(q=8)$	$(q=6)$	$(q=8)$	$(q=6)$	$(q=8)$
0	1·973	—	4·5	—	0·096 ± 0·000	—
1	1·939	—	4·8	—	0·091 ± 0·001	—
2	1·908	—	5·2	—	0·082 ± 0·001	—
3	1·880	—	5·6	—	0·070 ± 0·002	—
4	1·854	1·910	6·1	6·4	0·057 ± 0·003	0·045 ± 0·003
5	1·830	1·880	6·7	7·0	0·041 ± 0·005	0·027 ± 0·003
6	1·808	1·852	7·4	7·7	0·022 ± 0·007	0·005 ± 0·005

The energy E of a crystal at the absolute zero point is

$$E = \Phi + N\Sigma\tfrac{1}{2}h\nu, \tag{5·29}$$

where the second term represents the zero-point energy. Table XV shows the data available. The experimental values are very uncertain and the estimated limits of experimental errors are probably narrow rather than wide.

Table XV

Salt	$-E$ (calories)*	$N\Sigma\frac{1}{2}h\nu$ (calories)†	$\frac{qR_0}{Ce^2}\phi_s(x_0)$ (ergs) exp. value	s (Table IX)	q	$\frac{qR_0}{Ce^2}\phi_s(x_0)$ (ergs) (From Table XIV)
NaCl	181 ± 5	1·7	0·11 ± 0·03	1·3	6	0·09 ± 0·00
KI	154 ± 5	1·0	0·06 ± 0·03	3·6	6	0·06 ± 0·00
RbBr	151 ± 5	0·9	0·10 ± 0·03	4·4	6	0·05 ± 0·01
CsI	141 ± 5	0·7	0·04 ± 0·03	5·1	8	0·025 ± 0·01

* Mayer 1930; Helmholz and Mayer 1934.
† Mayer and Helmholz 1932.

6. The structure of the lattice and the dependence of interatomic distance on the number of geometrically equivalent nearest neighbours

We consider function ϕ_s as independent of q. This will of course mean a certain approximation.

A lattice with index 1 is then more stable than a lattice with index 2 provided that

$$-\frac{C_1}{x_{01}} + q_1\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\phi_s(x_{01}) < -\frac{C_2}{x_{02}} + q_2\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\phi_s(x_{02}). \tag{6·1}$$

As $\ln(-\phi_s'(x))$ within the interval under consideration (x_{01}, x_{02}) can be replaced by a straight line, the formula

$$\phi_s(x_{01}) = \phi_s(x_{02}) + \frac{1}{\mu_s}\left(\phi_s'(x_{01}) - \phi_s'(x_{02})\right) \tag{6·2}$$

is valid. By the aid of the condition of equilibrium we calculate

$$\frac{\rho_0^{(i)}+\rho_0^{(k)}}{e^2}\,\phi_s'(x_0) = -\frac{C}{qx_0^2}, \tag{6·3}$$

$$x_{01} = x_{02}\left(1+\frac{1}{\vartheta_s}\ln\frac{q_1C_2}{q_2C_1}\right) \sim x_{02}\left(1+\frac{1}{\vartheta_s}\ln\frac{q_1}{q_2}\right), \tag{6·4}$$

where, as before, $$\vartheta_s = -(x_0\mu_s+2). \tag{6·5}$$

According to (6·1)–(6·5) a lattice with the co-ordination number q_1 is more stable than a lattice with the co-ordination number q_2 if

$$\textit{either}\quad q_1>q_2,\ \frac{R_{02}q_2}{C_2e^2}\phi_s(x_{02})<Q_s \quad \textit{or} \quad q_1<q_2,\ \frac{R_{02}q_2}{C_2e^2}\phi_s(x_{02})>Q_s, \tag{6·6}$$

where

$$Q_s = \frac{q_2}{q_1-q_2}\left\{\frac{\dfrac{C_1}{C_2}}{1+\dfrac{1}{\vartheta_s}\ln\dfrac{q_1}{q_2}}\left(1-\frac{1}{(\vartheta_s+2)\left(1+\dfrac{1}{\vartheta_s}\ln\dfrac{q_1}{q_2}\right)}\right)-\left(1-\frac{1}{\dfrac{q_2}{q_1}(\vartheta_s+2)}\right)\right\}.$$

If $q_2 = 6$ and alternatively $q_1 = 8$, $q_1 = 4$ be entered in (6·6), Q_s obtains the following values (Table XVI) for univalent lattices:

Table XVI

s	$Q_s\begin{cases} q_1 = 8, & C_1 = 1·7626 \\ q_2 = 6, & C_2 = 1·7476\end{cases}$	$Q_s\begin{cases} q_1 = 4, & C_1 = 1·6385 \\ q_2 = 6, & C_2 = 1·7476\end{cases}$
0	0·041	0·143
1	0·040	0·145
2	0·039	0·148
3	0·038	0·152
4	0·037	0·156
5	0·036	0·160
6	0·035	0·165

A comparison between Tables XIV and XVI shows that the alkali halides cannot crystallize with the co-ordination number 4, as for all values of s a structure with $q = 6$ is more stable than a structure with $q = 4$. A face-centred lattice ($q = 6$) is also more stable than a space-centred lattice ($q = 8$) for small values of s, while a transition to a space-centred lattice occurs when s passes a value situated between 5 and 5·5. From Table IX it appears that only the salts CsCl, CsBr, CsI show s values sufficiently high to enable them possibly to form space-centred lattices. According to the theory these salts lie quite on the border between the two lattice types and are followed in respect of high s values by RbCl, RbBr, RbI. As is known, CsCl, CsBr and CsI crystallize in space-centred lattices, but on being heated pass into face-centred lattices (Wagner and Lippert 1936*a*, *b*), while RbCl, RbBr and RbI form face-centred lattices which, however, are transformed under sufficient pressure (Bridgman 1928). In agreement with the theory, the other alkali halides form only face-centred lattices. The lattice structures observed thus confirm that the value of s passes the number 5 between RbCl and CsCl in Table IX.

Goldschmidt (1932) has found experimentally that the interatomic distance increases by 3 per cent at the transition from a face-centred structure to a space-centred one. According to our theory such a transition happens for $s \sim 5$, $x_0 \sim 1{\cdot}83$, $\mu_s \sim 6{\cdot}7$, $\vartheta_s \sim 10$. Formula (6·4) gives with $q_1 = 8$, $q_2 = 6$, $\vartheta_s = 10$

$$x_{01} = 1{\cdot}029 x_{02},$$

in good agreement with Goldschmidt's rule.

For bivalent lattices with $\vartheta_s = -(\mu_s x_0 + 2) \sim 4$, Q_s $(q_1 = 8)$ takes the value 0·05 and Q_s $(q_1 = 4)$ the value 0·12. According to (5·28) and (6·6) a lattice with $q = 8$ is thus completely excluded in respect of the bivalent salts, whereas lattices with $q = 4$ and $q = 6$ are possible, as these salts lie near the border of the two lattice types. The bivalent salts crystallize in face-centred lattices, with the exception of MgTe, which forms a lattice with $q = 4$. However, the constant s is certainly higher for MgTe than for MgO, which, like other bivalent salts, forms a face-centred lattice. In accordance with the theory also MgTe ought therefore to crystallize with the co-ordination number $q = 6$. The incorrectness of this conclusion shows that the postulates of the theory are not fulfilled in respect of MgTe. It can easily be seen that this really is the case. For MgTe in a face-centred lattice, the negative ions would penetrate each other if we attribute to them the radii indicated by Goldschmidt. In such a case it is obvious that our basic postulate—according to which only the repulsion between nearest neighbours with opposite electric charges need be taken into consideration when calculating the potential energy of the lattice—will not hold good. Consequently, in some extreme cases certain atomic configurations can be excluded as energetically impossible on account of the relative size of the atoms or ions. This point of view was first put forward by Magnus (1922) in connexion with the question of complex chemical compounds and has later been successfully applied by Goldschmidt in the case of crystal lattices.

7. Theoretical interpretation of empirical results

The general form of $\phi^{00}(R)$ for small values of x is rather interesting. According to (2·24) $\phi^{00}(R)$ may be represented by a function

$$\phi^{00}(R) = \frac{e^2}{2\rho_0}\left(f_1(x) + \left(\frac{\rho_0}{a_0}\right)^2 f_2(x)\right), \tag{7·1}$$

where the relative importance of f_2 gradually diminishes when x decreases.

The reciprocal action of the outermost shells of two rare gas atoms has been investigated theoretically by Grönblom (1935). That the inner electrons play no important role in problems of this nature is well known and has been pointed out, i.e. by Bleick and Mayer (1934). We denote the nuclei by a and b, and the outermost electrons of a and b by $1, \ldots, 8$ and $1', \ldots, 8'$ respectively. We further denote the characteristic functions for $1, \ldots, 8$ and $1', \ldots, 8'$ by ψ_a and ψ_b respectively. The characteristic function for the two atoms regarded as one system will then be expressed as follows:

$$\Psi = \sum_{mn} C_{mn} P_m^+ P_n^- \Psi_0,$$

where
$$\Psi_0 = \psi_a(1)\,\psi_a(2)\ldots\psi_a(8)\,\psi_b(1')\,\psi_b(2')\ldots\psi_b(8').$$

P^+ and P^- respectively signifies the permutation of the electrons with positive or negative spin. $C_{mn} = \pm 1$, and is to be chosen so that Ψ is antisymmetrical in respect of all electrons. However, it appears, as also pointed out by Bleick and Mayer, that only those permutations are of importance to the final result, by which *one* electron from a is permuted with *one* electron from b. In this the possibility of dealing with the problem approximately as an H_2 problem is included. For the disturbance energy one arrives at the expression (Grönblom 1935)

$$\left.\begin{aligned} \phi^{00}(R) = {} & e^2\iint\left(\frac{1}{R}+\frac{1}{r_{12}}-\frac{1}{r_{a_2}}-\frac{1}{r_{a_1}}\right)\psi_a(1)^2\,\psi_b(2)^2\,dV_1\,dV_2 \\ & -8\frac{e^2}{R}\iint\psi_a(1)\,\psi_a(2)\,\psi_b(1)\,\psi_b(2)\,dV_1\,dV_2 \\ & -\frac{e^2}{2}\iint\frac{\psi_a(1)\,\psi_a(2)\,\psi_b(1)\,\psi_b(2)}{r_{12}}\,dV_1\,dV_2 \\ & +4e^2\iint\left(\frac{1}{r_{a_2}}+\frac{1}{r_{b_1}}\right)\psi_a(1)\,\psi_a(2)\,\psi_b(1)\,\psi_b(2)\,dV_1\,dV_2. \end{aligned}\right\} \tag{7·2}$$

The writer has shown (Wasastjerna 1932*b*) that the electron distribution for the outermost shell of atoms and ions of rare gas type can be approximately expressed by the general formula

$$D(r) = \frac{1}{\rho_0}B(\xi) = \frac{1}{\rho_0}\frac{5}{3}(5\xi)^4\exp(-5\xi), \tag{7·3}$$

where $\xi = \dfrac{r}{\rho_0}$, r being the distance from the centre of the atom. For each of the eight outermost electrons of both atoms Grönblom chooses a characteristic function

$$\psi = N_r\,r\exp\left\{-\frac{5r}{2\rho_0}\right\},$$

which corresponds to the electron distribution (7·3). From (7·2) he then obtains a potential energy, which can be written

$$\phi^{00}(R) = \frac{e^2}{2\rho_0}(A_0x^7+A_1x^6+\ldots+A_8x^{-1})\exp(-10x) = \frac{e^2}{2\rho_0}f_1(x), \tag{7·4}$$

where $A_0, \ldots, A_8$ are constants and where $x = \frac{R}{2\rho_0}$. A few terms of no importance at the intervals which come into question have been left out. Expression (7·4) meets condition (7·1). As an experiment we propose to assume that the first term in the polynomial appearing in (7·4) predominates. This assumption leads to the suggestive formula

$$f_1(x) \propto \frac{1}{x} B^2(x), \tag{7·5}$$

which gives the approximate theoretical value $\mu = \frac{f_1''(x)}{f_1'(x)} = -4\cdot 7$ for $x = 1\cdot 5$, where, according to § 4*a*, the second term in (7·1) can be neglected. The corresponding experimental value (figs. 1, 2) is $\mu(x) = -4$.

On the other hand, for large distances R, (7·1) gives

$$\phi^{00}(R) = \frac{e^2 \rho_0}{2a_0^2} f_2(x), \tag{7·6}$$

where, according to (3·8), $f_2(x) = -0\cdot 18x^{-6}$.

According to London the van der Waals energy is given by

$$\phi^{00}(R) = -\tfrac{3}{4}\alpha^2 E_j R^{-6}, \tag{7·7}$$

where $\alpha = \frac{3I}{4\pi N}$, $I = 10^{33}\rho_0^4$ (according to 2·18) and $E_j \rho_0 = 2 \times 10^{-19}$ (according to Table III). Formula (7·7) can thus be expressed by (7·6), where

$$f_2(x) = -0\cdot 09x^{-6}.$$

The experimental values of the van der Waals forces for rare gas atoms are thus exactly twice as large as the theoretical ones.

Addendum

For crystal lattices the van der Waals energy can be written $-\frac{Nw}{R^6}$, where w is a constant which can be calculated from experiments by formula (cf. 4·2)

$$-\frac{w}{R^6} = qs \frac{e^2}{\rho_0^{(i)} + \rho_0^{(k)}} f_2(x).$$

In Table XVII the experimental values w are compared with values theoretically calculated by J. E. Mayer (1933).

TABLE XVII

Salt	$w_{\text{exp}} \times 10^{62}$	$w_{\text{theor}} \times 10^{62}$	Salt	$w_{\text{exp}} \times 10^{62}$	$w_{\text{theor}} \times 10^{62}$
NaF	0·2	0·5	RbF	5·8	2·8
NaCl	2·0	1·8	RbCl	17·4	6·9
NaBr	2·7	2·7	RbBr	22·1	9·0
NaI	3·9	4·8	RbI	30·0	13·3
KF	2·8	1·7	CsF	9·8	4·9
KCl	11·4	4·5	CsCl	29·0	15·3
KBr	14·6	6·0	CsBr	36·3	20·7
KI	20·2	9·2	CsI	48·4	29·7

The experimental values for Na-salts are rather uncertain, as they depend to a considerable extent on how the graphical interpolation is done (§ 4 *b*). For other salts the experimental values of the VAN DER WAALS energies are again about twice as large as the theoretical ones, and there is thus a rather serious discrepancy to be faced.

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8. SUMMARY

A method is developed according to which it is possible to analyse, by the aid of accessible experimental data, the question of the dependence of the potential energy on the interatomic distance for atoms and ions with closed shells. The results of the analysis have been made the foundation for a theoretical calculation of a number of physical properties of crystals. In many instances the results of the calculations can be compared with experimental data. In other instances information is obtained concerning data, which have previously been entirely unknown or about which great uncertainty has prevailed. Finally, a theoretical interpretation is given to the empirical results.

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