

that are best for the polarographic reduction (pH 1-2) would appear to favor the formation of one of the dihydroacids rather than phthalide.

A few experiments were made with terephthalic acid or with sodium terephthalate. When 0.01 M sodium terephthalate was added to an equal volume of a buffer of pH 3.6, most of the acid precipitated but the curve showed a small wave (about 3 mm. = 0.4 microampere). At pH 8 either with or without barium present there was only a faint indication of a wave—so faint that it could not be ascribed to the terephthalate.

Summary

A polarographic study has been made of the reduction of *o*-phthalic acid and its salts over the pH range 1-8, and the following are the principal findings.

1. The distribution of total phthalate between the forms: undissociated molecules, biphthalate ions, and phthalate ions has been calculated from pH 0-8 and the polarographic results have been interpreted with reference to the theoretical distribution.

2. Three reproducible polarographic waves due to phthalate are produced in unbuffered solutions near pH 4 with multivalent cations present. In the absence of the latter, the first

wave obtained is always of a composite nature.

3. Although the number of the waves and the heights of the waves obtained from phthalates depend on the pH of the buffer used, the wave heights from buffered solutions can be used for quantitative studies.

4. The effect of small successive additions of barium chloride, barium acetate, calcium chloride, and lanthanum chloride to well-buffered phthalate at pH 3.6 diminishes the first wave systematically but not linearly.

5. The amount of undissociated phthalic acid that is derived from the polarographic measurements agrees roughly with the theoretical distribution of the undissociated form as a function of pH (Fig. 1).

6. Approximate half wave potentials have been noted for the phthalate waves at various pH values.

7. The slopes of typical curves have been analyzed by constructing the plot of $\log i/(i_d - i)$ against reduction potential. The reduction of the acid at pH 1-2 gives a graph of the same slope as cadmium. The other phthalate waves are apparently of composite nature. The maleic acid wave gives a graph that deviates from the theoretical slope.

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Apparent Volumes of Individual Ions in Aqueous Solution¹

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Introduction

The apparent molar volume of electrolytes at infinite dilution (Φ_0) is one of the properties which can be expected to be exactly additive for a given solvent at definite temperature and pressure. The partition of these values into the apparent volumes of individual ions is of special interest because this is the only kind of volume of individual ions to which exactly defined values can be assigned.

According to the wave mechanical picture of a free atom or ion, the density of its electron distribution diminishes asymptotically as a function of the distance from the nucleus²; thus it is not

(1) Presented in part at the 102nd Meeting of the American Chemical Society, September 11, 1941.

(2) See, e. g., L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940.

possible to assign a definite radius or volume to a free ion. Within a molecule, crystal, or solution, the electronic system of an ion interpenetrates that of the oppositely charged ions or of the solvent molecules. Therefore the partition of lattice distances or crystal volumes into ionic radii² or volumes³ can be performed only when some appropriate definitions or assumptions are made.⁴ The fact that interionic distances in molecules and crystals and the volumes of crystals show systematic deviations from additivity⁵ leads to the same result. However, the value of the volume which an ion at infinite dilution adds to

(3) W. Biltz, "Raumchemie der Festen Stoffe," Verlag Leopold Voss, Leipzig, 1934.

(4) See the criticism [K. Fajans, *Z. physik. Chem.*, **B24**, 125 (1934)] of Wasastjerna's derivation of ionic crystal radii.

(5) K. Fajans, *J. Chem. Phys.*, **9**, 281-283, 379 (1941).

that of the solvent is a definite quantity under given conditions and is independent of the counter ion.

Former derivations of the apparent molar volumes of individual ions are based either on information obtained from the partition of the molar refraction,⁶ or on the assumption that the ratio of the apparent volumes of aqueous cesium and chloride ion⁷ or potassium and fluoride ion,⁸ or cesium and iodide ion⁹ is the same as the ratio of the cubes of the radii assigned to these ions in crystals. The results of these four previous partitions gave values for the apparent volume of the chloride ion of 18 to 23 cc./mole (see also references 10-12).

The starting point of the present approach to the problem is the fact that the apparent volume of ammonium chloride in aqueous solution is approximately equal to the volume of two moles of water and that the temperature dependence of these volumes near 35° is practically identical. When one also considers that on the whole ammonium chloride changes numerous properties of water to a smaller extent than any other electrolyte, and that the ammonium ion seems to fit closely into the structure of liquid water, one is led to the conclusion that the apparent volume of each of the ions, ammonium and chloride, is equal at 35° to that of one mole of water.

1. Apparent Volume of Ammonium Chloride.

—Figure 1 shows the apparent molar volume at infinite dilution (Φ_0) as a function of temperature for ammonium chloride and a few other electrolytes which have Φ_0 values equal to the volume of two moles of water at some temperature near 35°.

The Φ_0 values used in this paper are derived by extrapolation according to the linear relation¹³⁻¹⁶ between Φ and \sqrt{c} (c is the normality of the solution). This relation applies to all salts treated in this paper over a considerable concentration range above 1 *N*. For the alkali halides the extrapolated Φ_0 values are additive within about

(6) W. Geffcken, *Naturwissenschaften*, **19**, 321 (1931).

(7) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(8) Y. Kobayashi, *J. Sci. Hiroshima Univ.*, **9A**, 241 (1939).

(9) O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(10) J. Traube, *Z. anorg. Chem.*, **8**, 73 (1895).

(11) K. Fajans, *Naturwissenschaften*, **9**, 729 (1921).

(12) J. W. Ingham, *J. Chem. Soc.*, 2059 (1929).

(13) O. Masson, *Phil. Mag.*, **8**, 218 (1929).

(14) O. Redlich, *Naturwissenschaften*, **19**, 251 (1931); *J. Phys. Chem.*, **44**, 619 (1940); O. Redlich and P. Rosenfeld, *Z. physik. Chem.*, **A155**, 65 (1931); *Z. Elektrochem.*, **37**, 705 (1931).

(15) W. Geffcken, see reference 6 and *Z. physik. Chem.*, **A155**, 1 (1931).

(16) A. F. Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

0.2 cc./mole¹⁵; thus they give a set consistent in itself although they are not true Φ_0 values.¹⁷

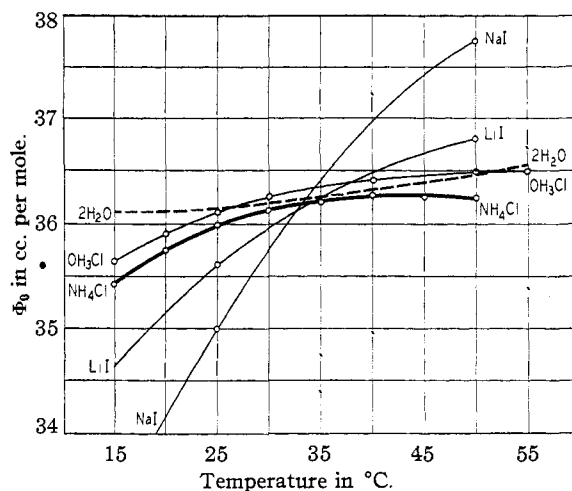


Fig. 1.—Comparison of the temperature dependence of the apparent molar volume (Φ_0) of aqueous solutions of ammonium chloride and other electrolytes at infinite dilution¹⁷ with that of two moles of water.

The difference between the similarly extrapolated Φ_0 values for potassium nitrate (38.0 cc. at 25°) and sodium nitrate (27.4 cc.) deviates considerably from the corresponding average difference between the halides (10.1 cc.). Even larger deviations occur with the hydroxides, sulfates and carbonates. Obviously the curves for these electrolytes exhibit an individual behavior in the dilute region, also. In such cases an average was taken to obtain the Φ_0 values for the individual ions.

The Φ vs. \sqrt{c} curves for most strong acids have a complicated form.^{5,32} However, the curve for hydrochloric acid at 25° measured by G. Hedstrand (see Geffcken¹⁵) is linear above 1 *N* and was used for the derivation of the corresponding Φ_0 value of the hydrogen ion.

The Φ_0 vs. t curve for hydroxonium chloride in Fig. 1 is based on the values of hydrochloric acid given by Åkerlöf and Teare¹³ for 5-16 molal (*m*) solutions from 0-80°. The extrapolation to Φ_0 of

(17) Extrapolation to infinite dilution from density data at 25° for dilute solutions (down to 0.01 *N*) of sodium and potassium chlorides, sodium bromide and ammonium nitrate gives values which differ from the Φ_0 values mentioned above by 0.45, 0.32, -0.1 and -0.3 cc./mole, respectively [see A. Kruis, *Z. physik. Chem.*, **B34**, 1 (1936), and the earlier papers quoted there]. Since these differences go parallel to the differences (0.5, 0.3, -0.1 and -0.7) between the slope of the Φ vs. \sqrt{c} curve in the concentrated region and the limiting slope (1.9 cc. \times (mole/liter)^{-1/2}), one can try to derive true Φ_0 values for other electrolytes by extending this parallelism. One obtains, e. g., a better additivity for hydroxides and nitrates; however, until more experimental data for dilute solutions are available, the method of extrapolation mentioned above is preferable.

(18) G. Åkerlöf and J. Teare, *THIS JOURNAL*, **60**, 1226 (1938).

the Φ vs. \sqrt{c} lines from these high concentrations is less certain than from Hedestrand's values at 25°. The volume of a mole of water at the corresponding temperature was added to the Φ_0 values of hydrochloric acid.

The curve for ammonium chloride of Fig. 1 is based on density measurements of Shinkichi and Horiba¹⁹ from 0–50° at 10° intervals, and of Shibata and Hölemann²⁰ at 25, 35 and 45°, both for c values between 1 and 5 mole/liter.²¹ The values for Φ_0 extrapolated linearly from these data are given in Fig. 1 and it can be seen that they fit excellently into one curve.

The sources of the other values used in this paper are given in connection with Tables II–IV.

The comparison of the Φ_0 vs. t curves of electrolytes with that of two moles of pure water in Fig. 1 shows that the curve of ammonium chloride at 35° approaches that of water most closely: the absolute values are 36.2 and 36.25 cc., respectively, and the slope of the ammonium chloride curve at 35° is, within the experimental errors, equal to that of water (0.012 cc./deg.). The comparison of the numerical values is given in Table I.

TABLE I

APPARENT VOLUME OF AMMONIUM CHLORIDE AND HYDROXONIUM CHLORIDE AT INFINITE DILUTION¹⁷ IN CC./MOLE AND THE VOLUME OF 2 MOLES OF LIQUID WATER

t , °C.	NH ₄ Cl ^{19,20}	2H ₂ O	OH ₂ Cl ¹⁸
0	33.9	36.04	34.3
10	35.0	36.04	35.3
20	35.75	36.10	35.9
25	36.0	36.14	36.2 ¹⁵
30	36.1	36.19	36.2
35	36.2	36.25	..
40	36.3	36.31	36.4
45	36.25	36.39	..
50	36.25	36.47	36.5
60	...	36.65	36.4

The curve for hydroxonium chloride is next nearest to that for two moles of water; the latter intersects it (at 26 and 52°) as well as the curves for lithium iodide (34°) and sodium iodide (33°). However, at these temperatures of intersection the slope of the water curve differs distinctly from that

(19) Shinkichi and Horiba, *J. Coll. Sci. Tokyo*, **2**, 1 (1917).

(20) Z. Shibata and P. Hölemann, *Z. physik. Chem.*, **B13**, 347 (1931).

(21) Φ values of ammonium chloride for concentrations between 0.1 and 4 N at 25° have been obtained by J. N. Pearce and G. G. Pumpkin, *THIS JOURNAL*, **59**, 1221 (1937). They agree well with the above-mentioned measurements of Shibata and Hölemann; the slope of the Φ vs. \sqrt{c} line above 1 N is 1.5 for both. The slope is about 1.7 between 1 and 0.1 N and the corresponding Φ_0 value is about 0.2 cc. smaller than that given in Table I [see also A. B. Lamb and R. E. Lee, *ibid.*, **35**, 1666 (1913), and G. Jones and S. K. Talley, *ibid.* **55** 624 (1933)].

of hydroxonium chloride and strongly from those of the two iodides.

We can show now that dissolved ammonium chloride has very little effect on a number of other properties of liquid water.

2. Other Properties of Dissolved Ammonium Chloride.—From measurements of the heat of dilution, Frank and Robinson²² calculated ΔS , the difference between the partial molal entropy of water in aqueous solutions of electrolytes (S_1) and the entropy of pure water (S_1^0). They give these values for 19 mono-monovalent strong electrolytes at concentrations between 0.1 and 4 m at 25°. Ammonium chloride and hydrochloric acid are among the five electrolytes (lithium chloride, sodium hydroxide and potassium hydroxide are the other three) for which the increase or decrease of the entropy of the water of dilution has the smallest absolute value. Frank and Robinson state: "the ammonium ion exerts a stabilizing influence on the water structure by virtue of its tetrahedral shape and ability to form hydrogen bonds."

This stabilizing action is indicated by the fact that the ΔS for ammonium chloride has the distinct negative value -0.02 cal. \times deg.⁻¹ \times mole⁻¹ at 2 m , this being the minimum of the curve (ΔS is zero at 0 and 3.5 m). On the other hand, for sodium iodide, whose Φ_0 value also approaches V_{2H_2O} , the ΔS vs. m curve rises steeply from the value zero at infinite dilution to $+0.14$ at 3 m .

On the whole, one can state that at 25° both the ammonium and chloride ion produce but little change in the entropy, *i. e.*, in the order of the particles within the liquid.²³

The viscosity of solutions of strong electrolytes is partly higher and partly lower than that of pure water (see Fig. 2). Among 25 mono-monovalent electrolytes, the data for which at 25° were taken from the "International Critical Tables," ammonium chloride solutions show the smallest deviation (less than 1%) from water.²⁴ The curve for ammonium chloride at 30°, obtained by interpolation of the data from "I. C. T." for 0, 10, 25 and 40°, approaches that of pure water below 2 m

(22) H. S. Frank and A. L. Robinson, *J. Chem. Phys.*, **8**, 933 (1940).

(23) Concerning the possibility of the balancing of the effects of the two ions, see Section 5.

(24) See also the attempt of Ingham¹² to connect the viscosity of highly concentrated solutions of ammonium and chloride ions with their apparent volumes. He discusses the alternatives that the apparent volumes of the two ions are equal to each other (22 cc./mole) and that the viscosity of water is lowered by one ion as much as it is raised by the other ion.

still closer than that for 25°. However, the viscosity of hydrochloric acid solutions increases strongly with concentration and for the 4 *m* solution is higher than for water by as much as 24%.

Stewart²⁵ has measured the *electron diffraction* of water and of solutions of sixteen electrolytes. His results show that ammonium chloride and ammonium acetate change the curve of the intensity *vs.* the angle of diffraction less than any of the other electrolytes.

Some indication is given also by *infrared absorption*. From measurements of Plyler and Barr,^{25a} the following shifts of the maximum of the 4.72 μ band of liquid water can be deduced for 5 *N* solutions: for ammonium fluoride -0.10μ , chloride $+0.04$, bromide $+0.08$, for sodium bromide $+0.14 \mu$. Thus the absolute value of the shift is smallest for ammonium chloride.

3. Structure of Water and Role of Deformation Phenomena in the Hydration of Ions.—As ammonium chloride changes the properties of water so little, it is of importance to find out the relation of each of its ions to the solvent water.

According to Bernal and Fowler,⁷ the tetrahedral arrangement of the water molecules in the tridymite form of ice is preserved to some extent in liquid water. They have concluded that the higher the temperature²⁶ or the concentration of dissolved electrolytes, the more the loose structure is broken in favor of arrangements of higher coordination number. Bernal and Fowler consider the nearly tetrahedral angle between the lines connecting the two protons with the oxygen nucleus as one of the factors responsible for this arrangement.

The interaction of two water molecules can be expected to lead to the following deformation effects as a result of the mobility²⁷ of the protons within the electronic shell and the polarizability of the latter. The shell of water molecule 1 will

(25) G. W. Stewart, *J. Chem. Phys.*, **7**, 869 (1939).

(25a) E. K. Plyler and E. S. Barr, *J. Chem. Phys.*, **6**, 316 (1938).

(26) See also J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938).

(27) A displacement of protons was used as an explanation of the wurtzite structure and instability of solid ammonium fluoride [see V. M. Goldschmidt, *Norske Videnskaps Akad. Oslo*, No. 2, p. 67 (1926)], and of the peculiarities of ammonium and hydrxonium salts (acids) in respect to their refraction and other properties [K. Fajans, *Z. physik. Chem.*, **A137**, 361 (1928)]. A direct indication for such a proton displacement in case of bonded water molecules is given by the interpretation [P. C. Cross, J. Burnham and P. A. Leighton, *THIS JOURNAL*, **59**, 1134 (1937)] of Raman frequencies leading to an O-H distance 0.986 Å. as compared with that in water vapor 0.958 Å. [D. M. Dennison, *Rev. Mod. Phys.*, **12**, 175 (1940)]. Concerning the deformation of electronic shells see, *e. g.*, K. Fajans, "Chemical Forces and Optical Properties of Substances," Cornell Lectures, 1931.

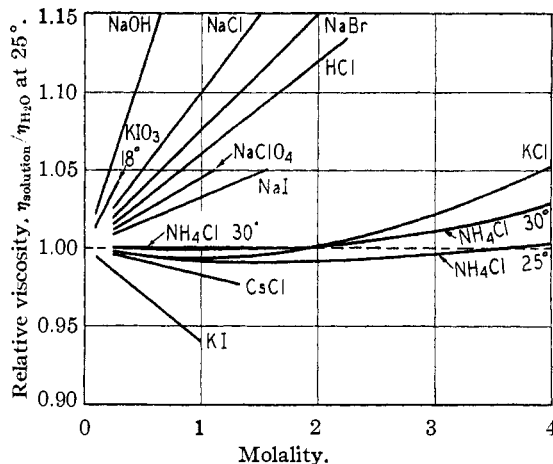


Fig. 2.—Viscosity of aqueous solutions of electrolytes relative to that of water at 25° (for ammonium chloride also at 30°) for different concentrations.

be attracted in the direction of one of the protons of molecule 2, and this proton will be displaced towards molecule 1. One can expect the deformation energy involved to be of importance in the total energy of binding of the water molecules and more generally in that of the "hydrogen bond" or "hydrogen bridge" or "bonding by the proton."²⁸

So it is likely that in an aqueous solution of an ammonium ion, one water molecule is oriented in the direction of each of the four protons (tetrahedrally arranged within the electronic shell of that ion) and that the protons are shifted toward the water molecules. Therefore the ammonium ion can be expected to fit into the tetrahedral structure of liquid water. In section 4, some properties of the dissolved ammonium ion will be discussed which indicate clearly that its relation to the surrounding water is different from that of alkali ions. In the case of the hydration of these spherically symmetrical cations, there is no obvious reason for strong directed forces, and probably more than four water molecules surround the larger alkali ions in the first sphere.

However, the electronic shells of the halide ions, interpenetrating those of the water molecules, will be deformed in the direction of the neighboring protons which in turn will be displaced toward the ion.²⁹ It is thus conceivable, although less evi-

(28) W. M. Latimer and W. H. Rodebush, *THIS JOURNAL*, **42**, 1431 (1920); Pauling²; M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936); E. Bauer and M. Magat, *J. Phys. Radium*, **9**, 319 (1938).

(29) The small fluoride ion displaces the proton of a neighboring water molecule so strongly that a noticeable hydrolysis of fluoride solutions results. For similar reasons the doubly charged oxygen ion is practically completely changed in aqueous solution to the hydroxide ion.

dent than for the ammonium ion, that due to these directed forces the chloride ion also fits into the structure of the liquid.³⁰

4. Properties of the Aqueous Ammonium Ion.—A number of properties of aqueous solutions of ammonium salts can be connected with the idea that the ammonium ion fits into the tetrahedral structure of liquid water without increasing its packing density. Only a brief indication will be made here.

(a) While the volumes of numerous crystallized ammonium salts are very nearly equal to those of rubidium salts (see *e. g.*, Table V), the Φ_0 values of the ammonium salts are larger than those of the rubidium salts by 5.9 cc. at 0°, 4.3 at 25° and 3.4 at 50°. The rubidium ion obviously disturbs the loose tetrahedral structure of liquid water thus causing a higher coordination number and smaller apparent volume. Rise of temperature brings about an increase of the coordination number of pure water,²⁶ and therefore diminishes the influence of the breaking effect of the ions; this explains why $\Phi_{\text{NH}_4^+} - \Phi_{\text{Rb}^+}$ decreases with increasing temperature.

The fact that ammonium salts diminish the compressibility of water to a considerably smaller extent than rubidium salts⁴¹ must also be connected with the difference in coordination number.

(b) The increase of the apparent volume of electrolytes with concentration is due mainly to the screening of the electrostrictive^{30a} action of the ions on water by the approach of the counter ions.¹⁴ Thus one can expect that one of the factors determining the slope of the Φ vs. \sqrt{c} line (concerning other factors see reference 5) will be the strength of the electrostriction in dilute solution. The fact that these slopes at 25° for ammonium chloride (1.5 cc. \times (mole/liter)^{-1/2}),²⁰ bromide (1.2),³¹ and iodide (0.8)³¹ are considerably smaller³² than those for the corresponding rubidium salts (2.3, 2.0 and 1.6, respectively)¹⁵ must

(30) The polarization of the electronic shells of the noble gases by the protons of water must be one of the factors responsible for the formation of hydrates of noble gases. It is of interest to note that a hydrate of the least polarizable rare gas, neon, is not known, while the stability of the others [*A. ca.* 5H₂O, Kr·5H₂O, and Xe·6 or 7H₂O, see de Forcrand, *Compt. rend.*, **181**, 15 (1925)] increases with the polarizability of the rare gas.

(30a) In this paper the term electrostriction is used as by P. Drude and W. Nernst (1894) in the broader sense, not excluding the diminution of the volume of the water due to the breaking of its loose structure by dissolved ions; see, however, ref. 37.

(31) Calculated from the density data in the "1. C. T."

(32) Ammonium nitrate has, even in very dilute solution (0.01 *N*), a slope (1.4) which is considerably smaller than the limiting slope of 1.9 [see Kruis¹⁷ and W. Geffcken and D. Price, *Z. physik. Chem.*, **B26**, 81 (1934)].

be at least partly due to the smaller breaking action²⁵ of the ammonium ion.

(c) Ammonium nitrate does not have the maximum in the curve of apparent molar refraction vs. concentration which is shown by the alkali halides³³ as well as by potassium nitrate,³⁴ thalious nitrate,³⁴ and silver nitrate³⁵ at about 1 *m*. As the maximum was connected³³ with the action of ions on water, this behavior of ammonium nitrate indicates a peculiarity in the hydration of the ammonium ion.³⁶

5. Empirical Relation Concerning the Temperature Dependence of Φ_0 .—It was shown in sections 1 and 2 that among numerous dissolved mono-monovalent electrolytes, ammonium chloride near 35° resembles water most in respect to apparent volume and its temperature dependence, and is among the salts which produce the smallest change in entropy, viscosity, infrared absorption, and electron diffraction. This variety of properties makes it improbable that the peculiarities of ammonium chloride are due to a balancing of influences of opposite sign exerted by its two ions.

As to the ammonium ion, it seems plausible (see section 3) that with its four protons, it fits into the tetrahedral structure of liquid water, and that this is responsible for the differences in the behavior of the dissolved ammonium ion as compared with its nearest analog, the rubidium ion (see section 4).

From these statements one can conclude that near 35° both the ammonium and the chloride ion approach water in respect to the properties involved.

We wish now to show that, in all probability, the close coincidence of the temperature coefficients of the volumes of ammonium chloride and of 2 moles of water near 35° is due to the equality of the apparent volume of each of the ions with the volume of one mole of water.

In Fig. 3 the experimental values of Φ_0 relative to their values at 25° are plotted as a function of temperature. From the curves given and the corresponding curves for other alkali halides, the

(33) A. Kruis, *Z. physik. Chem.*, **B34**, 13, 82 (1936).

(34) A. E. Brodskii, Zh. M. Shershever and N. S. Filippova, *Chem. Abstracts*, **33**, 9074 (1939).

(35) N. Bauer, "Dissertation," University of Michigan, 1941.

(36) See also the abnormal behavior of ammonium nitrate in respect to the dependence of partial molar volume on pressure [L. H. Adams and R. E. Gibson, *THIS JOURNAL*, **54**, 4520 (1932)]. Significant is the crossing of the curves of the osmotic coefficient vs. concentration of ammonium halides and ammonium nitrate with those of the corresponding rubidium salts [G. Scatchard and S. S. Prentiss, *ibid.*, **54**, 2696 (1932); **55**, 4355 (1933)].

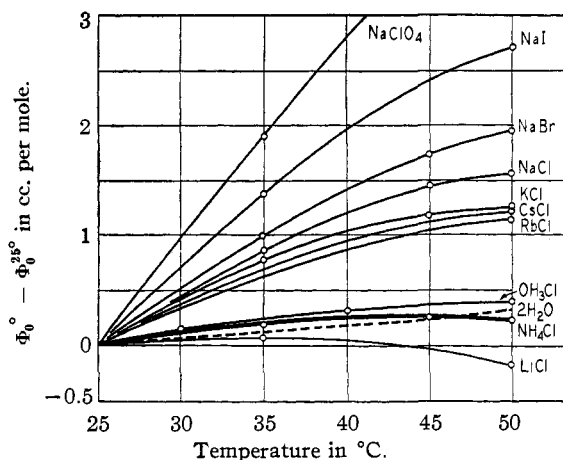


Fig. 3.—Change of the apparent molar volume of several electrolytes at infinite dilution¹⁷ from 25° to the temperature of the abscissa.

$d\Phi_0/dt$ values were derived for 35°. Since the Φ_0 values at various temperatures are additive within the errors involved,¹⁵ so also are the derived temperature coefficients. Thus the $d\Phi_0/dt$ values for ammonium bromide, iodide and perchlorate, not known experimentally, could be derived from that of ammonium chloride and the average differences between the chloride ion and the other anions.

In Fig. 4 the differences between the $d\Phi_0/dt$ values for a number of salts (the alkali and hydroxonium chlorides as well as the halides, the nitrate and the perchlorate of ammonium) and the dV_{2H_2O}/dt are plotted against $\Delta_{salt} = \Phi_0 - V_{2H_2O}$. One finds that the curves connecting the values for ammonium chloride, bromide and iodide for which $\Delta_{salt} \geq 0$, and those for sodium, potassium and rubidium chlorides for which $\Delta_{salt} < 0$ are approximately linear. Since the Φ_0 values are additive, obviously this linearity for the salts with the common ion can be expressed by the following equation for single ions

$$d\Delta_{ion}/dt = a + b |\Delta_{ion}| \quad (1)$$

where $\Delta_{ion} = \Phi_{ion} - V_{H_2O}$ and the values of a and b are different for the alkali and halide ions.

The behavior of cesium chloride requires an explanation. In Fig. 3 the curves of the chlorides, for which measurements of Baxter (see reference following Table IV) and Geffcken¹⁵ show good agreement, have the abnormal sequence sodium, potassium, cesium, rubidium. Therefore in Fig. 4 cesium chloride does not appear on the continuation of the straight line connecting the three other alkali chlorides. This does not

contradict Eq. (1) if we assume that Δ_{ion} has a different sign for cesium than for the other alkali ions and that for an imaginary alkali ion (alk^+), for which $\Phi_{Rb^+} < \Phi_{alk^+} < \Phi_{Cs^+}$ and $\Delta_{alk^+} = 0$, the $d\Delta_{alk^+}/dt$ has the smallest value among the alkali ions.

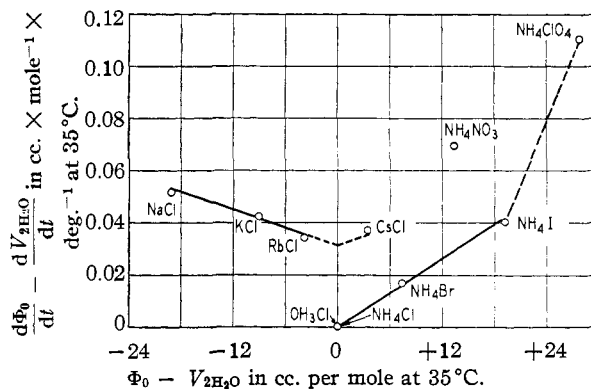


Fig. 4—The figure shows, for ammonium halides and alkali chlorides in aqueous solution at 35°, that the greater the absolute value of the difference between their apparent molar volume (Φ_0) and the volume of two moles of water, the more the temperature dependence of Φ_0 exceeds that of V_{2H_2O} .

This leads to the dotted parts of the alkali chloride lines from which it is seen that the smallest value for the alkali chlorides at 35° occurs at about $|\Delta_{alk^+} + \Delta_{Cl^-}| = 0$. Since $\Delta_{alk^+} = 0$, it follows that $\Delta_{Cl^-} \sim 0$. Therefore the following must be nearly true (see end of section 6) at 35°:

$$\Phi_{Cl^-} = \Phi_{NH_4^+} = \Phi_{alk^+} = V_{H_2O} = 18.1 \text{ cc./mole} \quad (2)$$

These semi-quantitative conclusions are in full agreement with the idea of the fitting of the ammonium ion as well as of the chloride ion into the structure of liquid water. The meaning of Eq. (1) can be expressed as follows. The more the apparent volume of an alkali or halide ion differs from the volume of one mole of water, the more its $d\Phi_{ion}/dt$ value differs from dV_{H_2O}/dt .

Taking into account the indications concerning the similarity of the properties of aqueous ammonium chloride and water (see Section 2), it appears reasonable to assume that at 35°

$$d\Phi_{Cl^-}/dt = d\Phi_{NH_4^+}/dt = dV_{H_2O}/dt = 0.006 \text{ cc./deg.} \quad (3)$$

This leads to the following values of the constants in (1)

$$a_{hal^-} = 0 \quad b_{hal^-} = 0.0022 \text{ deg.}^{-1} \quad (4a)$$

$$a_{alk^+} = 0.031 \text{ cc.} \times \text{deg.}^{-1} \quad b_{alk^+} = 0.0011 \text{ deg.}^{-1} \quad (4b)$$

As a consequence, $d\Delta_{alk^+}/dt = a_{alk^+} = 0.031 \text{ cc.} \times \text{deg.}^{-1}$. This and relation (3) indicate that

a halide ion having the apparent volume of water at 35° also has the same temperature coefficient as water, as well as does the ammonium ion, but an alkali ion of the same volume would have a higher temperature coefficient (see the explanation in Section 6).

The constants (4b) which were derived from the experimental values for sodium chloride, potassium chloride and rubidium chloride when used in Eq. (1) with the value of Φ_{Cs^+} (see Table II), give a calculated value of $d\Phi_0/dt$ for cesium chloride of 0.048 as compared with the experimental value of 0.050. The agreement is better than one would expect, in view of the approximate nature of the above quantitative relations and of the experimental errors involved.

6. Discussion of the Temperature Dependence of Φ_0 .—The partition given by relation (2) can be supported by theoretical considerations. Gibson and Loeffler³⁷ pointed out as the two opposing factors necessary to explain the maximum in the Φ_0 vs. t curves (seen in Fig. 1 for ammonium chloride and hydroxonium chloride, in Fig. 5 for Sr^{++}).

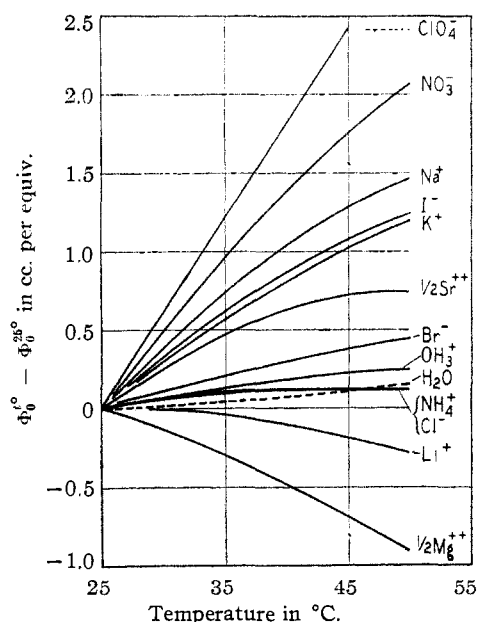


Fig. 5.—The temperature dependence of the apparent volume of individual ions, based on the provisional assumption that between 25° and 50° the $d\Phi_0/dt$ values for the ammonium and chloride ions equal each other.

(a) The effect of the ions in increasing the packing density of water, which gives a negative component to the apparent volume of the ions. This

(37) R. E. Gibson and O. H. Loeffler, *THIS JOURNAL*, **63**, 443, 2287 (1941).

component will be of decreasing importance with rising temperature since this rise favors the breaking of the tetrahedral structure of pure water (see Section 4a). Therefore effect (a) explains why the $d\Phi_0/dt$ values of electrolytes can be positive. The experimental results of Gibson and Loeffler led them to the conclusion that effect (a) is a little stronger for the bromide than for the chloride ion.

(b) The attractive forces between the ions and water dipoles. The thermal expansibility diminishes in general with increasing forces; thus this effect tends to diminish the slope of the Φ_0 vs. t curves, and if the forces are sufficiently strong, it can overbalance the influence of (a) and even cause a negative $d\Phi_0/dt$ (see the curve for lithium chloride in Fig. 3 and for Li^+ and Mg^{++} in Fig. 5).

Besides effects (a) and (b), the following factors must be taken into consideration.

(c) From the result that the gradation of the $d\Phi_0/dt$ values is $Cl^- < Br^- < I^- < ClO_4^-$ (see Figs. 3 and 4) while that for the temperature dependence of the apparent molar refraction (dR/dt) is³⁸ $ClO_4^- < Cl^- < Br^- < I^-$, one can conclude that the water dipoles have a distinct tightening effect on dissolved easily polarizable anions analogous to the tightening of anions by cations.⁵ This effect should add to the $d\Phi_0/dt$ values of anions a positive component which increases with the polarizability of the anion.³⁹

(d) The loosening effect of water dipoles on cations can be assumed to contribute to the expansibility of electrolyte solutions a negative component dependent on the polarizability of the cation.

In order to understand the experimental gradation of the $d\Phi_0/dt$ values of different ions we list below also the gradations in respect to the strength of the effects (b),^{14,48} (c) and (d) which can be theoretically predicted; the signs + and - indicate whether the effect has an increasing or decreasing influence on $d\Phi_0/dt$

$$(d\Phi_0/dt): \quad Cl^- < Br^- < I^- < NO_3^- < ClO_4^- \quad (5)$$

$$(d\Phi_0/dt): \quad Na^+ > K^+ > Cs^+ > Rb^+ > NH_4^+ \quad (6)$$

$$(b), -: \quad Cl^- > Br^- > I^- > ClO_4^- \quad (7)$$

$$(b), -: \quad Na^+ > K^+ > Rb^+ > Cs^+ \quad (8)$$

$$(c), +: \quad ClO_4^- < Cl^- < Br^- < I^- \quad (9)$$

$$(d), -: \quad Na^+ < K^+ < Rb^+ < Cs^+ \quad (10)$$

(38) K. Fajans, P. Hölemann and Z. Shibata, *Z. physik. Chem.*, **B13**, 362, 365 (1931).

(39) This will be discussed in a future paper, and it will be shown that the peculiar gradation of the expansion coefficients of solid alkali halides [see K. Fajans and H. Grimm, *Z. Physik*, **2**, 308 (1920)] is also due to the influence of the polarization of ions.

The effects (c) and (d) influence the "true volume" of the ions and the change of the apparent molar refraction (R) with temperature can be taken as a measure of the order of magnitude of these effects, although dR/dt is influenced also by the effect of the ions on water. One finds³⁸ for the fraction $(R_{45^\circ} - R_{25^\circ})/(\Phi_{45^\circ} - \Phi_{25^\circ})$ the values: 0.017 for sodium perchlorate, 0.06 to 0.07 for five alkali halides, and 0.2 for ammonium chloride.

Thus the effects (c) and (d) contribute only a small fraction to the large positive slopes in Figs. 3 and 5, which therefore must be due mainly to effect (a)+.

From the fact that among the alkali ions Na^+ has the largest $d\Phi_0/dt$ value although it exerts the strongest forces on the water (effect b), it follows that effect (a) must be stronger for Na^+ than for the larger alkali ions. Lithium ion is not included in this discussion for reasons mentioned in Section 8c.

In the case of the anions, the increase of $d\Phi_0/dt$ with increasing size of the ions could be due to the increasing influence of the forces (effect b). Thus it is not possible, without a quantitative treatment, to obtain definite information about the gradation of effect (a) beyond the indication of Gibson and Loeffler that this effect is stronger for the bromide than for the chloride ion. However, the slopes for the individual ions given in Fig. 5 show that near 35° not only the sodium but also the perchlorate ion has a large positive slope.⁴⁰ As the perchlorate like other ions must considerably increase the forces within the liquid, the large slope of ClO_4^- shows that effect (a) is strong for this ion.

So one sees that ClO_4^- which is much larger and Na^+ which is considerably smaller than the water molecule, both exert strong breaking effects^{40a} and in Fig. 5 show the most positive $d\Phi_0/dt$ values for the anions and cations, respectively.

We arrive at the conclusion that the size of

(40) Although Fig. 5 is based on the provisional stipulation that the apparent volume of the ammonium and chloride ion are also equal to each other at temperatures different from 35° , it cannot be so much in error as to leave any doubt concerning the above statement.

(40a) An indication in the same direction is given by the observation that NaClO_4 has a stronger effect on the absorption of the 3μ band of water than KCl or MgCl_2 [see E. Ganz, *Ann. Physik*, **28**, 445 (1937)]. The result of R. Suhrmann and F. Breyer [*Z. physik. Chem.*, **B20**, 17 (1933)] based also on infrared absorption shows that the strength of the "Depolymerization effect" of ions on water, which seems to be identical with the breaking effect, has the gradation $\text{Cl}^- < \text{Br}^- < \text{I}^-$. See also A. M. Buswell, R. C. Gore and W. H. Rodebush, *J. Phys. Chem.*, **45**, 543 (1941).

the ions relative to water is of importance for the distortion of the water structure. This is also strongly supported by the following gradation, shown by the data of Frank and Robinson,²² of the change which ions exert on the entropy of water, *i. e.*, on the order of the arrangement of its molecules: $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{NO}_3^-$ and $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+$.

The small slope for ammonium chloride near 35° is thus in full agreement with the main conclusion of this paper according to which both of its ions fit into the water structure.

For the ammonium ion one can assume that it does not extensively break the tetrahedral arrangement of water molecules and even partly stabilizes it,²² *i. e.*, hinders the increase of the coordination number of pure water with rise of temperature. It is easily seen, although it may appear surprising, that this stabilizing effect gives a positive component to the $d\Phi_0/dt$ value just as the breaking effect (a) does. Thus one can understand why $d\Phi_{\text{NH}_4^+}/dt$ is positive (see relation 3), in spite of the negative influence of effect (b)⁴¹ and (d).

The fact that K^+ , Rb^+ and Cs^+ , which are nearest to NH_4^+ in respect to forces and size, have considerably higher $d\Phi_0/dt$ values than the latter shows clearly that in a quantitative respect the influence of the breaking effect on $d\Phi_0/dt$ is stronger than that of the stabilizing effect.

The positive temperature coefficient of the chloride ion (see relation 3) can be due to the overbalancing of the negative effect (b), partly by effect (c) and partly either by a stabilizing effect or by a breaking effect.

A future quantitative estimation of the different effects will allow a more detailed discussion of the Φ_0 vs. t curves and will show the degree of accuracy⁴² of relation (2) and (3).

Taking into account the variety of effects involved, one can understand that the simple linear relation (1) for the halide ions does not apply to anions of other structure, *e. g.*, perchlorate, nitrate (Fig. 4), formate and acetate.

7. Apparent Volume of Individual Ions.—

On the basis of relation (2), the following table is obtained.

(41) That the ions of ammonium chloride exert stronger forces on water molecules than the latter on each other is shown by the fact that the compressibility of water is decreased by dissolved ammonium chloride [see B. Lunden, *Svensk. Kem. Tid.*, **53**, 86 (1941)].

(42) The use of true Φ_0 values (see ref. 17) may cause a small change in the partition and in the temperature at which relations (2) and (3) hold best. The viscosity curve of ammonium chloride in Fig. 2 approaches water most closely not at 35° but at 30° .

TABLE II

APPARENT VOLUMES OF IONS IN INFINITELY DILUTE¹⁷
AQUEOUS SOLUTIONS AT 35° IN CC./EQUIVALENT

$\frac{1}{2}\text{Ba}^{++}$	-5.8	OH^-	-4.6
Li^+	-0.9	Cl^-	18.1
Na^+	-0.8	Br^-	25.3
H^+	+0.1	I^-	37.2
Rb^+	14.3	ClO_4^-	45.6
NH_4^+	18.1		
OH_3^+	18.2		
Cs^+	21.7		

As a considerably greater number of exact density data are available for 25° and other temperatures than at 35°, *provisional* individual ionic values were obtained by equating the apparent volume of the ammonium ion and chloride ion at other temperatures also (see Section 6).

TABLE III

Φ_0 VALUES FOR INDIVIDUAL IONS IN AQUEOUS SOLUTION
AT 25° IN CC./EQUIVALENT

H^+	0.2	F^-	-1.8
Li^+	-0.9	Cl^-	18.0
Na^+	-1.7	Br^-	25.1
K^+	8.4	I^-	36.7
Rb^+	13.7	OH^-	-4.8
Cs^+	21.1	NO_3^-	29.4
NH_4^+	18.0	ClO_3^-	35.1
OH_3^+	18.3	BrO_3^-	36.4
Ag^+	-1.2	IO_3^-	25.1
Tl^+	9.4	ClO_4^-	44.5
$\frac{1}{2}\text{Be}^{++}$	-7	MnO_4^-	ca. 42
$\frac{1}{2}\text{Mg}^{++}$	-10.7	HSO_4^-	26.5
$\frac{1}{2}\text{Ca}^{++}$	-9.5	HCO_3^-	22.3
$\frac{1}{2}\text{Sr}^{++}$	-9.2	CNS^-	40.6
$\frac{1}{2}\text{Ba}^{++}$	-6.6	HCOO^-	26.3
$\frac{1}{2}\text{Mn}^{++}$	-7	CH_3COO^-	40.5
$\frac{1}{2}\text{Fe}^{++}$	-9	$\frac{1}{2}\text{CO}_3^{--}$	-1.4
$\frac{1}{2}\text{Co}^{++}$	-9	$\frac{1}{2}\text{SO}_4^{--}$	7.7
$\frac{1}{2}\text{Cu}^{++}$	-13.3	$\frac{1}{2}\text{S}_2\text{O}_8^{--}$	ca. 17
$\frac{1}{2}\text{Zn}^{++}$	-13	$\frac{1}{2}\text{C}_2\text{O}_4^{--}$	ca. 8
$\frac{1}{2}\text{Cd}^{++}$	-6.6	$\frac{1}{2}\text{CrO}_4^{--}$	9.1
$\frac{1}{2}\text{Hg}^{++}$	-10	$\frac{1}{2}\text{Cr}_2\text{O}_7^{--}$	36.7
$\frac{1}{2}\text{Pb}^{++}$	-14		
$\frac{1}{3}\text{Al}^{+++}$	-14.3		
$\frac{1}{3}\text{Fe}^{+++}$	-10		

8. Discussion of Individual Φ_0 Values.—The knowledge of the individual Φ_0 values allows one to draw several conclusions.

(a) **Dependence of Individual Φ_0 Values on Temperature.**—On the basis of the provisional assumption that the temperature dependence of the apparent volume of the ammonium and chloride ions are equal, the Φ_0 vs. t curves for other ions can be obtained. Figure 5 gives the resulting curves for a number of ions. The comparison

TABLE IV^a

Φ_0 VALUES FOR 15–20°

-15°		-20°	
NH_4^+	17.7	NH_4^+	17.9
$\frac{1}{3}\text{Cr}^{+++}$	-13	$\frac{1}{2}\text{Ni}^{++}$	-17
Cl^-	17.7	Cl^-	17.9
CN^-	21	N_3^-	25
$\frac{1}{2}\text{SO}_3^{--}$	4	NO_2^-	25
$\frac{1}{2}\text{SeO}_4^{--}$	11	VO_3^-	27
$\frac{1}{2}\text{MoO}_4^{--}$	15	H_2PO_4^-	31
		$\frac{1}{2}\text{WO}_4^{--}$	17
SH^-	19	$\frac{1}{2}\text{SiO}_3$	-2

^a In addition to the references cited in Section 1, the sources of the density data (or Φ values) used in compiling Tables II–IV were as follows: G. P. Baxter, *THIS JOURNAL*, **38**, 70 (1916); A. Heydweiller, *Ann. Physik*, **37**, 739 (1912); J. Traube¹⁰; "International Critical Tables"; Landolt-Börnstein "Tabellen"; Tables Annuelles; and the following more recent publications (in the case of a series of papers by one author, only the latest one is given): G. Åkerlöf and co-workers, *THIS JOURNAL*, **63**, 1086 (1941), [HCl, NaOH, KOH]; R. C. Cantelo and H. E. Phifer, *ibid.*, **55**, 1334 (1933), [CoSO₄]; K. Fajans and co-workers, "Refractometric Investigations," salts investigated are listed in *Z. physik. Chem.*, **B29**, 153 (1935); R. E. Gibson³⁷ and co-workers, [KNO₃, Na₂SO₄, BeSO₄, K₂CrO₄]; F. T. Gucker, Jr., *Chem. Rev.*, **13**, 111 (1933), [LiOH, NaOH, KOH, CaCl₂]; G. Jones and co-workers, *THIS JOURNAL*, **62**, 338 (1940), [KMnO₄]; J. N. Pearce and co-workers, *ibid.*, **59**, 2689 (1937), [KCNS, NH₄Cl, LiNO₃, Li₂SO₄, Na₂SO₄, K₂SO₄, CuSO₄, Ca(NO₃)₂, Al(NO₃)₃]; B. Pesce, *Gazz. chim. ital.*, **65**, 448 (1935), [Ca(NO₃)₂, Cu(NO₃)₂, Sr(ClO₄)₂, Na₂Cr₂O₇]; R. A. Robinson, *THIS JOURNAL*, **59**, 84 (1937), [TiNO₃, TiClO₄, TiC₂H₃O₃, and alkali nitrates and acetates]; A. F. Scott, *J. Phys. Chem.*, **40**, 461 (1936), [Ca(NO₃)₂, alkali halides]; J. B. Stark and E. C. Gilbert, *THIS JOURNAL*, **59**, 1818 (1937), [KCNS, NH₄NO₃]; G. M. Watson and W. A. Felsing, *ibid.*, **63**, 410 (1941), [HCOONa, H₃CCOONa]; H. E. Wirth, *ibid.*, **62**, 1128 (1940), [HCl, K₂SO₄]; N. Bauer,³⁸ [AgNO₃].

of Na⁺ and Mg⁺⁺ can be added to that of the singly charged ions of the same sign given in Section 6. Sodium ion shows between 25° and 50° the steepest rise among the cations; magnesium ion has a negative slope. As effect (d) discussed in Section 6 is negligible for these ions of small polarizability, it is obvious that, while $d\Phi_0/dt$ of Na⁺ is influenced mainly by the breaking effect (a), for the slope of the doubly charged magnesium ion, the effect (b) of the forces must be of decisive importance.

(b) **Hydrogen Ion.**—The apparent volume of the proton (+0.2 cc. at 25°) in Table III is larger than that of the sodium ion (-1.7 cc.) while in the gaseous state the opposite is true. This apparent contradiction and the fact that the heat of hydration of the proton is larger than that of the

sodium ion by as much as 160 kcal.,⁴³ led to the conclusion¹¹ that the proton is not symmetrically surrounded by water molecules, but forms OH_3^+ , the existence of which was first assumed on the basis of catalytic experiments.⁴⁴ Thus the smaller Φ_0 value of sodium ion is due to the fact that it exerts stronger forces and has a stronger breaking effect than the larger hydroxonium ion which is nearest to the ammonium ion in respect to fitting into the water structure.⁴⁵ However, it appears remarkable that the apparent volume of the proton given in Tables II and III has a small positive value while the apparent molar refraction of the proton is negative (-0.6 cc.).⁴⁶ The explanation can be partly based on the fact that the deviation of our Φ_0 values from true values for infinite dilution¹⁷ may be large for the hydrogen ion since the extrapolation for acids is especially uncertain (see Section 1). The increase of the size of the hydroxonium ion due to a loosening effect (d) of the surrounding water molecules can also be of some influence.

(c) **Lithium and Beryllium Ions.**—The Φ_0 vs. t curves of lithium salts cross those for sodium salts: the fact that below 30° aqueous lithium ion appears to be larger than sodium ion (see Fig. 1) indicates its close relation to one⁴⁷ of the surrounding water molecules. This explains why lithium in Figs. 3 and 5 is closer to hydroxonium ion than to sodium ion. Similarly the apparent volume of the beryllium ion appears to be larger than that for the magnesium ion (see Table III).

(d) **Gradation of Ionic Volumes in Solid and Dissolved State.**—Table V shows that the gradation of the apparent volumes of aqueous ions can differ considerably from that observed in

crystal lattices. Besides the ammonium and rubidium ion (see Section 4), the thallium ion shows nearly the same volume in the crystallized cubic perchlorates.⁴⁸ However, the apparent volume of this non-rare gas ion with twenty electrons in its outer shell is considerably smaller than that of the other two. This is not surprising because in solid and vapor halides, thallium shows inter-ionic distances varying from that of sodium to almost that of cesium.⁵

Another interesting comparison is that of bromates and iodates. For crystallized potassium salts the molar volume of the iodate (53.8 cc.) is slightly larger than that of the bromate (51.1), but in aqueous solution the apparent volume of the iodate ion is smaller by 11 cc. (see Table V). One can connect this peculiarity with the fact that in crystallized bromates, the coordination number of bromine is 3, while in iodates⁴⁹ that of iodine is 6. It is reasonable to assume that in aqueous solution I^{5+} has 3 oxygens and 3 water molecules as nearest neighbors. The resulting strong interaction with water explains not only the small apparent volume of the iodate ion in aqueous solution but also why it causes high viscosity (see Fig. 2), and shows low mobility, strong dependence of apparent molar refraction on concentration, and a pronounced change of the Raman spectrum of water.

(e) **Comparison of Anions with Cations.**—Of great interest is the comparison of halide and alkali ions of the same rare gas structure. The anhydrous fluoride ion is considerably larger than sodium ion. The nuclear distance for the electron density maximum of the L-shell is 1.4 times larger in the free gaseous fluoride ion than in the sodium ion.⁵⁰ The usual crystal radii in Å. are² F^- (1.3), Na^+ (1.0), K^+ (1.3). In respect to Φ_0 , however, at 25° , F^- (-1.8 cc.) is slightly smaller than Na^+ (-1.7) and much smaller than K^+ (8.4). This confirms the conclusion, based on the comparison of the gradation of the apparent volumes with that of the heats of hydration of ions,¹¹ that the fluoride ion in spite of its larger size in the free gaseous state exerts stronger forces on the water than does the sodium ion. This influence of the sign of the ionic charge was explained with K. F. Herzfeld¹¹ by the unsym-

	NH_4^+	Rb^+	Tl^+
$V_{\text{MClO}_4}^{\text{cryst.}}$	68.4	69.2	69.2
$\Phi_{\text{M}^+}^{25^\circ}$	18.0	13.7	9.4
	BrO_3^-	IO_3^-	
$V_{\text{KXO}_3}^{\text{cryst.}}$	51.1	53.8	
$\Phi_{\text{XO}_3^-}^{25^\circ}$	36.4	25.1	

(43) K. Fajans, *Verh. der d. phys. Ges.*, **21**, 549, 709 (1919); M. Born, *Z. Physik*, **1**, 45 (1920).

(44) H. Goldschmidt and O. Udby, *Z. physik. Chem.*, **60**, 728 (1907); see also Latimer and Rodebush, ref. 28.

(45) H. E. Wirth, *This Journal*, **62**, 1128 (1940).

(46) K. Fajans and G. Joos, *Z. Physik*, **23**, 31 (1924); K. Fajans and R. Lühdemann, *Z. physik. Chem.*, **B29**, 150 (1935).

(47) V. K. LaMer and T. H. Grønwall, *J. Phys. Chem.*, **31**, 898 (1927).

(48) H. Braekken and L. Harang, *Z. Krist.*, **75**, 538 (1930).

(49) See "Strukturbericht," Vol. 1 and II, Akad. Verlag., Leipzig, 1931 and 1933.

(50) Calculated by Mr. Norman Bauer from the wave functions according to D. R. Hartree, *Proc. Camb. Phil. Soc.*, **24**, 89 (1928); *Proc. Roy. Soc. (London)*, **151**, 96 (1935).

metrical position of the dipole within the water molecule (see also ref. 7).

(f) **Distance between Particles in Crystals and Solution.**—The behavior of dissolved ammonium chloride suggests strongly that near 35° both of its ions fit in some way into the structure of liquid water. If one tries to give a precise geometric meaning to this, it is simplest to assume that the ammonium and chloride ion can replace one molecule of water in its tetrahedral structure. This leads to the following comparison: the distance between neighboring molecules in liquid water at 35° is 2.96 Å,²⁶ the interionic distance in crystallized ammonium chloride is 3.34 Å. for the coordination number eight, 3.27 for the coordination number six, and according to rules found for crystals⁵¹ would be expected to be about 3.1 for the coordination number four. In order to account for the difference between 2.96 and 3.1 Å., it should be recalled that according to the above paragraphs (d) and (e) it is not generally possible to identify even the gradation of the size of analogous ions in crystals and solution. For the present comparison of the absolute values of the distances, the following factor among others can be of importance in an aqueous solution: If an ion replaces a water molecule without breaking the given structure of water, the ionic forces will cause the interpenetrating water molecules surrounding the ion in the first and second spheres to come closer to each other and to occupy a smaller volume than in pure water; this leaves more space for the ion. Thus one cannot consider the difference between the distances 2.96 and 3.1 Å. as an objection to the idea that ammonium and chloride ions fit into the structure of water.

(g) **Comparison with Former Partitions.**—Paragraphs (d) and (e) make it understandable why the partitions of the apparent molar

(51) V. M. Goldschmidt, *Norske Videnskaps Akad. Oslo*, No. 8, p. 69 (1926); L. Pauling, see ref. 2.

volumes, based on the ratios of the usual crystal radii of anions and cations (see introduction), gave distinctly differing results according to the pair chosen. The apparent volume of the chloride ion is given as 22.5 (20°),⁷ 23.5 (25°)⁸ and 20.4 (25°)⁹ as compared with our result of 18.0 cc./mole at 25°. The latter value coincides with the lower limit given with Geffcken⁶ on the basis of the assumption, $\Phi_{H^+} = 0$.⁵²

Summary

1. A partition of the apparent molar volumes (Φ_0) of strong electrolytes into values of individual ions is made on the basis of the behavior of aqueous ammonium chloride near 35°. The Φ_0 values of the electrolytes were obtained by extrapolation to infinite dilution from density measurements above 1 *N*. From the close similarity of several of the properties of ammonium chloride to that of the solvent, water, it is concluded that near 35°, ammonium and chloride ions both fit into the structure of liquid water and that the apparent volume of each is equal to the volume of one mole of water (18.1 cc./mole).

2. It is shown that for ions which are either much larger (ClO_4^-) or smaller (Na^+) than water molecules, the thermal expansibility of their aqueous solutions is strongly influenced by the breaking of the loose water structure.

3. The displacement of protons within water molecules and within the ammonium and hydroxonium ions is brought into relation with the mechanism of hydration of ions and molecules.

4. The comparison of anions with cations and of ions of different structure shows that the gradation of their apparent volumes in aqueous solution can be considerably different from that of their size in crystals.

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(52) See also B. B. Owen and S. R. Brinkley, Jr., *Chem. Rev.*, **29**, 461 (1941).