IONIC SIZE

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CONTENTS

I. INTRODUCTION

The term "ionic size" is admittedly vague. It refers, on the one hand, to various molar (apparent, partial) volumes and, on the other, to internuclear distances and ionic radii. To obtain the latter from the former usually involves some structural assumptions such as packing. Similarly, although internuclear distances are relatively easy to obtain, various assumptions made in determining ionic radii from these may lead to large differences in the resulting values.

It is well known that the internuclear distance between the anion and cation in a compound depends greatly on the environment. For example, in a sodium chloride molecule this distance is about 0.5 A. less than in the crystal, because in the latter forces on the ion act in all directions. Similar statements apply to solutions. Moreover, the same measurement may give rise to different values, depending on the method of calculation. Indeed, as the authors will try to show, the ionic radius is an operational concept which has a specific meaning and value only for specified experimental conditions and methods of calculation. It would appear that "ion size" can be thought of as the volume influence exerted by an ion under the particular conditions, the method of measurement, and the application of theory being used.

The purpose of this paper is to describe and compare the various methods which are used to measure and calculate ion-size parameters. Where necessary for illustration values are given, but it is not intended to present an exhaustive compilation of numbers or a bibliography of all papers in this field. To some extent the relative emphasis given various topics reflects the authors' personal interest and knowledge.

The almost ubiquitous appearance of ion size in calculations of various kinds needs hardly to be pointed out. Frequently various values of ionic radii are used without awareness of the conditions for which these were derived. The authors hope that by bringing together material which is usually scattered among different areas of research the need for further work will become more apparent and other workers will be stimulated to help carry it out.

II. The Isolated Ion

From a consideration of the classical atom or ion with its fixed electron orbits the size or radius of the particle can easily be visualized as the distance of the outermost electron shell from the nucleus. This "classical" picture of the atom proposed by Bohr (32) gives for the ionic radius

$$r = \frac{h^2}{4\pi^2 m\epsilon^2} \cdot \frac{n^2}{Z} = 0.528 \times 10^{-8} \text{ cm.} \times \frac{n^2}{Z} \tag{1}$$

where h is Planck's constant, ϵ is the electronic charge, $m = 9.035 \times 10^{-28}$ g, n is the principal quantum number, and Z is the atomic number. From the known quantum numbers of the ions in their normal (unexcited) states the ionic radii can be calculated. Equation 1 is, however, only applicable to a unielectronic atom; for a many-electron atom, electrons in the outer shells will be partly shielded from the positive nuclear charge by electrons closer in. Consequently the effective nuclear charge will be reduced. In general $Z_{\text{eff}} = Z - S$, where S is a screening constant. The evaluation of S depends on wave-mechanical considerations and is beyond the scope of this paper. It is evident, however, that the ionic radius must now be identified with the maximum in the electron density for the outermost electron. (Since the density is not zero for larger distances this view introduces a certain vagueness into the term "radius".)

Slater (185) has described a simple method for calculating screening constants of the lighter atoms but it is not too good for ions and the outer electrons of atoms. Hartree (90) has calculated screening constants and radii for several ions, using the self-consistent field approximation. This method consists in assuming a volume density of electric charge, calculating the motion of the electrons in this field, and obtaining a new charge distribution. By a method of successive approximations one arrives at a state when the calculated field becomes equal to the assumed field. For a more complete description the references cited should be consulted.

Hartree's result can be expressed in the form

$$\bar{r} = \frac{r_{\mathrm{H}}}{Z - \sigma} \tag{2}$$

where

$$r_{\mathrm{H}} = \frac{1}{2}\,[3n^2 - l(l + 1)] \tag{3}$$

and σ is a screening factor which, for the lighter atoms, is close to Slater's value of S. The method for its calculation is quite involved and has been carried out for relatively few ions.

A combination of Hartree's and Slater's methods is easy to apply and gives fairly good agreement for the lighter ions with the more involved Hartree method. The method consists in retaining Hartree's equation but substituting Slater's S for the Hartree σ, or replacing Slater's n^2 by Hartree's r_{H}, i.e., $r_{\mathrm{SH}} = r_{\mathrm{H}}/(Z - S)$. Tables 1 and 2 reproduce the values of Slater and Hartree, respectively.

As an example consider potassium ion. Its electronic configuration is

TABLE 1

Contribution of one shielding electron of given quantum number to shielding constant of shielded electron (185)

Shielded Electron	Shielding Electron				
	1*s*	2*s*	2*p*	3*s*	3*p*
1*s*	0.35	0	0	0	0
2*s*	0.85	0.35	0.35	0	0
2*p*	0.85	0.35	0.35	0	0
3*s*	1.00	0.85	0.85	0.35	0.35
3*p*	1.00	0.85	0.85	0.35	0.35

TABLE 2

*Values of r_H for various quantum levels**

Quantum level	(1*s*)	(2*s*)	(2*p*)	(3*s*)	(3*p*)	(3*d*)	(4*s*)
r_H	1.5	6	5	13.5	12.5	10.5	24

* Reference 90, p. 125.

TABLE 3

Ionic radii and screening constants from the Slater–Hartree equations

Ion	S	σ	Radii (in Atomic Units)		
			Slater	Hartree	Slater–Hartree
Li$^+$	0.35	—	0.38	—	0.57
Na$^+$	4.15	4.72	0.58	0.80	0.73
K$^+$	11.25	10.26	1.16	1.43	1.61
Be^{++}	0.35	—	0.27	—	0.41
Mg^{++}	4.15	4.68	0.51	0.68	0.64
Ca^{++}	11.25	10.10	1.03	1.27	1.43
Al^{+++}	4.15	4.61	0.45	0.60	0.57
F$^-$	4.15	5.02	0.83	1.26	1.03
Cl$^-$	11.25	10.85	1.57	2.03	2.18

$1s^22s^22p^63s^23p^6$. Hence $S = 2(1.0) + 8(0.85) + 7(0.35) = 11.25$, compared with the more accurate $\sigma = 10.26$. The outermost orbital is $3p$; hence $r_H = 12.5$. This gives for the radius $12.5/(19 - 11.25) = 1.61$ A., as against 1.43 A. for the Hartree calculation. In table 3 are listed ionic radii and screening constants for ions of several light atoms, the corresponding Hartree values being listed when available.

In every case where comparison is possible the method suggested here yields radii which lie considerably closer to the Hartree values than those obtained by Slater's method. The difference between the two methods is particularly striking for the heavier ions. It is interesting to note that quantum-mechanical radii are much smaller than—usually about half of—those obtained by crystallographic methods (*cf.* Section IV). However, the Hartree and similar radii represent maxima in the electronic wave functions and the electron density is usually appreciable beyond this.

III. IONS IN THE GAS PHASE

A. COLLISION RADII

Information available on ionic size in the gas phase depends essentially on the measurement of some property related to collisions between particles. These collisions may involve electrons, ions, atoms, or molecules.

1. Chemical kinetics

Collisions which result in the production of new chemical species at a measured rate may be classified under the heading of gas kinetics. As in the case of other approaches, the value of the radius of an ion found from gas kinetics depends on the type of measurement made and the method of calculation.

For unlike molecules Hinshelwood (93) writes for the number of collisions, Z, per cubic centimeter per second,

$$Z = N_A N_B \sigma_{AB}^2 \left[8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} \tag{4}$$

where N_A and N_B are the numbers of molecules of the two kinds per cubic centimeter, σ_{AB} is the mean of the molecular diameters, and M_A and M_B are the respective molecular weights.

For calculations of reaction velocity constants the collision frequency Z is multiplied by the factor $e^{-E/RT}$, which gives the fraction of the reactant particles which have energy to react, and by a factor P which represents deviation from theory. E is the energy of activation for the reaction. This gives for the kinetic rate expression,

$$K' = \frac{PN_0\sigma_{AB}^2}{1000} \left[8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} e^{-E/RT} \tag{5}$$

where N_0 is Avogadro's number.

This equation can be applied to kinetic rate data between ionic reactants. Amis and LaMer (13) found, assuming P to be unity, that even in solution the reaction between bromophenol blue and hydroxide ion gave σ_{AB} to be 7.10 and 5.51 A., respectively, when the solvents were ethyl alcohol–water and methyl alcohol–water in that order.

Equation 5 was independently obtained by Trautz (200) and Lewis (136) by letting $s = 1$ in the more general equation

$$K' = \frac{PN_0}{1000} (r_A + r_B)^2 \left[8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} e^{-E/RT} \left(\frac{E/RT}{(s-1)} \right)^{s-1} \tag{6}$$

obtained from classical molecular statistics of reactions of the second order. In this equation $2s$ is the number of squared terms into which the critical energy E can be resolved, and $r_A + r_B$ is the sum of the radii of the reaction particles.

Moelwyn-Hughes (146) applies this to reactions between oppositely charged ions in the presence of neutral molecules.

If N_+, N_-, and N represent the concentrations of cations, anions, and neutral molecules, respectively, the rate of discharge of the ions is

$$-\frac{dN_-}{dt} = -\frac{dN_+}{dt} = k_3'NN_+N_- \tag{7}$$

If the neutral particle is unaffected by the reaction, its concentration remains constant and the reaction is apparently of the second order. Hence,

$$k_2' = k_3'N \tag{8}$$

The observed second-order rate constant for the union of ions proves to be linear with total pressure in air, carbon dioxide, nitrous oxide, sulfur dioxide, and carbon monoxide over a range of pressures extending from less than 200 mm. to almost 800 mm. (198).

Moelwyn-Hughes (146) writes for the collision frequency between cations and neutral molecules the expression

$$Z = N_+(r + r_+)^2(8\pi kT/u_+)^{1/2} \tag{9}$$

where

$$u_+ = \frac{mm_+}{m + m_+} \tag{10}$$

For the relevant ternary collisions, the frequency is the product of Z of equation 9 and the chance that an anion shall have its center within a volume $(4/3)\pi R^3$ from the cation-molecule pair. The change is approximately $(4/3)\pi R^3N_-$. Taking the radius of capture to have the equipartition value of

$$R = \frac{e^2}{kT} \tag{11}$$

the frequency of collision between the cation-molecule pairs and the anions is

$$Z = NH_+N_-\left(\frac{8}{3}\right)\pi(r + r_+)^2(2\pi kT/u_+)^{1/2}(e^2/kT)^3 \tag{12}$$

The frequency of collision between the anion-molecule pairs and the cations would be given by a similar expression.

This treatment involves the sum of the radii of an ion and a neutral molecule. It accounts for the order of the reaction and for values of k_3' which vary, at a total constant concentration, as $T^{-5/2}$. It has numerous drawbacks, however; it predicts an infinite velocity at the absolute zero of temperature and a constancy of k_2'/N as opposed to the maximum actually found (122). Some assumption would have to be made to break the sum $(r + r_+)$ into its component parts.

Moelwyn-Hughes (146) gives another equation which, applied to particles of the same masses and radii, is

$$Z = N_+N_-9(2r)^5(3kT/2m)^{1/2} \tag{13}$$

This equation is subject to disadvantages similar to those found in equation 12.

From the magnitudes of their specific rates and their temperature dependence

Stevenson and Schlissler (192) concluded that the collision areas were about three times greater than the ordinary kinetic theory collision areas for the following gaseous reactions:

$$\begin{aligned}
&D_2^+ + D_2 \rightarrow D_3^+ + D\\
&A^+ + H_2 \rightarrow AH^+ + H\\
&A^+ + HD \rightarrow AH^+ + D\\
&A^+ + DH \rightarrow AD^+ + H\\
&A^+ + D_2 \rightarrow AD^+ + D\\
&CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3
\end{aligned}$$

The loss of two electrons by negative ions upon collision with atoms and molecules was studied by Dukel'skiĭ and Fedorenko (49). Cross-sections for the change of charge $I \rightarrow I^+$, $Br^- \rightarrow Br^+$, $Na^- \rightarrow Na^+$ increase with increasing ion energies and are lower in hydrogen and helium than in argon and nitrogen. These cross-sections are of the order of 10^{-17} to 10^{-16} sq. cm., values which would give cross-sectional radii of about 0.2 to 0.6×10^{-8} cm.

2. Inelastic collisions of the second kind

In an elastic collision the total kinetic energy is conserved. In inelastic collisions of the first kind some of the kinetic energy of the colliding particles is converted into internal energy—such as rotational, vibrational, or electronic—of one or both of the colliding particles.

Klein and Rosseland (107) reason from the standpoint of microscopic reversibility that if the kinetic energy of a free electron can be converted into internal energy of an atom with which the electron collides, then an electronically excited atom upon collision with another particle should be able to convert some of its internal energy into kinetic energy. Such collisions are called inelastic collisions of the second kind.

Deactivation of energy-rich particles by collision with their own kind or another kind is an example of inelastic collisions of the second kind. Specifically the quenching of fluorescence by collision of the excited particles with other particles represents inelastic collisions of the second kind.

The equation

$$Z = \frac{kT}{3\eta}\,\frac{(r_A + r_B)^2}{r_A r_B}\,N_A N_B \qquad (14)$$

has been derived (147, 152, 186) from kinetic rate theory and the Stokes-Einstein equation for the frequency of collisions of particles of radii r_A and r_B in a medium of viscosity η at an absolute temperature T when the numbers of the particles per cubic centimeter are N_A and N_B.

Moelwyn-Hughes compares the specific velocity constant k_4' for the deactivation of particle A with particle B, thus,

$$A^* + B \rightarrow A + B$$

with equation 14 and writes

$$k_4' = \frac{kT}{3\eta}\,\frac{(r_A + r_B)^2}{r_A r_B}\,\frac{N_0}{1000} \qquad (15)$$

TABLE 4

Total cross-sections for scattering protons by argon and helium

Gas	Proton Energy	Cross-section in Units a_0^2	Gas-kinetic Cross-section in Units a_0^2	Gas	Proton Energy	Cross-section in Units a_0^2	Gas-kinetic Cross-section in Units a_0
	e.v.				*e.v.*		
Helium	90	3.75	2.6	Argon	73	16.4	7.3
	800	2.00			650	10.7	

For particle A much larger than particle B, as in the quenching of quinine ion with chloride, bromide, or iodide ion, one may write:

$$k_4' = \frac{kT}{3\eta}\frac{r_A}{r_B}\frac{N_0}{1000} \tag{16}$$

Thus the ratio r_A/r_B can be determined from kinetic data and if either r_A or r_B is known from some other source, the other may be found. Moelwyn-Hughes gives the ratio r_A/r_B for the quenching of the fluorescence of quinine ion in water by chloride, bromide, and iodide ion to be, respectively, 1.92, 2.27, and 2.55 A., where the subscript B refers to the halide ion.

3. Elastic collisions

In the elastic collision of atoms and ions with atoms, the total elastic cross-section is comparable with the gas kinetic cross-section and only a small proportion of scattering occurs at angles greater than 12° (134). A comparison of the total cross-sections for the scattering of protons by argon and helium is given in table 4 (see reference 134). Massey and Bishop (134) discuss the principle of the method for the determination of mean effective total cross-section averaged over the distribution of relative velocities fixed by the temperatures of the particles. The equation

$$\bar{\lambda} = (2\pi^{1/2}/\bar{Q}_{AB}N_B)\bar{\psi}(\alpha) \tag{17}$$

is given by these authors for calculating mean effective total cross-section $\bar{Q}_{AB}$ in terms of the mean free path $\bar{\lambda}$, the concentration N_B of particles B in particles per cubic centimeter, and a function $\bar{\psi}(\alpha)$, important values of which are listed in a table.

$$\alpha = M_A T_B/M_B T_A \tag{18}$$

Easterman, Foner, and Stern (51) found that λ for a definite velocity could be determined and $\bar{Q}_{AB}$ calculated from the equation

$$\lambda_v = \pi^{1/2}W^2/N_B\bar{Q}_{AB}\psi(W) \tag{19}$$

where

$$W = v(M_B/2T_B)^{1/2} \tag{20}$$

and

$$\psi(W) = we^{-w^2} - (2w^2 + 1)\int_0^w e^{-z^2}dz \tag{21}$$

In table 4 it is seen that the radius of total cross-section for the scattering of protons by helium gas ranges from about 0.8 to 1.1 A. and that the kinetic cross-sectional radius is about 0.9 A.; there is hardly the same agreement in the case of argon, which gives a range of the radius of total cross-section of scattering to be about 2.3 to 1.2 A., while the gas kinetic cross-sectional radius is 1.15 A.

Again all these radii are sums of the radii of the colliding particles and would have to be resolved into their component parts by some assumption.

Holstein (94) in a study of the mobilities of positive ions in their parent gases found the effective "collision radius" of the ions to be large compared to atomic dimensions. For helium the collision radius was found to be 8 Bohr radii; for other gases the collision radius was even greater.

For very slow ions Zeigler (219) measured the effective cross-section, which included both charge transfer and scattering for angles above 2°, and also the cross-section q_u for charge transfer alone. The latter cross-section was obtained by making use of the theoretical difference in distribution between scattered and exchanged ions. Neon, argon, and xenon were investigated at ion energies of 0.8, 1.0, and 1.2 e.v., respectively. The corresponding values of q and q_u are 5, 9, and 13 and 4.4, 5.5, and 10.3 $\times 10^{-15}$ sq. cm., respectively. These would correspond to collision radii for the ions of from about 4 to 6 $\times 10^{-8}$ cm.

4. *Collision cross-sections*

(a) Charge transfer

Massey and Burhop (132) have discussed these phenomena in great detail. The point of importance here is that in the field the quantity obtained is not an ionic radius or volume but a collision cross-section which depends on the condition of the experiment (91, 164, 204), particularly on the kind of energy of the particles taking part in collision. This is perhaps easiest to see for the case of the collision of an atom or an ion with an electron. The structure of the atom is quite open, and the probability that an electron will be captured or scattered by it obviously depends on the velocity of the electron. Thus the effective cross-section is a statistical quantity dependent on the fraction of passing electrons affected. The arguments on the basis of classical and quantum theory have been clearly presented by Arnot (17). For example, the collision cross-section of alkali metal atoms derived from impact with rare gases differs considerably with the nature of the rare gas. For argon the cross-sections are about ten times as large as for helium (52, 133, 173, 174). Hornbeck and Wannier (96) have shown that the effective cross-sections for ion–atom collisions of rare gases are quite different from the viscosity cross-sections. For example, for helium the collision cross-section for He^+–He is 54.3×10^{-16} cm.; for viscosity it is 14.9×10^{-16} cm.

Maecker, Peters, and Schenk (129) studied ionic and atomic cross-sections in the plasma of various gases. Measurements of the water-stabilized high-power arc led to the following equation for the ionic cross-section, Q_+:

$$Q_+ = e^4(kT)^{-2} \ln \frac{kT}{e^2n^{1/3}} \pm 15\% \tag{22}$$

In this equation n is the electron concentration and the other symbols have their usual significance.

Frost and McDowell (66) observed ionization to all four excited states of the nitrogen molecular ion when nitrogen in a mass spectrometer was subjected to electrons with an energy spread of 0.1 e.v. produced by a pulse technique. The interatomic distances are given for the various states of the N_2^+ ion.

Cross-sections of overcharged slow ions in their own gases were compared from experimental and theoretical data by Kagan and Perel (103).

Ions were produced and counted by Nolan and O'Connor (150) by bubbling air through water, two ion tubes, a diffusion box, and a photoelectric counter. The mobility of ions produced in this way ranged from 0.05 to 0.001 cm. $sec.^{-1}$ $volt^{-1}$ at an age of 20 sec. The radii ranged from 0.7×10^{-6} cm. for fast ions to 2.7×10^{-6} cm. for slow ions. Charges varied inversely as the radius squared. Extreme values were 127 electronic charges on fast ions and 7 on slow ones.

Porter, Chupka, and Inghram (163) obtained the following estimated relative cross-sections: $Ag^+:Au^+:SiO^+:SiO_2^+:O_2^+:O^+ = 1.5:1.5:1:1.5:2:1:0.5$. The various cross-sections involved have a maximum variation of 4.

Erikson (54) interpreted the separation of the maxima for streams of positive and negative ions in air of a velocity less than 500 cm. per second to mean that there were ions of different sizes in the air. In the case of older ions the separation of the maxima is due to the aging of the positive ion, whereby it loads up and thus moves more slowly in the electric field.

(b) Photoionization

A photon may be absorbed by an atom or a molecule if there is within the atom or molecule some change which is not forbidden by quantum restrictions and which corresponds to the energy of the photon.

The absorbed quantum may result in the production of heat, excitation of the atom or molecule, dissociation in the case of the molecule, dissociation and excitation of one of the fragments produced, fluorescence (when there is an immediate reradiation of part of the quantum at a different wavelength), phosphorescence (when there is a time lag in this reradiation), or ionization.

From photoionization the size of the ion may be determined.

Watanabe (208) by improved energy measurements showed that the photoionization cross-sections of nitric oxide in the region 1070–1340 A. were about 40 per cent too low. At 1215.6 A. the photoionization and the total cross-sections were 2×10^{-18} and 2.4×10^{-18} $cm.^2$, respectively. The difference was ascribed to an absorption band. These values of cross-section would correspond to radii which would be extremely small.

The photoionization cross-section of ammonia rose gradually with decreasing wavelength in the region 1220–1060 A. and reached a value of 9×10^{-18} $cm.^2$ at 1060 A. Even this maximum value of cross-sectional area would yield a corresponding radius of less than 0.2 A., assuming that the area comprises the major circle of a sphere.

Photoionization, like other approaches, leads under certain circumstances to charged agglomerates which may be one or two orders of magnitude larger than ordinary ions. Thus aerosols of neutral particles may become charged by photochemical action. Such large agglomerates may have several or even many elementary charges. This is in contrast to the elementary ions, which have charges limited by the number of extranuclear electrons in the atom of the element.

Vassails (202) irradiated filtered air briefly with ultraviolet light in an ionization chamber 1 m. long and 11 cm. in diameter. He attributed the observed increase of conductance to the formation of large ions with a mobility of 10^{-3} cm. per second. The experimental method involved sweeping the normal ions from the chamber in about 1 sec. The charge for the large ions was then measured over a period of 30 min., using a quadrant electrometer. The concentration of the ions was about 100 per cubic centimeter. The ions are formed from an aerosol of neutral particles arising from the photochemical action. The particles capture molecular ions arising from natural ionization. The majority of the particles were visible in the ultramicroscope and were of a size of about 5×10^{-6} cm. The ions were found to carry ten or fewer elementary charges. The most effective radiation for producing the large ions in air lies between 10 and 200 A. Gases which give rise to condensed products or solids by photochemical action increase the formation of the large ions if introduced before irradiation, but diminish it if introduced afterward.

The examples presented above for various approaches to ion size are not exhaustive, but are illustrative of the range in ion size found by different and even by the same procedure when conditions vary. Thus the energy of the bombarding particles or of the photon of radiant energy influences the sizes of the ions observed.

Busse (38) by experiments on ions produced in both moist and dry air by a variety of methods proved that there was an essentially continuous distribution of sizes of the ions.

Thus the meaning which can be attached to the term "ionic size" in the sense in which it is usually understood in crystals and even in solution is different from the sense in which it is used in the gas phase.

B. SALT MOLECULES IN THE VAPOR

1. *Internuclear distances*

When ordinary ionic crystals such as sodium chloride are vaporized, salt molecules are formed. Internuclear distances have been determined for many of these. A compilation of the literature up to 1950 is given in the Landolt-Börnstein *Tabellen* (119). From a comparison of crystal symmetry with the vapor state it is clear that interatomic distances in the latter should be smaller. In the sodium chloride crystal a sodium ion is pulled equally in all directions by its six nearest (chloride ion) neighbors. In the molecule the attraction by one chloride ion is not balanced by a pull in any other direction. The difference between the spacing in the crystal and in the vapor may amount to more than 10 per cent. A comparison for several simple salts is given in table 5.

Interatomic distances are not strictly additive. This is true both for compari-

TABLE 5

Interatomic distances for several inorganic compounds in crystal and vapor

Compound	Interatomic Distance		Compound	Interatomic Distance	
	Vapor	Crystal§		Vapor	Crystal§
	A.	*A.*		*A.*	*A.*
NaCl	2.51*	2.814	CsI	3.41	3.94
NaBr	2.64	2.975	$PbBr_2$‡	2.60†	3.31, 2.99
NaI	2.90	3.235	PbI_2	2.79	—
CsCl	3.06	3.568	$SnCl_2$	2.42	—
CsBr	3.14	3.724	$SnBr_2$	2.55	—

* L. R. Maxwell, S. B. Hendricks, and V. M. Moseley: Phys. Rev. **52**, 968 (1937) for all alkali halides.

† M. W. Lister and L. E. Sutton: Trans. Faraday Soc. **37**, 406 (1941).

‡ Metal-halogen distance.

§ R. W. G. Wyckoff: *The Structure of Crystals*, p. 400 ff. The Chemical Catalog Co., Inc., New York (1924).

son within the vapor phase and also between vapor and crystal. For example, in the vapor $\Delta r(\text{NaBr} - \text{NaCl}) = 0.13$, whereas $\Delta r(\text{CsBr} - \text{CsCl}) = 0.08$. Within the crystal these differences are nearly the same. Wyckoff (213) has divided salts into two groups: those whose ions have essentially constant crystal radii and those whose ions do not. The alkali halides, as well as several other simple halides, fall in the first of these groups. The differences between crystal and vapor are nearly the same. Thus $\Delta r_v(\text{NaBr} - \text{NaCl}) = 0.13$ and $\Delta r_c(\text{NaBr} - \text{NaCl}) = 0.16$. This agrees with the intuitive view that the forces holding anions and cations together in the vapor are the same as those in crystals. Hence the mutual polarization or distortion of the ions is much the same in the two phases except that in the crystal these are symmetrical. One would thus expect monatomic ions to be more nearly spherical and the radii more nearly additive in the crystal.

2. Ionic radii

It follows from the above section that ionic radii in salt molecules in the vapor will be less than the corresponding distances in the solid. Moreover, since ions in the vapor are more distorted, the ions will be less spherical and the term "radius" less meaningful. One may define "ionic radius" here as that distance which, when combined with the corresponding distance for an ion or opposite charge, yields the correct (experimental) internuclear distance. A good approximation can be obtained by preserving the same ratio of ionic radii as in the crystal. It is to be expected that this procedure will be most effective for salts in which the hypothesis of constant atomic radii holds, e.g., in the alkali halides.

In anticipation of material to be presented in Section IV,B table 6 lists internuclear distances and ionic radii for salt molecules, where Pauling's (156) crystal radii have been used as standard. These have been derived for small deforming forces for ions in a sodium chloride structure. Interatomic distances in the salt molecule were taken from the compilation by Landolt-Börnstein (119).

The cation sizes remain rather constant, independent of the anion (halides only). In every case the internuclear distance in the salt molecule is known to within ±0.03 A. Thus, the assumption made that the ratio r_+/r_- is the same

TABLE 6

Ionic radii for salt molecules in the vapor

Ion	r	Other Ions in Molecule	Crystal r (Pauling)
	A.		A.
Na^+	0.88 ± 0.01	Cl^-, Br^-, I^-	0.95
K^+	1.20 ± 0.02	Cl^-, Br^-, I^-	1.33
Rb^+	1.31 ± 0.01	Cl^-, Br^-, I^-	1.48
Cs^+	1.47 ± 0.01	Cl^-, Br^-, I^-	1.69
Pb^{++}	1.00 ± 0.01	Br^-, I^-	1.21
Cd^{++}	0.80 ± 0.01	Cl^-, I^-	0.97
Zn^{++}	0.62	I^-	0.74
Cl^-	1.60 ± 0.02	Na^+, K^+, Rb^+, Cs^+, Sn^{++}	1.81
	1.43 ± 0.02	Tl^+, Cd^{++}	
Br^-	1.73 ± 0.03	Na^+, K^+, Rb^+, Cs^+, Sn^{++}	1.95
	1.54	Tl^+	
I^-	1.96 ± 0.05	Na^+, K^+, Rb^+, Cs^+, Sn^{++}	2.16
	1.80 ± 0.01	Cd^{++}, Zn^{++}	
	1.61	Pb^{++}	

in crystal and vapor holds here. The ratio $r_+(\text{crystal})/r_+(\text{vapor})$ increases gradually from 1.08 for Na^+ to 1.15 for Cs^+, as would be expected from the increase in polarizability with size. For the anions r_- is not nearly so constant. For the alkali metals and tin(II) r_- is constant, but for their association with thallium(I), cadmium(II), and lead(II) the radii differ considerably. Evidently the charge on the cation is not a factor. No explanation for this is evident.

In all cases listed the internuclear distances in the crystal are 10–15 per cent greater than in the vapor. Data on interionic distances in salt molecules are still somewhat scarce.

Pauling (162) has recently derived a simple expression for the interatomic distances in gas molecules of alkali halides. He uses the Born expression for the repulsive potential and neglects ionic polarization to obtain

$$r = (r_+ + r_-)(nB_0)^{1/(n-1)}$$

where B_0 is a characteristic repulsive coefficient and n is the Born exponent. Good agreement with experimental results is obtained.

O'Konski and Higuchi (151) use the expression $r = (a^2 + b^2)^{1/2}$, where a and b are the respective distances from the center of the monomer to the cationic and anionic centers. For sodium chloride $b/a = 1.35$ and the effective radii of sodium ion and chloride ion are 1.54 and 1.94 A., values which are quite different from those given in table 6.

IV. Ionic Crystals

This review will present only a brief summary of the immense amount of work that has been done on crystals. Discussion of the well-known method of x-ray diffraction will be omitted.

A very extensive compilation of ionic radii and volumes is given in the Landolt-Börnstein *Tabellen* (120). In view of the general availability of this work no such compilation is given here.

A. IONIC VOLUMES

The molar volumes of electrolytes can be determined simply from the density and gram-formula weight, V = gram-formula weight/density. V is of course temperature-dependent, the cubical expansion coefficient being positive. A set of additive ionic volume increments has been derived by Biltz (24).

B. INTERNUCLEAR DISTANCES

The standard methods of x-ray crystallography yield essentially internuclear distances between centers of charge. In general, these are not additive in the ionic radii, although for crystals of high symmetry, e.g., the alkali halides, they may be nearly additive. A brief discussion of ionic radii follows.

C. CRYSTAL RADII

An ion is essentially an open and largely empty structure which is subject to distortion and deformation by forces outside. One would thus expect the radius of a given ion to be different in different salts. The extent of the difference depends on both the nature of the ions and the kind of packing occurring in the crystal. Wyckoff (213) classifies salts on the basis of whether radii of the constituent ions are additive. Since by far the largest amount of data on crystals yields internuclear distances, one cannot escape the problem of how to divide this distance into cationic and anionic components in a given crystal, quite aside from developing generally additive radii. One possibility is to select one salt whose ions are assumed to have equal size on heuristic grounds. For example, potassium ion and chloride ion both have the argon configuration; one can thus assign (equal) radii to these ions and derive further radii from them. Even here, though, further consideration of the greater nuclear charge for potassium ion implies a slightly smaller size for this ion.

A more direct experimental method for determining ionic radii directly is based on electron-density maps. In a crystal of (say) sodium chloride the electron density is a maximum at the centers of the sodium ion and chloride ion and drops nearly to zero in between. The point of zero density can be taken as the dividing line between the ions. The computation involved is considerable and the method has been virtually unused. One exception is the work of Havinghurst (92) on some alkali halides. This author studied the electron distribution in sodium chloride, sodium fluoride, lithium fluoride, and calcium fluoride. He found that the size of the fluoride ion in the last three salts is virtually constant at 1.25 A. (Pauling's value is 1.33 A.), as might be expected from the small size of that ion, but that the size of the sodium ion decreased from 1.18 A. in sodium chloride to 0.88 A. in sodium fluoride. Evidently the sodium ion is already large enough to be deformed considerably by the intense field of the fluoride ion.

D. DEVELOPMENT OF ADDITIVE RADII

The purpose of a system of additive ionic radii is to obtain a single value characteristic of an ion which, when combined with the corresponding value for an ion of opposite charge, will yield the correct (internuclear) distance. From

TABLE 7

Additivity of ionic radii in the alkali halides

	Li		Na		K		Rb
F	2.01	(0.30)	2.31	(0.35)	2.66	(0.16)	2.82
	(0.56)		(0.50)		(0.48)		(0.47)
Cl	2.57	(0.24)	2.81	(0.33)	3.14	(0.15)	3.29
	(0.18)		(0.16)		(0.15)		(0.14)
Br	2.75	(0.22)	2.97	(0.32)	3.29	(0.14)	3.43
	(0.25)		(0.26)		(0.24)		(0.23)
I	3.00	(0.23)	3.23	(0.30)	3.53	(0.13)	3.60

the above discussion this is evidently a difficult task. Several authors have tried to develop such radii based on somewhat different models and assumptions. In this section only brief outlines of the methods will be given.

The earliest system of ionic radii was developed by Goldschmidt (79), who based his data on 1.32 A. for O^{--} and 1.33 A. for F^-, calculated by Wasastjerna (207) from molar refraction data; i.e., since the polarizability α is proportional to r^3, the internuclear distance can be divided according to $(\alpha_1/\alpha_2)^{1/3}$. More recent "Goldschmidt radii" are based on 1.40 A. for O^{--} and 1.36 A. for F^-. For crystals in which the additivity holds, e.g., the alkali halides, the method is applicable. Data on these are given in table 7. Pauling (157) has developed a set of semiempirical ionic radii for ions forming crystals of the sodium chloride type. One further restriction is their use in crystals for which the radius ratio of cation to anion is near 0.75. The system is based on the empirical internuclear distances in sodium fluoride, potassium chloride, rubidium bromide, cesium iodide, and lithium oxide. It may be noted that the above alkali halides consist of isoelectronic ions. For such ions Pauling assumes the ionic radius (i.e., the position of the outermost electrons) to be inversely proportional to the effective nuclear charge. This leads to the expression

$$R = \frac{C_n}{Z - S} \tag{23}$$

for the ionic radius, where C_n is a constant determined by the total quantum number of the outermost electrons in the ion. Z is the nuclear charge and S is a screening constant obtained from x-ray data and quantum-mechanical calculations (see Section II).

On this basis the internuclear distances of the above salts are divided and radii for the constituent ions are obtained. Further application of this equation yields *univalent* radii for all ions having the configuration of a rare gas. These radii are those which the multivalent ions would possess if they were univalent but retained all their electrons. They cannot be added to obtain the correct internuclear distances in crystals. The crystal radii are obtained from the univalent radii by multiplying the latter by a factor $Z^{-2/(n-1)}$, where Z is the nuclear charge and n is the Born repulsive exponent.

It should be emphasized that the crystal radii derived by Pauling should only be used when $r_+/r_- = 0.75$. When the anions are proportionately larger than this, anion–anion contact will occur (for $r_+/r_- \simeq 0.414$). As r_+/r_- approaches this value "double repulsion" occurs, i.e., the repulsive forces are larger than they would be for either anion–cation or anion–anion contact alone. As a result the cation–anion distance is larger than the sum of the radii and the anion–anion distance is also larger than twice the crystal radius. For the alkali halides Pauling has formulated a theory which takes this effect into account and is in agreement with experiment.

Pauling also applies his theory successfully to most of the alkaline earth oxides, selenides, and tellurides which crystallize in the sodium chloride structure. In crystals of unsymmetrical valence type, e.g., calcium fluoride, the correct interionic distance cannot be obtained by simple addition of ionic radii, since the attractive and repulsive forces are different. The ratio of equilibrium distances for the two structures is

$$\frac{R_{\mathrm{CaF_2}}}{R_{\mathrm{NaCl}}} = \left[\frac{B_{\mathrm{CaF_2}}}{B_{\mathrm{NaCl}}} \cdot \frac{A_{\mathrm{NaCl}}}{A_{\mathrm{CaF_2}}}\right]^{1/(n-1)} \tag{24}$$

where B is the number of cation–anion contacts per stoichiometric molecule (eight for calcium fluoride, six for sodium chloride) and A is the Madelung constant. However, in most cases this correction is unnecessary and the interatomic distance is close (within a few hundredths of an Angström unit) to the sum of the radii.

Pauling discusses the effect of a change in coördination number on interionic distance. In no case is the correction change in distance more than 5 per cent. In table 8 a comparison of Pauling's interatomic distances with the experimental radii is given. Agreement is excellent for all but the lithium salts, where anion–anion repulsion occurs.

Zachariasen (217) has also derived an equation which considers the Born repulsion and the effect of coördination numbers.

Ahrens (2) supports Pauling's arguments and corrects some previously determined radii on the basis of $O^{--} = 1.40$ A. and for shrinkage due to polarization. Stockar (195) has extended Pauling's method to some positive monatomic ions not previously calculated. He uses the equation

$$r = a + be^{-\lambda(N-N_0)} \tag{25}$$

where a is the limiting value for a particular electronic configuration, and N and N_0 are, respectively, the atomic numbers of the element in question and of the end element of the preceding period; e.g., for chromium $N = 24$ and $N_0 = 18$.

TABLE 8

Pauling's radii: comparison with experiment

	Li^+	Na^+	K^+	Rb^+	Cs^+		Li^+	Na^+	K^+	Rb^+	Cs^+
F^- radius sum	1.96	2.31	2.69	2.84	3.05	Br^- radius sum	2.55	2.90	3.28	3.43	
observed	2.01	2.31	2.67	2.82	3.01	observed	2.75	2.98	3.29	3.43	
Cl^- radius sum	2.41	2.76	3.14	3.29		I^- radius sum	2.76	3.11	3.49	3.64	
observed	2.57	2.81	3.14	3.29		observed	3.02	3.23	3.53	3.66	

TABLE 9

Ionic radii of Yatsimirskiĭ (216)

Ion	r	Ion	r	Ion	r	Ion	r
	A.		*A.*		*A.*		*A.*
Ni^+	0.96	Ti^{++}	0.77	Ga^{++}	0.85	In^{++}	1.07
Pd^+	1.05	V^{++}	0.73	Ge^{++}	0.93	Sn^{++}	1.17
In^+	1.38	Cr^{++}	0.81	Pd^{++}	0.96		
Pt^+	1.16	Cu^{++}	0.80	Ag^{++}	0.95		

For each configuration b and λ are constants fitted to Pauling's radii. This leads to the expression

$$r = a + [b_0 - K(N - N_0')]e^{-\lambda(N-N_0)} \qquad (26)$$

Stockar gives values of a, b_0, K, and λ for each period and then calculates radii.

Santen and Wieringen (180) have discussed Stockar's results for elements in the iron group and show that trivalent ions with the $3d^4$ and $3d^5$ structures have somewhat higher radii then predicted by Stockar on the basis of (a) regularities between radii, ionic charge, and ionization potential or (b) the relation $r = k/I^{3.5}$, where I is the ionization potential.

Yatsimirskiĭ (216) also stresses the importance of ionization potentials in the calculation of radii. He derives the relation $I = (A \log N + B)r^{3/2}$ and evaluates A and B for ions in the first and second periods; he then uses the above equation to calculate r (see table 9).

Kordes has derived relations between the molar refraction of crystals and their radii. For compounds having the sodium chloride structure he finds (109) for the ionic refraction

$$R = 0.602kr_u^{4.5} \qquad (27)$$

where r_u is Pauling's univalent radius and k is a constant depending on the electronic configuration. For ions of the rare-gas structure (2/2, 8/8) $k = 1$; for ions with eighteen outer electrons (18/8) $k = 2.25$. In an AB compound with the sodium chloride structure ($k = 1$) the molar refraction is (110)

$$\text{MR} = 0.602(r_{+u}^{4.5} + r_{-u}^{4.5}) \qquad (28)$$

If the experimental internuclear distance $D = r_+ + r_-$ is known, ionic radii can be calculated from the measured molar refraction. For salts in which both ions have the same rare-gas structure (sodium fluoride, potassium chloride, rubidium bromide, α-cesium iodide) the calculated radii are in good agreement with Goldschmidt's values.

Kordes then assumes (111) that the molar refraction is proportional to some function of $(r_+^3 + r_-^3)$ for sodium chloride structures when Goldschmidt's radii are used. He then obtains

$$\text{MR} = 0.602(r_+^3 + r_-^3)_{\text{VI}}^{c} \text{ cm.}^3 \qquad (29)$$

where the constant $0.602 = (6.02 \times 10^{23})(10^{-8})^3$ when the radii are in Ångström units, and the constant $c = 1.365$ for the refractive index determined with the sodium D line. For salts not crystallizing in the sodium chloride structure the right-hand side of equation 29 is multiplied by $1/f$, where f is a structure factor analogous to that used by Pauling; i.e.,

$$f = \frac{D_{\mathrm{CN}}}{D_{\mathrm{VI}}} = \frac{\mathrm{CN}}{6} \cdot \frac{A_{\mathrm{VI}}}{A_{\mathrm{CN}}} \tag{30}$$

e.g., for coördination number 4 (ZnS) $f = 0.95$.

Radii calculated by this method agree well with others (Goldschmidt, Pauling, etc.). It is to be noted that no radius is used in this calculation. Kordes' equation has been used to determine ionic radii for the metals of Group VIII (211).

Povarennykh (165) has derived the equation

$$R_{\mathrm{M}^+} = d_{\mathrm{MF}}[R_{\mathrm{F}} - k(R_{\mathrm{F}^-} - R_{\mathrm{F}^0})]$$

for the effective radius of M^+ in the compound MF. R_{F^-} and R_{F^0} are the purely ionic and atomic radii of F^- and F^0, and k is the per cent covalent binding in MF. Radii calculated agree well with those obtained by other methods; e.g., $\mathrm{Na}^+ = 0.93$, $\mathrm{K}^+ = 1.29$, $\mathrm{O}^{--} = 1.46$, $\mathrm{Cl}^- = 1.85$ A.

There have been numerous attempts to derive relations between atomic and ionic radii. As a recent example only the papers by Somayajuli and Palit are cited (189, 190). They found that the anionic volumes are linearly related to the squares of the atomic radii, the proportionality constant differing somewhat for different families in the Periodic Table. Cationic radii are linearly related to their metallic radii.

V. Molten Salts

In molten salts the ions no longer occupy rigid positions. However, although the long-range order existing in the solid is destroyed, short-range order persists. Recent work on the x-ray and neutron diffraction of molten salts shows that within one or two ions away from a given ion certain distances are preferred. If these distances correspond to nearest neighbors in contact, they may be identified with internuclear distances and compared with the corresponding crystal parameter. One would not expect these to differ greatly. Hence the considerable increase in molar volume on melting and the subsequent expansion on further heating are explained in terms of hole formation in the liquid (99) and a decrease in the coördination number (218). Janz (99) has discussed some of these problems. Kinetic aspects (conductance, transference, diffusion) will not be considered here, but the discussion will be restricted to molar volumes and internuclear distances.

A. MOLAR VOLUMES

The molar volume of a molten salt can simply be determined from its density and gram-formula weight. The recent literature in this field has been summarized by Janz, Solomons, and Gardner (99a), who also give references to older work. Of particular interest is the work by Van Artsdalen and Yaffe (201) on the densities of pure alkali halides and their mixtures. They point out that for both the densities vary linearly with temperature from a few degrees above the melting point to the highest temperatures measured. Also, the equivalent volumes in the mixtures are linear functions of the mole fraction, although this is not true of the conductance.

The molar volumes of liquid salts are generally linear with temperature. The coefficient of expansion for the alkali halides at corresponding temperatures $\theta = T°\text{K.}/T_m°\text{K.}$, where T_m is the melting point, varies in a regular way from salt to salt. All potassium, rubidium, and cesium chlorides, bromides, and iodides have nearly the same expansion coefficient. The lithium salts are about 30 per cent lower, with the sodium salts intermediate. Smooth curves can be obtained for plots of molar volume against molecular weight, interionic crystal distance, etc.

Johnson, Agron, and Bredig (100, 101) have examined volume changes on melting in the alkali halides. In all salts of the sodium chloride structure expansion on melting ranges from 10 per cent in cesium chloride to 31 per cent in lithium fluoride. The situation in the cesium halides is particularly interesting. The expansion of cesium iodide and cesium bromide is about 27 per cent (from the simple cubic solid) and that of cesium chloride 10 per cent. However, the solid modification just below the melting point for cesium chloride is face-centered cubic, the solid–solid transition from simple cubic occurring about 200°C. below the melting point. If the molar volume for the cubic form is extrapolated to the melting point, then the expansion to the liquid is the same as for the bromide and the iodide. The expansion of the bromide and iodide on melting results from the disappearance of long-range order and a lowering of the coördination number from 8 to 6, whereas only the former occurs in cesium chloride. For the other alkali halides the situation is not so clear. In general, a volume change of about 15 per cent is to be expected (170) when the cubic close packing of equisized spheres is destroyed. This can explain the 19 per cent change for potassium fluoride without having to assume a lowering of the average coördination number below 6. For salts whose expansion is much greater than 15 per cent a decrease in the average coördination number is the most likely explanation. Information on such changes in coördination can be obtained by comparing diffraction patterns in the solid and liquid states.

Bloom, Knaggs, Molloy, and Welch (27) have measured the molar volumes of a number of binary systems and find these additive for the $NaNO_2$–$NaNO_3$, $CdCl_2$–CdI_2, and KI–NaCl systems, whereas in the KBr–$BaBr_2$, LiCl–$CdCl_2$, KCl–NaI, and CdI_2–KI systems there are deviations which indicate that covalency is more pronounced in the mixtures than in the pure compounds. Bloom and Heymann (26) have found complex formation in only a few systems, e.g., $PbCl_2$–KCl and $CdCl_2$–KCl.

B. INTERNUCLEAR DISTANCES

Internuclear distances and structural information on molten salts are obtained by x-ray diffraction. Information in this field is very scarce. Lark-Horovitz and Miller (123) published some work on the lithium, sodium, and potassium chlorides which showed that interatomic distances in the melts are nearly the same as in the corresponding solids. Ritter and coworkers have published liquid structure determinations of aluminum chloride (89), indium iodide (210), tin(IV) iodide (211), and cadmium iodide (212). All of these salts exhibit considerable covalent character in the liquid state. For example, the sum of the covalent radii of cadmium and iodine is 2.76 A., whereas the sum of the ionic radii is 3.13 A. In liquid cadmium iodide this distance is 2.90, compared with 2.99 A. in the solid and 2.58 A. in the vapor. However, the molecule in the vapor is linear I—Cd—I; the angle in the solid is 90° and in the liquid 110°. Thus, both arrangements and distances in the liquid resemble the solid. In aluminum chloride, on the other hand, the characteristic distances are those of the vapor and hence give evidence for the existence of Al_2Cl_6 molecules.

VI. IONIC SIZE IN SOLUTION

A. EQUILIBRIUM METHODS

1. Methods yielding volumes

(a) Partial and apparent molal volumes

This topic has been reviewed recently by Harned and Owen (87), who give numerous references to previous work. Their conclusions will be stated and then, following Eucken (57), mechanistic arguments will be emphasized.

Partial and apparent molal volumes are derived from the density of solutions. The apparent molal volume is

$$\phi_v = \frac{V - n_1 V_1^0}{n_2} = \frac{1000}{cd_0}(d_0 - d) + \frac{M_2}{d_0} \tag{31}$$

At infinite dilution the apparent and partial molal volumes are equal. It is these quantities which are of greatest theoretical interest, since at infinite dilution interionic effects are absent and ion–solvent effects can be studied independently of them.

Partial and apparent molal volumes are dependent on temperature and concentration. The dependence on the latter can be well represented by the expression derived by Masson (135)

$$\phi_v = \phi_v^0 + S_v\sqrt{c} \tag{32}$$

or to higher concentrations by

$$\phi_v = \phi_v^0 + S_v\sqrt{c} + bc^{2/3} \tag{33}$$

b is quite small for most electrolytes. The limiting theoretical value of the slope S_v is 1.86 ± 0.02 cm.^{3} l.$^{1/2}$/mole$^{1/2}$ at 25°C. for univalent electrolytes (169). $\phi_v^0 = \bar{V}^0$ for electroytes is additive in the ionic volumes, and this additivity extends to fairly high concentrations. The splitting up of $\bar{V}^0$ into its ionic components requires at least one additional assumption.

Owen and Brinkley (154) take $\bar{V}_i^0$ for hydrogen ion as zero, which yields $\bar{V}^0$ for HCl as the volume of the chloride ion. All other ionic volumes are determined on this basis. Eucken (57) assumes that cesium ion and iodide ion are little hydrated and that their volumes in solution are proportional to the cube of the crystal radii. E-An Zan (50) has listed ϕ_v for many electrolytes over a range of

TABLE 10

Partial ionic molal volumes at 25°C.

Ion	$\bar{V}_i^0$ (Owen and Brinkley	$\bar{V}_i^0$ (Eucken)	$\bar{V}_i^0$ (Fajans and Johnson)	Ion	$\bar{V}_i^0$ (Owen and Brinkley)	$\bar{V}_i^0$ (Eucken)	$\bar{V}_i^0$ (Fajans and Johnson)
H^+	0.0		+0.2	Cs^+	21.1	18.7	21.1
Li^+	−1.1	−3.5	−0.9	Cl^-	18.1	20.8	18.0
Na^+	−1.6	−4.5	−1.7	Br^-	25.1	27.6	25.1
K^+	+8.5	+5.7	+8.4	I^-	36.7	39.5	36.7
Rb^+	13.7	11.0	13.7				

concentrations and temperatures calculated on this basis. Fajans and Johnson (62) give extensive arguments that the values of ϕ_v^0 for ammonium ion and chloride ion are equal to that for water (18.0 ml.) and calculated other ionic volumes on that basis. A comparison of ionic volumes based on these three assumptions is shown in table 10.

For the cations Eucken's values are 2–3 ml. per mole lower, while for the anions they are higher by about the same amount, reflecting the difference in the assumptions made. There is no clear basis for preferring one set of values over the other. For example, one might argue that the hydrogen ion should have a greater tightening effect on the water structure than the lithium ion and hence that its $\bar{V}^0$ should be more negative. This would result in an increase of the anion volumes toward Eucken's figures. On the other hand, if one argues that cesium ion should be somewhat hydrated, then Eucken's values for the cations would be increased and those for the anions decreased in the direction of Owen and Brinkley's results.

Couture and Laidler (41) have studied the relation between $\bar{V}_i^0$ and the crystal radii of monatomic ions. Using Goldschmidt's (50) radii they find for the volumes (using the assumption that $\bar{V}^0_{H^+} = 0$) $\bar{V}^0_+ = 16 + 4.9r^3 - 20Z_+$ and $\bar{V}^0_- = 4 + 4.9r^3 - 20/|Z_-|$; i.e., the volume decreases by 20 ml. for each unit charge on the ion. The two equations can be made to coincide if one takes $\bar{V}^0_{H^+} = -6$ ml. Then $\bar{V}^0_\pm = 16 + 4.9r^3 - 26\,|Z_\pm|$. If $V_\pm$ is taken to depend on the actual ionic volume plus changes in the water structure, the former term should be $2.5r^3$ instead of the $4.9r^3$ if crystal radii are used. The difference can be accounted for by a free-volume term and the somewhat smaller ionic radius in the crystal

TABLE 11

Ionic partial molal volumes

Ion	$\bar{V}_0$ conv. ($H^+ = 0$)	$\bar{V}_0'$ ($H^+ = -6$)	$0.25nr$	Ion	$\bar{V}_0$ conv. ($H^+ = 0$)	$\bar{V}_0'$ ($H^+ = -6$)	$0.25nr$
NO_2^-	26.5	32.5	1.32	HPO_4^{--}	8.3	20.3	2.21
$H_2PO_4^-$	29.4	35.4	1.47	CO_3^{--}	−1.7	10.3	1.99
$H_2AsO_4^-$	35.5	41.5	1.57	ClO_4^-	46.4	52.4	2.92
HCO_3^-	23.5	29.5	1.33	MnO_4^-	43.2	49.2	3.09
ClO_3^-	36.4	42.4	2.16	SO_4^{--}	16.4	28.4	2.90
BrO_3^-	35.6	41.6	2.38	SeO_4^{--}	21.5	33.5	3.05
HSO_4^-	31.4	37.4	2.17	CrO_4^{--}	20.3	32.3	3.00
$HSeO_4^-$	31.4	37.4	2.29	MoO_4^{--}	29.5	41.5	3.23
NO_3^-	29.3	35.3	1.98	WO_4^{--}	26.3	38.3	3.35
SO_3^{--}	9.5	21.5	2.09	AsO_4^{--}	14.9	3.1	3.15

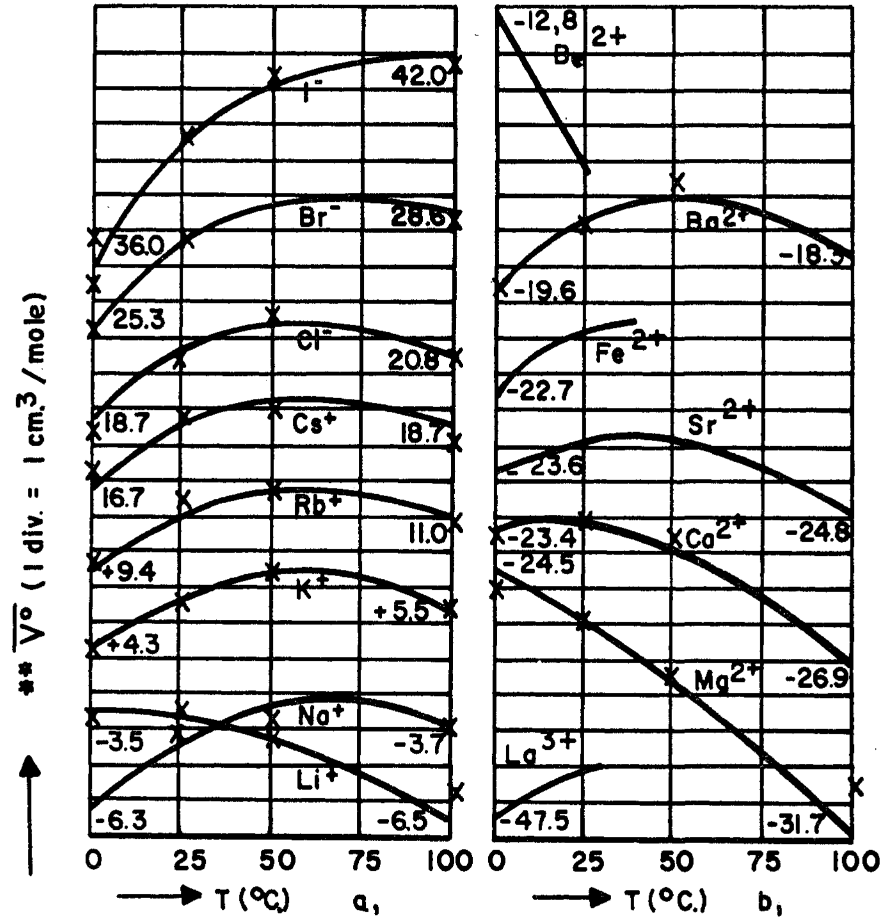

FIG. 1. Temperature dependence of the ionic partial molal volume

For polyatomic oxyanions (43) the situation is somewhat more complicated. The equation for the effective radii will be given in Section VI,A,3. Here the partial molal volumes of several oxyanions will be listed, both on the conventional ($\bar{V}_{H^+} = 0$) basis and on that preferred by Couture and Laidler ($\bar{V}_{H^+} = -6$) (see table 11).

Ionic partial molal volumes are temperature-dependent. Figure 1 shows Eucken's (57) data for several common ions. Notable is the maximum in the plots, although the largest anion, iodide ion, has its maximum above the boiling point of water, whereas cations having the strongest electrostatic fields (except for La^{3+}) have theirs below the freezing point.

The partial molal volume is the sum of two effects: the actual volume of the ion and any changes occurring in the solvent. At low temperatures the structure of the water is ice-like and open, and one can imagine small ions fitting into the open spaces. For these ions, having intense fields, the primary volume change comes from the electrostriction of the water around the ions, resulting in a net decrease in volume. Eucken considers volume changes in the solvent as the sum of three terms: (*a*) the volume change in the primary hydration shell (*cf.* Section 3) $V_{\mathrm{H\,I}} = -\Delta V_{\mathrm{H_2O}} H_{\mathrm{I}}$, where $\Delta V_{\mathrm{H_2O}}$ is the contraction per mole of water and H_{I} is the primary hydration number. Use of data of Balandin (18) on divalent metal chlorides yields $\Delta V_{\mathrm{H_2O}} \simeq 3.5$–$4$ cm.^{3} per mole. For most ions H_{I} is relatively temperature-independent. (*b*) A certain amount of water is withdrawn from the solvent into the hydration shell, altering the actual concentration. This results in a breakdown of the water structure outside the hydration shell. expressed as $\Delta V_2 < 0$. (*c*) A secondary hydration shell consists of water molecules in a structure more open than that of pure water itself; this hydration decreases rapidly with increasing temperature ($\Delta V_{\mathrm{H\,II}}$). In addition there is the actual volume contributed by the ions themselves (V_{J}). A plot of the various contributions is shown in figure 2. Eucken has calculated the various contributions to $\bar{V}^0$ for several ions at various temperatures. These are given in table 12. In each case the calculated volume of the bare ion in solution is somewhat smaller than

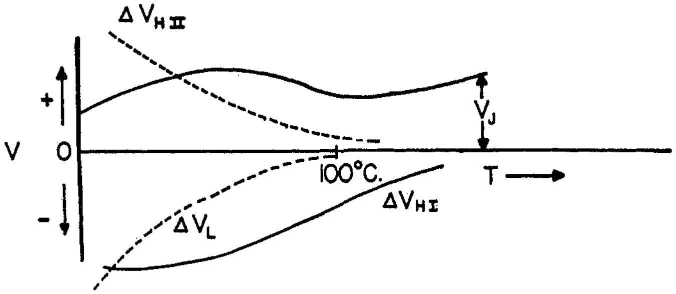

FIG. 2. Contributions to the ionic partial molal volume

TABLE 12

Contributions to the partial molal volume of ions (after Eucken)

Ion	T	H_{I}	H_{II}	ΔV_{L}	$V_{\mathrm{H_2O}}$	V of Bare Ion	$*V^0$	V (crystal)
	°C.							
I^-	0	6.03	2.27	−6.7			36.9	
	25	5.78	1.96	−3.5		39.5	39.4	26.8
	50	5.35	1.73	−1.3			41.0	
	100	4.68	1.26	−0.3			41.3	
Cl^-	0	6.55	5.04	−8.3			18.6	
	25	6.20	4.30	−4.1	−0.67	19.6	20.6	15.0
	50	5.87	3.65	−1.8			21.2	
	100	5.00	2.60	−0.3			20.5	
Rb^+	0	7.37	6.04	−9.3			9.8	
	25	7.05	5.00	−4.6			11.3	
	50	6.69	4.10	−2.0	−1.00	11.2	11.6	8.4
	100	5.64	2.68	−0.3			10.3	
Mg^{++}	0		7.46	−10.3			−24.5	
	25	8.00	5.94	−5.1	−4.50	0	−25.8	0
	50		4.72	−2.2			−27.6	
	100		3.05	−0.4			−30.7	

its volume in the crystal. The zero volume for magnesium ion in the crystal is calculated from compounds with anion–anion contact.

The literature on apparent and partial molal volumes in nonaqueous solvents is scarce. Bateman (20) has measured the apparent molal volumes of barium chloride and strontium chloride in ethanol–water mixtures in concentrations from 0.05 to 0.5 molar. For both salts ϕ is a maximum near 60 per cent ethanol at every concentration. Filippova (63) has reviewed earlier work on alcohols and amines.

Rutskov (175) has calculated some ionic volumes based on the assumption that V_1, the volume of an ion in solution, is independent of the degree of disssociation, the nature of the salt, and temperature. If V_2 is the ionic volume in the crystal, then $V_1 - V_2$ is the volume change on the solution of the crystal. If $V_1 - V_2 < 0$, Rutskov finds the solubility low, and good if $V_1 - V_2 \geqslant 0$. Thus, for sodium, potassium, rubidium, and chloride ions $V_1 - V_2 = 0$; for ammonium ion $V_1 - V_2 = +10$; for sulfide ion, $V_1 - V_2 = +10$; for thiocyanate ion, $V_1 - V_2 = +8$ (all in milliliters per gram-equivalent). In crystal hydrates Rutskov finds the volume of the first mole of water to be 12 ml., and that of the sixth mole 16–17 ml.

Recently Stokes and Robinson (196) have applied Glueckauf's (77) free-volume statistics to the calculation of ionic partial molal volumes. Using the results of Alder (3) that spheres randomly packed into a medium of equal density occupy 0.58 of the total volume, they assume that spherical ions which dissolve without significant electrostriction contribute to the volume of the system an amount $4Nb^3(3 \times 0.58)$ per ion of radius b, i.e., the ionic molar volume is

$$\bar{V}^0 = \frac{4\pi N b^3}{3 \times 0.58} = 4.35 \times 10^{24} b^3 \tag{34}$$

Using data on the alkali metal bromides and iodides whose $\bar{V}^0$ is a linear function of the Pauling anion radius, they obtain anionic volumes and calculate cationic ones by difference. The additivity relation is then used to determine volumes for a large number of other ions. The results are approximately 4 cm.^{3} per mole larger for anions and smaller for cations than those proposed by Bernal and Fowler (22) on the assumption that the ionic volumes of cesium chloride in water were proportional to their ionic volumes in the solid state. Stokes and Robinson find for hydrogen ion $\bar{V}^0 = -7.2$ ml., a value close to that given by Couture and Laidler (41). The resulting values are then used to find the Debye–Hückel a parameter (*cf.* Section VI,A,2,(c)).

(b) Molar refraction

The calculation of ionic radii from refraction data—solid, gas, or solution—is based on some relations between the polarizability and the radius r. Thus, for example, Wasastjerna (207) derived ionic radii by considering the ions as conducting spheres. In that case $\alpha = r^3$. The procedure for obtaining ionic radii has been described in Section IV. The basic theory has been described in some detail by Glasstone (75). Much of the early work on electrolytes has been summarized by Fajans (61). Fajans' theory, as well as more recent work, is summarized and examined by Böttcher (30), who criticizes (27, 31) Fajans' (60) interpretation of deviations from additivity in the molar refractions of ions and shows that such deviations can be explained quantitatively by a correction of the Lorenz–Lorentz formula for the difference in the internal field of different particles. He obtains

$$\frac{(n^2 - 1)(2n^2 + 2)}{12\pi n^2} = \sum_i N_i \alpha_i^*$$

where n is the index of refraction of the solutions, and N_i is the number of particles of the i^{th} kind per cubic centimeter. α_i^* is then related to the ionic radius

$$\alpha_i^* = \frac{\alpha_i}{1 - \frac{\alpha}{r_i^3} \cdot \frac{2n^2 - 2}{2n^2 + 1}}$$

where r_i is the radius of the particle, measured from its center to where the liquid begins. In water and water–glycerol solutions, values of r_i do not differ greatly from Pauling's crystal radii; e.g., Böttcher gives 1.75 (Pauling, 1.81) for chloride ion and 1.12 (Pauling, 1.33) for potassium ion.

2. *Methods yielding internuclear distances*

(a) X-ray diffraction

Although the earliest papers appeared more than twenty years ago (138, 168, 194), determination of the structure of electrolytic solutions is still a largely neglected field. What work has appeared is on aqueous solutions. Since even in liquid structure many problems remain, this neglect is not surprising, for the interpretation of solution data is more difficult. As Prins (168) points out, scattering from the solvent is always present and the data admit of a considerable variety of structural possibilities. Consequently the study of dilute solutions, which would be of the greatest interest, is the most difficult and work has been carried out mainly on concentrated solutions. For example, Brady and Krause (35) in studying potassium hydroxide and potassium chloride used 11 per cent by weight as their most dilute concentration.

X-ray data do not, of course, yield ionic radii, but peaks of the scattering curves represent favored (most probable) distances in the solution and are commonly interpreted as nearest-neighbor distances, while the area under a given peak corresponds to the number of nearest neighbors at that distance. For example, in a potassium hydroxide solution (35) peaks were found at 2.87 A. (18.8 per cent KOH), at 2.92 A. (11.4 per cent), and at 4.75 A. The approximate ionic radii from crystals (1.33 A. for potassium and hydroxide ions and 1.38 A. for water) being known, the smaller distances can be identified as K^+-H_2O and OH^--H_2O ($\sim$2.71 A.) and H_2O-H_2O (2.72 A.), whereas the peak at 4.75 A. is identified with the second-nearest H_2O neighbor. Areas under the peaks are compatible with several different structures, and arguments used to distinguish between these do not unequivocally rule out all but one. For example, in potassium chloride the authors arrive at a hydration number $\geqslant 5.4$ for chloride ion, which they interpret as an increase in the tendency for the close-packing of water.

Vaughan, Sturdivant, and Pauling (203) have determined the structures of several complex ions—$PtBr_6^{--}$, $PtCl_6^{--}$, $Nb_6Cl_{12}^{++}$, $Ta_6Br_{12}^{++}$, $Ta_6Cl_{12}^{++}$—in ethanol solution. They find that intermetallic distances in these structures are in reasonable agreement with those predicted from Pauling's theory (158) of intermetallic bonds when the usual ionic radius is assigned to the halide ions.

Much more work in this field is needed. A combination of structural information with data such as molal volumes, which measure a total change for solute plus solvent, should lead to a better understanding of solutions.

(b) Dipole moments

When an electrolyte is dissolved in a nonpolar solvent the dissociation constant is extremely low ($K < 10^{-12}$) and at low concentration essentially only ion-pairs are present. These can be thought of as quasi-molecules characterized by a dipole moment. Methods for the calculation of dipole moments from dielectric constants are well established (187). The only such study was carried out by Kraus and coworkers (72, 95) for a series of salts in benzene at 25°C. Of interest here is that a values obtained from these measurements are rather small. (For a comparison with other methods see table 22.) Certainly the method has not received the attention it deserves. A comparison of a values in different solvents as well as in the gas phase would certainly be of interest.

(c) Fitting activity coefficients

The development of the theory of activity coefficients is too well known and has been treated too extensively by other authors to warrant review here. For treatments of this topic the reader is referred to works by Glasstone (74), Harned and Owen (88), Stokes and Robinson (172), and Eucken (59). One could sum up the situation briefly by saying that the fitting of activity coefficients to concentrations above that where the Debye–Hückel limiting law holds requires the introduction of an internuclear distance, i.e., a distance between the centers of oppositely charged ions, a. However, since frequently a is significantly larger than the sum of the crystal radii, this is interpreted in terms of a solvation model: the required distance corresponds to a partial interpenetration or overlapping of the hydration spheres. Eigen and Wicke (53) have applied this idea in great detail.

The point that the authors wish to make here is that at the present state of the theory not too much meaning can be attached to numerical values of a; one can only expect them to be reasonable. Thus, for the few cases in which a is *smaller* than the sum of the crystallographic radii, special *ad hoc* explanations are usually required. For all others one would expect a to depend on the electrolyte, the concentration, and the equation by which it is calculated.

3. *Methods yielding ionic radii: solvation models, ionic free energies, and entropies*

Theories of ionic solvation have recently been reviewed by Conway and Bockris (40) and by Bockris (28). These authors divide solvation theories into two types: those considering the solvent as a continuous dielectric medium and those considering it as an assembly of molecules, i.e., structural theories. Both types postulate changes in the solvent as a result of the presence of ions, but the latter yield primarily solvation numbers, i.e., a number of solvent molecules attached more or less firmly to the ion under a specified set of conditions. Obviously the term radius is virtually meaningless here, for how far is the radius to extend? Should it include only the bare ion or part or all of the first (primary) hydration sheath? (*Cf.* Section VI,A,2,(a).)

If the solvent is a continuous medium one may speak of an "effective" ionic radius of the "bare" ion or of a cavity in the dielectric all or part of which is occupied by the ion. Calculations of this type are usually based on experimental heats or free energies of hydration. In order to split these thermodynamic quantities for electrolytes into their ionic components, some extrathermodynamic assumptions are necessary. For a discussion of these the work of Conway and Bockris (40) should be consulted.

The authors restrict consideration here to calculations directly applicable to ionic size. The earliest theory of solvation was due to Born (34), who considered the ion as a rigid sphere of radius r and charge $Z\epsilon$ in a continuous medium of dielectric constant D and calculated the electrostatic free energy of solvation as

$$\Delta F = -\frac{NZ^2\epsilon^2}{2r}\left(1 - \frac{1}{D}\right) \tag{35}$$

If crystal radii and the macroscopic dielectric constant of water are used, values of ΔF obtained are too high. Webb (209) corrected Born's theory for the change in dielectric constant near the ion, while Latimer, Pitzer, and Slansky (125) proposed "effective Born radii" which would make the free energy of both anions and cations fall on the theoretical curve (ΔF vs. Z/r). In general, anionic radii were required to be 0.1 A. and cationic radii 0.85 A. larger than their crystal radii. This was explained structurally in terms of the orientation of water molecules in the hydration sheath; those around the anions have their hydrogen atoms turned in, those around the cations their oxygen atoms. Latimer (124) has derived a set of effective radii based on the linearity of the ΔS vs. Z/r plot. Table 13 shows a comparison of ionic radii calculated by Webb and Latimer for several ions. Columns 4 and 5 show a comparison of crystal radii obtained by Latimer (by subtracting 0.1 A. from the value for the anion and 0.85 A. from the value for the cation) with Pauling's values. The agreement between Latimer's and Pauling's crystal radii is excellent. Webb's values for anions are about 0.3 A. larger for anions and ~0.54 A. larger for the cations than the crystal radii. The sum of these differences is 0.98 A. compared with Latimer's value of $0.85 + 0.10 = 0.95$ A. Evidently the two theories of hydration both require a certain average effective radius, but differ in the way in which the contribution of the water in the hydration sphere is to be distributed between anions and

TABLE 13

Ionic radii from hydration theories

Ion	r (Latimer)	r (Webb)	r*	r (Pauling)	r (Webb) $-r$ (Pauling)
	A.	*A.*	*A.*	*A.*	*A.*
F^-	1.45	1.75	1.35	1.33	0.42
Cl^-	1.91	2.24	1.81	1.81	0.43
Br^-	2.05	2.38	1.95	1.95	0.43
I^-	2.26	2.60	2.16	2.16	0.44
Li^+	1.48		0.65	0.60	
Na^+	1.80	1.51	0.95	0.95	0.56
K^+	2.18	1.87	1.33	1.33	0.54
Rb^+	2.33	2.02	1.48	1.48	0.54
Cs^+	2.54	2.19	1.69	1.69	0.50
Cd^{++}	1.62		0.77	0.97	
Ca^{++}	1.84		0.99	0.99	
Sr^{++}	2.00		1.15	1.13	
S^{--}	2.09		1.99	1.84	
Ba^{++}	2.25		1.40	1.35	
Al^{+++}	1.38		0.53	0.50	
Fe^{+++}	1.43		0.58	0.60	
In^{+++}	1.56		0.71	0.81	

* Obtained by Latimer by subtracting 0.1 A. from the value for the anion and 0.85 A. from the value for the cation.

cations. In Webb's theory 0.43 A. is to be added to the anions and 0.54 A. to the cations. Presumably any other method would lead to the sum total increment of ~0.95 A. per ion-pair, but the distribution might be different. Passoth (155) has criticized Latimer's use of Webb's theory, which gives the wrong dependence on $D(r)$. He uses the correction given by Sack (176), which yields for the hydration energy

$$\Delta H = -N\frac{\epsilon^2}{2}\left(\frac{1}{r_i} - r_i\int\frac{2}{D_r + D_\theta}\cdot\frac{1}{r^2}\,dr\right) \tag{36}$$

The values given for the alkali metal ions are approximately 0.4 A. smaller, and those of the halides about the same amount larger, than Latimer's values.

Recently Laidler (115) and Laidler and Couture (42) have reëxamined the problem of ionic entropies. Accepting Gurney's (81) argument that the partial molal entropy of the hydrogen ion is −5.5 e.u., they derive for the "absolute" entropy of monatomic ions

$$\bar{S}^0 = 10.2 + \frac{3}{2}\ln M - 11.6z^2/r_u \tag{37}$$

where r_u is Pauling's univalent ionic radius. This contrasts sharply with the z/r dependence derived by Powell and Latimer (167) on the basis of $\bar{S}_{H^+} = 0$

$$\bar{S}^0 = 37 + \frac{3}{2}\ln M - \frac{270z}{r_e} \tag{38}$$

where r_e is an "effective" radius $= r_e^+ = r_{\text{crystal}} + 2.0$ A., $r_e^- = r_c + 1.0$ A. Couture and Laidler point out that $\bar{S}^0$ can be considered the sum of an electrostatic term $\bar{S}_e = (z^2\epsilon^2/2rD)(\partial \ln D/\partial T) = 9.42z^2/r$ e.u. in water at 25°C., which is just the Born entropy, and a nonelectrostatic term

$$\bar{S}_{\text{n.e.s.}} = \frac{3}{2} \ln M + 10.2 \tag{39}$$

which can be derived from free-volume theory, i.e., considering the translation of an ion in a free volume v_f.

$$S_{\text{n.e.s.}} = R\left[\frac{3}{2} + \ln\ (2\pi mkT)^{3/2}v_f/h^3\right] \tag{40}$$

Allowing for a "cratic" (125) term due to the mixing of the ions with water $= R \ln (1000/55.5) = 7.9$ e..u, they obtain $v_f = 0.73$ cu. A. For oxyanions the situation is similar, though somewhat more involved. The relation is $\bar{S}^0 = 40.2 + \frac{3}{2} R \ln M - 27.2Z^2/0.25nr$, where the first two terms represent the nonelectrostatic part and r is the radius of the circumscribed sphere $= r_{12} + 1.40$ A.; r_{12} is the distance from the central atom to the center of the surrounding oxygens (sum of Pauling's covalent radii) and 1.40 A. is the oxygen radius. n is the number of charge-bearing ligands attached to the central atom, e.g., $n = 4$ for sulfate ion. This model is also applied to the calculation of partial molal volumes. The volumes and radii for many oxyanions are listed in Section VI,A,1,(a).

Relations have also been derived between the heats of hydration and ionic radii. Thus Robertson (171) used the Born equation as corrected by Bernal and Fowler (22) and found that ΔH^0_{hydr} is proportional to $r^{-2/3}$ for cations and $r^{-3/2}$ for anions, as compared with r^{-1} for the uncorrected Born equation.

Kapustinskiĭ and Yatsimirskiĭ (105, 215) derived an equation relating the heat of hydration to ionic radii, based on an equation of Kapustinskiĭ for lattice energy (104). For several tetrahedral and triangular ions

$$\Delta H = 287.2\, \Sigma n(\nu_1\nu_2/(r_1 + r_2)\{1 - [0.345/(r_1 + r_2)]\} \tag{41}$$

where n is the number of ions in the substance and ν_1, ν_2 are the cationic and anionic valences. Values of r calculated for anions differ within 2 per cent depending on the cation. The "radius" of nonspherical anions is larger with larger cations. Thus for the nitrate ion $r = 1.86$ A. in $CsNO_3$ and 1.94 A. in $[Co(NH_3)_5Cl](NO_3)_2$; for the chlorate ion $r = 1.98$ in $RbClO_3$ and 2.05 in $[Ni(H_2O)_4](ClO_3)_2$, presumably because the smaller cation can penetrate more into the anion. In general r lies between the minimum distance of maximum penetration and the radius of the circumscribed sphere. The distance d between the center of the complex anion and cation is not equal to the sum of the radii, $r_1 + r_2$, calculated for a circumscribed octahedron, but for a given lattice type d/r is constant. For example, for the barite structure ($BaSO_4$, $SrSO_4$, $PbSO_4$) $d/r = 1.05$; for the calcite structure ($CaCO_3$, $MnCO_3$, $NaNO_3$) $d/r = 0.90$.

Similarly, for a given type of anion the ratio of r to the radius of the circumscribed sphere is constant. Thus, for triangular ions (NO_3^-, CO_3^{--}) it is 0.67; for tetrahedral ions (ClO_4^-, MnO_4^-, BF_4^-, SO_4^{--}, CrO_4^{--}, MoO_4^{--}) it is 0.79.

TABLE 14

Anionic radii (105, 215)

Ion	r	Ion	r	Ion	r
	A.		A.		A.
BO_3^{--}	1.91	ClO_4^-	2.36	PO_4^{---}	2.38
BeF_4^{--}	2.45	MnO_4^-	2.40	CrO_4^{--}	2.4
IO_4^-	2.49	CO_3^{--}	1.85	MoO_4^{--}	2.54
NO_3^-	1.89	SeO_4^{--}	2.43	SiO_4^{---}	2.4
ClO_3^-	2.00	TeO_4^{--}	2.54	AsO_4^{---}	2.48

This permits calculation of ionic radii for ions whose circumscribed sphere is known. Anionic radii are listed in table 14.

B. KINETIC METHODS

In this section those methods which depend on the measurement of ions in motion are discussed. These include principally diffusion, in which motion takes place under a gradient of concentration (more accurately chemical potential), and conductance and transference, in which the gradient is electrical. Usually some assumption, such as the Kohlrausch law of independent ion migration, is required to determine parameters for individual ions. Since diffusion and conductance involve essentially the same phenomenon, it is not surprising that several equations relate these two. Since the viscosity of the medium is involved, this quantity will enter many of the equations. Although ion-pair contact distances are obtained from conductance measurements a discussion of these is placed in a separate section, since they involve different equations and yield essentially internuclear distances. This review is certainly not meant to be exhaustive. For the basic theory and much experimental work the reader is referred to the book by Harned and Owen (84).

1. Viscosity

There are a few relations which involve only the viscosity of electrolyte solutions.

Onsager and Fuoss (153) define the electrostatic contribution η^* to be the increase in the viscosity η of an electrolyte solution over the viscosity η^0 of a solvent. The equation for η^* is

$$\eta^* = \eta - \eta^0 \tag{42}$$

All viscosities are measured at the same temperature. These authors derived an expression relating the fractional part that η^* was of η in terms of the Debye κ and the radius r of an ion. The equation is

$$\frac{\eta^*}{\eta} = \frac{\kappa r}{80} = \frac{\eta - \eta^0}{\eta} \tag{43}$$

and shows that in the first approximation the relative change in viscosity is proportional to the ratio between the radius of the ion and that of its atmosphere. These authors derived other equations relating η^* to ionic strength and other properties of the solution.

Merckel (137) found that the viscosity of aqueous electrolyte solutions is a pure lyotropic property and is related to the lyotropic number and to the hydration of the ions in a linear manner. Since the viscosity of the solution is related to the hydration of the ions, it is conceivably related to ionic size. This point is rather difficult to check quantitatively, since Merckel's data do not include ion sizes and hydration numbers for the ions in the regions of concentration investigated, which was principally 0.2 and 0.5 normal.

Tollert (199) found that the trend of specific ionic viscosity in 0.1 N concentration for the alkali chlorides agreed with the trend of the ionic radius in the solid lattice. The specific ionic viscosities of the alkali metals gave similar plots to the crystalline ionic radii in the alkali chlorides when plotted against the atomic number of the metals.

Viscosity data on solutions of sodium and potassium chlorides in water at 18°C. were taken from the Landolt-Börnstein-Roth tables (117). These data were for concentrations ranging from 10 to 30 weight per cent of the salts. Calculations by means of equation 43, using the viscosities of these solutions at these concentrations, gave r values for the electrolyte which varied strongly with concentration and which were an order of magnitude greater for sodium chloride than for potassium chloride. Perhaps the equation does not apply to electrolytes at such high concentrations, but differences in viscosity for dilute solutions would probably be so small as to make accurate measurement difficult.

Debye (146), taking the rotating sphere of radius a, related relaxation time τ, the viscosity η of the medium, and a by the equation

$$\tau = \frac{4\pi\eta a^3}{kT} \tag{44}$$

where k is the Boltzmann constant and T the absolute temperature. Presumably for a dipolar substance, e.g., hydrogen chloride in the pure state or in an inert solvent, if the relaxation time and the viscosity were known, the radius a of the molecule could be found. This radius might be related to the radius of the unsolvated or gaseous hydrogen and chloride ions if a way of proportioning the distances could be found. The molecular radius involved in the relaxation phenomenon is that along the axis in which the molecular dipole lies.

Smyth (187) gives the radii of many dipolar molecules calculated from relaxation times in a pure state and in inert solvents. He found that these radii were too low and that they tended to be lower the higher the viscosity of the medium in which measurements were made.

Thus if this approach were found to yield the radii of ionizable dipoles and by some method of resolution the radii of ions, these radii would be small.

2. Diffusion

Glasstone, Laidler, and Eyring (76) derived the equation for the diffusion coefficient D_1 of large molecules to be

$$D_1 = \frac{kT}{a\pi r\eta} \tag{45}$$

where k is the Boltzmann gas constant, T the absolute temperature, η the viscosity, r the radius of the diffusing particles, and a is a factor of the order of unity which allows for the fact that a large molecule B may diffuse owing to the movement of a small molecule A around the B molecule, but that in moving around the large B molecule, the A molecule may not take the shortest path.

The Stokes–Einstein equation

$$D = \frac{kT}{6\pi r\eta} \tag{46}$$

makes $a = 6$, but this involves the approximation of considering the solvent as a continuous medium.

For small molecules Glasstone, Laidler, and Eyring find the diffusion coefficient to be

$$D_s = \frac{kT}{l\eta} \tag{47}$$

hence D_1 and D_s are related by the equation

$$D_1 = D_s \frac{l}{a\pi r} \tag{48}$$

where l is the distance between successive equilibrium positions of the solvent molecule.

It is reasonable to assume that the equation of Glasstone, Laidler, and Eyring can be applied to the diffusion of ions in liquid media as has the Stokes–Einstein equation.

For a single ion Eucken (56) writes for the relationship between the velocity of migration V of the ion constituent and the diffusion coefficient D of the ion the equation

$$D = \frac{VRT}{Z\mathfrak{F}} \tag{49}$$

For an electrolyte as, for example, a strong salt where both ions are involved in the diffusion and in the transport of electricity, Eucken writes

$$D = \frac{2V^+V^-RT}{Z\mathfrak{F}(V^+ + V^-)} \tag{50}$$

Remembering that the equivalent conductance of an ion λ is related to V by the equation

$$V = \frac{\lambda}{\mathfrak{F}} \tag{51}$$

one can write from Eucken's equation (equation 49) and that of Glasstone, Laidler, and Eyring (equation 45)

$$\lambda = \frac{10^7 Z\mathfrak{F}^2}{Na\pi r\eta} \tag{52}$$

where the 10^7 factor accounts for the fact that k in the Glasstone, Laidler, and Eyring equation is in ergs and R in the Eucken equation is in joules. If infinitely

TABLE 15

Ionic radii and difference in successive positions of the solvent molecule calculated from diffusion and conductivity data

Ion	$D^0 \times 10^5$	λ^0	r_l $a = 1$	$r_{s\text{-}e}$	l	r_{52} $a = 1$	r_{52} $a = 6$	l_{53}
	$cm.^2 sec.^{-1}$	$ohm^{-1}\ cm.^2$	*A.*	*A.*	*A.*	*A.*	*A.*	*A.*
H^+	9.34	350	1.99	0.332	4.93	1.57	0.262	4.94
Li^+	1.04	39	17.9	2.99	44.2	14.1	2.35	44.4
K^+	1.74	74	10.7	1.69	26.4	7.74	1.24	23.4
Na^+	1.35	50.5	13.8	2.30	34.1	10.9	1.82	34.3
Cs^+	2.11	79	8.83	1.47	21.8	6.97	1.16	21.9
Tl^+	2.00	75	9.31	1.55	23.0	7.34	1.22	23.1
Pb^{++}	0.98	73	19.0	3.17	47.0	15.1	2.52	47.4
Cd^{++}	0.72	54	25.9	4.31	63.9	20.4	3.40	64.1
Zn^{++}	0.72	54	25.9	4.31	63.9	20.4	3.40	64.1
Cu^{++}	0.72	54	25.9	4.31	63.9	20.4	3.40	64.1
Ni^{++}	0.52	52	35.8	5.97	88.5	21.2	3.54	66.5
OH^-	5.23	196	3.56	0.59	8.80	2.81	0.47	8.83
Cl^-	2.04	76	9.13	1.52	22.6	7.35	1.23	22.8
NO_3^-	1.92	72	9.70	1.62	24.0	7.65	1.28	24.0
CH_3COO^-	1.92	41	9.70	1.62	24.0	13.4	1.23	42.2
IO_3^-	1.09	41	17.1	2.85	42.2	13.4	1.23	42.2
BrO_3^-	1.44	54	12.9	2.16	32.0	10.2	1.70	32.0
SO_4^{--}	1.08	81	17.3	2.88	42.6	13.6	2.26	42.7
CrO_4^{--}	1.07	80	17.4	2.90	43.0	13.8	2.30	43.2
$Fe(CN)_6^{---}$	0.89	100	20.9	3.49	51.7	11.0	1.84	34.6
$Fe(CN)_6^{----}$	0.74	110.5	25.2	4.20	62.2	9.96	1.66	31.3

dilute solutions are considered, D and λ become D^0 and λ^0. An equation in terms of λ for small ions would be

$$\lambda = \frac{10^7 z \mathfrak{F}^2}{N l \eta} \tag{53}$$

and again at infinite dilution λ^0 would replace λ in equation 53.

Kolthoff and Lingane (108) list values of D^0 and λ^0 for individual ions.

The D^0 values inserted into the Glasstone, Laidler, and Eyring equation for large ions give the values for the radii, r_l, recorded in table 15. In the table are also recorded the values of $r_{s\text{-}e}$ from the Stokes–Einstein equation and the distance l between successive equilibrium positions of the solvent molecule calculated from Glasstone, Laidler, and Eyring's equation for small ions. The values of r_{52} and l_{53} calculated from equations 52 and 53 are given in the table and can be compared with values of r_l and l.

Calculation of the radii using the Glasstone, Laidler, and Eyring equation for large ions with a taken as unity gives radii of the ions listed which are too large. Perhaps all these ions would be classified as small ions. The Stokes–Einstein equation gives more reasonable values for the radii of these ions. Equation 52, using a as unity, gives radii smaller, except in the case of acetate ion, than does the Glasstone, Laidler, and Eyring equation for large ions using a as unity. Equation 52 with a as unity gives radii which are too large for the ions listed, but if a is taken as 6, as in the Stokes–Einstein equation, the magnitudes of the radii are fairly reasonable and somewhat less than the corresponding values calculated by the Stokes–Einstein equation.

The values of the distance l between successive equilibrium positions of the solvent are calculated by the Glasstone, Laidler, and Eyring equation for small ions and recorded in column 6 of the table; those calculated by equation 53 are recorded in column 9 of the table. These values as given by either calculation are apparently several ionic diameters and have about the same values for corresponding ions by both calculations.

Harned and coworkers (82, 83) used the Onsager and Fuoss (153) equation for the diffusion coefficient to relate diffusion data for electrolytes in dilute aqueous solution to theory. The equation relates the diffusion coefficient of an electrolyte to its concentration activity coefficient, the equivalent conductance at infinite dilution of the constituent ions, the distance of closest approach of the ions, and the viscosity, dielectric constant, and temperature of the solvent. In the case of potassium chloride, data and theory were in remarkable agreement for the distance of closest approach a of 3.8 A. For calcium chloride an a value of 4.944 A. was used, but in this case the data and theory were not in agreement.

Harned and Levy conclude that since theory and data agree for potassium chloride but not for calcium chloride in dilute aqueous solutions, the Fuoss and Onsager estimate of the electrophoretic effect was either wrong or incomplete for this unsymmetrical type of electrolyte.

Adamson (1) found poor agreement between present data and the electrophoretic treatment of mean diffusion coefficients of electrolytes. He considered an additional effect arising from the counter diffusion of the solvent, but found that this approach yields hydrodynamic radii for electrolytes which are quite large and in concentrated solutions tend to approach an upper limit equal to the radius of the atmosphere.

The hydrodynamic radii, r, calculated for several salts at several molarities are given in table 16. The reciprocals of the Debye kappa (atmosphere radii) corresponding to the concentrations used are included.

Adamson outlined the mathematical basis for the relaxation effect computed for the self-diffusion of ions and presented an alternative theory based on the absolute rate treatment of diffusion. He found that present self-diffusion data are insufficiently precise for adequately testing limiting laws, and that in concentrated solutions, systematic differences appear to exist between the various experimental methods employed.

TABLE 16

Hydrodynamic radii calculated from diffusion data for several salts

Salt	0.001 *M*		0.002 *M*		0.003 *M*		0.005 *M*		0.010 *M*	
	r	$\frac{1}{\kappa}$	r	$\frac{1}{\kappa}$	r	$\frac{1}{\kappa}$	r	$\frac{1}{\kappa}$	r	$\frac{1}{\kappa}$
	A.		*A.*		*A.*		*A.*		*A.*	
Li_2SO_4	12.6	56			10.6	32	9.9	25		
Cs_2SO_4	14.1	56	12.5	39	11.5	32				
KNO_3	7.4	96			6.8	56			5.9	31
$LaCl_3$			13.9	28			11.1	18	9.9	12

3. Conductance

(a) Mobility and conductance

The calculation of ionic radii from ionic constituent mobility U^0 and ionic mobility u^0 per unit field and from ionic equivalent conductance λ^0 are inextricably related and will therefore be considered together. Ionic constituent mobility per unit field and ionic equivalent conductance at infinite dilution are related by the equation

$$\lambda^0 = \mathfrak{F}U^0 \tag{53a}$$

where $\mathfrak{F}$ is the faraday (96,494 coulombs).

The ionic constituent mobility U of an ion of mass m and charge $z\epsilon$ is related to the field strength E by the equation

$$m\frac{\mathrm{d}U}{\mathrm{d}t}\; Ez\epsilon - CU \tag{54}$$

which at the steady state where $\mathrm{d}U/\mathrm{d}t$ equals zero gives

$$U = \frac{Ez\epsilon}{C} \tag{55}$$

Therefore,

$$U^0 = \frac{z\epsilon}{C} \tag{56}$$

In these equations C is a constant.

Eucken (58) derived equation 57 in the form

$$U^0_{\pm} = \frac{10^{-3}z\epsilon\mathfrak{F}}{300(6\pi\eta r)} = \frac{(10^{-3})(z)(477)(10^{-10})(96{,}494)}{300(6\pi\eta r)} = \frac{0.815 \times 10^{-11}z}{\eta r} \tag{57}$$

for the ionic mobility of a plus or minus ion of valence z. Using this equation Eucken calculated the radii of various positive and negative ions (see table 17). Uncorrected and corrected values calculated from equation 57 are given together with crystal radii.

TABLE 17

Ion radii in water solution at 25°C. calculated from equation 57 and compared to those from crystallographic measurements

Ion	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Mg^{++}	Ca^{++}	Ba^{++}
U^0_+ at 18°C	0.0327	0.0434	0.0645	0.064	0.068	0.0543	0.0455	0.0575	0.0552
r (uncorrected) in A	2.36	1.79	1.20	1.20	1.13	1.41	3.40	3.00	2.80
r (crystallographic) in A	~0.70	0.97	1.33	1.49	1.67	1.13	~0.78	~1.00	~1.80
r (corrected) in A	3.40	2.76	2.32	2.28	2.28		4.65	3.21	3.92
Ion	F^-	Cl^-	Br^-	I^-	NO_3^-	ClO_3^-	ClO_4^-	MnO_4^-	CH_3COO^-
U^0_- at 18°C	0.0466	0.0654	0.0675	0.0660	0.0617	0.0549	0.0583	0.053	0.035
r (uncorrected) in A	1.66	1.18	1.14	1.17	1.25	1.40	1.32	1.45	2.2
r (crystallographic) in A	1.33	1.81	1.96	2.20	2-2.5	~2.7	~2.9	~2.7	~3.0
r (corrected) in A		2.14	2.27	2.28					

The corrections were necessary, since Stokes' law gives values of radii which are too low for small ions whose size approaches the size of the solvent molecules. Eucken (55) introduces a constant less than 1 in the denominator of equation 57 to correct for the small size of small ions and lets the factor approach 1 for large ions. This method of calculation allows all radii for ions in solution calculated by equation 57 to exceed the corresponding crystallographic radii in size. The uncorrected radii calculated by equation 57 were not always larger than the corresponding crystallographic radii,—for example, for silver ion and many of the negative ions.

Eucken has discussed the effect of the aggregate of eight water molecules in solvent water on the mobilities and hence size of ions.

Moelwyn-Hughes (144) takes C in equation 56 to be $6\pi\eta r$ from Stokes' law, where η is the viscosity of the medium and r is the ionic radius. Hence,

$$U^0 = \frac{z\epsilon}{6\pi\eta r} \tag{57}$$

For water at 18°C. η is 0.01041 poise, and therefore for ions of all valences Moelwyn-Hughes (146) writes

$$r \text{ (in A.)} = \frac{0.243}{U^0} \tag{58}$$

Moelwyn-Hughes (145) has listed the ionic constituent mobilities, ionic equivalent conductances, and ionic radii of many ions, both negative and positive. He concluded that except for large ions the radii are unreasonably small and vary in a direction contrary to the crystal radii. For example, from these calculations the radii of the H^+, Li^+, Na^+, K^+, Rb^+, and Cs^+ ions are, respectively, 0.253, 2.36, 1.80, 1.21, 1.16, and 1.155 A. In the crystal state the radii from x-ray data of the Li^+, Na^+, K^+, Rb^+, and Cs^+ ions are 1.52, 1.86, 2.25, 2.43, and 2.62 A., respectively (142).

Thus the elementary theory is not applicable to small ions but does explain Walden's rule for large ions. Since ionic constituent mobility is proportional to ionic equivalent conductance, the product of either with the viscosity is constant for an ion of given charge and radius, as is evident from equation 57. Also for a uni-univalent electrolyte (128)

$$\eta\Lambda_0 = \eta(\lambda_0^+ + \lambda_0^-) = \frac{\epsilon\mathfrak{F}}{6\pi}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{59}$$

This gives for the radius in Ångström units of an ion of radius (z) (205):

$$r \text{ (in A.)} = \frac{0.814}{\eta\lambda_0}\,|z| \tag{60}$$

Moelwyn-Hughes (145) found r_+ for the tetraethylammonium ion to be 3.05 A. and r_- also to be 3.05 A. for picrate ion in a variety of nonaqueous solvents. The radii for other ions were individually more reasonable than the corresponding radii in water. However, the radii of the elementary ions were found to vary in the wrong direction among themselves. The radii for lithium, sodium, and potassium ions were 3.86, 3.42, and 3.01 A., respectively.

Walden and Birr (206) found that the solvation numbers of the ions could be found by calculating the difference between the molecular volumes of the solvated and the unsolvated ions. Moelwyn-Hughes (145), using this procedure, found that the solvation number decreased from a value of 6 for lithium ion to 4 for potassium ion, and from 3 for chloride ion to 1 for iodide ion. These data were in harmony with the average solvation numbers found for these ions by Walden and Birr.

Kressman and Kitchener (114), in a study of exchange equilibrium constants and ionic sizes, calculated, from the equation given by Walden (equation 60) and using the ionic equivalent conductances at infinite dilution given in the Landolt-Börnstein tables (114), the hydrated radii of ions at 25°C. They used the crystalline radii given by Pauling (159). The values of the hydrated ionic radii given by these authors for Li^+, Na^+, K^+, Rb^+, and Cs^+ are 2.31, 1.78, 1.22, 1.18, and 1.16 A., respectively. These compare favorably with the values found by Moelwyn-Hughes from mobility data and recorded in table 17. As calculated by Kressman and Kitchener, over half the ions listed have hydrated radii which are smaller than the corresponding crystalline radii. Also, the hydrated radii of sodium and potassium ions are smaller, as calculated by Kressman and Kitchener, than the radii of the same ions as calculated by Secoy (183) applying kinetic theory to critical phenomena for aqueous solutions of uni-univalent electrolytes. Secoy's work will be mentioned again later.

Hughes and Hartley (47) found from conductance data and using the Stokes equation that ions are smaller in water than in alcohols or acetone and that the addition of water to an alcoholic electrolyte solution diminishes the ionic radii. In table 18 the radii of several ions in different organic solvents and in water are given. The values in water correspond well and show the same trend of those found by Moelwyn-Hughes and by Kressman and Kitchener. Some radii quoted from Wasastjerna (207) are listed along with similar data from Pauling (161) and Moelwyn-Hughes (141). Wasastjerna divided the observed interatomic

TABLE 18

Ionic radii in Ångström units at 25°C. in various solvents

Ion	Water	Methanol	Ethanol	Acetone	Lattice		
					Wasastjerna	Moelwyn-Hughes	Pauling
	A.	*A.*	*A.*	*A.*	*A.*	*A.*	*A.*
Li^+	2.3	3.78	5.16	3.40	0.72	0.758	0.60
Na^+	1.79	3.27	4.04	3.21	1.01	1.012	0.95
K^+	1.22	2.78	3.45	3.10	1.30	1.341	1.33
$N(C_2H_5)_4^+$	2.76	2.43	2.67	2.85			
Cl^-	1.21	2.91	3.11	2.40	1.72	1.811	1.81
Br^-	1.18	2.69	2.95	2.29	1.92	1.973	1.95
I^-	1.20	2.45	2.63	2.36	2.19	2.228	2.16
ClO_4^-	1.33	2.11	2.23	2.23			
Picrate$^-$	2.98	3.20	2.82	2.98			

TABLE 19

Application of equation 60 to the picrate ion

Solvent	$\lambda_0\eta$	V_m	r_{pi}	Solvent	$\lambda_0\eta$	V_m	r_{pi}
		cm.^{3}	*A.*			*cm.*^{3}	*A.*
Water	0.273	18	3.3	Pyridine	0.297	81	3.9
Methanol	0.261	40.4	3.7	Nitrobenzene	0.293	100	4.1
Ethanol	0.279	58.6	3.8				

distance by assuming that ionic refractions are roughly proportional to ionic volumes. Moelwyn-Hughes explains the variation in crystal radii reported by him when compared to other data as arising from his values being based on recent work.

Kortüm and Weller (112) used the equation derived by applying Stokes rotation to the hydrodynamic theory of ion mobility

$$\lambda_{i,0} = \frac{0.815}{\eta_{\text{macro}}\left(1 - \dfrac{0.21V_m}{r_i^3}\right) r_i}$$

to solve for the radius r_i of the ion. In this equation $\lambda_{i,0}$ is the equivalent conductance of the ion at infinite dilution, η_{macro} is the macroviscosity of the medium, V_m is the molar volume of the solvent, and r_i is the radius of the ion in Ångström units. A summary of his calculations for picrate ion is given in table 19.

By considering the ion as moving among different three-dimensional aggregates of solvent of volume fraction p, Kortüm and Weller corrected the macroviscosity to effective viscosity and derived the equation:

$$\lambda_{i,0} = \frac{0.815(1 + 2.5P)}{(1 + 0.5p)\eta_{\text{macro}}\left(1 - \dfrac{0.21V_m}{r_i^3}\right) r_i} \qquad (61)$$

Table 20 shows how the solvated radius of the lithium ion varies with mole per cent ethanol in a water–ethanol mixture. Thus the radius of the solvated ion increases as the amount of the solvent component with the larger molar volume (ethanol) increases.

Fuoss (68) used the Einstein equation

$$\eta = \eta_0\left(1 + \frac{5}{2}\phi\right) \qquad (62)$$

to correct η_0, the viscosity of the pure solvent, to η, the viscosity of a solution containing ϕ volume fraction of solute. The hydrodynamic radius R of the

TABLE 20

The solvated radius of the lithium ion as a function of the mole per cent ethanol in water–ethanol mixtures

Mole per cent ethanol	0	10	20	30	40	60	80	100
r_{Li^+} in A	3.18	3.30	3.47	3.72	3.89	4.30	4.68	5.13

cations which was dependent on the concentration c of solute was related to ϕ by the equation

$$\phi = \left(\frac{4\pi R^3}{3}\right)\left(\frac{N_c}{1000}\right) = Sc \tag{63}$$

where N is Avogadro's number. Then Λ', which includes both the effect of ion association and ion atmosphere but not the viscosity effect, is related to Λ_0, the equivalent conductance at infinite dilution, by the equation

$$\Lambda' = \Lambda_0 - \frac{5\Lambda_0 S}{2} c \tag{64}$$

The slope of the straight-line plot of Λ' versus c for tetraisoamylammonium nitrate was used to calculate S and from S the hydrodynamic radius R of the tetraisoamylammonium cation for various percentages of dioxane in dioxane–water solutions at 25°C. These hydrodynamic radii for this cation were practically constant for the various solvent mixtures, the range being from 7.3 A. in pure water to 8.4 A. in 50 per cent dioxane in water. The hydrodynamic radius of tetrabutylammonium cation in tetrabutylammonium bromide in water had an average value of 5.98 in the concentration range 0.0175 to 0.290 equivalent per liter of the salt in water at 25°C.

The solvent correction of Kortüm and Weller increases the mobility and equivalent conductance of an ionic species, owing to decrease in the effective viscosity as compared to the macroscopic viscosity of the medium. The solute correction of Fuoss decreases the mobility and equivalent conductance of an ionic species, owing to an increase in the effective viscosity as compared to the macroscopic viscosity.

Amis (7) found that the deviation from Walden's rule, calculated as ionic radii, indicated solvation in the case of certain ions in certain solvents to be selective, with the ions clinging preferentially to the more polar component of the solvent (in the cases studied, water) even at relatively low concentrations (20 weight per cent) of this component. An effective distance of electrostatic attraction of ions and molecules is fairly constant for different solutes in different mixed solvents. The equation was derived by assuming that the distance r_s of effective electrostatic attraction between an ion and a molecule is the sum of the radius r_i^0 of the nonsolvated ion and a term proportional to the electrostatic attractive force between the ion and the dipolar molecules of solvent. If r_i^0 in the sum is neglected and the term involving the force is substituted in the Walden rule equation the value for r_s, the distance of effective electrostatic attraction of the ion and the dipole, becomes

$$r_s = \sqrt[3]{\frac{1000\pi\eta K\mu\Lambda_0}{D\mathfrak{F}}} \tag{65}$$

where μ is the moment of the dipole molecule of the solvent.

The average value for r_s was found to be 12.72 ± 0.32 A. when the data for potassium chloride in water, methanol, and water–methanol at three temperatures and the data for tetramethylammonium chloride and tetraethylammonium picrate in both ethyl and methyl alcohol were used in the calculation.

Brull (37) from ionic mobility data deduced the values of ionic radii and compared these with the "a" parameters of the Debye–Hückel theory and with extensions of this theory. He concluded that the "a" parameters of these theories are only empirical corrective coefficients to make theoretical results conform to experimental data (*cf.* Section VI,A,2,(c)). Brull concludes, however, that the "a" parameters of Bonino (33) have an unquestionable theoretical significance, both because the parameters can be calculated from the radii and the deformabilities of the ions and because it is possible to deduce the parameters from other experiments, e.g., mobility measurements, which do imply directly the concept of thermodynamic activity from which the parameters were determined by Bonino.

Gorin (80) has derived the conductance equation

$$\Lambda = \frac{\Lambda_0 + (r_- \lambda_{0,+} + r_+ \lambda_{0,-})\kappa}{1 + (r_+ + r_-)} \tag{66}$$

for binary electrolytes. He used the Debye–Hückel theory to calculate the potential at the surface of an ion. He assumed, however, that an applied external field does not sensibly distort the ionic atmosphere. Thus he neglects the asymmetry potential in his derivation. Gorin's equation will not therefore reduce to the Onsager limiting law. The equation has the limiting slope represented by the equation:

$$\frac{\mathrm{d}\Lambda}{\mathrm{d}\kappa} = -(r_+ \lambda_{0,+} + r_- \lambda_{0,-}) \tag{67}$$

Harned and Owen (86) give a table of estimated ionic radii at 25°C., using the Gorin equation. Their values are listed in table 21.

Talat-Erben (197) used an ellipsoidal model for organic chain anions. He related the mobility U of the ion of charge $z\epsilon$ to the equatorial radius b of the ellipsoid and the ratio α of the radius of revolution a and the equatorial radius. The equation relating these quantities is

$$U = \frac{z\epsilon h}{8\pi\eta b}\left[\frac{2\alpha^2 - 1}{(\alpha^2 - 1)^{3/2}} \arg ch\, \alpha - \frac{\alpha}{\alpha^2 - 1}\right] \tag{67a}$$

Using this approach Talat-Erben was able to show a linear relation between the length of the chain and the number of carbon atoms in the ion, and to calcu-

TABLE 21

Ionic radii estimated by the Gorin equation at 25°C.

Electrolyte	Λ_0	$\lambda_{0,+}$	$\lambda_{0,-}$	$\left(\frac{\mathrm{d}\Lambda}{\mathrm{d}\sqrt{C}}\right)_{C\to 0}$	r_+	r_-
					A.	*A.*
HCl	426.06	349.73	76.33	−156.5	0.945	1.921
KCl	149.86	73.53	76.33	−96.1	1.978	1.933
NaCl	126.45	50.12	76.33	−90.6	2.562	1.937
LiCl	115.03	38.70	76.33	−88.7	3.095	1.976

late the characteristic angle between the carbon–carbon bonds. This angle agreed in magnitude with the angle determined from the theory of the regular tetrahedra.

(b) Ion-pairs

All measurements on and theories of ion-pairs involve one ion-size parameter —the "contact distance" a, i.e., the distance between the positive and negative centers of charge when the ions are in contact. Hence the fundamental problem here (as elsewhere) is to divide this distance into its anionic and cationic components. Moreover, the term "ionic radius" must be relatively devoid of meaning unless the ions are approximately spherical. For many large organic ions, such as picrate, this is certainly not the case. Such ions are perhaps better thought of as ellipsoidal.

The contact distance a has been obtained from two kinds of measurements: dipole moment and conductance. The former are discussed in Section VI,A, 2,(b).

Conductance data yield ion-size parameters by two methods.

(*1*) From Λ_0 values and the application of Stokes' law the radius of the equivalent solvodynamic sphere can be calculated. This method has been discussed in Section VI,B,5,(a) above.

(*2*) From various equations which relate the ion-pair dissociation constant K, the dielectric constant D of the medium, and a. The procedure for the calculation of K itself from conductance data is itself a complex process and will not be reviewed here (69, 184). For solvents of low dielectric constant ($K < 0.01$) the methods used have been subjected to considerable scrutiny. Recently Fuoss (67) has extended the method to solvents of higher dielectric constant so that in principle K can be obtained for any ion-pair in any solvent. The calculation of a from K and D is by no means straightforward. The a's obtained seem to depend on the method of calculation. These methods are briefly discussed in Sections (1) to (4) below; in (5) the equations are compared.

(1) The Bjerrum equation (25)

Historically, this is the earliest treatment of ion-pairs. It assumes that the ions can be treated as rigid unpolarizable spheres in a medium of fixed macroscopic dielectric constant. All ion–solvent interactions as well as nonpolar quantum bonds are excluded.

By assuming a Maxwell–Boltzmann distribution for the ions Bjerrum shows that for a distance $q = \epsilon^2/2DkT$ the probability has a minimum. For distances $q \leq r \leq a$ Bjerrum considers the ions associated. Harned and Owen (85) have discussed this theory in some detail. Only certain implications of the theory will be discussed here: The solvent influences the extent of dissociation through its macroscopic dielectric constant D. It follows that (*a*) K should be the same for the same salt in different solvents having the same dielectric constant (at constant temperature) and (*b*) a should be independent of solvent altogether. However, it is known that prediction (*a*) is only good within an order of magnitude and that a varies with solvent as much as 2 A. for large ions, e.g., for tetrabutylammonium picrate there is a variation of 40 per cent. It has been suggested that the theory masks specific solute–solvent interactions. The voluminous literature has recently been summarized by Kraus (113).

(2) The Denison–Ramsey equation (47)

Whereas the Bjerrum equation is essentially statistical, the Denison–Ramsey theory is thermodynamic. Only ions in contact are counted as ion-pairs; hence the free energy of dissociation is $\Delta F^0 = N\epsilon^2/aD$. This approximation restricts the theory to solvents of low dielectric constant, in which there are few ions at intermediate distances. The solvent is treated as a continuous medium. One would thus expect this theory to yield the same a values as the Bjerrum theory in solvents of low dielectric constant from experimental K's. However, for tetrabutylammonium picrate a_B and a_{DR} differ by more than 1 A. in several different solvents. An explanation for this difference has recently been given (64).

(3) The Gilkerson equation (73)

Gilkerson's treatment is based on statistical mechanics; it assumes that the Kirkwood free-volume theory (106) is applicable to ions and ion-pairs. It differs from previous equations in that specific solute–solvent interaction is taken into account. However, it permits a calculation of a only on the assumption that a for a given electrolyte is independent of solvent and temperature. Gilkerson obtains $a = 2.51$ A. for tetrabutylammonium picrate compared with values between 5 and 7 A. calculated from the Bjerrum and Denison–Ramsey equations.

(4) The Fuoss–Kraus theory (70)

For solvents in which the dissociation is relatively large ($K > 0.01$) the earlier methods of Fuoss and Kraus and Shedlovsky (69, 184) did not permit an accurate calculation of K. A new derivation by Fuoss removes this limitation. This theory will not be discussed here, but reference will be made to a part of their paper more related to ion size. One defect of the Bjerrum theory is that it predicts a "limiting value of the dielectric constant" for a given electrolyte beyond which no association occurs at all. Moreover, it, as well as the Denison–Ramsey theory, makes allowance only for charge-charge forces. Fuoss and Kraus observed that for several salts in dioxane–water mixtures the association constant of the ion pair $A = K^{-1}$ is a linear function of D^{-1}. This led them to suggest that A is of the form

$$A = A_0 \exp(u/kT) \tag{68}$$

where u is an electrostatic free energy. However, if it is assumed that $u = \epsilon^2/aD$, the value of a obtained is unreasonably small when compared to a values obtained from conductance plots. They therefore express u as

$$u = (\epsilon^2/aD) + (\mu/d^2D) \tag{69}$$

where μ is the dipole strength and d is the distance from the center of the cation to the electrostatic center of the dipole. Using this expression, reasonable and consistent a values are obtained. It should be emphasized that in order to carry out the computation of A in solvents of high dielectric constant, data in solvents of lower dielectric constant must be available and it must be assumed that for a given salt a remains constant independent of solvent composition. This limits the method to mixed solvent systems. Moreover, conductance data of high precision (±0.02 per cent) are required. It would be interesting to extend the Fuoss–Kraus analysis to other solvent systems. For example, Powell and Martell (166) have measured the conductance of tetraethylammonium and tetrabutylammonium picrates in anisole–nitrobenzene mixtures. Fuoss and Kraus suggest that the application of this equation can make their method a useful tool in the elucidation of ionic structure. The viscosity correction introduced by these authors has been discussed in Section VI,B,1.

(5) Comparison of the methods

Below is given the equation for the dissociation constant of an ion-pair as given by the above theories. The Bjerrum equation is

$$K^{-1} = \left(\frac{4\pi N}{1000}\right)\left(\frac{\epsilon^2}{DkT}\right)^3 Q(b) \tag{70}$$

where

$$Q(b) = \int_2^b e^Y Y^{-4}\,\mathrm{d}Y \tag{71}$$

$$Y = \epsilon^2/rDkT \tag{72}$$

$$b = \frac{\epsilon^2}{aDkT} \tag{73}$$

One of us (64) has shown recently that a good approximation for "(b)" is given by

$$Q(b) \simeq e^b/b^3 \tag{74}$$

and equation 70 then becomes

$$K_{\mathrm{B}}^{-1} = \left(\frac{4\pi N}{1000}\right)\left(\frac{\epsilon^2}{DkT}\right)\frac{e^b}{b^3} \tag{75}$$

Simplifying, one obtains:

$$K_{\mathrm{B}}^{-1} = \frac{4\pi N a^3}{1000}\,e^b \tag{76}$$

The equation derived by Denison and Ramsey can be written as:

$$K_{\mathrm{DR}}^{-1} = e^b \tag{77}$$

It follows that $K_{\mathrm{B}}^{-1} = K_{\mathrm{DR}}^{-1}$ only when $4Na^3/1000 = 1$. This is the case only for $a = 5.1$ A., which is in the range of large organic ions. For other ions the theories differ considerably. Looked at in another way one would in general expect the two theories to yield different a values from the same experimental K.

TABLE 22

a values for tetrabutylammonium picrate in several solvents

Solvent	*a* Values			
	Bjerrum (equation 70)	Denison-Ramsey (equation 77)	Gilkerson (equation 78)	From dipole moment
	A.	*A.*	*A.*	*A.*
Benzene	—	—	—	3.72
Anisole	4.93	6.25	2.51	—
Chlorobenzene	4.80	5.58	—	—
o-Dichlorobenzene	4.06	5.17	—	—
Ethylene chloride	5.77	6.52	2.51	—
Pyridine	7.91	6.72	—	—

The equation derived by Gilkerson is

$$K_{\mathrm{G}}^{-1} = \left(\frac{2\pi\mu kT}{h^2}\right)^{-3/2} (gv\sigma)^{-1} \exp(-E_S/RT) \exp(e^2/aDkT) \tag{78}$$

where $\mu = m_+m_-/(m_+ + m_-)$, E_S is the difference in the solvation energy of the ion-pair and the free ions, $(gv\sigma) = (g_+g_-v_+v_-\sigma_+\sigma_-)/(g_\pm v_\pm \sigma_\pm)$, v_i is the volume available to the particle, g is the internal rotational and vibrational contribution to the partition function, and σ is a factor taken to be 1. a and E_S can be calculated from Gilkerson's equation only on the assumption that a is invariant with solvent. A comparison of a values for tetrabutylammonium picrate is given in table 22.

It is clear that the Bjerrum and Denison–Ramsey equations are solvent-sensitive, although both define a as the distance between centers of ions in contact. Sadek and Fuoss (178) have suggested that the Bjerrum equation includes the solvent, perhaps as a molecule trapped between the two ions. It is not at all clear, however, why the directly measured dipole moment gives a smaller value, i.e., no molecule is trapped when one measures the dielectric constant but is trapped in measurements of conductivity.

The Gilkerson equation seems a step in the right direction in considering specific solute–solvent interaction (through the solvent dipole moment) but unfortunately must *postulate* the constancy of a with change in solvent. The Fuoss–Kraus equation, on the other hand, tends to support a continuum model for the solvent. It is evidently satisfactory for dioxane–water mixtures but has not yet been tested elsewhere. It does require extremely precise measurements of conductance (±0.02 per cent). In some other cases the continuum model also seems to be quite satisfactory. Thus Lichtin and Pappas (127) and Lichtin and Leftin (126) found a remarkable adherence to the simple sphere-in-continuum theory of both association behavior and, for elemental electrolytes, mobility in liquid sulfur dioxide solvent. They found that the Bjerrum distances of closest approach (a) calculated from data at two temperatures deviate from the crystallographic or van der Waals radii by 0 to 8 per cent, and that experimental limiting conductances (Λ_0) of the elemental electrolytes differ by 0 to 10 per cent from those calculated by substitution of ionic radii into the Stokes law equation.

TABLE 23

Comparison of ionic radii at 0°C.

Ion	van der Waals Radius	Bjerrum Radius	Stokes Radius	Ion	van der Waals Radius	Bjerrum Radius	Stokes Radius
	A.	*A.*	*A.*		*A.*	*A.*	*A.*
Cations:				Anions:			
K^+	1.33	(1.33)	(1.33)	Cl^-	1.81	1.63	1.84 (2.22)*
$(CH_3)_4N^+$	3.30	3.30	1.44	Br^-	1.95	1.95	2.10
$(C_2H_5)_4N^+$	4.65	4.9	1.71	I^-	2.17	2.20	2.20
$(n\text{-}C_3H_7)_4N^+$	5.9	7.8	1.94	BF_4^-	2.8	1.26	2.73
$C_7H_7^+$	3.90	3.4	1.64	ClO_4^-	3.0	1.33	2.66
Methylpyridinium$^+$	4.13	3.4	1.47	Picrate$^-$	5.10	4.9	6.13
$(C_6H_5)_3C^+$	7.0	9.8	2.10				

* The value of the Stokes radius for chloride ion given outside the parentheses was based on triphenylmethyl chloride; that inside the parentheses was based on potassium chloride.

From Bjerrum *a* values, Bjerrum radii were calculated assuming that the Bjerrum radius of an ion is not affected in liquid sulfur dioxide by the nature of its counter-ion and that Bjerrum and crystallographic radii of the potassium ion are the same. The crystallographic or van der Waals radius of ions of planar symmetry was identified with the maximum van der Waals radius about the center of gravity as determined from known bond distances and angles and atomic masses. This radius defines a spherical region occupied by the rotating ion. In table 23 are listed van der Waals, Bjerrum, and Stokes radii for several ions.

Goldenberg and Amis (78) found that, for uranyl chloride in the ethanol–water system at 25°, 35°, and 45°C., constant *a* values were obtained from the Denison–Ramsey equations over the entire range of solvent composition. At these three temperatures *a* was, respectively, 4.47, 4.32, and 4.19 A. The dissociation was taken to be $UO_2Cl_2 = UO_2Cl^+ + Cl^-$.

In many cases, particularly in mixed solvents, the failure of the continuum theory is quite striking. In a series of papers by Fuoss and coworkers (139, 177, 179) in which the conductance of tetrabutylammonium bromide was measured in several mixed solvents, one of the components being methanol, it was shown that the addition of less polar solvents such as benzene, heptane, carbon tetrachloride, and methyl ethyl ketone, while lowering the dielectric constant of the solvent, led to an increase in K and a decrease in the conductance; *a* values in these systems varied widely. The results were explained by the depolymerization of methanol on the addition of other solvents and the resulting increased solvation of the ions by methanol. This leads to lower mobility and to a larger electrostatic size with an attendant increase in K.

Davies and Monk (45) have measured the dissociation constant of silver acetate in several mixed-solvent systems and find that the Bjerrum *a* is much smaller than the crystallographic radius of the silver ion alone. Wynne-Jones (214) has derived an equation relating values of K to the dielectric constant and the *average* radius of the two ions

$$\ln (K_2/K_1) = z_1z_2\epsilon^2/(rkT)(1/D_2 - 1/D_1) \tag{78}$$

TABLE 24

Average ionic radii of silver acetate in mixed solvents

		Water-Acetone	Ethanol-Water	Dioxane-Water
Dissociation constant K	r in A.	1.42	1.43	3.10
Solubility	r in A.	0.85	1.01	1.63

which is very similar to an equation for the solubility ratio of a salt in two solvents derived by Born (34) and Scatchard (181).

$$\ln (S_1/S_2) = z_1z_2\epsilon^2/(2rkT)(1/D_2 - 1/D_1) \tag{79}$$

This equation gives values of r which are too small, but Davies and Monk suggest that the solubilities should be corrected by introducing the activity solubility product. They compare values of r for silver acetate obtained from equation 78 in three mixed-solvent systems.

From Stokes' law $r_{\text{Ac}^-} = 2.2$ and $r_{\text{Ag}^+} = 1.5$; hence $r = 1.8$. Monk (149) has also listed r values for a number of salts in nine different solvents. His data show that r depends more on the solvent than on the salt.

Denny and Monk (48) measured the dissociation constants of alkaline thiosulfates in water. They found that as the crystal radii decreased a increased and concluded that K is dependent on the hydrated ionic radii. This point is also illustrated by data on the alkaline earth nitrates (102) and sulfates (44). In water ionic radii of several thiosulfates are bigger than in ethanol–water and methanol–water, implying reduced hydration in mixed solvents (23). It seems reasonable to conclude that although the continuum theory is satisfactory in several cases, perhaps because of a compensation of various effects, it cannot account for all observations. Particularly when preferential solvation in mixed solvents occurs, a theory based on molecular interactions is required. Such a theory is not available.

(6) The assignment of ionic radii

The division of the ion-pair contact distance a into its components depends on essentially heuristic arguments. One assumes, perhaps on the basis of considerations of molecular models, that some electrolyte contains two equisized spheres. Another method which has been used in aqueous solutions is to assume that ions of the same limiting mobility have the same (perhaps solvated) size. This requires knowledge of transference numbers for the electrolytes. Unfortunately, no such data in solvents of very low dielectric constant are available. It is obvious that the extrapolation from finite concentrations to infinite dilution would be as difficult as that of the equivalent conductance. It has recently been shown (126) that for several quasi-spherical ions in sulfur dioxide Bjerrum a values are approximately equal to the sum of the anionic and cationic crystallographic radii, whereas in most solvents $a < r_+ + r_-$, indicating mutual compression of the ions. The authors suggest that in sulfur dioxide polarization effects (which tend to diminish a) are balanced by ionic solvation, which eliminates contiguous ion-pairs.

From a consideration of molecular models tetrabutylammonium and picrate ions would appear to be of approximately equal size; $r_+ = 6$ A. However, as is evident from table 22, a is less than 6 A. in several solvents. This can be explained by (*1*) charge localization on the phenolic oxygen of the picrate ion and (*2*) the pointing away of the butyl chains from the picrate ion when the pair is formed (191). This latter possibility cannot occur with $(CH_3)_4N^+$. Moreover, Lichtin and Leftin find for tetramethylammonium bromide $r_+ + r_- = a = 5.25$ A. Using the Pauling radius (160) for bromide ion of 1.95 A. yields for $(CH_3)_4N^+$ the value 3.20 A. If it is assumed that the ratio r_+/r_- for tetramethylammonium bromide is independent of solvent, then ionic radii for the two ions can be calculated for this salt in other solvents. However, no other conductance measurements on this salt have yet been carried out. Another possibility is to accept the assumption of Fowler and Kraus (65) that $\lambda_0^+ = \lambda_0^-$ for tetrabutylammonium triphenylborofluoride $(C_4H_9)_4NF \cdot B(C_6H_5)_3$, and that therefore $r_+ = r_-$. From molecular models the most compressed conformation is $r_\pm = 6.0$ A. In table 25 are listed a values for this salt in several solvents. As pointed out previously, a depends both on the solvent and on the method of calculation. Moreover, either set of a values is less than the sum of the model radii, $r_+ + r_- = 12$ A. This is in accord with the generalization pointed out by Lichtin and Leftin. It is easy to show that the division of a values leads to unreasonable ionic radii. The last column of table 25 gives the ionic radius of $(C_4H_9)_4N^+$. First, it is strongly solvent dependent and therefore of limited usefulness. Secondly, if one considers the a value of tetrabutylammonium bromide in pyridine (4.55 A.) and subtracts the radius for $(C_4H_9)_4N^+$ in pyridine (from table 22), the resulting radius of the bromide ion is only 0.59 A. Considering that the ion is fairly spherical and that its crystallographic radius is 1.95 A., this implies unreasonably large distortion.

One might well conclude that ion-pair contact distances are not suitable for the determination of ionic radii. All that one might expect is to obtain, by using a particular equation (e.g., the Bjerrum equation), a self-consistent set of values which give a considerable amount of valuable information on ionic configuration in solution.

C. THE RADII OF IONS AND ION COMPLEXES DETERMINED FROM CONSIDERATIONS OF CHEMICAL KINETICS

1. *Statistical and polar considerations of ion–molecule as compared to ion–ion reaction rates*

There are many approaches from the standpoint of chemical kinetics in solution which may be used to determine ion-size parameters. Some of these will be discussed in the following pages.

TABLE 25

a values of tetrabutylammonium triphenylboroftuoride, $(C_4H_9)_4N \cdot BF(C_6H_5)_3$

Solvent	a_B	a_{DR}	$a_B/2$
	A.	*A.*	*A.*
Acetone	8.80	6.90	4.40
Pyridine	7.92	7.02	3.96
Ethylene chloride	6.42	6.42	2.79

Ingold (98), considering the statistical requirements and polar influence which are among the factors influencing the speed of hydrolysis of symmetrically constituted dicarboxylic esters in a dielectric medium of dielectric constant 80 at 298°K., derived the equation for the ratio of the velocities of the stages of the hydrolyses to be

$$\frac{k_1'}{k_2'} = \frac{(v_1 + v_2)^2}{2v_1v_2} e^{6.97\times10^{-8}/r} \tag{80}$$

where k_1' and k_2' are the specific velocity constants for the first and second stages of hydrolysis, v_1 and v_2 are the catalytic coefficients for the hydrolysis of the first and second ester groups, respectively, and r is the distance between the mean ionic center in the carboxylate ion of the ionic ester $ROCO(CH_2)_nCOO^-$ and the mean focus of the reaction with the hydroxide in the carboxylic ester group. For the special case of a symmetrically constituted dicarboxylic ester $v_1 = v_2$ and equation 80 becomes

$$\frac{k_1}{k_2} = 2e^{6.97\times10^{-8}/r} = 2e^{7\times10^{-8}/r} \tag{81}$$

Since the hydroxide ion must attack the unsaturated carboxy linking and not the saturated ether linking, Ingold points out that the distance r would, to a first approximation, be independent of the nature of the alcohol radical R. Table 26 seems to justify this supposition.

TABLE 26

The radii of esters along the long axis

Ester	k_1/k_2	Mean	r	Mean r	r of Ion
			A.	A.	A.
Methyl oxalate	(10^4)	(10^4)	(2.9)	(2.9)	(3.4)
Ethyl oxalate	(10^4)		(2.9)		(3.9)
Methyl malonate	(92)	(91)	(3.8)	(3.8)	(3.9)
Ethyl malonate	(90)		(3.8)		(4.4)
Methyl succinate	9.66	9.64	5.61	5.62	4.8
Ethyl succinate	9.62		5.63		5.3
Methyl glutarate	6.45	6.42	6.81	6.83	5.4
Ethyl glutarate	6.40		6.85		5.9
Methyl adipate	4.95	4.97	8.34	8.30	6.2
Ethyl adipate	5.00		8.26		6.6
Methyl pimelate	4.34	4.34	9.57	9.57	6.8
Methyl suberate	3.91	3.91	10.97	10.97	7.5
Methyl azelate	3.61	3.61	12.38	12.38	8.2

Ingold points out that these r values all agree to within half an Ångström unit with the distances derived from the first and second dissociation constants of the corresponding free acids (71). The largest difference occurs with oxalic acid (0.47 A.), but here, as in the case of malonic acid (difference 0.37 A.), Ingold says that agreement is hardly to be expected.

While the r values given here are not radii of the ions listed as such, they do seem to measure the distances between reactive centers in the ions. If the dimensions be taken as that between the carbonyl carbon atoms at the two ends of the ester-ion and if the length of the single-bonded oxygen at the hydrolyzed end of the ester-ion and the length of the alkoxy group at the unhydrolyzed end of the ester-ion be added to the r value, then one-half of this sum would approximate the radius of the ester-ion along its long axis. From Fisher–Hirschfelder models, the methoxy group adds a maximum of about 3.5 A. and the ethoxy group about 4.5 A. to the length of an ester chain. The single-bond oxygen adds about 0.5 A. to the chain length. The above method of calculation gives the radii of the esters along the long axes, as recorded in the last column of table 26.

LaMer (116), applying the above theory, wrote for the relation of the specific velocity constants for the displacement of bromine by thiosulfate ion in methyl α-bromopropionate and methyl bromoacetate to the corresponding specific velocity constants for the displacement of bromine by the thiosulfate ion in the acid anions of the corresponding hydrolyzed esters, the equation

$$\log\left(\frac{k'_{\text{ester}}}{k'_{\text{ion}}}\right) = \frac{z_A z_B \epsilon^2}{2.3DkT}\,\frac{1}{r} \tag{82}$$

where r is the distance of closest approach of the charges at the moment of chemical reaction.

At infinite dilution and for water at 25°C. the equation becomes:

$$\log\left(\frac{k'_{\text{ester}}}{k'_{\text{ion}}}\right)_{\mu=0} = z_A z_B\,\frac{3.06}{r} \tag{83}$$

where μ represents ionic strength. The limiting value of the $(k'_{\text{ester}}/k'_{\text{salt}})_{\mu=0}$ is 131 for the α-bromo compounds and 58 for the bromoacetate compounds. The corresponding r values using equation 83 are 2.88 A. and 3.47 A. While these r values probably correspond to a separation of active centers of the two reactant ions at the instant of reaction, some idea of the ionic dimensions is gained from these data.

Moggridge and Neuberger (148) found that η-acetylmethylglucosaminide, α-methylglucoside, and β-methylglucoside at 80°C. are hydrolyzed in the presence of 1 N hydrochloric acid at rates which are, respectively, 350, 100, and 180 times faster than the rate of hydrolysis of methylglucosaminide hydrochloride. Applying equation 82 to this reaction gives respective r values of 1.3 A., 1.7 A., and 1.5 A. in the three cases.

The r values are rather small compared to the values obtained from the reactions involving the displacement of bromine from organic acid anions and esters

TABLE 27

Critical ionic separation in the reaction between thiosulfate and bromoacetate ions in aqueous solution

Method	r
	A.
The absolute value of P* at zero ionic strength	3.94
The variation of ΔE† with respect to temperature at constant ionic strength	3.31
The comparison of the rates of ion-ion and ion-molecule reactions	3.47

* P is probability in the collision theory and dP is the probability that any molecule will have energy within the limits E and $E + dE$.

† ΔE is the energy of activation in calories per mole.

by thiosulfate ions. Thus there is no simple relation between these dimensions and the sizes of the ions themselves.

2. Collision theory considerations, the temperature coefficient of energy of activation, and relative rates of ion–ion and ion–molecule reactions

Moelwyn-Hughes (140) discusses four ways of obtaining values of r. He compares the r values for the reaction between thiosulfate and bromoacetate ions obtained by three of these methods and finds the various values of r reasonable in themselves and to agree fairly well with one another. The comparison is given in table 27.

3. The dependence of the specific velocity constant on the dielectric constant of the solvent for ion–ion reactions

The fourth method mentioned by Moelwyn-Hughes was derived by Scatchard (182) for the effect of changing dielectric constant of the solvent upon the reaction velocity at zero ionic strength. The dielectric constant is varied by varying the proportions of the components in a mixed solvent. The equation for calculating r is

$$\frac{\partial \log k'_{\mu=0}}{\partial(1/D)} = -\frac{z_A z_B \epsilon^2}{2.303 rkT} \qquad (84)$$

Amis and LaMer (13) applied equation 84 to the data for the reaction of tetrabromophenolsulfonphthalein ion with hydroxide ion in both methyl alcohol–water and ethyl alcohol–water as solvents. The values of r in the two cases were 1.22 A. and 1.49 A., respectively, thus showing a specific solvent effect. These r values are of the right order of magnitude but seem rather small in actual size considering the complexity of the tetrabromophenolsulfonphthalein ion.

Amis and Price (15) by the same method found r values of 2.2 A. and 2.5 A. for the reaction of ammonium ion with cyanate ion in methyl alcohol–water and glycol–water media, respectively. Thus while there are specific solvent effects, the values of r obtained are gratifying from the standpoint of theory.

4. The coulombic energy approach for ion–ion reactions

Amis (4) calculated the r values in both methyl alcohol–water and ethyl alcohol–water for the tetrabromophenolsulfonphthalein–hydroxide ion-pair using

TABLE 28

Representative values of r calculated by various methods

Ions*	Solvent	r from ln k' vs. $1/D$	r from $\Delta E_{\text{coul.}}$	r from $\Delta E_{\text{f.c.}} - \Delta E_D$	r from ln $Z_{\text{f.c.}}$ − ln Z_D	r from log k' vs. κ
		A.	*A.*	*A.*	*A.*	*A.*
$B\phi B^{--} + OH^-$	Glycerol-water				1.75	
$B\phi B^{--} + OH^-$	Ethanol-water	1.22	2.0	1.2	1.2	1.06
$B\phi B^{--} + OH^-$	Methanol-water	1.49	2.0	1.3	1.3	1.65
$NH_4^+ + OH^-$	Methanol-water	2.2	2.0	2.0	2.0	1.38
$NH_4^+ + OH^-$	Glycol-water	2.5	5.0	2.5	2.5	1.16
$S_2O_4^{--} + I^-$	Ethanol-water	1.76		0.90	0.90	1.58

* $B\phi B^{--}$ stands for the negative bivalent bromophenolsulfonphthalein ion; $\Delta E_{\text{coul.}}$ is coulombic energy of activation: $\Delta E_{\text{f.c.}}$ and $Z_{\text{f.c.}}$ are the energy of activation and the Arrhenius frequency factor, respectively, in solvents of fixed composition; and ΔE_D and Z_D are the energy of activation and the Arrhenius frequency factor, respectively, in solvents of constant dielectric constant.

the coulombic energy approach. The r value in both solvents was 2 A. For the ammonium ion–cyanate ion reaction in methyl alcohol–water the r value was 2 A. and in glycol–water it was 5 A., using the coulombic energy approach.

5. Application of calculations of nonelectrostatic potential

Amis and Jaffe (12) made calculations of the r parameter, using the nonelectrostatic potential, and obtained values comparable to those found above for the same ions in the same solvents, as shown in column seven of table 28. In table 28 are listed representative values of r calculated in the various ways from kinetic data.

The calculations from nonelectrostatic potentials were made using the equation given by Amis and Jaffe, namely:

$$\frac{\mathrm{d}\ln \mathrm{k}'}{\mathrm{d}T} = a_T = -\frac{1}{k}\left[\Phi_1(r_0) + \frac{z_A z_B \epsilon^2 e^{\kappa(a-r_0)}}{D r_0(1+\kappa a)}\right] \tag{85}$$

For the calculations the limiting form of the equation at infinite dilution was used. Taking the values of d ln $k'/\mathrm{d}T$, $\Phi_1(r_0)$, D, and T recorded by Amis and Jaffe, the r_0 values were calculated for the ionic species given. In the above equation $\Phi_1(r_0)$ is the nonelectrostatic potential and the other quantities have their usual significance.

6. Primary salt effect and dielectric constant effect upon rates of ion–molecule reactions

Amis and coworkers (5, 6, 11, 16, 36) have originated an equation which enables one to calculate the r-functions of ion-dipolar molecule complexes from the primary salt effect and dielectric constant effect upon the reaction rates between the two types of particles. The equation is

$$\ln k' = \ln k'_{\substack{D=\infty \\ \kappa=0}} + \frac{Z_B \epsilon\mu}{DkTr_0^2} + \frac{Z_B\epsilon \cos\theta}{DkTr}\left(\mu_0^* - \frac{\mu^*(1+\kappa r)}{e^{\kappa r}}\right) \tag{86}$$

In this equation κ is the Debye kappa, $Z_B\epsilon$ is the charge on the ion, θ is the angle which the line drawn between the centers of charge in the dipole makes with

TABLE 29

r_0 values applying equation 86 to effect of ionic strength and dielectric constant upon reaction rates between ions and dipolar molecules

Reactants	Added Electrolyte	Solvents	r_0, Ionic Strength Effect	r_0, Dielectric Constant Effect
			A.	*A.*
H_3O^+ + sucrose	$BaCl_2$ HCl	Water	6.0*	
H_3O^+ + sucrose	$CaCl_2$ HCl	Water	6.0*	
H_3O^+ + sucrose	KCl HCl	Water	2.5*	
H_3O^+ + sucrose	$NaCl$ HCl	Water	2.5*	
H_3O^+ + sucrose	HCl	Water	3.5*	
H_3O^+ + ethylene acetal	$HClO_4$	Water	4.0*	
OH^- + diacetone alcohol	Various uni-univalent salts and hydroxides	Water	3.1*	
OH^- + diacetone alcohol	Uni-bivalent salts and uni-univalent hydroxides	Water	4.6*	
OH^- + diacetone alcohol	Uni-univalent hydroxides	Water	4.8*	
OH^- + diacetone alcohol	$NaOH$	Water–ethanol		6.0†
H_3O^+ + sucrose	HCl	Water–dioxane		5.5†
$S_2O_3^{--}$ + ethyl bromomalonate	KNO_3	Water–methanol	4.0¶	2.5‡¶
OH^- + ethyl acetate	$NaOH$	Water–ethanol		0.98‡
OH^- + ethyl acetate	$NaOH$	Water–acetone		1.8‡
OH^- + methyl propionate	$NaOH$	Water–acetone	4.0§	1.4‡§
H_3O^+ + ethyl acetate	HCl	Water–dioxane		9.2‡
H_3O^+ + ethyl acetate	HCl	Water–acetone		5.2‡
H_3O^+ + methyl propionate	HCl	Water–acetone		3.4‡

*Reference 11. † Reference 5. ‡ Reference 6. § Reference 16. ¶ Reference 36.

the line drawn from the ion to one of these centers of charge, μ is the moment of the dipole in vacuo, μ^* is the Onsager enhanced moment, μ_0^* is the enhanced moment at zero ionic strength, r_0 is the distance of approach between the ion and the dipole for reaction to take place, D is the dielectric constant of the medium, k is the Boltzmann gas constant, and T is the absolute temperature.

Some values of r_0 found from the dependence of reaction rates between ions and dipolar molecules on ionic strength and dielectric constant and calculated using equation 86 are recorded in table 29. The constants determined from the dependence of the rate on ionic strength were calculated by transforming equation 86 into the form

$$W = \frac{z^2}{1 + z + \frac{z^2}{2} + (n^2/2D)(1 + z)} \tag{87}$$

where

$$z = \kappa a = \kappa r_0, \tag{88}$$

and

$$W = \frac{(\ln k' - \ln k'_{\kappa=0})2DkTr_0^2}{\epsilon Z_B \mu_0^* \cos \theta} \tag{89}$$

Plots of W vs. z^2 were made, and the proper values of the parameters r_0, μ_0^*, and n selected to make the experimental data fit the theoretical curve.

TABLE 30

Values of r_0 obtained by applying equation 90 to effect of dielectric constant upon the reactions indicated

Reactants	Solvents	r_0
		A.
H_3O^+ + ethyl acetate	Water-dioxane	3.3
H_3O^+ + ethyl acetate	Water-acetone	3.0
H_3O^+ + methyl propionate	Water-acetone	3.0
OH^- + ethyl acetate	Water-dioxane	2.5
OH^- + ethyl acetate	Water-acetone	2.4
OH^- + ethyl acetate	Water-isopropyl alcohol	2.3
OH^- + ethyl acetate	Water-*tert*-butyl alcohol	2.2
OH^- + ethyl acetate	Water-1-propanol	2.1
OH^- + ethyl acetate	Water-ethanol	2.0
OH^- + ethyl acetate	Water-methanol	1.8
H_3O^+ + formanilide	Water-ethanol	3.3
H_3O^+ + form-*o*-toluidide	Water-ethanol	3.3
H_3O^+ + form-*p*-toluidide	Water-ethanol	3.3
o-Nitroacetanilide	Water-ethanol	3.4
Acetanilide	Water-ethanol	3.4
Acet-*m*-toluidide	Water-ethanol	3.4
H_3O^+ + acetamide	Water-ethanol	2.8
H_3O^+ + propionamide	Water-ethanol	2.8
OH^- + acetamide	Water-ethanol	2.1
OH^- + propionamide	Water-ethanol	2.1

The values of r_0 from the dielectric constant data were secured by plotting $\ln k'$, preferably at zero ionic strength, versus $1/D$, setting the slope of the curve equal to $z_B \epsilon \mu / kTr_0^2$, and solving for r_0.

In table 30 are listed values for r_0, the distance between the ion and dipolar molecule indicated for reaction to take place and calculated by using the Landskroener and Laidler (121) equation, which is

$$\ln k' = \ln k_0' + \frac{\epsilon^2}{2kT}\left(\frac{1}{D} - 1\right)\left(\frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_0}\right) + \frac{3\epsilon^2}{8kT}\left(\frac{2}{D} - 1\right)\left(\frac{G_A}{r_A^3} + \frac{G_B}{r_B^3} - \frac{G_\pm}{r_0^3}\right) \qquad (90)$$

In this equation k is the observed specific velocity constant, k_0' is the specific velocity constant at some reference dielectric constant, z_A is the valence of reactant A, z_B is the valence of reactant B, $(z_A + z_B)$ is the valence of the intermediate complex, D is the dielectric constant, T is the absolute temperature, k is the Boltzmann gas constant, and ϵ is the electric charge; G_A, G_B, and $G_\pm$ are complex functions of the charges and structures of reactant A, reactant B, and the intermediate complex, respectively. Definite models of reactant molecules and of complex have to be assumed in order to determine the charges, distances, and Legendre polynomials which make possible the determination of the G-factors.

After the radii, r_A and r_B, of the reactants and the G-factors are determined from the models, the radius, r_0, of the complex is found from the slope of the $\ln k'$ versus $1/D$ plot. For the acid hydrolysis of esters or amides, r_A, the radius of the hydronium ion, was taken as 1.7 A.; for the base hydrolysis of esters or amides, r_B, the radius of the hydroxide ion, was taken as 1.4 A. Thus the radii of the hydronium and hydroxide ions as well as those of the complex were estimated.

Amis and Holmes (10), using the coulombic energy approach, found an r value of 2 A. for the sucrose–hydronium ion molecule–ion pair in dioxane–water.

7. *Differences in energy of activation and in the Arrhenius frequency factor in media of fixed composition and fixed dielectric constant*

Amis and Holmes (10) and also Amis and Potts (14) found that differences between energies of activation measured in solvents of fixed composition and in solvents of fixed dielectric constant gave reasonable values of the r parameters. In like manner Amis and Cook (9) found acceptable r values using the differences between Arrhenius frequency factors measured in solvents of fixed composition and in solvents of fixed dielectric constant.

8. *Evaluations of the distance function for solvolytic reactions*

Bateman, Church, Hughes, Ingold, and Taher (19) have derived for solvolytic reactions the kinetic equation

$$\frac{dx}{dt} = k_1(a - x)\ \text{antilog}_{10}(1.806 \times 10^8 \sigma x) \tag{91}$$

where $\sigma = z^2 r$ has the dimensions of length, since z is the fraction of electronic charge transferred in the ionization to form a carbonium ion and is therefore dimensionless, and r is the length that the ionizing bond has stretched. Thus r at the moment of ionization is the distance between the two ions when the bond is ruptured and chemical reaction has therefore occurred. In this state z is unity, i.e., the whole electronic charge has been transferred, and $\sigma = r$. Bateman, Church, Hughes, Ingold, and Taher calculated σ for $z = 0.5$ ($z^2 = 0.25$) for the solvolysis of alkyl halides; in the case of the solvolysis of *tert*-butyl bromide in "90%" aqueous acetone they found r to be 2.59 A., using the Morse function, and σ to be 0.25×2.59 A. or 0.65 A. The kinetic data for the solvolysis gave $\sigma = 0.74$ A., a value which is certainly in agreement with the calculated value. This σ-factor was calculated for many solvolytic reactions of alkyl halides and found to vary from about 0.7 A. to 2.73 A.

All the calculations of the distance function listed above, except those of Ingold (98), involve the distance between the centers of two particles. The distance function could in each case be resolved into the dimensions of two particles by making assumptions as to the equality of the two dimensions or as to the value of either. In the case of Ingold's calculation the radius of the ion in the long dimension was actually found, and since this dimension was measured internal to the ester-ion, it is independent of external effects such as solvation.

From the tables the distance factor is seen to be a function of the valence type of electrolyte used in controlling the ionic strength and is also a function of the solvent used in controlling the dielectric constant of the media. Table 28 shows that the value of the distance factor for the same reactants in the same solvents is dependent upon the method used in measuring it and on the theory of its evaluation.

9. Evaluation of the r-function for electron-exchange reactions

Electron-exchange reaction-rate theories allow the calculation of the radii of the reacting species and the r-function of the complex. Marcus, Zwolinski, and Eyring (131) found from their electron tunneling hypothesis for electron-transfer reaction rates that the critical intercationic distance r^*_{ab} between the electron-exchanging cations A and B varied from 3.4 A. for the Fe^{2+}–$FeCl_2^{1+}$ system to 9.3 A. for the Ce^{3+}–Ce^{4+} system. They used the radius r_0 of the classical orbit for the exchanging electron as 4.3 A. Their equation relating r^*_{ab} and r_0 is

$$r_{ab}^{*2} = \frac{3\epsilon^2 N_a N_b h r_0^{1/2}}{8\pi\epsilon k D T (mz^*)^{1/2}} \tag{92}$$

In this equation $N_a\epsilon$ and $N_b\epsilon$ are the respective charges on the electron-exchanging ions A and B, h is Planck's constant, k is the Boltzmann constant, D is the dielectric constant, T is the absolute temperature, m is the mass of the electron, ϵ is the electronic charge, and z^* is the number of positive electronic charges on the central atom of the complex ion.

Cohen, Sullivan, Amis, and Hindman (39) found that for the Np(V)–Np(VI) electron-exchange reaction $r^*_{ab} = 5.04$ A. when the other parameters in equation 92 had reasonable values. These authors found that the rate of the exchange reaction was independent of the dielectric constant in water–glycol and in water–sucrose as solvents. This was not in accord with the electron tunneling hypothesis.

Marcus (130) derived an expression for the rate constant k' of electron transfer to be

$$k' = Z \exp(-\Delta F^*/RT) \tag{93}$$

where Z is the collision number in solution and ΔF^* is given by the equation

$$\Delta F^* = \frac{1}{2a}\left[\left(\frac{e_1^* e_2^*}{D_s} + \frac{(\Delta e)^2}{4}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)\right)\right] \tag{94}$$

In this equation e_1^* and e_2^* are the charges on the reactants, $\Delta e = (e_1 - e_1^*) = (e_2 - e_2^*)$, e_1 and e_2 are the charges on the products, $2a = r$ is the sum of the radii of the two ions involved in the electron transfer, D_{op} is the square of the refractive index of the solvent, and D_s is the static dielectric constant of the solvent. Using this theory Marcus found $2a$ to range from 5.7_2 A. for the MnO_4^{2-}–MnO_4^- reaction to 9.6 A. for the $Mo(CN)_8^{4-}$–$Mo(CN)_8^{3-}$ reaction. Actually, Marcus records values of a, which is assumed to be the radius of each of the ions involved. The parameter $2a$ would correspond to r^*_{ab} given by Marcus, Zwolinski, and Eyring.

Amis (8), using a hydronium-bridge mechanism, derived the following expression relating r_{ab} and r_0:

$$r_{ab}^2 = \frac{3hf'(z)\epsilon r_0^{1/2}}{8\pi k T D'[m(z_a^* + z^*)]} \tag{95}$$

where $f'(z) = 2(z_a + z_b) + z_a z_b$, z_a and z_b are the valences of ion A and ion B, respectively, z_a^* is the charge on the central atom of the complex ion whose central coördinated ion has the smallest ionization potential, z_ϵ^* is the charge on the hydronium ion, D' is the dielectric constant of the component of the solvent having the higher dielectric constant under conditions of complete dielectric saturation, and the remaining quantities are defined as in the theory of Marcus, Zwolinski, and Eyring.

Using this approach r_{ab} for the Np(V)–Np(VI) reaction was found to be 10.0 A. when r_0 was taken as 6.87 A. This value of r_{ab} is nearly double the value for r_{ab} for this reaction using the Marcus, Zwolinski, and Eyring approach. The difference in the value of r_{ab} arises from the differences in both the assumed models and the mathematical manipulations. Amis (8) assumes a hydronium-ion bridge between the two ions which are exchanging electrons. Marcus, Zwolinski, and Eyring do not include a bridge in their model. Thus the former theory would be expected to yield a greater value of r_{ab}.

VII. Discussion and Conclusions

In this section the spread of values obtained by different methods of calculation for each of the types of system described in Sections II to VI is compared. After that, some general comparisons between these systems will be presented.

A. THE ISOLATED ION

As shown in table 3 the various "radii" agree within 30 per cent. It must be emphasized that these radii represent maxima in the wave functions of the outer electrons and are thus radii only by convention. Since these wave functions may drop to near zero over an appreciable fraction of the total radius, it is difficult to assign a physical meaning to the values obtained. If, however, one composes quantum-mechanical solutions for two-atom (or more complicated) molecules with physically determined internuclear distances, one can demand that the theoretical model conform to the experimental one (183a).

B. IONS IN THE GAS PHASE

(*1*) Methods based on the collision of particles, whether atomic or subatomic, yield cross-sections for particular conditions. Thus the type of particle used as probe and its velocity influence the value of the cross-section far more than the particle being investigated. All one can say is that the radii obtained from these cross-sections are ordinarily of atomic dimensions, i.e., from a few tenths to several Ångström units.

(*2*) Salt molecules in the vapor: Internuclear distances can be determined quite accurately (±0.03 A.). To split these distances into effective (or additive) ionic radii requires assumptions either about relations to the solid or about force expressions. Depending on which method is used the same internuclear distance may yield radii which differ by a factor of 2.

C. IONIC CRYSTALS

Molar volumes can be easily determined, but this volume consists of both ionic volume and empty space. The volume is temperature-dependent, an increase in temperature mainly increasing the size of the holes. Thus there is no good way of obtaining ionic radii from volumes, unless detailed information on packing is available.

Internuclear distances in crystals can be determined quite accurately. In many cases, particularly the alkali halides, these are known to within 0.001 A. Extensive compilations, such as the Landolt-Börnstein tables, commonly list values to 0.01 A. The splitting up of the internuclear distance into its ionic components requires assumptions about interionic forces and/or some "standard" radius. It is encouraging that radii obtained by different methods generally agree within 0.1 A., i.e., about 10 per cent. These radii are thus less subject to error than those obtained by other methods, and it is not surprising that they have been used so widely.

D. MOLTEN SALTS

The statement made about crystal volumes above applies with even greater force here. Very little work has been done on internuclear distances, but results so far suggest that these are not too different from corresponding values in the crystal, differences being accounted for by changes in ionic or covalent character from solid to liquid.

E. IONIC SIZE IN SOLUTION

1. Equilibrium methods

(a) Volumes

Electrolyte volumes in solution include not only the actual volume of the ions, but changes in the orientation and packing of the solvent molecules from that of the pure liquid. The determination of partial molal volume may thus serve as a powerful tool for examining the structure of solutions, but so far the method has hardly been applied to nonaqueous systems. The determination of ionic from molal volumes requires additional assumptions (e.g., $\bar{V}_{\mathrm{H}^+} = 0$). Thus the same molal volume may yield different ionic volumes. At present there seems to be no good reason for preferring one method over another. In general, differences in $\bar{V}^0_{\pm}$ do not exceed 7 ml./gram-ion, but this may be 30 per cent of the total volume.

(b) Internuclear distances

Omitting theories of ionic activity coefficients which frequently include some solvent in the effective ionic size, these distances are measured by x-ray diffraction and by dipole moments. The former has been used so far only on a few concentrated aqueous solutions, while the latter is necessarily restricted to solvents of very low dielectric constant, preferably nonpolar ones. Thus there is no case in which the two methods have been applied to the same systems.

X-ray studies of solutions are of great interest, since they give information on internuclear distances in solution more directly than any other method. Indications so far are that ionic radii in solution do not differ greatly from those in crystals.

(c) Ionic radii

Methods which yield radii directly are essentially based on the measurements of some energy such as heat of solution. This energy is then split up into its corresponding ionic components in conformity with some hydration model.

Linear relations between some thermodynamic function and a distance function are especially popular. Radii thus obtained are usually larger than crystal radii, which is taken as an indication that some solvent is included. Recent refinements separate the energy into electrostatic and nonelectrostatic terms, or they consider the solvent to be simultaneously a homogeneous fluid of a certain dielectric constant and an assembly of molecules capable of specific orientation. So far, detailed distribution functions for electrolytic solutions have not been worked out.

2. Kinetic methods

Little has been done on viscosity. Radii are concentration-dependent, which is a good sign that the solvent is included. Although both conductance and diffusion are active fields of research, the problems here are much the same. When ions move they carry solvent with them, and some of this is undoubtedly included in the effective ionic size. Not only may different measurements yield different results but the same measurement may yield different radii depending on the method of calculation. This is particularly true of ion-pair contact distances, where differences of several Ångström units are not unusual.

3. Chemical kinetics

The statements in the above section apply here also. Moreover, since chemical reactions involve the collision of particles, the distance parameter may be a radius sum or an average radius. For unsymmetrical particles, such as large organic ions and molecules, the relative orientation of the reacting species may be important. To some extent the spread of values only defines our ignorance.

Although ions are deformable this deformation probably does not exceed 20 or 30 per cent with change in environment, this being the extent of change in the move of an ion from the crystal to a salt molecule in the vapor. In that case an essentially symmetrical charge distribution is replaced by a highly unsymmetrical one. In solution, charge distributions may be nearly as unsymmetrical, e.g., in ion–ion reactions, but in general they will be both more symmetrical and weaker, e.g., in ion–dipole interaction. It would be difficult to imagine a case where distortion would be much greater.

If one accepts crystal radii, according to whatever scheme they may have been derived from internuclear distances, as representing the effective radii of ions in other environments as well, the above argument implies that any values which differ greatly from crystal radii (with the exception of quantum-mechanical and gas-phase collision radii) must include in one form or another the effects of interaction with the environment. In some cases, such as partial molal volumes (particularly when these are negative), the influence of such effects is obvious. In conductance or diffusion, where the same experimental data yield radii which depend more on the method of calculation than on the system studied, the way in which different equations may implicitly include different amounts of solvent is usually not well understood. The fact that in this field as well as in chemical kinetics ionic radii are strongly solvent-dependent and that there is good evidence for selective solvation in mixed solvents shows that radii include this solvent. It would seem that a comparison of crystal radii with (say) solution radii—or better, "distance functions"—should shed much light on ion–solvent interaction. A thorough analysis of equations in the various areas seems to be called for.

An additional problem arises whenever a quantity characteristic of an electrolyte (volume, interionic distance) is to be split into its ionic components. Such divisions are usually made on heuristic grounds, all of which may appear eminently and equally reasonable and still lead to differences as large as 20 or 30 per cent. Particularly in kinetics the method of dividing an internuclear distance may affect considerably mechanisms which are based on comparison of interaction energies, since these are sensitive to distance.

In some areas, such as that of ion-pairs, even internuclear distances differ widely, both with the method of measurement and with that of calculation. Considerable work will be necessary to discover reasons for these differences.

In conclusion, the assertion made in the introduction is repeated, namely, that the ionic size is an operational concept which has a definite value only for specified conditions of measurement and calculation and that in many cases this size is a description of the influence of the ion on its environment, rather than the radius or volume of a "bare" ion. It is *not* implied, however, that all methods of investigation and all results are equally valid and equally useful. What is needed is a clearer understanding of molecular forces which will allow us to distinguish, more clearly than is yet possible, between the space occupied by a particle and the influence which it exerts. There is probably a kind of uncertainty principle which prevents this distinction being made too precisely, but these limits have not yet been reached.

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