THE ENTROPY OF AQUEOUS IONS AND THE NATURE OF THE ENTROPY OF HYDRATION

WENDELL M. LATIMER

Department of Chemistry, University of California, Berkeley, California

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A knowledge of the partial molal entropies of ions in aqueous solutions extends the applications of the third law of thermodynamics to reactions involving electrolytes by means of the equation relating the free energy, ΔF, the reaction heat, ΔH, entropy, ΔS, and the absolute temperature, T:

$$\Delta F = \Delta H - T\Delta S \tag{1}$$

These partial molal entropies are fundamental thermodynamic quantities, and give definite evidence regarding the nature of the forces acting between the ions and the solvent molecules.

The most direct method of obtaining ionic entropies involves a knowledge of the entropy of a salt, and its entropy of solution, the latter quantity being calculated from the free energy and heat of solution by equation 1. The sum of the entropies of the ions in solution is then given as the ΔS of solution plus the entropy of the solid salt. Since it is more convenient to use relative values for the ionic entropies instead of these sums, the entropy of H^+ has been chosen as zero and all values are given in reference to this arbitrary choice. Many examples of this method of obtaining ionic entropies are to be found in table 1. All values are given for the standard state which is chosen, again arbitrarily, as the hypothetical 1 molal solution with the heat content of the ions at infinite dilution.

There are also a good many other reactions involving aqueous ions for which both the heat and free energy are known, as, for example, the solution of potassium in dilute acid and the combination of chlorine and hydrogen to form hydrochloric acid. For some of these, the reaction heats are large and the data are not of great accuracy. However, the best of the available data for these reactions are also summarized in table 1. This table has been taken, unless otherwise noted, from a paper by Latimer, Schutz, and Hicks (6) and this reference should be consulted for the details of these calculations.

The values for the entropies of the substances appearing in table 1 have all been obtained from specific heat measurements, using the third law of

TABLE 1

Summary of entropy calculations

ΔH^0 and ΔF^0 in calories per mole. ΔS^0 in calories per degree per mole. The entropy data for the elements and compounds used in these calculations are summarized in table 2 of ref. 6

REACTION	$\Delta H^0_{298.1}$	$\Delta F^0_{298.1}$	$\Delta S^0_{298.1}$	
				$\bar{S}^0_{Cl^-}$
$\frac{1}{2}H_2+AgCl(s)=H^++Cl^-+Ag(s)$	−9600	−5125	−15.01	13.49
$HCl(g)=H^++Cl^-$	−17880	−8598	−31.14	13.52
$\frac{1}{2}H_2+\frac{1}{2}Cl_2(g)=H^++Cl^-$	−39940	−31373	−28.75	13.52
	−39940	−31367	−28.77	13.50
				$\bar{S}^0_{Ag^+}$
$AgCl(s)=Ag^++Cl^-$	15980	13297	9.0	18.5
	15980	13329	8.9	18.4
$Ag+\frac{1}{2}Cl_2(g)=Ag^++Cl^-$	−14330	−12890	−4.8	18.4
$Ag+H^+=Ag^++\frac{1}{2}H_2$	25540	18448	23.8	18.3
				$\bar{S}^0_{Hg_2^{++}}$
$2Hg(l)+2H^+=Hg_2^{++}+H_2$	40160	36854	11.1	16.5
$Hg_2Cl_2(s)=Hg_2^{++}+2Cl^-$	23740	24446	−2.4	16.2
				$\bar{S}^0_{Br^-}$
$\frac{1}{2}Br_2+\frac{1}{2}H_2=Br^-+H^+$	−28945	−24577	−14.65	19.3
$AgCl(s)+Br^-=AgBr(s)+Cl^-$	−4457	−3461	−3.3	19.4
$AgBr(s)+\frac{1}{2}H_2=Ag(s)+H^++Br^-$	−5135	−1673	−11.6	19.5
				$\bar{S}^0_{I^-}$
$AgI(s)=Ag^++I^-$	26710	21889	16.2	25.4
$\frac{1}{2}H_2+\frac{1}{2}I_2=H^++I^-$	−13660	−12361	−4.3	25.2
$HI(g)=H^++I^-$	−19550	−12676	−23.0	26.5
$Ag(s)+\frac{1}{2}I_2(s)=Ag^++I^-$	11870	6087	19.4	24.9
				$\bar{S}^0_{Tl^+}$
$Tl+H^+=Tl^++\frac{1}{2}H_2$	935	−7760	29.2	28.5
$Tl+\frac{1}{2}Cl_2(g)=Tl^++Cl^-$	−38790	−39105	1.0	29.1
	−38930	−39105	0.6	28.7
$TlCl=Tl^++Cl^-$	10125	5086	16.9	29.2
$Tl+\frac{1}{2}Br_2(l)=Tl^++Br^-$	−27990	−32337	14.5	28.4
$Tl+\frac{1}{2}I_2(l)=Tl^++I^-$	−12720	−20082	24.7	28.0
$TlI=Tl^++I^-$	17530	9938	25.5	28.6
				$\bar{S}^0_{NO_3^-}$
$TlNO_3=Tl^++NO_3^-$	9970	1790	27.4	36.9
				$\bar{S}^0_{Ba^{++}}$
$Ba(NO_3)_2=Ba^{++}+2NO_3^-$	10200	3200	23.5	0.8
				$\bar{S}^0_{OH^-}$
$H_2O=H^++OH^-$	13329	19122	−19.4	−2.5
				$\bar{S}^0_{Ca^{++}}$
$Ca(OH)_2=Ca^{++}+2OH^-$	−3385	6960	−34.7	−11.4
				$\bar{S}^0_{Mg^{++}}$
$Mg(OH)_2=Mg^{++}+2OH^-$	−1180	15410	−55.6	−35.5

TABLE 1—*Continued*

REACTION	$\Delta H^0_{298.1}$	$\Delta F^0_{298.1}$	$\Delta S^0_{298.1}$	
				$\bar{S}^0_{K^+}$
$KCl = K^+ + Cl^-$	4119	−1207	17.9	24.3
$KBr = K^+ + Br^-$	4726(2)	−1546	21.0	24.1
$K + H^+ = K^+ + \frac{1}{2}H_2$	−60340	−67431	23.8	24.7
				$\bar{S}^0_{S^{--}}$
$H_2 + S(s) = 2H^+ + S^=$	10040	23450	−45.0	−6.2
$H_2S(g) = 2H^+ + S^=$	15300	31290	−53.6	−5.4
				$\bar{S}^0_{SO_4^{--}}$
$Ag_2SO_4 = 2Ag^+ + SO_4^=$	4210	6722	−8.4	2.8
$BaSO_4 = Ba^{++} + SO_4^=$	5455	13718	−27.7	3.0
$CaSO_4 \cdot 2H_2O = Ca^{++} + SO_4^= + 2H_2O$	270	6308	−20.2	3.8
				$\bar{S}^0_{Na^+}$
$NaCl = Na^+ + Cl^-$	1019	−2524	11.9	15.7
	1019	−2161	10.7	14.4
$NaBr = Na^+ + Br^-$	−44(2)	−4231	14.0	14.7
$Na + H^+ = Na^+ + \frac{1}{2}H_2$	−57520	−62588	17.0	13.9
				$\bar{S}^0_{Pb^{++}}$
$Pb + 2H^+ = Pb^{++} + H_2$	−600	−5877	17.7	2.1
$Pb + Cl_2(g) = Pb^{++} + 2Cl^-$	−80330	−68567	−39.5	2.4
$PbCl_2 = Pb^{++} + 2Cl^-$	5060	6483	−4.8	2.1
				$\bar{S}^0_{Fe^{++}}$
$Fe + Hg_2Cl_2(s) = Fe^{++} + 2Cl^- + 2Hg(1)$	−37500	−32585	−16.5	−28.0
$Fe + 2TlCl(s) = Fe^{++} + 2Cl^- + 2Tl$	−3170	5455	−28.9	−27.6
$Fe + 2H^+ = Fe^{++} + H_2$	−20800	−20240	−1.9	−26.6
				$\bar{S}^0_{Fe^{+++}}$
$Fe^{++} + H^+ = Fe^{+++} + \frac{1}{2}H_2$	11240	17230	−20.1	−63.1
$Fe^{+++} + Ag = Ag^+ + Fe^{++}$	14300	1218	43.9	−63.0
				$\bar{S}^0_{Al^{+++}}$
$CsAl(SO_4)_2 \cdot 12H_2O = Cs^+ + Al^{+++} + 2SO_4^= + 12H_2O$	13560	12910	2.18	−71.7
				$\bar{S}^0_{Li^+}$
$Li + H^+ = Li^+ + \frac{1}{2}H_2$	−66380	−68248	6.2	−1.8
				$\bar{S}^0_{Rb^+}$
$Rb + H^+ = Rb^+ + \frac{1}{2}H_2$	−61210	−67473	21.0	22.8
				$\bar{S}^0_{Cu^{++}}$
$Cu + 2H^+ = Cu^{++} + H_2$	16640	15912	2.4	−21.0
				$\bar{S}^0_{Cd^{++}}$
$Cd + 2H^+ = Cd^{++} + H_2$	−16510	−18348	6.2	−12.7
				$\bar{S}^0_{Sn^{++}}$
$Sn + 2H^+ = Sn^{++} + H_2$	−2390	−6276	13.0	−5.9
				$\bar{S}^0_{Hg^{++}}$
$Hg + 2H^+ = Hg^{++} + H_2$	41590	39679	6.4	−6.5
				$\bar{S}^0_{Zn^{++}}$
$Zn + 2H^+ = Zn^{++} + H_2$	−36720	−34984	−5.8	−27.2

TABLE 1—*Concluded*

REACTION	$\Delta H^0_{298.1}$	$\Delta F^0_{298.1}$	$\Delta S^0_{298.1}$	
				$\bar{S}^0_{ClO_3^-}$
$KClO_3 = K^+ + ClO_3^-$	10120	1277	29.7	39.3
				$\bar{S}^0_{BrO_3^-}$
$Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O$	15360	7170	26.5	38.7
$KBrO_3 = K^+ + BrO_3^-$	9540	1690	26.3	37.4
				$\bar{S}^0_{IO_3^-}$
$AgIO_3 = Ag^+ + IO_3^-$	13200	10200	10.1	27.7
$KIO_3 = K^+ + IO_3^-$	6340	1770	15.3	26.9
				$\bar{S}^0_{ClO_4^-}$
$KClO_4 = K^+ + ClO_4^-$	12115	2690	31.6	43.1
				$\bar{S}^0_{C_2O_4^{--}}$
$CaC_2O_4 \cdot H_2O = Ca^{++} + C_2O_4^{=} + H_2O$	5090	11790	−22.5	9.3
				$\bar{S}^0_{CO_3^{--}}$
$CaCO_3 + C_2O_4^{=} + H_2O$ $= CaC_2O_4 \cdot H_2O + CO_3^{=}$	−7460	−306	−24.0	−13.1
$C + \frac{3}{2}O_2 + H_2 = 2H^+ + CO_3^{=}$	−161100	−125760	−118.5	−12.5
$CaCO_3 = Ca^{++} + CO_3^{=}$	−2780	10922	−46.0	−12.6
				$\bar{S}^0_{HCO_3^-}$
$CaCO_{3\,calc.} + CO_2 + H_2O = Ca^{++} + 2HCO_3^-$	−8588⁽³⁾	7980(3)	−55.6	23.0
$CaCO_{3\,arag.} + CO_2 + H_2O = Ca^{++} + 2HCO_3^-$	−8550(3)	7788(3)	−54.8	22.8
				$\bar{S}^0_{Sr^{++}}$
$SrCO_3 + CO_2 + H_2O = Sr^{++} + 2HCO_3^-$	−6740(3)	9052(3)	−53.0	−7.8

thermodynamics, and it is obvious from the consistency of the data that this method may be applied to salts of non-magnetic ions and their aqueous solutions without serious danger of errors due to zero point entropy or transitions at very low temperatures. It should also be noted that the checks obtained are, for almost every ion, more numerous than the cases listed under that ion. For example, if we use our values for iodide, iodate, ferrous, ferric, and sulfate ions, we can then calculate by five additional methods the entropy of silver ion. The maximum deviation from the mean (which includes also the error in the negative ion) is 0.8 E.U. A summary of values for all the ions which have been determined is given in table 2.

One of the most useful applications of the ionic entropies to thermodynamic problems is the calculation of oxidation–reduction potentials for those elements which are either so highly electropositive or highly electronegative that direct equilibrium measurements are impossible in water solutions. A summary of the calculations for a number of such elements is given in table 3, together with similar calculations for a few examples in which direct comparison may be made with the experimental values.

The agreement in the first three cases indicates the reliance which may be placed in the calculations, but unfortunately the entropy values which have been used to calculate the ΔS terms and also the reaction heats for many of the other reactions are not known with sufficient accuracy to place the same confidence in all of the last six examples. However, these values are certainly to be preferred to any of the attempts to measure these equilibria directly.

TABLE 2

Entropies of aqueous ions at 298.1°

Values are given in calories per degree per mole

IONS	ENTROPIES	IONS	ENTROPIES
Li^+	1.8	Fe^{++}	−27.4±0.7
Na^+	14.7±1.0	Fe^{+++}	−63.0
K^+	24.6±0.5	Al^{+++}	−71.7
Rb^+	22.8	F^-	−5.0
Tl^+	28.6±0.3	Cl^-	13.5±0.1
Hg_2^{++}	16.4±0.5	Br^-	19.4±0.4
Ag^+	18.4±0.2	I^-	25.7±0.7
Mg^{++}	−35.5	NO_3^-	36.9
		ClO_4^-	43.1
Ca^{++}	−11.4	ClO_3^-	39.3
Ba^{++}	0.8	BrO_3^-	37.7±1.0
Cu^{++}	−21.0	IO_3^-	27.1±1.0
Zn^{++}	−27.2	OH^-	−2.5
Cd^{++}	−12.7	CO_3^{--}	−12.7±0.5
Sn^{++}	−5.9	SO_4^{--}	3.5±0.5
Hg^{++}	−6.5	$C_2O_4^{--}$	9.3
Pb^{++}	2.2±0.2	S^{--}	−5.8±1.0
Sn^{++}	−7.8	HCO_3^-	−22.9

TABLE 3

Calculation of oxidation–reduction potentials

REACTION	$\Delta H^0_{298.1}$	$\Delta S^0_{298.1}$	$\Delta F^0_{298.1}$	E^0 CALCD.	E^0 EXPTL.
$Ag + H^+ = Ag^+ + \frac{1}{2}H_2$	25540	24.0	18390	−0.798	−0.799
$Pb + 2H^+ = Pb^{++} + H_2$	−600	17.8	−5910	−0.127	−0.128
$\frac{1}{2}I_2 + \frac{1}{2}H_2 = H^+ + I^-$	−13660	−3.9	−12480	−0.536	−0.539
$Mg + 2H^+ = Mg^{++} + H_2$	−110200	−12.1	−106600	+2.31	
$Ca + 2H^+ = Ca^{++} + H_2$	−129800	+8.8	−132400	+2.86	
$Sr + 2H^+ = Sr^{++} + H_2$	−130200	+11.4	−133600	+2.90	
$Ba + 2H^+ = Ba^{++} + H_2$	−128600	+19.6	−134500	+2.91	
$Al + 3H^+ = Al^{+++} + \frac{3}{2}H_2$	−127000	−31.7	−117500	+1.70	
$Cl^- + \frac{1}{2}F_2 = F^- + \frac{1}{2}Cl_2$	−39900	−16.0	−35100	−1.52	

The measurement of the free energy of solution, i.e., to form the hypothetical 1 molal solution, of very slightly soluble salts or of very highly soluble salts is often a problem of unusual difficulty. A knowledge of the ionic entropies and the entropy of the salts permits the accurate calculation of this free energy from the heat of solution, and, conversely, if the solubility of a salt is known, the heat of solution may be calculated by equation 1. If both the heat of solution and molal solubility are determined experimentally, one may calculate this activity coefficient of the salt in solution, but not many of the heats of solution and entropy values are of sufficient accuracy to justify this procedure at present.

It was pointed out by Latimer and Buffington (4) in their initial paper upon ionic entropies, that the so-called entropy of hydration is a function of the size and charge of the ion.

$$\Delta S_{\text{hydration}} = f\left(\frac{e^2}{r}\right) \tag{2}$$

The hydration entropy is defined as the difference between the partial molal entropy of the ion in solution and the entropy of the ion as a gas which, provided it is all translational entropy, may be calculated by the Sackur equation.

$$S_{298.1} = \frac{3}{2} R \ln M + 26.03 \tag{3}$$

where M is the molecular weight and the constant is for the gas at 1 atmosphere and 298.1°A.

In figure 1 these hydration entropies have been plotted against the ionic radii as given by Pauling (7). The values fall fairly well upon straight lines, showing that specific hydration effects are small in comparison to the electrostatic action of the charge upon the water dipoles. The values for the entropies of the ions in solution are not absolute but are relative to hydrogen equal to zero, so it is not to be expected that the lines for the monovalent positive and negative ions should coincide; however, if the hydration entropies are the same function of the radii, the lines should be parallel. Now theoretical considerations suggest that the effective radius of an ion in solution is the distance from the center of the ion to the center of the water dipole. Since the negative ions have the hydrogens of the water directed in and the positive ions have the hydrogen directed out, the effective radii of the negative ions will be but slightly greater than the crystal radius, while those for the positive ions will be considerably larger. If we choose this increase in the positive ion radii as 0.7 A.U., the curve for the positive ions in figure 1 is shifted to the position of the dotted line, and is approximately parallel to that of the negative ions. The difference between the two lines should now be due to the difference in the relative and absolute entropies of the aqueous ions, and is in fact in close agreement with the recent determination of the absolute partial molal entropy of chloride ion by Eastman and Young (8), who obtain as a provisional value 18.1 ± 0.5 E.U. in comparison to our value relative to $H^+ = 0$ of 13.5 E.U. The difference 4.6 E.U. should then be added, in the case of the monovalent negative ions, and subtracted for the monovalent positive ions, in order to convert the relative entropies to absolute entropies, i.e., the two curves in figure 1 should differ by 9.2 E.U. The agreement is shown in figure 2 in which the absolute entropies of hydration have been plotted against the reciprocal of the effective radii as defined above.

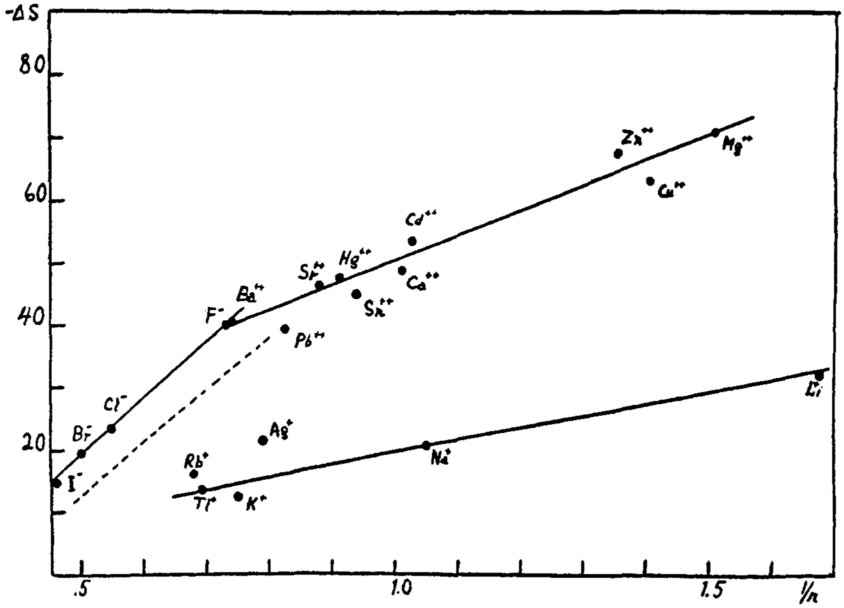

FIG. 1. Relative entropy of hydration against reciprocal ionic radius

Latimer and Kasper (5) were able to show that the entropy of hydration of the larger monovalent ions could be accounted for entirely as the decrease in entropy of the water due to the pressure set up in the polarizable medium by the charge on the ion. The change in entropy with pressure is given by the expression

$$dS = -\left(\frac{dV}{dT}\right)_P dP \qquad (4)$$

For a differential unit of volume the entropy change is obtained by integrating this expression with respect to the pressure and the total entropy change about the ion is then obtained by integrating over the total volume of the water outside the ion cavity.

$$\Delta S = -\int_r^\alpha \int_1^P \frac{1}{V^0}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_P \mathrm{d}P\, 4\pi r^2 \mathrm{d}r \tag{5}$$

For the pressure they used the expression

$$P = \frac{(3 + 2D)(D - 1)}{40D^2}\,\frac{e^2}{r^4} = 375{,}000\,\frac{e^2}{r^4}\text{ kg. per cm.}^2 \tag{6}$$

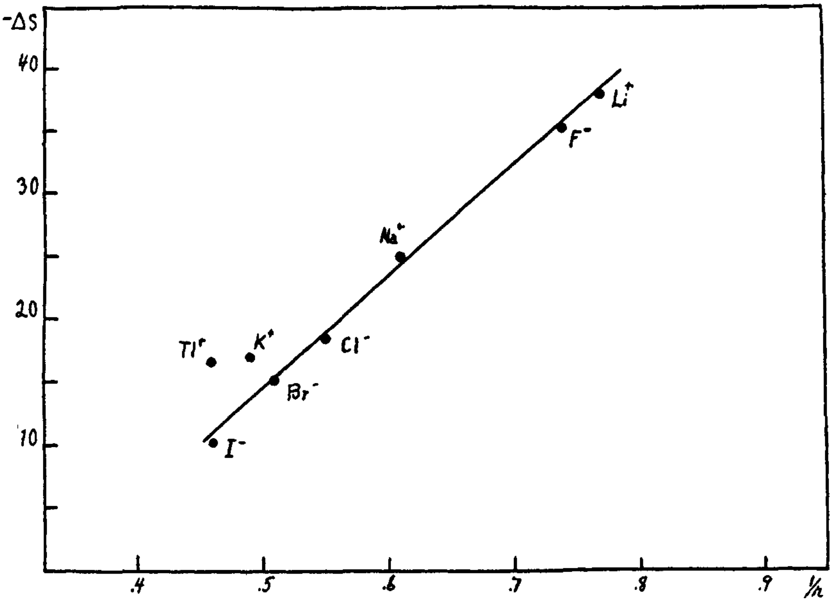

FIG. 2. Absolute entropy of hydration against effective ionic radius

where e is the charge in faradays, r is expressed in Ångström units, and the constant is for water at 25°C. The deviation of the actual pressure at very high values from that given by the expression is a matter of some conjecture, but they believe its use is justified for a rough approximation for the larger ions. Using Bridgman's (1) value of the coefficient $\frac{1}{V^0}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)$ as 3.2×10^{-4}, the integration of equation 5 becomes

$$\Delta S = -22\,\frac{e^2}{r}\text{ cal. per degree per mole} \tag{7}$$

where the constant is for the reaction involving no change of entropy with volume, i.e., for 1 mole of ions in 24.4 liters of solution at 25°C. A test of equation 7 with a number of ions is given as table 4.

The agreement is not very good in several of these examples and is still worse for the smaller ions, as might be expected from an assumption regarding the electrical pressure. However, when we recall that the calculation involves only two experimental constants for water and our previously chosen effective radii, it does give considerable justification for our picture of the entropy of hydration as due to the compression of the water about the ions by the electrostatic field. The determination of ionic entropies in other solvents would help to solve many of these problems and would give a much more complete understanding of ionic solvation. However at present the solubilities, activity coefficients, and heats of solution of salts in non-aqueous solvents are too meager to permit the calculation for even a single case.

TABLE 4

A test of equation 7

ION	S_{gas}	$\bar{S}_{1M}$	$\bar{S}_{absolute}$ 1/24.4 molal	EFFECTIVE RADIUS	ΔS	
					Exptl.	Equation 7
Na^+	35.4	10.1	16.5	1.65	18.9	13.3
K^+	37.0	20.0	26.4	2.03	10.6	11.0
Br^-	39.0	24.0	30.4	1.95	8.6	11.3
Cl^-	36.7	18.1	24.5	1.81	12.2	12.1
I^-	40.5	30.3	37.0	2.16	3.8	10.2
Ba^{++}	40.7	−8.4	−2.0	2.05	42.7	43.0

There are still a fairly large number of aqueous ions for which we have not obtained entropy values. Some of these, as for example phosphate and chromic ions, are difficult to determine, because hydrolysis corrections are large and heats of hydrolysis are not accurately known. In other cases, such as the rare earths, heats of solution and activity coefficients must be obtained. The paramagnetic ions are difficult, since it is necessary to to carry the specific heats measurements to much lower temperatures in order to avoid errors which may arise from low temperature transitions and errors in extrapolation. For example, we have a complete specific heat curve for ferrous oxalate from 298° to 14°A., but at the latter temperature the curve is still far from obeying the T^3 law. However we believe that most of these experimental problems will be solved in the next few years, and that many new ions will be added to our table of ionic entropies.

REFERENCES

(1) Bridgman: Proc. Am. Acad. Arts Sci. **48**, 300 (1913).
(2) Hammerschmidt and Robinson: J. Am. Chem. Soc. **54**, 3120 (1932).
(3) International Critical Tables, Vol. V. McGraw-Hill Book Co., New York (1929).
(4) Latimer and Buffington: J. Am. Chem. Soc. **48**, 2297 (1926).
(5) Latimer and Kasper: J. Am. Chem. Soc. **51**, 2293 (1929).
(6) Latimer, Schutz, and Hicks: J. Chem. Physics **2**, 82 (1934).
(7) Pauling: J. Am. Chem. Soc. **49**, 765 (1927).
(8) Young, M. B.: Thesis, University of California, 1935.

DISCUSSION

Dr. Onsager suggested that the entropy of an ion could be computed theoretically as the temperature coefficient of the work required for charging.

Dr. Latimer answered that the entropy deficiency expected on this basis would amount to about one-third of the observed effect.

Dr. Onsager emphasized the importance of this disagreement. Any satisfactory theory of ionic entropies must take into account the anomalous dielectric properties of the solvent in the neighborhood of an ion.