molecules; (3) geometrical compounds (Cu_3Au) ($CuAu_3$) (Bain) in which definite proportions are an accident of symmetry in homogeneous atomic dispersions; (4) Wernerian compounds ($CaCl_2I$) (Wyckoff) (K_2PtCl_4) (Dickinson) in which the crystal is built up of both simple and complex ions; (5) mixed ionic compounds ($3CaO \cdot Al_2O_3$).

There remains to be discovered a sixth type,[1] namely, the molecular compound in which molecules of the constituents crystallize together without losing their original identity. As in the case of Type 3, it may be expected that this will be an accidental effect of the symmetry of a homogeneous molecular dispersion of one substance in the other.

Acknowledgments.—It is a pleasure to express our appreciation to the General Electric Company, Schenectady, N. Y., the Calumet Baking Powder Company, Chicago, Ill., and to the Aluminum Company of America, New Kensington, Pa., for placing at our disposal facilities without which this research would have been exceedingly difficult, if not impossible; and to Dr. E. A. Harrington, who first showed that the x-ray diffraction pattern of an impure tricalcium aluminate contained lines corresponding to those from a body-centered cube.

Summary

1. The most probable crystal structure of tricalcium aluminate has been determined and the alternate possibilities stated.

2. The structure of tricalcium aluminate has been shown to be mixed ionic.

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THE THEORETICAL EVALUATION OF THE ENTROPIES OF AQUEOUS IONS

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It has been suggested by Latimer and Buffington[1] that the entropy change, ΔS, for the process

$$\text{Ion (gas)} = \text{Ion (aq.)}$$

is a function of the charge, e, on the ion, and the radius, r, of the ion cavity in the water solution; $\Delta S = f(e^2/r)$. This relation was noted from an inspection of the experimental values of the entropies of solution and was stated in the form of an empirical equation. The theoretical evaluation of this function will be considered in this article.

The total entropy of hydration may be considered as due to two effects: $\Delta S_{(1)}$, the entropy change arising from the polarizability of the medium,

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[1] Latimer and Buffington, This Journal, **48**, 2297 (1926).

and $\Delta S_{(2)}$, the entropy change due to the compression of the water, arising from the electrostatic attraction of the water molecules.

The first effect can be obtained by considering the temperature coefficient of the free energy of the process of charging the ion in the gas and water phases. For this free energy, we have the expression first set forth by Born[2] and Fajans[3] and later developed in the works of Hückel,[4] Zwicky[5] and Webb.[6]

The original Born work, which of late has been supported (in so far as the dielectric constant is concerned) by Latimer,[7] Scatchard[8] and Bjerrum,[9] takes the ordinary dielectric constant to be operative. Hückel advanced the idea that the effective dielectric constant must be less than that of pure water in accounting for the course of the activity–coefficient curve. Webb actually succeeded in calculating such an effective dielectric constant, but, unfortunately, the method which involves the selection of an effective moment, and the application of the Langevin theory to water as a normal liquid is open to serious question, especially in the case of entropies.

It is interesting, nevertheless, to see what result the old picture gives us. Thus, using the Born expression

$$\Delta F_{(1)} = -\frac{e^2}{2r}\left(1 - \frac{1}{D}\right) \tag{1}$$

and by differentiation

$$\Delta S_{(1)} = \frac{e^2}{2rD^2}\left(\frac{\mathrm{d}D}{\mathrm{d}T}\right)_P = \frac{-\Delta F_{(1)}}{D^2}\left(\frac{\mathrm{d}D}{\mathrm{d}T}\right)_P\left(\frac{1}{1 - \frac{1}{D}}\right) \tag{2}$$

From Kockel,[10] for 25°, the dielectric constant of water is 78; its temperature coefficient is equal to -0.4. Placing these values in Equation 2 we obtain $\Delta S_{(1)} = 6.3 \times 10^{-5}\,\Delta F_{(1)}$ cal. per degree per mole. The magnitude of this quantity is about half that found experimentally for the total entropy of hydration. However, we cannot attach much significance to the numerical result as the temperature coefficient of the dielectric constant of pure water may not be even of the same order of magnitude as that for water under the enormous electrical field about the ion. From

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[2] Born, *Z. Physik,* 1, 4 (1920).

[3] Fajans, *Ber. physik. Ges.,* **21**, 549, 709 (1919).

[4] Hückel, *Physik. Z.,* **26**, 93 (1925).

[5] Zwicky, *ibid.,* **26**, 664 (1926); *Proc. Nat. Acad.,* **12**, 86 (1926).

[6] Webb, This Journal, **48**, 2589 (1926).

[7] Latimer, *ibid.,* **48**, 1234 (1926).

[8] Scatchard, *Trans. Faraday Soc.,* **23**, 454 (1927); *Trans. Am. Electrochem. Soc.,* **51**, 13 (1927).

[9] Bjerrum and Larsson, *Z. physik. Chem.,* **127**, 358 (1927); Bjerrum, *Trans. Faraday Soc.,* **23**, 434 (1927).

[10] Kockel, *Ann. Physik,* **77**, 417 (1925).

the calculations which we are to make it appears that $\Delta S_{(1)}$ must in reality be small in comparison with the other effect. This failure of Equation 2 will be considered in a later paragraph.

The second entropy change accompanying hydration, that is, the change of entropy of the water with pressure, is given by the thermodynamic expression $\mathrm{d}S = -(\mathrm{d}V/\mathrm{d}T)_P\mathrm{d}P$. For a differential unit of volume the entropy change is obtained by integrating this expression with respect to the pressure. The total entropy change about the ion is then given by integrating over the total volume of the water outside the ion cavity. Expressing volume as a function of the radius, we obtain

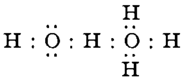
$$\Delta S_{(2)} = -\int_r^{\infty}\int_1^{P} \frac{1}{V^0}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_P \mathrm{d}P\ 4\pi r^2\mathrm{d}r \tag{3}$$

From considerations similar to those of Lorentz for the force density in a polarizable medium in an electric field, Zwicky[5] has developed an expression for the pressure at a distance, r, from a charge, e. The value of this expression depends upon the polarization of the medium by the field. For small fields the polarization is proportional to the field strength and the expression becomes

$$P = \frac{(3 + 2D)\ (D - 1)}{40\pi D^2}\ \frac{e^2}{r^4} \tag{4}$$

The deviation of the actual pressure at very high values from that given by this expression, due to the electrical saturation of the water, is a matter of some conjecture. The dielectric constant of water may be considered as the sum of three effects: (1) the electronic displacement—this factor is given by the classical relation between the index of refraction and the dielectric constant; (2) the ionic displacements, that is, the stretching of the molecule with respect to hydrogen and hydroxide ions; (3) the orientation of the water molecules in the electric field due to their permanent electrical moment. The value of $D_{(1)}$ is about 3 and it has been generally assumed that $D_{(3)}$ is very much larger than $D_{(2)}$ so that the problem may be treated by the methods developed by Langevin.[11] Now, although liquids undoubtedly do exist normally (or under special conditions) in the form of dipoles, we doubt very much whether this is true with associated liquids. Furthermore, it is well known that the theory does not give the correct temperature variation.

Latimer and Rodebush[12] in their discussion of associated liquids have suggested that the association is through "hydrogen bonds," *e. g.*,



$$\begin{array}{ccccccccc} & & & & & & \mathrm{H} & & \\ \mathrm{H} & : & \overset{..}{\underset{..}{\mathrm{O}}} & : & \mathrm{H} & : & \overset{..}{\underset{..}{\mathrm{O}}} & : & \mathrm{H} \\ & & & & & & \mathrm{H} & & \end{array}$$

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[11] See Webb, ref. 6, and Debye "Marx Handbuch der Radiologie," Akademische Verlagsgesellschaft, Leipzig, Germany, **1925**, Vol. 6, p. 618.

[12] Latimer and Rodebush, THIS JOURNAL, **42,** 1419 (1920).

and that the high dielectric is due to the displacement of the hydrogen held between the oxygen by forces which may, as an approximation, be proportional to the displacement over a considerable distance.

On the basis of either picture, a saturation effect is obtained at high field strengths. With the Langevin theory this would correspond to all of the dipoles being lined up. The other view corresponds to the complete break of the water molecule into hydroxyl and hydrogen ions and this is, of course, what actually happens with ions of sufficiently high field strength, *i. e.*, the ion is hydrolyzed.

However, considering the uncertain nature of these theories, we do not feel justified in attempting to calculate a saturation limit for water. Moreover, we are inclined to believe that the electrical polarization can be taken approximately proportional to the field strength to greater values of the latter than has generally been assumed. For this reason we will use Equation 4, which should hold as a rough approximate for the larger ions. For water at 25° this gives

$$P = 375{,}000 \frac{e^2}{r^4} \text{ kg./cm.}^2 \qquad (5)$$

where e is the charge in Faradays (*i. e.*, valence) on the ion and r is expressed in Ångstroms.

Large Positive Ions.—To integrate Equation 3 it is necessary to know the coefficient of expansion of water as a function of pressure. This has been determined by Bridgman[13] up to 1000 atmospheres. In order to avoid the problem of extrapolating his data to enormously higher pressures, we shall first consider the case of the larger ions. Using his average value for the coefficient $\frac{1}{V^0}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)$ as 3.2×10^{-4}, we obtain upon integrating Equation 3, employing also Equation 5

$$\Delta S_{(2)} = -22 \frac{e^2}{r} \text{ cal. per degree per mole} \qquad (6)$$

To evaluate this entropy change for any ion, we must know the radius of the ion cavity in the water solution. To obtain this we will employ the Born expression, Equation 1, and the experimental values for the free energy of solution, although in doing this we realize that the Born expression is not exact, since it does not include changes in thermal energy and the compression of the water, both quantities, however, being comparatively small, less than 10% for large ions.[14] It must be kept in

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[13] Bridgman, *Proc. Am. Acad. Arts Sci.*, **48**, 300 (1913).

[14] See Webb, ref. 6. Bjerrum, ref. 9, has also considered specific effects which he has treated from the standpoint of the free energy of solution of the discharged ion or corresponding rare gas. The Born expression, since it does not consider the thermal energy, is for a sort of hypothetical absolute zero and therefore is both ΔF and ΔH for the process considered.

It should also be noted that the close agreement of the radius of the ion cavity with mind, moreover, that the dielectric constant in this expression is the "effective" value, but since it is the quantity $(1 - 1/D)$ which is involved, the value of the radius is changed but slightly unless the dielectric constant becomes extremely small, a condition which certainly is not the case for the large ions.

To obtain the free energy values, a revision has been made in energy values calculated by Latimer,[7] *i. e.*, the ΔE values have been converted to ΔF. Account has also been taken of the association of sodium and potassium into Na_2 and K_2. The values obtained agree approximately with the calculations of Webb.[6]

The experimental entropies of the ions in terms of the entropy of H^+ as zero are those given by Latimer and Buffington.[1] These relative values have been converted to absolute entropies using Eastman's[15] value for chloride ion in 0.01 M solution, 28.0 at 15°. Estimating $\bar{c}_p$ as -12.0,[16] we obtain for the hypothetical 1 M solution at 25° $S_{Cl^-} = 18.3$.

The entropies have then been calculated for the concentration corresponding to the molal gas volume at 25° and 1 atmosphere, *i. e.*, $^1/_{24.4}$ M, to eliminate any entropy change arising from a change in volume upon solution. Finally, ΔS of solution of the gas ion is obtained by subtracting the entropy of the ion as a monatomic gas as given by the Sackur equation.[17]

The data employed and the results are summarized in Table I.

TABLE I

SUMMARY OF DATA USED IN CALCULATING THE ΔS OF SOLUTION AT 25°. ΔF IN k CAL. AND ΔS IN CAL./DEG.

	ΔF of soln.	Radius in Å.	S of ion, 1 M soln. $S_{H^+} = 0$	Absolute S in 1 M soln.	Absolute S in 1/24.4 M soln.	S of gas ion	$-\Delta S$ of solution	
							Exp.	Eq. 3
Na^+	−100	1.64	15	13	20	35.1	15	13.5
K^+	−81	2.03	22	20	26	36.6	10.6	11
Rb^+	−78	2.10	25	23	29	39.0	10	10.5
Ag^+	−111	1.52	16	14	20.4	39.7	19	14.5
Tl^+	−79	2.06	26.5	24.5	30.5	41.5	11	10.7
Ba^{++}	−307	2.13	4	0	6	40.4	34	40

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the old values of Bragg for the radius of the positive ions in crystals is entirely accidental and that the latter are actually considerably smaller (about 0.7 Å.). See Pauling, THIS JOURNAL, **49,** 765 (1927).

It is, of course, more reasonable to expect that the size of the ion cavity in water would be somewhat greater, and the really important fact remains that the relative size of the positive ions in crystals and in solutions is approximately the same. It may also be that the Born expression gives the radius as the distance from the center of the ion to the center of the water dipole, *i. e.*, the radius of the ion plus the radius of an oxygen ion.

[15] Eastman, THIS JOURNAL, **50,** 292 (1928).

[16] Based on the work of Randall and Rossini, unpublished.

[17] See Lewis, Gibson and Latimer, THIS JOURNAL, **44,** 1008 (1922).

A comparison of the last two columns of Table I shows an excellent agreement between the experimental entropies of solution and those calculated from Equation 3. If these calculations are correct, we must conclude that the entropy of hydration results largely from the change of entropy of the water about the ion due to compression, and that $\Delta S_{(1)}$, the dielectric effect, is small. This may be interpreted as meaning that there is but small entropy change in the orientation of electric dipoles, but a large effect in the loss of thermal energy of the compressed (or tied up) water molecules. This is, of course, just the opposite to the magnitude of these two effects in the free energy of hydration.

The reasons for the failure of Equation 2 are not entirely clear. In addition to the uncertainty regarding the temperature coefficient of the dielectric constant of water under high electric fields, it may also be pointed out that the validity of the equation assumes the constancy with temperature of the radius of the ion cavity. Moreover, it must be kept in mind that the Born expression gives a sort of hypothetical free energy (*cf.* note, ref. 14) which agrees closely with the experimental value only because the magnitude of the entropy factor is small in comparison.

For the large ions Equations 6 and 1 may be combined to give

$$\Delta S = 1.35 \times 10^{-4} \Delta F \text{ cal./deg.} \qquad (7)$$

This is the approximate straight-line relation pointed out by Latimer and Buffington.[1]

Small Ions.—Equation 6, when applied to the smaller ions or to the large ions of higher valence, leads to values which are too high, indicating that at very high pressures the coefficient of expansion of water must be very much smaller. This effect may be noted for Ba^{++} listed in Table I. The theorem proposed by G. N. Lewis[18] that at infinite pressure the entropy of a substance is zero (*i. e.*, the integral $\int_1^\infty \left(\frac{dV}{dT}\right)_P dP$ must be equal to the entropy of water at 25°) might be used to extrapolate the coefficient to high pressures. However, the uncertainty in the shape of the curve appears to render it inadvisable to attempt these calculations at this time.

Large Negative Ions.—The entropies of solution of the negative ions have not been included in Table I because of the uncertainties regarding the electron affinities of these ions. If the values for entropies were of somewhat higher accuracy, the calculation might be reversed and Equation 7 used to calculate ΔF of solution and from this the electron affinities. However, it does seem worth while to show that the electron affinities of chloride, bromide and iodide, as calculated from the crystal lattice energies,[19]

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[18] G. N. Lewis, *Z. physik. Chem.*, 130, 532 (1927).

[19] Or the values of Angerer and Müller from absorption spectra of the alkali halides, which are in approximate agreement. See Franck and Jordan, "Anregung von Quantensprungen durch Stösse," Springer, Berlin, 1926.

lead to calculated entropy values in approximate agreement with the experimental. The data are summarized in Table II. The entropies of chloride, bromide and iodide are also from the paper by Latimer and Buffington, but instead of taking the values in agreement with the halogen acids, these values have been averaged with those obtained from the silver, thallous and lead salts. The resultant change is, however, small.

TABLE II

SUMMARY OF DATA

	$^1/_2\,X_2 = X_{(g)}$ ΔF	$^1/_2\,X_2 + E^-{}_{(g)} = X^-{}_{(aq.)}$ ΔF	Electron affinity	ΔF of soln.	S, 1 M X^- $S_{H^+} = 0$	Absolute S 1/24.4 M X^-	S of $X^-{}_{(g)}$	$-\Delta S$	
								Exp.	Eq. 3
Cl^-	32	−132	86	78	16.5	24.7	36.4	11.7	10.8
Br^-	18	−126	86	58	21.8	30.0	38.8	8.8	8.1
I^-	21	−112	79	54	26.5	34.7	40.2	5.5	7.5

The agreement between the calculated and experimental entropies of solution is probably within the accuracy with which the latter are known and may be considered as substantiating the electron affinities. At the same time, the reasonableness of the result further confirms our theoretical calculation of the entropies of hydration.

These calculations constitute an independent check upon the theory which considers the properties of solutions of strong electrolytes as due to the effect of an electrostatic charge located at the center of a cavity in the dielectric medium. The results seem especially significant in view of the fundamental nature of the ionic entropies and the fact that both the relative and absolute entropies are singularly free from large experimental uncertainties.

Summary

Calculations have been made which indicate that the entropy of hydration of aqueous ions arises largely from the enormous pressures developed about the ion and the resulting decrease in the entropy of the water due to compression.

The entropies of solution of the halide ions are shown to be in agreement with the estimated electron affinities of these elements.

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