1. The conversion of the chlorides or nitrates to bromides with 8 *N* hydrobromic acid.
2. Separation of sodium, potassium and barium bromides from magnesium, strontium and calcium bromides using isoamyl alcohol.
3. Separation of sodium and barium bromides from potassium bromide using ethyl alcohol.
4. Precipitation of sodium and barium chlorides with 12 *N* hydrochloric acid from the ethyl alcohol solution.
5. Separation of magnesium from calcium and strontium by ignition of the nitrates.
6. Separation of strontium from calcium by dissolving calcium nitrate in 16 *N* nitric acid.

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STUDIES ON THE PERIODIC SYSTEM. III. THE RELATION BETWEEN IONIZING POTENTIALS AND IONIC POTENTIALS

BY G. H. CARTLEDGE

RECEIVED MARCH 7, 1930 PUBLISHED AUGUST 5, 1930

In the preceding papers of this series[1] the author has developed a quantitative periodic function, the ionic potential ϕ, which is defined as the ratio of the charge of an atomic ion to its crystal radius, that is

$$\phi = \frac{z}{r} \tag{1}$$

In the previous papers the numerical values of the ionic potentials were calculated in arbitrary units, taking z as the valence and r as the ionic radius in Ångström units. It has been shown that the values of the ionic potential may be used to trace the order of variation in numerous properties of ions and compounds, such as the development of acidic properties of hydroxides, the electrical conductance and volatility of chlorides, and others. It is the purpose of the present paper to show the relationship between the ionic potential and the ionizing potential; from this relationship it is found that information regarding the polarizability of the ions may be obtained.

In order to make the desired comparisons it will be convenient to express the ionic potential in volts. The potential of a positive ion of valence z and charge ze e. s. u. is ze/r_c in electrostatic units, if r_c is the ionic radius in cm. As the volt is one three-hundredth of the electrostatic unit of potential, we have for ϕ_v, the ionic potential in volts

$$\phi_v = 300\,\frac{ze}{r_c}\ \text{volts} \tag{2}$$

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[1] Cartledge, THIS JOURNAL, 50, 2855, 2863 (1928).

but ϕ was previously defined arbitrarily as the ratio of the valence to the radius in Ångström units, so we have

$$\phi_v = \frac{300 \times 4.774 \times 10^{-10}}{10^{-8}}\,\phi = 14.3\phi \qquad (3)$$

In Table I the values of ϕ_v as well as the ionization potentials[2] are given for reference. In the case of the ionization potentials the data refer to the removal of the *last* electron in producing the ion represented by the symbol. The ionizing potential is denoted by V.

Table I

Ionic and Ionizing Potentials (Volts)

	H^+					
ϕ_v	...					
V	13.54					
	Li^+	Be^{++}	B^{3+}	C^{4+}	N^{5+}	
ϕ_v	23.9	92.3	215	380	645	
V	5.37	18.1	37.8	64.2	...	
	Na^+	Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}
ϕ_v	15.0	44.4	85.9	140	210	296
V	5.12	14.97	28.32	44.95	64	...
	K^+	Ca^{++}				
ϕ_v	10.4	28.9				
V	4.32	11.82				
	Rb^+	Sr^{++}				
ϕ_v	9.65	25.3				
V	4.16	10.98				
	Cs^+	Ba^{++}				
ϕ_v	8.45	21.2				
V	3.88	9.96				
	87^+	Ra^{++}				
ϕ_v		...				
V	...	10.23				

The Theoretical Relation between Ionic and Ionizing Potentials.—The theoretical relationship between the ionic and ionizing potentials may be qualitatively derived by using the Bohr model of the atom, augmented by considerations growing out of the more recent picture given by the wave mechanics. According to the considerations of Bohr, the valence electron rotating in its orbit has both kinetic and potential energy. If r is the radius of the orbit, the kinetic energy is $e^2/2r$ and the potential energy is $-e^2/r$. The total work done in bringing up the electron from an infinite distance is the sum of these energies, $-e^2/2r$, and is measured by the ionization potential. In comparing the ionic potential with the ionizing potential, the *potential* energy of the electron is the important quantity,

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[2] Foote and Mohler, *Bull. Nat. Res. Council*, 9, No. 48 (1924).

and this is numerically twice the ionization work. The ionic potential, therefore, will be compared with double the ionization potential.

It is not possible to make a theoretical estimate of the relation between these quantities, however, since the Bohr model gives no information as to the relation of the crystal radius of the ion to the electronic orbit of the neutral atom. A closer approach to this information may be obtained from the wave mechanics conception of the atom.[3]

In Fig. 1, the solid curves of which are taken from Pauling's paper, the electron distribution in the sodium and chloride ions is given as a function of the distance from the nucleus. The distance to which these ions approach each other in the sodium chloride crystal is such that a slight penetration of their electronic fields takes place; that is, the crystal radius r_c corresponds to the distance at which the electron distribution becomes approximately equal to zero, as indicated in the figure. If we assume for the moment that the valence electron of the sodium atom may be added without disturbing the spherical distribution of the *K* and *L* electrons in the ion, according to the dotted, qualitative extension of Pauling's curve, r_e in the figure will represent the electron radius which determines the ionization work. With the situation as represented in the diagram, the doubled ionizing potential should be less than the ionic potential by an amount equivalent to the work done in moving the static electron from r_c to r_e.

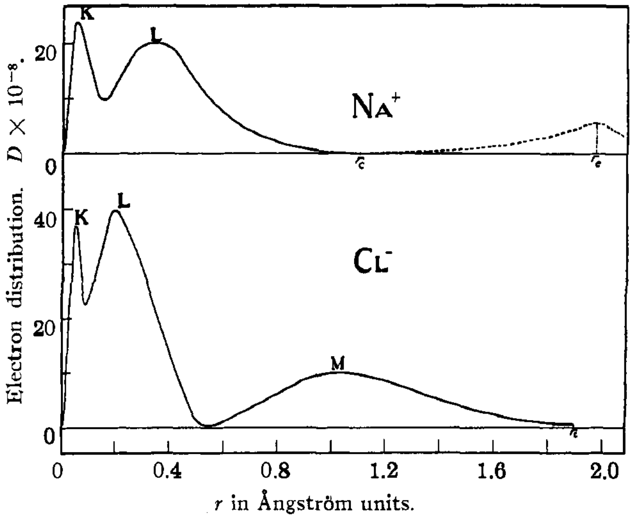

Fig. 1.

That this difference should be definitely related to the ionic potential may be indicated as follows. The work done, *w*, is given by

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[3] Pauling, This Journal, 49, 765 (1927).

$$w = -\int_{r_c}^{r_e} \frac{ze^2dr}{r^2} = ze^2\left(\frac{1}{r_c} - \frac{1}{r_e}\right) \text{ ergs} \tag{4}$$

$$w = \frac{ze^2}{10^7\, r_c}\left(1 - \frac{r_c}{r_e}\right) \text{ joules} \tag{5}$$

but ϕ_v is the potential at r_c and $2V$ is the potential at r_e, so if Δ_v is the difference $\phi_v - 2V$ we have, with e still in e. s. u.

$$w = \frac{\Delta_v e}{3 \times 10^9} = \frac{ze^2}{10^7\, r_c}\left(1 - \frac{r_c}{r_e}\right) \text{ joules} \tag{6}$$

or, from (2)

$$\Delta_v = \phi_v\left(1 - \frac{r_c}{r_e}\right) \text{ volts} \tag{7}$$

Although it is not possible to predict from either atomic model just what value the fraction r_c/r_e will have in general, further consideration of Fig. 1 will furnish an estimate for the limiting case of a rigid ion of lithium-like structure. The minimum in the electron-distribution curve between the peaks associated with the K and L shells corresponds to the crystal radius r_c in an ion having only the K shell, whereas the L peak corresponds to the radius r_e of the valence electron. The difference between these distances divided by the distance of the L maximum should therefore be approximately equal to the factor $1 - (r_c/r_e)$ in Equation 7. When these distances are measured as closely as the original figure permits, both the Na^+ and Cl^- curves give a value of 0.52. In the sodium and chloride ions the K and L shells are quite rigid, and for such a case Equation 7 accordingly becomes

$$\Delta_v = 0.52\phi_v \tag{8}$$

Of the univalent positive ions, the lithium ion is assuredly the most rigid, and it is observed that the equation above corresponds closely to the facts:

$$\phi_v = 23.9 \qquad 2V = 10.74 \qquad \Delta_v = 13.2 = 0.55\phi_v$$

That the relationship cannot be of general applicability, however, is indicated by the consideration that the ions are not rigid. The valence electron has about it an electric field of enormous magnitude, and by its proximity to the ion produces a deformation or polarization which is far greater than the effects produced by light waves or by the proximity of oppositely charged ions. The effect of polarization by electrons has been investigated by Schrödinger.[4] The result of such polarization, in the present case, will be to decrease r_e with respect to r_c; that is, the term $1 - (r_c/r_e)$ (which is equal to Δ_v/ϕ_v) will become smaller as the polarizability of the ion increases. That this actually occurs is shown in Table II, which gives the values of Δ_v/ϕ_v.

It is clear that as far as the fifth series the proportionality factor increases in passing from Group I to the higher groups. The increasing charge and decreasing size of the ions makes the polarizability of these ions steadily

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[4] Schrödinger, *Ann. Physik*, [4] **77**, 43 (1925).

TABLE II

RATIO $\Delta_v:\phi_v$

→Decreasing polarizability→

↑Decreasing polarizability↑

Group	I	II	III	IV	V
Series II	Li^+ 0.55	Be^{++} 0.61	B^{3+} 0.65	C^{4+} 0.66	
III	Na^+ 0.32	Mg^{++} 0.33	Al^{3+} 0.34	Si^{4+} 0.36	P^{5+} 0.39
IV	K^+ 0.173	Ca^{++} 0.183			
V	Rb^+ 0.138	Sr^{++} 0.134			
VI	Cs^+ 0.082	Ba^{++} 0.061			

less. There is no *a priori* basis for estimating the extent of the change in going down a group, but the deformability of the alkali ions, for example, increases rapidly in passing from lithium to cesium,[5] which corresponds to the great decrease in the ratio observed in the table. From the empirical relation between the ionic and the ionizing potentials we may, therefore, reason backward to obtain further information as to the ionic deformabilities.

Empirical Relation of the Potentials.—When, for the ions of a given periodic series, the differences between the ionic potential and the doubled ionizing potential are plotted against the ionic potential, a smooth curve is obtained suggesting a relation of the type

$$\Delta_v = a\phi_v^b \tag{9}$$

Accordingly, if log Δ_v is plotted against log ϕ_v, as in Fig. 2, it is found that the data for the lithium and sodium series give straight lines. The curves are essentially parallel for the periodic Series II, III and IV. The slope becomes about unity for Series V (rubidium and strontium), whereas with cesium and barium the slope is less than unity. Corresponding to the greater polarizability of the ions in going down a group, the curves lie progressively below each other. The curves for the ions of Series II and III are best represented by the equations

$$\text{Series II} \quad \Delta_v = 0.461\phi_v^{1.061}$$
$$\text{Series III} \quad \Delta_v = 0.274\phi_v^{1.055}$$

The data for potassium and calcium undoubtedly establish a similar curve for series IV, which could be extrapolated to estimate the ionizing potential that scandium would have if the third valence electron were in the 4_0 shell, and similarly for the remaining ions in the series.

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[5] Compare the molecular refractions of the ions, for example, Fajans and Joos, *Z. Physik*, **23**, 1 (1924).

When we plot Δ_v against ϕ_v for the ions of a particular group, as shown in the upper left portion of Fig. 2, an almost linear curve is obtained. This curve may be extrapolated to $\Delta_v = 0$, at which condition the ionic potential and doubled ionizing potentials are equal; that is, *the valence electron exerts so great a polarizing effect upon the ion that the electron comes as close to the nucleus as the "surface" of a negatively charged ion does.* At still smaller values of ϕ_v the electron comes inside the crystal radius. From the values of ϕ_v at which $\Delta_v = 0$, it may be calculated that this occurs, for univalent ions, when the crystal radius is 1.99 Å., and, for bivalent ions, when the crystal radius is 1.54 Å. These radii are only 0.3 Å. and 0.2 Å. larger than the radii of the cesium and barium ions, respectively.

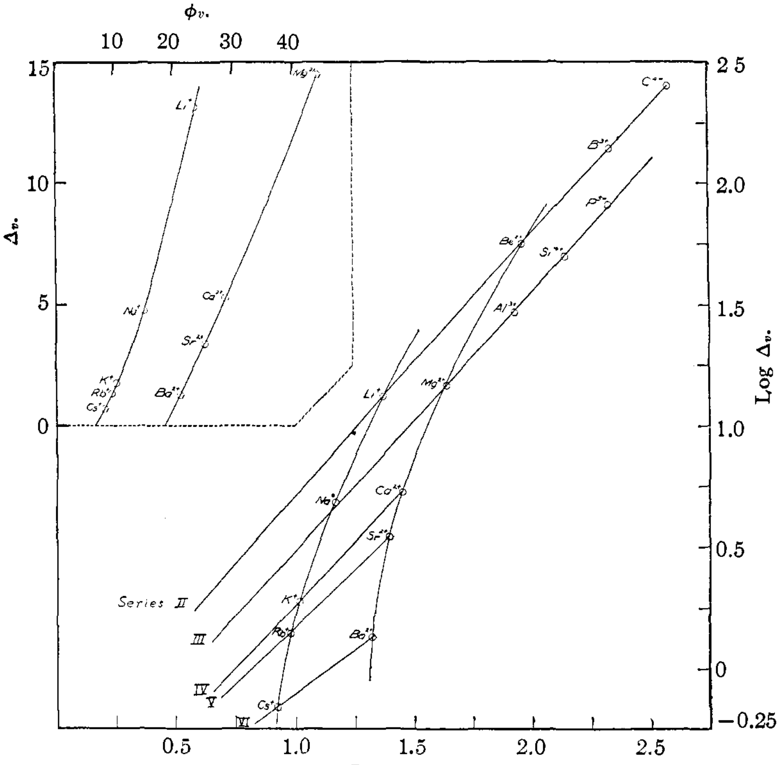

Fig. 2.

The fact that in barium ions the crystal radius is even closer to the critical size (for $\Delta_v = 0$) than it is in cesium may readily account for the fact that, in Fig. 2, the cesium–barium curve has a slope so much less than the curves above it. In spite of the increase in charge, which generally decreases polarizability, the nearer approach of the barium valence electron to the ion "surface" gives a greater polarization in barium than in cesium (Δ_v/ϕ_v = 0.082 for Cs^+ and 0.061 for Ba^{++}).

The Ionic Polarizability.—On account of the close relationship obviously existing between the polarizability of the ions and the difference in the potentials under consideration, it will be interesting to compare the ionic polarizabilities as measured by other types of phenomena. Reference has already been made[4] to the work of Schrödinger, in which the polarization of the ion by the valence electron is calculated from spectral data. Another related type of phenomenon is the ionic refraction, data for which are given by Fajans and Joos.[5] The required data are assembled in Table III, in which p represents the index of refraction as calculated by Schrödinger,[6] p' the ionic refraction[5] and Δ_v/ϕ_v has its previous significance.

TABLE III

IONIC POLARIZABILITIES

	$\frac{\Delta_v}{\phi_v}$	p	p'		$\frac{\Delta_v}{\phi_v}$	p	p'
C^{4+}	0.664	1.4	..	Mg^{++}	0.326	30	..
B^{3+}	.647	2.6	..	Na^+	.32	26(?)	0.50
Be^{++}	.608	4.2	..	K^+	.17	326	2.23
Li^+	.553	15	0.20	Rb^+	.138	711	3.58
Si^{4+}	.358	14	..	Cs^+	.082	1160	6.24
Al^{3+}	.342	19	..				

The data of Schrödinger are plotted against Δ_v/ϕ_v in Fig. 3, from which it is obvious that a smooth curve fits nicely, although the table includes the entire alkali family, together with ions up to Group IV in Series II and III.

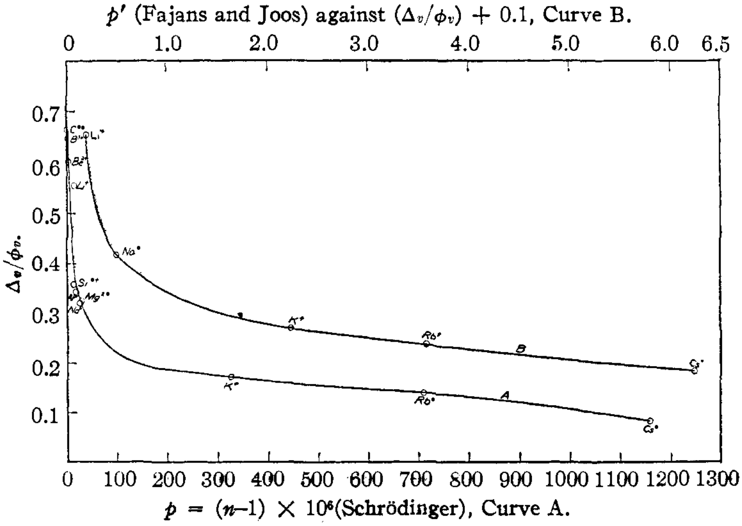

Fig. 3.

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[6] Schrödinger, Ref. 4, p. 66. The data for $(n-1) \times 10^6$ are used.

The ionic refraction of the alkali ions is also plotted against Δ_v/ϕ_v in Fig. 3, the Δ_v/ϕ_v values being increased 0.1 to prevent overlapping. It is obvious that the same sort of systematic relationship exists. The function Δ_v/ϕ_v is, therefore, a useful index to the polarizability of the ions.

Summary

1. The ionic potentials of the inert-gas type ions have been recalculated to volts and compared with ionizing potentials.

2. It is indicated that the valence electron of alkali and alkaline earth ions comes within the crystal radius with ions 0.3 Å. and 0.2 Å. larger than cesium and barium ions, respectively.

3. The ionic polarizability by light or by electrons varies systematically with the fractional difference between the ionic and ionizing potentials, which therefore may be used to estimate the polarizability.

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[CONTRIBUTION FROM THE FRENCH BATTERY COMPANY, MADISON, WISCONSIN]

THE REACTIONS OF AMMONIA ON THE SYSTEM $ZnCl_2$–NH_4Cl–H_2O

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RECEIVED APRIL 23, 1930 PUBLISHED AUGUST 5, 1930

The literature contains much information relating to the composition and preparation of the zinc–ammonium chloride double salts and the oxy and hydroxy forms as well, but little or no attention seems to have been given to the mechanism of the reactions, especially in relation to hydrogen-ion concentration.

It is the object of this investigation to study the formation of insoluble salts in aqueous solution where the ammonium chloride, zinc chloride, ammonia or ammonium hydroxide concentrations are varied. The actual experimental work covered the following ground: (1) determination of the *P*H of aqueous zinc chloride–ammonium chloride solutions in the range of solubility at 20°; (2) determination of the approximate quantity of ammonia which the solutions absorb to the point of formation of a permanent precipitate; (3) determination of *P*H of the supernatant liquors in equilibrium with these precipitates; (4) analysis of the precipitates obtained.

Experimental Procedure

The range of possible concentrations of zinc chloride–ammonium chloride in water at 20° (without supersaturation) was first shown graphically by plotting the aqueous solubilities of zinc chloride–ammonium chloride mixtures on triangular coördinate paper (Fig. 1). The solubility values were as determined by Meerburg.[1] Concentrations were selected to cover the entire range of possible solutions.

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[1] Meerburg, *Z. anorg. Chem.*, **37**, 206 (1903).