

cients in sodium, potassium and barium chlorides are much smaller than the earlier values. Wereide reports a large Soret effect in cane sugar solutions. My experiments, on the contrary, show no appreciable effect, although a change of 0.1% could have been readily observed by the interferometer.

The Soret coefficients of thallos and barium hydroxides are the largest that have ever been recorded.

The writer desires to acknowledge his indebtedness to Professor G. N. Lewis, who suggested the investigation and under whose supervision the work was carried out. He also wishes to express his thanks to Professor E. D. Eastman for the helpful interest he has taken in the investigation.

Summary

When a solution is maintained for some time in a temperature gradient, a concentration gradient is set up. This is known as the Soret effect.

The conductance method is used to determine the fractional change in concentration at the two ends of a cylindrical vessel, the upper end being maintained at a temperature 10° higher than the lower.

The Soret coefficient, defined as the fractional change in molality per degree, or $d \ln m/dT$, has been determined for a large number of solutions. This coefficient is found to vary from zero in the case of lithium nitrate and ammonium chloride to -1.2% per degree for barium hydroxide.

No explanation of the phenomenon is offered. The Soret coefficient is regarded as being determinable only empirically.

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THE FREE ENERGY OF HYDRATION OF IONS AND THE ELECTROSTRICTION OF THE SOLVENT

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1. Introductory

The evaluation of the free energy of hydration of an ion depends essentially upon a calculation of the difference in its potential energy in a vacuum and in water. This difference in the case of ions that do not combine chemically with water, is given practically entirely by the difference in the energy of the electrical fields that surround the ion in the two states,² that is, by the electrical work to be obtained at constant temperature and pressure from discharging the ion in a vacuum and subsequently charging

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² There is a comparatively small energy change corresponding with the compression of the solvent in the vicinity of the ion, which, however, may not be neglected. (Compare Part 3.)

it in water.³ The calculation of the difference in the energy of the electrical fields is practicable in view of the fact that around each ion in solution there is a cavity (assumed to be spherical)⁴ in which there are no water molecules, the radius of which cavity is several times that of the radius of a sphere fixed by the outer electron orbits of the ion. Since the energy of the field within the cavity is the same for the ion in a vacuum that it is for the ion in water, it is necessary to evaluate only the energy of a field, exterior to a given sphere, large in comparison with the size of the ion. The very obvious procedure of using the dielectric constant of water for calculating the energy of the field surrounding the ion in water cannot be followed on account of the electrical saturation effects resulting from the orientation of the solvent dipoles about the ion and the consequent, effectively inconstant, dielectric "constant." This energy is calculated by an application of the theory of Langevin,⁵ as made by Debye⁶ to dielectric constants. By this means the electric polarization of the water is calculated as a function of the moment of the water dipole,⁷ its optical polarizability, the field strength and the temperature. For the energy of the electrical field, exterior to a sphere of radius r_0 , arising from an ion of charge e , in a vacuum, the following expression of electrostatics suffices: $e^2/2r_0$. The radius r_0 of the cavity surrounding the ion in solution is an essential magnitude for the calculations that follow, and for the sake of brevity will be referred to subsequently as the radius of the ion.

The energy changes associated with the solution of ions in various solvents are important in that they permit a calculation of the absolute activities of ions (that is, with reference to a state independent of any solvent) and the relative solubilities of electrolytes.⁸ For the calculation of the solubility of an electrolyte without reference to its solubility in any other solvent, it is necessary to know, in addition, the lattice (free) energy of the crystal structure. Since it is the difference between the lattice (free) energy and the free energy of solvation of the ions which determines the solubility of an electrolyte (or more precisely, its activity at saturation), and since these quantities are large and very nearly equal, much greater

³ Similar ideas, but differently calculated and applied, have been employed by Born [*Z. Physik*, **1**, 4 (1920)], by Gyemant [*ibid.*, **30**, 240 (1924)] and recently by Latimer [THIS JOURNAL, **48**, 1234 (1926)]. For criticisms, see Webb, *Proc. Nat. Acad. Sci.*, **12**, 524 (1926).

⁴ See Part 6.

⁵ Langevin, *J. de phys.*, [4] **4**, 678 (1905); *Ann. chim. phys.*, [8] **5**, 70 (1905).

⁶ Debye, "Marx' Handbuch der Radiologie," Akademische Verlagsgesellschaft, Leipzig, 1925, vol. 6, pp. 618, 680.

⁷ An effective moment of the water molecule, obtained with the assumptions that the optical part of the dielectric constant of water is 3 and that the water molecules are not associated, is used.

⁸ Provided the molecular complexities of the solvents and the activity coefficients of the solutes are known.

accuracy than is at present possible in the calculation of lattice energies is necessary before even a rough calculation of the solubility can be made. The present paper deals principally with the evaluation of the free energy of hydration of ions; the problem of the electrostriction of the solvent is invoked as an aid to the assignment of radii to individual ions.

2. The Electrical Work of Charging an Ion in a Molecular Medium

The energy of the electrical field exterior to a sphere of radius r_0 , arising from the ion in solution, is obtained by calculating the energy density residing at points variably distant from the ion, at the end of a process by which the charge on the ion has been changed in infinitesimal steps from zero to its full value, and then by integrating the energy density over the entire volume of the solvent that surrounds the ion, that is, the limits of the integration are $r = \alpha$, and $r = r_0$, where r_0 is the radius of the ion. The ion in its discharged state is considered as a perfect solute, preserving exactly, however, its effective volume in solution. The picture of the ion in the solvent, effective for the energetics of its charging, is thus a spherical cavity in the solvent, at the center of which is the charge of the ion.

The first step in the calculation of the electrical work is to obtain the energy density residing at various points, at the end of the charging process. The following two equations taken from electrical theory furnish the starting point.

$$\begin{aligned} D &= E + 4\pi P \\ \delta w &= E(\delta D/4\pi) \end{aligned} \quad (1)$$

in which D is the dielectric displacement, E the electrical field strength, P the polarization per unit volume and w the energy residing in the medium, per unit volume, as a result of the charge. In order to calculate the polarization, it is necessary to know the internal field strength K , which is greater than E by a quantity proportional to P . The proportionality factor has been shown by Lorentz⁹ to be very nearly $4\pi/3$, for isotropic bodies; whence

$$\begin{aligned} K &= E + 4\pi P/3 \\ D &= K + 2\Lambda = e/r^2 \end{aligned} \quad (2)$$

where $\Lambda = 4\pi P/3$, e is the charge on the ion and r the distance from the center of the ion to the point being considered. The appropriate substitutions yield for the work of charging per unit volume, at a given point

$$w = E_m^2/8\pi + \int_0^{P_m} E(P)dP$$

where E_m and P_m are the values of E and P , respectively, at a point, at the end of the charging process. The total work of charging is obtained by integrating over the entire volume of solvent which surrounds the ion

⁹ Lorentz, "Theory of Electrons," B. G. Teubner, Leipzig, 1909, p. 138.

$$W = \frac{1}{8\pi} \int_{r_0}^{\infty} E_m^2 4\pi r^2 dr + \int_{r_0}^{\infty} \left(\int_0^{P_m} E(P) dP \right) 4\pi r^2 dr \quad (3)$$

This work is to be separated into two parts, W_1 and W_2 , corresponding with the two terms on the right of the preceding equation. Substitutions corresponding with Equation 2 lead to the following expression for W_1

$$W_1 = \frac{e^{3/2}}{4} \int_0^{K_0} \frac{1 + 2\Lambda'}{(K_m + 2\Lambda_m)^{3/2}} (K_m - \Lambda_m)^2 dK_m$$

where K_m and Λ_m are the values of K and Λ , respectively, at a point, at the end of the charging process; $\Lambda' = \partial\Lambda/\partial K$ and K_0 is the value of K_m corresponding with r_0 .

For the calculation of the second term of Equation 3, recourse is had to the Langevin theory, whence

$$\Lambda = \frac{4\pi}{3} n\alpha K + \frac{4\pi n}{3} \mu L(x)$$

$$\Lambda' = \frac{4\pi}{3} n\alpha + \frac{4\pi n\mu^2}{3kT} \left[-\frac{1}{\sinh^2 x} + \frac{1}{x} \right]$$

where n is the number of water molecules per cc.,¹⁰ α the optical polarizability of the water (per molecule), μ the permanent electrical moment of the water dipoles, $L(x)$ the Langevin function, that is, $L(x) = \coth x - (1/x)$, $x = \mu K/kT$, k is Boltzmann's constant and T is the temperature. The evaluation of W_2 in accord with the Langevin theory and Equation 2 follows.

$$W_2 = 3 \int_{r_0}^{\infty} \left(\int_0^{\Lambda_m} E d\Lambda \right) r^2 dr$$

$$\int_0^{\Lambda_m} E d\Lambda = K_m \Lambda_m - \frac{\Lambda_m^2}{2} - \int_0^{K_m} \Lambda dK$$

$$\int_0^{K_m} \Lambda dK = \frac{4\pi n\alpha K_m^2}{6} + \frac{4\pi n k T}{3} \int_0^{x_m} L(x) dx \quad (3a)$$

$$\int L(x) dx = \log \frac{\sinh x}{x}$$

whence
$$\int_0^{\Lambda_m} E d\Lambda = \Lambda_m K_m - \frac{\Lambda_m^2}{2} - \frac{4\pi n\alpha K_m^2}{6} - \frac{4\pi n k T}{3} \log \frac{\sinh \frac{\mu K_m}{kT}}{\frac{\mu K_m}{kT}}$$

and
$$W_1 + W_2 = e^{3/2} \int_0^{K_0} \frac{1 + 2\Lambda'}{(K_m + 2\Lambda_m)^{3/2}} \left[K_m^2 \left(\frac{1}{4} - \pi n\alpha \right) + \Lambda_m K_m - \right.$$

¹⁰ In this calculation, the number of water molecules per cc. is assumed to be constant. This is not true, as is shown further; however, the slight effect of pressure on the dielectric constant of water leads one to believe that no great error is made in the calculation of the polarization, on the assumption that n , α and μ may be treated as constants.

$$\left. \frac{\Lambda_m^2}{2} - 2\pi n k T \log \frac{\sinh x}{x} \right] dK_m \quad (4)$$

Upon substitution of numerical values in Equation 4, the total electrical energy, in kilogram calories, necessary to charge one mole of ions in water is found to be

$$W_1 + W_2 = 0.15115 \int_0^{K_0} \Omega(K_m) dK_m \quad (5)$$

where $\Omega(K_m)$ is defined by the preceding equation, and K_0 is related in the following way to the radius of the ion and the polarization of the solvent existing at the surface of the ion: $e/r_0^2 = K_0 + 2\Lambda_0$. The integral giving the value of the work of charging the ion in water has been evaluated by calculating the values of Λ_m and Λ' corresponding with various values of K_m and integrating graphically from $K_m = 0$ to $K_m = K_0$. These data are collected in Table I; Row 1 gives the values of K_0 , Row 2 the values of r_0 in Ångström units and Row 3 the energy in kilogram calories necessary to charge one mole of ions in water.

TABLE I

ELECTRICAL WORK OF CHARGING IONS OF VARIOUS RADII

K_0	1×10^4	2×10^4	4×10^4	6×10^4	8×10^4	1×10^5	1.5×10^5	2×10^5	3×10^5	4×10^5
r_0	4.165	3.090	2.318	1.948	1.715	1.551	1.285	1.122	0.9238	0.8036
$W_1 + W_2$	0.980 ^a	1.585	3.168	5.054	7.045	9.064	14.00	18.67	27.22	34.92

^a At low values of the field strength, that is, below 8×10^4 , the approximation is made that $\Lambda = \bar{c}K$, where \bar{c} is a constant, and the equations thus obtained are integrated directly; \bar{c} is assigned the value 0.9305 for values of K with which it is here used.

Curve A of Fig. 1 shows $\Omega(K_m)$ plotted against K_m . The abscissas are in c.g.s. electrostatic units, and the ordinates are in c.g.s. electrostatic units multiplied by 0.1666×10^{-5} .

3. The Compression Work

In addition to the electrical energy necessary for the charging of the ion in water, there is an expenditure of energy resulting from the compression of the solvent in the vicinity of the ion. The pressures giving rise to the compression are a result of the attraction of the solvent molecules by the ion.

The pressure existing at a given distance from the ion may be calculated in the following way. Let the center of gravity of the negative charges in a molecule coincide with the origin of a rectangular set of coördinates, and let the position of the center of gravity of the positive charges in the system of coördinates be designated by ξ , η , ζ . If the effective charge on the dipole is e , and if the components of the electric field at the origin are X , Y , Z , then for the component of the force in the x -direction

$$F_x = -eX + e \left(X + \frac{\partial X}{\partial x} \xi + \frac{\partial X}{\partial y} \eta + \frac{\partial X}{\partial z} \zeta \right)$$

In terms of the components of the polarization per unit volume, P_x, P_y, P_z , and in view of the transformation resulting from the fact that $\text{rot } E = 0$, the above expression reduces to the following form

$$F_x = \left(P_x \frac{\partial X}{\partial x} + P_y \frac{\partial Y}{\partial x} + P_z \frac{\partial Z}{\partial x} \right) dv$$

where dv is an element of volume. Since P and E have the same direction in the case of an isotropic medium, it follows that

$$F_x = \frac{P}{E} \left(X \frac{\partial X}{\partial x} + Y \frac{\partial Y}{\partial x} + Z \frac{\partial Z}{\partial x} \right) dv \quad (6)$$

and since by definition

$$E = \sqrt{X^2 + Y^2 + Z^2}$$

and

$$\frac{\partial p}{\partial x} = F_x/dv$$

where p is the pressure, the result is that

$$\frac{\partial p}{\partial x} = \frac{P}{E} \frac{\partial}{\partial x} \left(\frac{E^2}{2} \right)$$

and

$$p = \int_0^{E_m} P(E) dE$$

$$E = K - \Lambda$$

whence, by reference to Equation 3a

$$p = \frac{n\alpha K_m^2}{2} + nkT \log \frac{\sinh \frac{\mu K_m}{kT}}{\frac{\mu K_m}{kT}} - \frac{3}{8\pi} \Lambda_m^2$$

The pressures calculated with the aid of this formula are given in Row 3 of Table II. Row 1 gives the distance in Ångström units from the center of the ion; Row 2, the values of the internal field strength corresponding, in c.g.s. electrostatic units; Row 3, the pressure in megadynes per square centimeter.

TABLE II

PRESSURES EXISTING AT VARIOUS DISTANCES FROM ION

Distance from ion, Å	12.77	5.76	4.16	3.09	2.32	1.95
Field strength	10^6	5×10^6	10^6	2×10^6	4×10^6	6×10^6
Pressure	0.43	20.9	1.76×10^2	1.28×10^3	6.34×10^3	1.42×10^4
Distance from ion	1.71	1.55	1.28	1.12	0.924	0.804
Field strength	8×10^6	10^6	1.5×10^6	2×10^6	3×10^6	4×10^6
Pressure	2.47×10^4	3.74×10^4	7.97×10^4	1.36×10^5	2.93×10^5	5.08×10^5

The compression work per unit volume, w_r , according to thermodynamics, is

$$w_r = \int_{v_0}^{v_0 + \Delta v} p \frac{dv}{v} = \int_0^p \frac{p}{v} \frac{\partial v}{\partial p} dp = \int_0^p \kappa p dp$$

where κ is the coefficient of compressibility of the solvent and is itself a function of the pressure. At low pressures, κ is practically constant, and

consequently at great distances from the ion (that is, $K_m < 10^5$), $w_r = \kappa p_m^2/2$. At great pressures, however, κ decreases rapidly; for κ as a function of the pressure, an expression due to Tumlriz¹¹ is used

$$\kappa = -1/[\beta(\pi + p)^2 + p + \pi]$$

where β and π are constants at a given temperature, with the values 2.845×10^{-10} and 7.311×10^9 , respectively. At values of the field strength greater than 10^5 , the compression work w_r is obtained by plotting κp against p and integrating graphically. The total compression work W_c is obtained by integrating over the entire volume of solvent, that is,

$$W_c = \int_{r_0}^{\infty} (w_r) 4\pi r^2 dr$$

or in terms of the internal field strength and the polarization, the total compression work per ion is

$$W_c = 2\pi e^{3/2} \int_0^{K_0} (w_r) \frac{1 + 2\Lambda'}{(K_m + 2\Lambda_m)^{3/2}} dK_m = 2\pi e^{3/2} \int_0^{K_0} \varphi(K_m) dK_m$$

Curve B of Fig. 1 shows $\varphi(K_m)$ multiplied by 2×10^7 plotted as ordinates against the internal field strength as abscissas. The performance of the

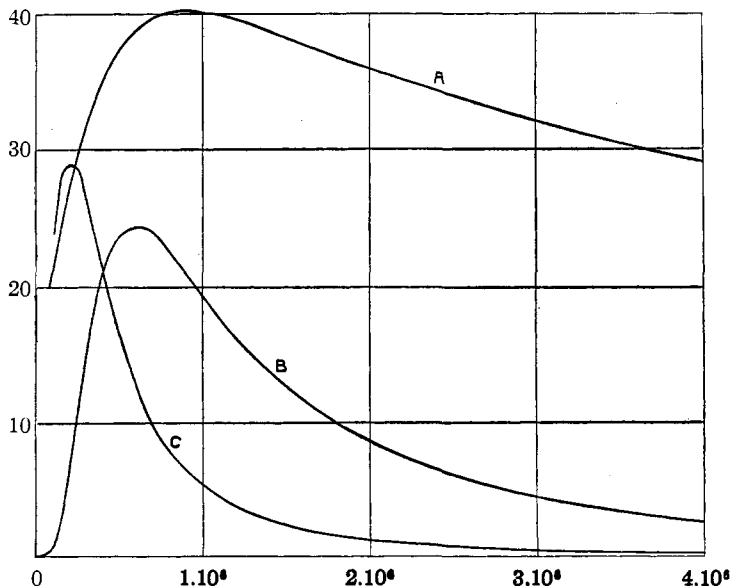


Fig. 1.—Various functions plotted against the internal field strength as abscissas.

graphical integration yields for the compression work in kilogram calories per mole of ions the values recorded in Table III.

¹¹ Tumlriz, *Sitzb. Akad. Wiss. Wien*, [IIa] 118, 203 (1909).

TABLE III
COMPRESSION WORK AS A FUNCTION OF THE RADII OF IONS

Radius (r_0), Å.	3.090	2.318	1.948	1.715	1.551	1.285	1.122	0.924	0.804
Compression work	0.01	0.15	0.38	0.60	0.80	1.17	1.41	1.69	1.85

4. The Free Energy of Hydration

The difference between the quantity of energy $e^2/2r_0$, and that calculated in the foregoing sections for charging an ion in water and compressing the solvent, gives the free energy of hydration of the ion being considered. The data for ions of various radii are collected in Table IV.¹² Row 1 contains the radii of the ions (in Å.); Row 2 contains the difference between the energy necessary to charge the ion in a vacuum and that necessary to charge the ion in water and to compress the solvent (in kilogram calories per mole of ions); Row 3 contains the virtual dielectric constant of the water, that is, the factor D' which would give the correct value for the electrical energy of charging the ion in water, when substitution is made in the formula $e^2/2D'r_0$.

TABLE IV
FREE ENERGY OF HYDRATION OF IONS OF VARIOUS RADII

Radius of ion	4.165	3.090	2.318	1.948	1.715	1.551	1.285	1.122	0.9238	0.8036
Free energy of hydration	38.7	51.8	67.9	79.3	88.6	96.6	113.3	127.1	149.8	168.7
D'	40.5	33.7	22.5	16.8	13.7	11.7	9.17	7.88	6.57	5.88

The validity of the free energy of hydration as a function of the radius of the ion, obtained in this way, depends principally upon the following assumptions: (1) that the Langevin theory gives the value of the polarization of the medium, (2) that the constants α and μ , as well as those of the compressibility formula, are given the correct values, (3) that the cavity surrounding the center of the ion in solution is spherical and (4) that the ions are unsolvated in a chemical sense. As regards the exactness of the Langevin theory and the correctness of the constants, little can be said more than that they probably reproduce the several quantities to within 10%. These quantities, however, are less than 15% of the quantities from which they are subtracted (for ions of radius greater than 0.9 Å.), and therefore for the difference between the energy necessary to charge the ion in a vacuum and in water, the values given are probably not in error by more than 1.5%. The fact that the radius of the cavity surrounding the ion is several times larger than the radius of the orbits of the outer electrons of the ion, is interpreted to mean that the form of the cavity approximates a sphere with considerable exactness. From evidence as to the actual volume occupied by the ions in solution (as calculated, see further)

¹² Calculations in this paper are made for a temperature of 25° and a pressure of one atmosphere.

it seems probable that the assumption regarding the absence of chemical hydration is true, at least for the ions of the alkali metals (except lithium), the halogens, silver and thallium. Ions such as those of zinc and hydrogen, if unsolvated chemically, are very compact. The deduction regarding the absence of chemical hydration in the case of the alkali metal ions, etc., follows from the fact that the necessary electrical effects are sufficient to account for the free energy of hydration, assignment of the radii being made on the basis of the actual volume of the ions in solution (Parts 5 and 6).

5. The Electrostriction of the Solvent

The free energy of hydration of ions having been calculated as a function of the radius, it is now necessary to attempt a calculation of some other property as a function of the radius, if an assignment of radii to actual ions is to be undertaken. This procedure is the result of there being no experimental data for the free energies of hydration of individual ions. The second property chosen for calculation is the partial molal volume of the ions in the infinitely dilute solution, that is, the change in volume (calculated on the basis of the mole) produced by the addition of an infinitesimal quantity of the ions to an infinitely dilute solution of the ions. This volume change arises from two causes: (1) the effective volume of the ions in solution, that is, the volume of the cavity surrounding the ion in the solvent and (2) the contraction of the solvent resulting from the attractions of the water dipoles by the ion. This contraction (the so-called electrostriction) is now to be calculated.

The change in volume per unit volume, at a point distant r from the center of the ion, resulting from changing the pressure from zero to p , is

$$\frac{-\Delta V_r}{V} = - \int_0^p \frac{1}{V} \frac{\partial V}{\partial p} dp = \int_0^p -\kappa dp$$

where the symbols are the same as those used in the evaluation of the compression work. At low pressures the coefficient of compressibility is practically constant and the expression is easily integrated, but at higher pressures, where both the coefficient of compressibility and the pressure become complicated functions of the field strength, resort is made to graphical methods.¹³

¹³ If the approximation be made that $\Lambda = \bar{c}K$, then p is equal to jK^2 , where c and j are constants. With the expression of Tumlirz for the coefficient of compressibility, $\Delta V_r/V$, may be obtained directly, whence

$$\frac{-\Delta V_r}{V} = j \int_0^x \frac{dx}{a + bx + cx^2} = j \frac{1}{\sqrt{b^2 - 4ac}} \left[\log \frac{2cx + b - \sqrt{b^2 - 4ac}}{2cx + b + \sqrt{b^2 - 4ac}} \right]_0^x$$

where $x = K^2$, $a = \beta\pi^2 + \pi$, $b = j(2\beta\pi + 1)$, $c = j^2\beta$. By weighting the averaged quantity \bar{c} , the values thus obtained agree closely with those obtained graphically.

The total decrease in volume of the solvent, resulting from compression by the ion, is obtained by integrating over the volume of solvent surrounding the ion, whence

$$-\Delta V = \int_{r_0}^{\infty} \left(\frac{-\Delta V_r}{V} \right) 4\pi r^2 dr$$

or, in terms of the field strength, the charge, and the polarization

$$-\Delta V = 2\pi e^{1/2} \int_0^{K_0} \left(\frac{-\Delta V_r}{V} \right) \frac{1 + 2\Lambda'}{(K_m + 2\Lambda_m)^{1/2}} dK_m$$

Curve C of Fig. 1 shows $\left[\frac{-\Delta V_r}{V} \frac{1 + 2\Lambda'}{(K_m + 2\Lambda_m)^{1/2}} \right]$ plotted against K_m . The abscissas are in c.g.s. electrostatic units, and the ordinates in the same multiplied by 2×10^{-17} . Table V gives the total decrease in volume (in cubic centimeters) attending the solution of one mole of ions in an infinite

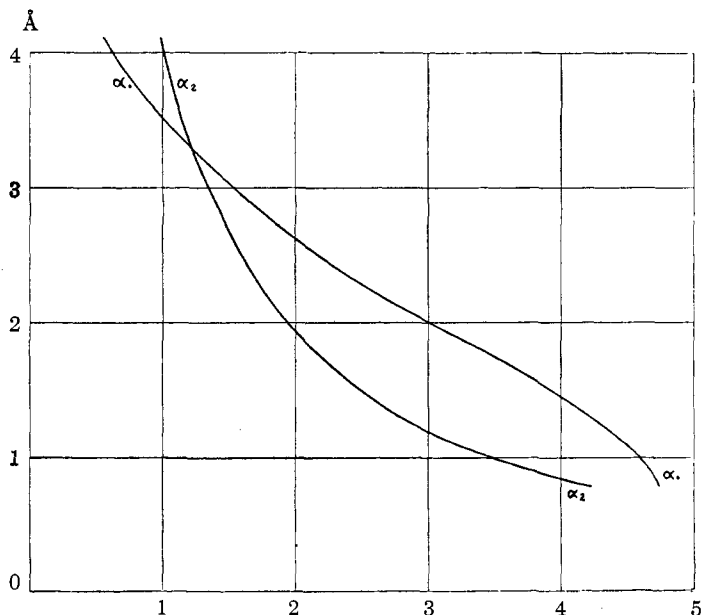


Fig. 2.—Volume contraction of solvent (α_1) and free energy of hydration (α_2) as a function of the radius of the ion. [Units arbitrary.]

quantity of water, as calculated for ions of various radii. The data of Table V are reproduced graphically in Fig. 2 (curve α_1). The radii of the

TABLE V
CONTRACTION OF SOLVENT PRODUCED BY IONS OF VARIOUS RADII

K_0	10^5	2×10^5	4×10^5	6×10^5	8×10^5	10^6	1.5×10^6	2×10^6	3×10^6	4×10^6
Radius	4.165	3.090	2.318	1.948	1.715	1.551	1.285	1.122	0.924	0.804
Contraction	1.40	3.59	7.66	10.27	11.84	12.86	14.21	14.83	15.44	15.69

ions are plotted as ordinates and the corresponding volume decrease (multiplied by 0.3) as abscissas.

6. Application of Data to Actual Ions, Comparisons, etc.

Two properties having now been calculated as a function of the radii of the ions of an electrolyte, these properties which have been measured only for the sum or difference of two ions may now be calculated for the individual ions. The equations for this purpose are of the following types:

$$\begin{aligned}\psi(r_A) + \psi(r_B) &= W_A + W_B \\ \frac{4}{3} \pi(r_A)^3 - f(r_A) + \frac{4}{3} \pi(r_B)^3 - f(r_B) &= \Delta V \text{ solution}\end{aligned}$$

where $\psi(r)$ and $f(r)$ are functions of r giving, respectively, the free energy of hydration of the ion and the volume contraction of the solvent. It is to be emphasized that the radius as a function of which the free energy of hydration is calculated is precisely the radius occurring in the equation for the volume calculation, that is, the radius of the sphere surrounding the center of the ion in solution, in which there are no solvent molecules. $W_A + W_B$ is the sum of the free energies of hydration of the two ions of an electrolyte, and is obtained empirically from a consideration of the following energy changes: (1) the algebraic sum of the standard electrode potentials of the corresponding elements, (2) the energy necessary to concentrate the solution to unit activity¹⁴ and (3) the energy necessary to transform the elements from the state in which their electrode potentials were measured to the state of an ionic gas at unit pressure.

Instead of applying the equations directly to any one electrolyte, the simplest of which would have necessitated the use of very uncertain data for the electron affinities of the halogens, the equations have been applied to the difference of the two quantities for sodium and potassium ions. The data for these ions are probably more exactly known than those for any other pair of ions that might be used. The difference between the free energies of hydration has been obtained from their standard electrode potentials,¹⁵ free energies of sublimation,¹⁶ and ionization potentials.¹⁷ The difference between the partial molal volume of the two ions at great dilution was calculated from the densities of the very dilute solutions of potassium chloride and of sodium chloride, as measured by Lamb and Lee.¹⁸ This difference was found to be 10.386 cc. (Much less precise experimental determinations of the densities of the solutions of the bromides and iodides of sodium and potassium, but at higher concentrations

¹⁴ Activity approaching mole fraction of solute as solution is indefinitely diluted.

¹⁵ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, chap. 30.

¹⁶ Ladenburg and Minkowski, *Z. Physik*, **6**, 163 (1921); **8**, 137 (1921).

¹⁷ Sommerfeld, "Atomabau und Spektrallinien," Vieweg, Braunschweig, 1924, p. 525.

¹⁸ Lamb and Lee, *THIS JOURNAL*, **35**, 1683 (1913).

where the measurements are less difficult, yield for this difference, respectively, 10.32 and 10.27 cc.), whence, for sodium and potassium ions

$$\begin{aligned}\psi(r_{\text{Na}}) - \psi(r_{\text{K}}) &= 17.128 \\ f(r_{\text{Na}}) - f(r_{\text{K}}) + \frac{4}{3}\pi L(r_{\text{K}})^3 - \frac{4}{3}\pi L(r_{\text{Na}})^3 &= 10.386\end{aligned}$$

where $\psi(r)$ and $f(r)$ are the functions of the radius of the ion having the meanings previously assigned them and L is the Avogadro number. Solution of the equation yields the following results: $r_{\text{K}} = 1.873 \times 10^{-8}$ cm.; $r_{\text{Na}} = 1.505 \times 10^{-8}$ cm.; $\psi(r_{\text{K}}) = 81.9$ kilogram calories per mole; $\psi(r_{\text{Na}}) = 99.0$ kilogram calories per mole.

The radii of the ions of the halogens may now be calculated from the densities of the solutions of their sodium or potassium salts, the radius of sodium or of potassium (found above), and the electrostriction correction. The corresponding free energies of hydration may be obtained by reference to Curve α_2 of Fig. 2,¹⁹ where the free energies of hydration of univalent ions (in kilogram calories, multiplied by 0.025, per mole) are plotted against the radius of the ion in Ångström units. In this manner the free energies of hydration of the ions of the halogens, alkali metals, silver and thallium have been obtained. In these cases the absence of chemical hydration is assumed. For the remaining ions for which data are given (Table VI), this assumption is not necessary; in the case of these ions sufficient data are available (free energies of sublimation, ionization and electrode potential) from experiment to calculate the difference between the free energies of hydration of these ions and that of sodium or potassium ion. This procedure implies the assignment of single potentials, but only for a sort of ideal electrode, that is, one for which the electrons exist as a gas and for which contact potentials are absent. It may be pointed out, however, that with an accurate value for the free energy of condensation of electrons on platinum, the single potentials of gaseous electrodes employing platinum as a conductor, may be calculated. Table VI has been compiled by the two methods of calculation given in this paragraph.

TABLE VI
FREE ENERGIES OF HYDRATION OF INDIVIDUAL IONS

Ion	Na ⁺	K ⁺	Rb ⁺	Co ⁺	F ⁻	Cl ⁻	Br ⁻	I ⁻
Radius	1.505	1.873	2.02	2.19	1.75	2.238	2.382	2.60
Free energy of hydration	99	81.9	76.9	71.5	87.0	70.1	66.2	61.0
Ion	H ⁺	Ag ⁺	Tl ⁺	Zn ⁺⁺	Cd ⁺⁺	Hg ⁺⁺	S ⁻	
Radius	<0.5	1.57	1.96	1.04	1.15	1.11	4.12	
Free energy of hydration	249.6	95.5	78.6	525	473	486	54	

¹⁹ The curve of Fig. 2 may also be used for ions of other valence. The necessary transformation will be evident from the form of Equation 4.

The values for the free energies of hydration of the halide ions make possible a calculation of the electron affinities of the halogens; these are given in Table VII. Row 1 gives the reaction being considered; Row 2 the total energy corresponding, that is, the electron affinity, calculated; Row 3, the experimental values obtained by various investigators,²⁰ spectroscopically. The comparison has some interest, but little importance can be attached to the approximate agreement, on account of the widely varying experimental results of others.

TABLE VII
ELECTRON AFFINITIES OF HALOGENS

Reaction	$\ominus + \text{Cl} = \text{Cl}^-$	$\ominus + \text{Br} = \text{Br}^-$	$\ominus + \text{I} = \text{I}^-$	$\ominus + \frac{1}{2}\text{F}_2 = \text{F}^-$ ^a
$E_{\text{calcd.}}$	89.2	72	62	50
$E_{\text{obs.}}$	89.3	67.5	59.2	

^a The electrode potential of fluorine, which has evaded measurement so far, and which was needed for this calculation, was calculated from the heat of formation of sodium fluoride (from sodium and fluorine), the entropy change corresponding, and the activity of sodium fluoride in its saturated solution. The entropy of sodium fluoride was calculated in the manner proposed by Latimer [THIS JOURNAL, 43, 818 (1921)], and the entropy of fluorine and the activity coefficient of sodium fluoride were estimated. The value arrived at for the standard fluorine electrode, that is, the potential of fluorine gas measured against a solution of its ions at unit activity (activity approaching molality as solution is indefinitely diluted) with reference to the similarly defined standard hydrogen electrode is 1.85 volts. The several quantities that were estimated were such as not to affect the final value markedly.

The procedure proposed at the outset for the calculation of the solubility of an electrolyte may, for the moment, be reversed, and accordingly the free energies of hydration used for the calculation of the lattice energies. The free energy of hydration gives the free energy resulting from the solution of one mole of ions (at unit pressure) in an infinite quantity of the solution at unit activity. To this is to be added the free energy obtainable from the reversible dilution²¹ of a quantity of the solution containing one mole of the electrolyte at the point of saturation. The free energy thus found is the free energy to be obtained when one mole of positive ions (at unit pressure) reacts reversibly with one mole of negative ions (also at unit pressure) to form one mole of the solid electrolyte. To this is to be added the energy corresponding with the entropy change of the reaction, and from it is to be subtracted the energy change corresponding with the volume change. The result is the lattice energy, that is, the internal energy change resulting from the separation of the ions of a crystal struc-

²⁰ Franck, *Z. Physik*, 5, 428 (1921). Steubing, *Ann. Physik*, 64, 673 (1921). Eder and Valenta, *Beitr. Photochem. Spektralanal.*, p. 358. v. Augerer, *Z. Physik*, 11, 167 (1922).

²¹ Unit activity (activity approaching mole fraction as the solution is indefinitely diluted) naturally corresponds with a highly supersaturated solution, except in a few cases where the activity coefficient becomes enormous.

ture. The following values, in kilogram calories, are thus obtained: potassium chloride, 169; sodium chloride, 187; silver chloride, 198; silver iodide, 198; thallos chloride, 173. The absence of activity coefficients for other electrolytes in their saturated solutions prevents further direct calculations of this kind. By means of a thermodynamic cycle Born²² obtains for sodium and potassium chlorides values four kilogram calories lower than the values calculated above, while Herzfeld²³ calculates in the same manner a value for silver chloride 2.6 kilogram calories greater than that given above. There are no available data for the two remaining salts with which the above values may be compared. It is to be pointed out that in the case of the bromides and iodides there is an essential disagreement between the results of the present calculations and the values of Born,

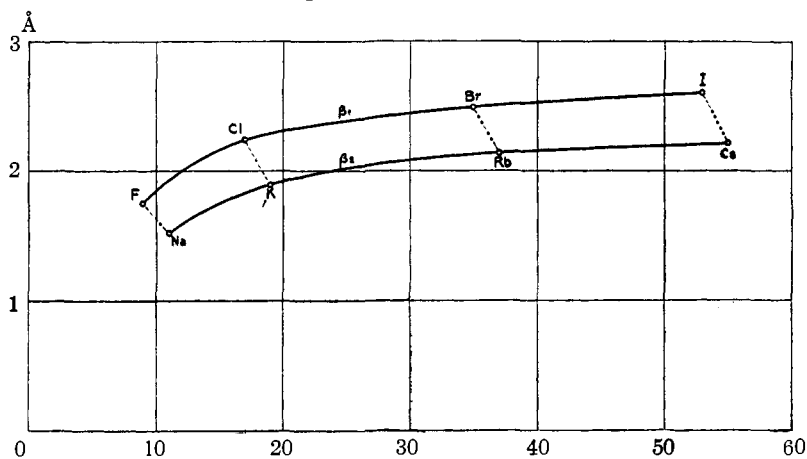


Fig. 3.—The radii of the commoner ions plotted against their atomic numbers.

as revealed by the fact that the electron affinities of bromine and iodine as calculated herein are 14 and 17 calories, respectively, smaller than those calculated by Born. In view of the uncertainty in the interpretation of electron-affinity data obtained from experiment and in view of the widely diverging results of different investigators, a decision as to the most probable values is almost impossible. The newer spectroscopic attempts of von Angerer and Müller²⁴ give an average value for chlorine of 87.5, for bromine, 80 and for iodine, 71.

Fig. 3 shows the radii of the ions of the alkali metals and of the halogens plotted against their atomic numbers. It is interesting to note that the

²² Born, "Atomtheorie des Festen Zustandes," Teubner, Berlin, 1923, p. 752. Here will be found reference to the older work on electron affinities.

²³ Herzfeld, "Kinetische Theorie der Wärme," Müller-Pouillet's "Lehrbuch der Physik," Friedrich Vieweg und Sohn Aktien-Gesellschaft, Braunschweig, 1925, p. 254.

²⁴ von Angerer and Müller, *Physik. Z.*, **26**, 643 (1925). Compare Ludlam and West, *Z. physik. Chem.*, **120**, 256 (1926).

radii of these ions follow the same order as that given by Bragg²⁵ and by Wasastjerna²⁶ for the radii of ions in crystals; moreover, the difference is roughly constant, the effective radii of the ions in solution being about 0.47 Å. greater than those of Bragg for radii in crystals.

The author expresses his thanks to Professor P. Debye of this Institute, whose advice in connection with this problem has been constantly sought and freely given.

Summary

The free energy of hydration of a chemically unhydrated ion is obtained as a function of its radius by calculating the difference in energy necessary to charge the ion in a vacuum and that necessary to charge the ion in water and to compress the solvent in the vicinity of the ion. Regard is taken of the fact that the dielectric constant of a molecular medium is not constant in the vicinity of an ion.

The partial molal volume of an ion at great dilution is calculated as a function of its effective radius in solution. This calculation requires a further one for the contraction of the solvent (electrostriction) due to the pressures resulting from the attraction of the solvent dipoles by the ion.

The solution of the two resulting equations, obtainable for an electrolyte whose free energy of hydration and partial molal volume are known, gives the radii of the individual ions, and hence their free energies of hydration. The free energies of hydration of the most common ions are obtained in this way, and the consequent calculations of electron affinities and lattice energies are made.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, GEORGE WASHINGTON UNIVERSITY
AND THE FIXED NITROGEN RESEARCH LABORATORY]

THE PHOTO- AND RADIOCHEMICAL INTERACTION OF HYDROGEN AND CHLORINE

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The development and present status of the theory of the photosynthesis of hydrogen chloride have been so recently and thoroughly summarized² that no further review is required. The synthesis by other radiative agencies such as α -, β -, γ - and x-rays was discussed and some of the possible relations to photochemical mechanism were earlier pointed out by Lind.³

²⁵ Bragg, *Proc. Roy. Inst. Gr. Brit.*, [III] **24**, no. 119, 614 (1925).

²⁶ Wasastjerna, *Soc. Scient. Fenn. Comm. Math.-Phys.*, **1**, p. 38 (1923).

¹ Frank Porter, *Thesis*, George Washington University, 1926.

² A. L. Marshall, *Trans. Am. Electrochem. Soc.*, Reprint 9, April, 1926. A. J. Allmand, *Ann. Repts. Chem. Soc.*, **22**, 333 (1925).

³ Lind, "Chemical Effects of α -Particles and Electrons," Chemical Catalog Co., New York, 1921.