COMPRESSIBILITY OF THE ALKALI HALIDES

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Abstract

Compressibility of eleven alkali halides and its variations with pressure and temperature have been determined by measurements by Bridgman's new method, up to 12,000 atm. for both 30° C and 75° C. The samples were all single simple cubic crystals each grown from the melt in a new way, described elsewhere. The error in the values of the compressibility at zero pressure, κ_0, is probably less than one per cent; in the values for variation with pressure, ψ_0, and temperature the error may be 5 and 20 per cent respectively. By extrapolation approximate values of κ_0 for absolute zero are found. *Periodic relations.* Both κ_0 and ψ_0 when plotted against the alkali ion for a series of salts of the same halogen ion, or vice-versa, show similar behavior. The curves break sharply at the ion similar to argon (K or Cl) the rate of increase suddenly decreasing. This behavior is also shown by the *grating space* as measured by Davey, and tends to corroborate *Bohr's theory of atomic structure* according to which there is a discontinuity in atomic formation at argon, additional electrons going into inner shells.

Interatomic forces in cubic crystals.—*The crystal potential energy as a function of volume, at absolute zero* is determined from the experimental results, and an empirical expression for it is developed which is extrapolated to a volume so large that the repulsive forces between the atoms are small. The remaining attractive force is found approximately equal to that given by the expression derived by Madelung assuming each ion is singly charged. Then assuming electrostatic cohesion, a series development is obtained for the repulsion betwe atoms. This is found not to vary as any single inverse power of the grating space, as demanded by the theory of Born for salts of Na, K and Rb; nor is there any discontinuity between Li and the other metals. Values for the *energy of dissociation of the crystal* into ions are given. As would be expected, the change of compressibility with temperature is related to the thermal expansion in such a way that an increase of temperature and decrease of pressure have the same effect on both volume and compressibility.

I. Introduction

FOR some time physicists have been familiar with the idea that a crystal of a polar compound, such as sodium chloride, is simply a great molecule, its constituents being ions of sodium and chlorine. In such a substance, the forces between the ions have at the same time the character of chemical forces, cohesive forces, and the forces which resist compression; and the study of the forces in one of these roles immediately throws light on the forces in the others. Since the ions are supposed to be electrically charged, the metals positively, the halogens negatively, they necessarily attract each other; and it naturally has often been suggested, for example by Langmuir, that this attraction actually is the cohesive,

or chemical, force, and that when it has pulled the ions together until they bump, so that the crystal "molecule" is in equilibrium, the substance is in its normal state.

This idea has been developed into a quantitative theory by several German physicists: Born,[1] Lande, Fajans, Herzfeld, and others. They all agree in assuming the cohesive forces to be the electrostatic attraction of the ions for each other, and Madelung[2] has found from potential theory what the value of the attraction, or rather the potential energy associated with it, actually is for various crystal lattices. The differences between the developments of the various men lie only in their treatment of what has been roughly termed the "bumping" of the ions, the repulsion which they exert on each other when they come very close together, and which increases very rapidly as the distance between ions decreases. Born assumes that two ions, apart from their electrostatic action, repel each other with forces varying as the inverse tenth power of the distance, unless they are lithium ions, when they repel according to the inverse sixth power; the others have more elaborate developments in inverse power series, leading to somewhat different numerical results. These values for the repulsion rest on assumptions that the ions act like cubes of eight static electrons, with a nucleus in the center; the special value for lithium arises because lithium, with its two electrons, can hardly have cubic symmetry. Although I shall not discuss it in this paper, it seems to me that the argument on which these values rest, carried over of course to a dynamic atomic model such as those which Bohr has recently suggested, strikes certain difficulties in the way of stability, which make the whole picture of the mechanism of the repulsion of doubtful truth. In any case, the theory of the repulsion has a far less certain basis than that of the cohesive electric attraction.

The sum of the attractive cohesive force, and the "bumping" repulsion, is zero in the normal state at absolute zero of temperature; if it is not zero, it must stand in equilibrium with an external pressure or tension. It is thus plain that the vehicle for studying these chemical, or cohesive, forces is the compressibility. The first numerical check which Born made on his theory was on the compressibility of the salts for which that constant had been measured. Of the simple cubic alkali halides, the simplest set of polar compounds, six had been done, by Richards and Jones:[3] NaCl,

[1] Born and Lande, Sitzber. d. Preuss. Akad. d. Wiss. p. 1048, 1918; Verh. d. D. Phys. Ges. 19, 210, 1918; Born, Verh. d. D. Phys. Ges. 21, 13, 533, etc., 1919; Fajans, Verh. d. D. Phys. Ges. 21, 539, etc., 1919; Fajans and Herzfeld, Zeits. f. Phys., 2, 309, 1920; Schwendenwein, Zeits, f. Phys., 4, 73, 1921.

[2] Madelung, Phys. Zeits. 19, 529, 1918

[3] Richards and Jones, J. Am. Chem. Soc. 31, 158, 1909

NaBr, NaI, KCl, KBr, KI. Born found fair agreement with his theory; the others also secured approximate agreement, but by no means exact. It seems likely from an examination of their results that the error lay in their values for the repulsion, in which they disagreed, rather than in the electrostatic attraction, which has a good theoretical foundation.

Bridgman[4] has very recently developed a new and much improved experimental method for measuring compressibility; and it is the purpose of this paper to state the results of an experimental investigation, by this method, on twice as many of the alkali halides as had been previously measured, and to see how much information these data are capable of yielding about the forces in the crystal. I wish to take this occasion to state my great indebtedness to Professor Bridgman for his constant interest and assistance during the research.

In previous theoretical work, it has been necessary to take the electrostatic nature of the cohesion for granted, and to assume that the approximate correctness of the results justified this. But the new measurements include not only the initial compressibility, but its initial change with pressure, which can be measured by use of a large pressure range (12,000 atmospheres). This gives a new term in the power series development of the potential energy of the crystal, and, by increasing the range of convergence, makes it possible to extrapolate to a negative pressure large enough so that the ions are theoretically pulled nearly out of contact, and the "bumping" repulsion has sunk to a low value, leaving principally the cohesive force by itself. This situation can naturally be more nearly reached with the soft salts, in which the ions touch loosely in the normal state, than in the hard ones. If now the cohesive force at the limit of extrapolation is compared with that to be expected on the electrostatic theory, it will be shown that the observed force approaches more nearly the theoretical as we pass to softer salts, departs from the theoretical in the direction to be expected on account of the remaining trace of repulsion, and approaches asymptotically almost exactly the correct value. This is as direct evidence for the electrostatic nature of the cohesion as could be desired.

If the electrostatic cohesion is regarded as established, then, since its theoretical value is known exactly, it is possible to put it on the known side of our equations, and concentrate the data on giving information about the other part of the force, the repulsive "bumping". First it is possible to see how far the theoretical assumptions of Born about this force are justified; in fact, we can set up for each salt, from experiment,

[4] Bridgman, Proc. Am. Acad., Jan., 1923

a fairly complete substitute for the function which Born assumed to be the inverse tenth power. But more important, we have here information about a series of ions, unaffected by chemical combination, and we can study the properties as we pass from one alkali to another, or one halogen to another. Actually, it is simpler not to try to eliminate the cohesive forces, but to consider periodic relations simply in the observed quantities. The number of salts studied is here, in contrast to previous work, large enough so that important information of this kind can be obtained, and the properties will be shown to have interesting connection with Bohr's recent theory of the periodic table.

II. Experimental Results

The experimental methods will be described in another place.[5] The measurement was performed by the new method used by Bridgman[4] in his recent work on the compressibility of metals. The samples were single crystals of the salts, artificially prepared in a new way by crystallization from the melted salt. Measurements of change of volume were made every thousand atmospheres up to 12,000 atmospheres, and at two temperatures, 30°C and 75°C. The change of volume is, within the limits of error of the experiment, a quadratic function of the pressure, so that the behavior at a single temperature can be described by two constants. If v is the volume of a certain quantity of substance, v_0 its volume under zero pressure, then the compressibility is defined as

$$\kappa = \frac{1}{v_0}\left(\frac{\partial v}{\partial p}\right)_T. \tag{1}$$

If κ_0 is the value of the compressibility under zero pressure, then the change of compressibility with pressure may be conveniently defined as

$$\psi_0 = \frac{1}{\kappa_0}\left(\frac{\partial \kappa}{\partial p}\right)_T = \frac{1}{\kappa_0 v_0}\left(\frac{d^2 v}{dp^2}\right)_T. \tag{2}$$

The two constants ψ_0 and κ_0, for a fixed temperature, together with the change of compressibility with temperature $(1/\kappa_0)(\partial\kappa/\partial\tau)_p$, are the quantities measured. The change of compressibility with pressure was found to be independent of temperature.

The values of compressibility are probably correct to one per cent, except for one or two of the most incompressible salts; the error in the change of compressibility with pressure in most cases is probably between two and five per cent, in a few cases more. The change of compressibility with temperature is much less accurate; errors of ten or even twenty per cent are not impossible.

[5] Slater; paper will probably appear in Proc. Am. Acad.

In Table I data are given for the eleven salts which I have measured. Of these, the lithium and rubidium salts and KF have not been previously measured, although measurements on some of them, as yet unpublished, have recently been made at low pressures in Professor Richards's laboratory. NaI is the only salt previously done which I have not measured. RbBr and RbI were found to have polymorphic transitions at high pressures, presumably changing to a body centered form similar to the caesium salts. The data given are for the low pressure, simple cubic modifications. The quantities tabulated in Table I are the compressibility at 30°C, the change of compressibility with pressure independent of temperature between 30°C and 75°C, and the average change of compressibility with temperature between 30°C and 75°C. The compressibility and change of compressibility with pressure both have the dimensions of the reciprocal of a pressure; they are expressed in reciprocal dynes per square centimeter. The change of compressibility with temperature is in reciprocal degrees centigrade.

TABLE I

Compressibility, and its change with pressure and temperature, at 30° C

Salt	$-\kappa_0$	$-\psi_0$	$(1/\kappa_0)\,(\partial\kappa/\partial T)_p$
LiF	$1.53(10)^{-12}$	$11.7(10)^{-12}$	$1.9(10)^{-4}$
LiCl	3.41	19.8	6.9
LiBr	4.31	24.5	8.4
NaCl	4.20	21.9	6.8
NaBr	5.08	25.5	7.5
KF	3.31	20.1	1.2
KCl	5.63	26.5	4.8
KBr	6.70	31.8	6.0
KI	8.54	39.1	6.0
RbBr	7.94	35	
RbI	9.58	43.0	6.8

For purposes of comparing various salts, these data, for 30°C, are satisfactory; but for theoretical use, when the temperature effects are to be neglected, the value of the compressibility for the absolute zero should be employed. The change of compressibility with temperature provides a means of approximately reducing the compressibilities to the absolute zero, if it is assumed that the change of compressibility with temperature is independent of temperature. This is probably not true; it seems likely for theoretical reasons that the change of compressibility with temperature should become small at very low temperatures. But the compressibility at absolute zero found in this way is certainly nearer the truth than the observed value at room temperature, which has been used for all previous theoretical work.

In Table II are given the compressibilities of the salts at absolute zero found by extrapolation. There are also given two quantities of theoretical interest, in which δ_0 is the grating space at no pressure (the distance between successive ions of the same sign, measured by Davey),[6] corrected to the absolute zero by assumed values of the thermal expansion, in cases where this has not been measured. The significance of these quantities will be explained later.

TABLE II

Compressibility and derived quantities at absolute zero.

Salt	$-\kappa_0$	$(1-9\delta_0^4/13.94e^2\kappa_0)$	$(3\psi_0/\kappa_0-10)$
LiF	1.4×10^{-12}	5.9	14.3
LiCl	2.7	8.0	11.9
LiBr	3.2	8.7	12.8
NaCl	3.3	9.1	9.8
NaBr	3.9	9.5	9.5
KF	3.2	7.9	8.9
KCl	4.8	9.7	6.5
KBr	5.5	10.0	7.1
KI	7.0	10.5	6.8
RbBr	6.5	10.0	6.2
RbI	7.6	11.0	6.8

III. SERIES DEVELOPMENT FOR CRYSTAL ENERGY

Before making numerical use of the data, it is necessary to derive the formulas for finding as much as possible about the energy of the crystal from the compressibility and its change with pressure. This discussion will refer to the absolute zero of temperature, so that, disregarding the electronic motions, the energy will be wholly potential.

Since no heat is to be absorbed in compression at the absolute zero, the first law states that $0=d\varphi+pdv$, where p is the pressure, and φ is the potential energy in a cube of volume v whose side is the grating space δ, now regarded as a variable. That is,

$$p = -d\varphi/dv. \tag{3}$$

It is desired to write κ and ψ, defined in Eqs. (1) and (2), in terms of derivatives of φ with respect to δ, instead of in terms of derivatives of v with respect to p, so that by inversion the derivatives of φ at zero pressure can be found in terms of κ_0 and ψ_0. This will be done in two steps. First, the derivatives of v with respect to p will be written in terms of derivatives of φ with respect to v; then these will be changed to derivatives with respect to δ.

[6] Davey, Phys. Rev. **21**, 143, 1923.

We have, from (3),

$$\frac{dp}{dv} = -\frac{d^2\varphi}{dv^2}, \quad \frac{dv}{dp} = -1 \bigg/ \frac{d^2\varphi}{dv^2}.$$

Then
$$\frac{d^2v}{dp^2} = \frac{dv}{dp}\frac{d}{dv}\left(\frac{dv}{dp}\right) = -\frac{d^3\varphi}{dv^3}\bigg/\left(\frac{d^2\varphi}{dv^2}\right)^3 = \frac{d^3\varphi}{dv^3}\left(\frac{dv}{dp}\right)^3.$$

Next let $v = \delta^3$, $d\delta/dv = 1/3\delta^2$. Denoting derivatives of φ with respect to δ by primes,

$$\frac{d\varphi}{dv} = \frac{d\varphi}{d\delta}\frac{d\delta}{dv} = \frac{\varphi'}{3\delta^2}; \quad \frac{d^2\varphi}{dv^2} = \frac{d}{d\delta}\left(\frac{d\varphi}{dv}\right)\frac{d\delta}{dv} = \frac{\varphi''}{9\delta^4} - \frac{2\varphi'}{9\delta^5};$$

$$\frac{d^3\varphi}{dv^3} = \frac{d}{d\delta}\left(\frac{d^2\varphi}{dv^2}\right)\frac{d\delta}{dv} = \frac{\varphi'''}{27\delta^6} - \frac{2\varphi''}{9\delta^7} + \frac{10\varphi'}{27\delta^8}.$$

We are interested in quantities at zero pressure. Denoting these by zeros, we have, from (3), $(d\varphi/dv_0) = 0$. Then $\varphi'_0 = 0$, and

$$\left(\frac{d^2\varphi}{dv^2}\right)_0 = -\frac{\varphi_0''}{9\delta_0^4}; \quad \left(\frac{d^3\varphi}{dv^3}\right)_0 = \frac{\varphi_0'''}{27\delta_0^6} - \frac{2\varphi_0''}{9\delta_0^7} = \frac{\varphi_0'''}{27\delta_0^6} - \frac{2}{\delta_0^3}\left(\frac{d^2\varphi}{dv^2}\right)_0.$$

Substituting these in the derivatives of v with respect to p, and these in (1) and (2), we have

$$\kappa_0 = -9\delta_0/\varphi_0''; \quad \psi_0 = \kappa_0^2\varphi_0'''/27 + 2\kappa_0. \tag{4}$$

These can now be solved for the derivatives, giving

$$\varphi_0' = 0; \quad \varphi_0'' = -9\delta_0/\kappa_0; \quad \varphi_0''' = (27/\kappa_0)/(\psi_0/\kappa_0 - 2). \tag{5}$$

Eq. (5) gives all the information about the energy which can be gained from these experiments. From them a Taylor's expansion can be immediately written down. Using $d = \delta/\delta_0$ as a variable, it is

$$\varphi = \varphi_0 - \frac{9}{2}\frac{\delta_0^3}{\kappa_0}\left\{(d-1)^2 - \left(\frac{\psi_0}{\kappa_0} - 2\right)(d-1)^3 + \ldots\right\}. \tag{6}$$

Eq. (6) is an empirical expression for the potential energy, and may be expected to represent the function only for values of d near enough to unity so that the remaining terms are small. To proceed further, it is desirable to inquire what the main features of the function may be expected to be.

The energy will show a minimum at the position of equilibrium, rising on each side. For values of d less than unity, there is no reason to suppose that the energy will not rise indefinitely, so that an indefinitely large amount of work can be done before reducing the volume of the crystal to zero. But for values of d greater than unity, the rise cannot be indefinitely large as it requires only a finite amount of work to pull the crystal apart so that its ions are a large distance from each other. Thus the curve may be expected to rise with increasing d, and approach

a horizontal asymptote. This part of the curve, where the force is attractive, will be much less steep than the other part, where it is repulsive. The energy will naturally be divided into parts: the slowly changing attractive energy, presumably electrostatic, and the repulsive energy, which is small at large distances, but becomes rapidly large near the position of equilibrium.

IV. THE COHESIVE ATTRACTION

We shall first seek information about the attractive energy. The method of doing this has already been described. We shall find the empirical value of the force, or of φ', for as large a value of d as we can; and we shall compare this with the theoretical value of φ'. The extrapolated value of φ' will first be found. To do this, we must consider more closely the nature of the empirical series. There are two terms. The first is a quadratic, a parabola rising indefinitely for values of d both less than and greater than $d = 1$. The two terms together form a cubic, rising higher than the parabola for d less than 1, but for greater values rising first, although not so high as the parabola, but passing through a point of inflection, a maximum, and finally falling. It seems most likely that all the higher terms for $d < 1$ will have the same sign, so that for $d > 1$ the series will be alternating. If the terms decrease regularly, the final value of the series will not be far from half way between the first and second approximation; it will certainly lie somewhere between them, and the mean will furnish a good approximation. It is hardly possible to use the series for values of d greater than that for which the cubic has its point of inflection. This value of d increases as the compressibility of the salt increases, from 1.055 for LiF to 1.093 for RbI. But at the point of inflection, the mean of the slopes of the first and of the second approximations should form a good value of φ'. This value may be compared with the value of φ' to be expected on the electrostatic hypothesis, and the value of the charge necessary to produce the observed φ' may be found. This charge may be expected for the incompressible salts to be considerably smaller than the charge actually present, since d for these salts is small and at the same time the ions are tightly packed together and they would have to be separated by a considerable distance before the repulsion vanished; for the compressible salts, on the other hand, the computed charge should be much nearer the actual charge. If the charge is the same for all the salts, and if the computed charge is plotted against compressibility, the curve should approach an asymptote for large values of compressibility, this asymptote representing the actual charge on each ion; if on the other hand the computed charge is plotted against the

reciprocal of the compressibility, and the curve extrapolated to zero, the intercept should be the actual charge. This will now be done.

At the point of inflection of (6), $\varphi'' = 0$, or $2 - 6(\psi_0/\kappa_0 - 2)(d - 1) = 0$, $d = 1 + 1/[3(\psi_0/\kappa_0 - 2)]$. At this point, the first term of φ' is $-3\delta_0^2/[\kappa_0(\psi_0/\kappa_0 - 2)]$ and the first two together $-3\delta_0^2/[2\kappa_0(\psi_0/\kappa_0 - 2)]$; the mean is $-9\delta_0^2/[4\kappa_0(\psi_0/\kappa_0 - 2)]$. The theoretical value of φ', as mentioned above, is a constant divided by δ^2; this constant has been computed from potential theory by Madelung,[2] who finds the value of φ' for a simple cubic lattice to be $13.94e^2/\delta^2$, where e is the charge on each ion. Setting this equal to the other expression for φ' gives

$$e = \frac{3}{2}\,\frac{\delta_0^2}{\sqrt{[-13.94\ (\psi_0 - 2\kappa_0)]}}\left\{1 + \frac{1}{3(\psi_0/\kappa_0 - 2)}\right\}.$$
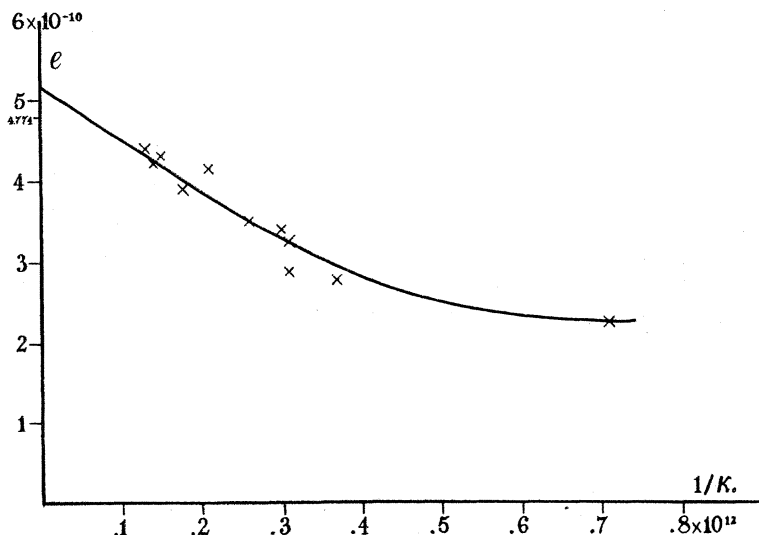

Fig. 1. Computed charge on ions, plotted against reciprocal of compressibility.

In Fig. 1, these values of e for the various salts are plotted against the reciprocals of the compressibility. The behavior of the curves is similar to what was expected. But more than that, the extrapolated value of e is 5.1×10^{-10} e.s.u., very close to the charge on the electron, showing that, if the attraction actually is electrostatic, the charge on each ion is one electronic charge. This seems to be very convincing evidence for the electrostatic nature of the cohesive forces.

V. THE ATOM REPULSION

Once the hypothesis is accepted that the source of the attractive force is electrostatic, the exact expression for this part of the energy becomes known, and by subtraction the Taylor's development of the repulsive

part of the energy can be found. This energy will be expected to sink to zero for values of d not far greater than unity; and the condition of approaching an asymptote, together with the requirement that the curve lie between the two approximation curves, is enough to fix the course of the function fairly completely. The region in which there is uncertainty, between the point where the second approximation ceases to represent the function and the point where the function is very small, is not large. By a simple method of interpolation, which need not be described here, it has been possible to fill in the intermediate part, thus affording a complete knowledge of the repulsive energy, and, by addition, of the total energy. One result of this is a knowledge of the magnitude of the energy of the crystal in the normal state. If the energy for infinitely large δ is taken to be zero, then the energy in the normal state is the sum of the negative energy of the attractive term, found simply from the grating space, and of the positive repulsive energy, determined from the empirical curves, and depending to some extent on the interpolation used in completing the curve. This last part of the energy amounts to about ten per cent of the whole. In Table III are the negative energies of the crystals in the normal state, calculated in the manner sketched. The

TABLE III

Lattice energies, from compressibility data, in kg-cal/g-mol

	Li	Na	K	Rb
F	231		182	
Cl	189	178	164	
Br	180	169	157	152
I			148	147

values are for absolute zero of temperature, and are naturally derived directly from the compressibility. The data are given in kg-cal/g-mol, for convenience in thermochemical applications. For the salts other than KF and those of Li, the figures are probably not in error by more than five kg cal. They differ by less than this in many cases from the values calculated by Born from his theory, which will be described next.

Born's formula for the energy, as indicated above is

$$\varphi = -13.94 \ e^2/\delta + b/\delta^n \tag{7}$$

where the first term is the electrostatic potential already considered, and the second is a hypothetical representation of the repulsive potential. The value of n is 9 for salts other than those of lithium, and 5 for those of lithium. It is well to see how nearly the data fit such a law.

The comparison could, of course, be made between the curves which can be drawn for the repulsive energy from experiment, and the inverse power law; but it is easier to make a more direct check. We can differ-

entiate (7), and substitute in (4), eliminating b by (5), and obtaining directly

$$\kappa_0 = -9\delta_0^4/(n-1)\ 13.94\ e^2; \quad \psi_0 = \kappa_0(n+10)/3.$$

These can be put in the form

$$n = 1 - 9\delta_0^4/13.94\ e^2\kappa_0 = 3\psi_0/\kappa_0 - 10. \tag{8}$$

Eq. (8) states a condition that must be satisfied by the experimental quantities if the repulsive energy is to be represented by a single inverse power term. The two quantities of (8) are given in Table II; and it is seen that, while they are of the same order of magnitude, they are by no means equal; the first shows a regular increase passing down the list, the second a regular decrease. Thus Born's assumption is not justified; even more, the assumption that $n=9$ for all salts except those of lithium, 5 for those of lithium, is incorrect. There is no discontinuity between the properties of lithium and of the other metals.

VI. RELATIONS IN THE PERIODIC TABLE

We have considered the character of the repulsive action for the separate salts; but more information about the ions can be obtained by treating them in the series to which they belong in the periodic table. The alkali halides form a very simple two parameter family of compounds, especially suited for investigating the comparative properties of the ions. For salts of a given halogen, there should be a regular progression of properties passing along from the lithium, sodium, potassium, to rubidium salts. Similarly, there should be a regular progression from the fluoride to the chloride, bromide, and iodide of the same metal. It is interesting to plot not only the compressibility and its change with pressure, but also the grating space, in this way, against both alkalis and halogens. This is done in Fig. 2 , where the abscissas represent the rare gas configurations which the corresponding ions resemble, equally spaced. The quantities plotted are the data for 30°, since these are more accurate than at the absolute zero. All these quantities increase as either of the ions increases in size. The interpretation of this is that as electrons are added to either kind of ion, the ions grow larger, the forces between them become less, they are less squeezed together initially, and a given external pressure has more effect in compressing them. But, in addition to this, and to the obvious regularity of the curves, it is seen that the curves plotted against the metals all show a break at potassium, and against the halogens at chlorine. These both correspond to the argon shell; and the fact that every one of the curves shows this behavior is convincing demonstration that there is some discontinuity at argon in the formation of the series
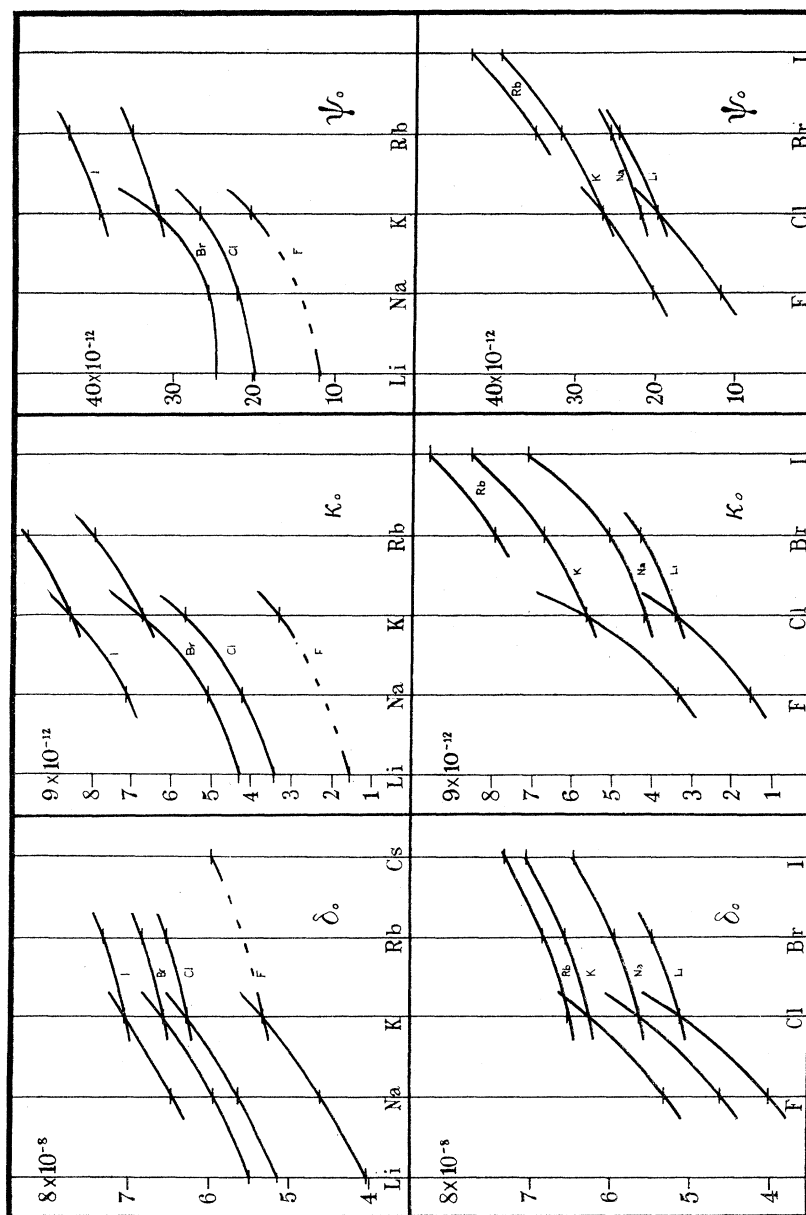
Fig. 2. Grating space, compressibility, and change of compressibility with pressure, at 30°C, plotted against metals and halogens.

of inert gases, and that it is really a property of the ion, not of the salts. The electrons added after argon have less effect on the external properties of the atom than those added before. But this is exactly in accord with Bohr's recent views of the relation between electron structure and the periodic table; at argon, the electrons added as the atomic weight increases stop going into the outer shell, but fill out the inner shell instead. Thus a discontinuity at this point would be strongly indicated theoretically.

VII. Temperature Effects

The discussion so far given refers merely to the absolute zero. No attempt at discussing the temperature effects will be given here. But almost any theory would demand that the effect of an increase of temperature on all the properties should be equivalent to a certain decrease of pressure, that is, that the change of compressibility with temperature should be to the change of volume with temperature (the thermal expansion) as the change of compressibility with pressure is to the change of volume with pressure (the compressibility). The thermal expansion has been measured, as far as I can find, for only four of the salts; but for these, this relation is found to be approximately fulfilled. This insures that any theory capable of describing the thermal expansion will at the same time give correctly the change of compressibility with temperature.

Jefferson Physical Laboratory,
  Harvard University,
    July 21, 1923.