Summary

The (hydrated) tervalent titanium ion is colorless, but it has a strong latent color, on account of which titanium trichloride is colored.

CAMBRIDGE A, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ENTROPY OF AQUEOUS IONS

BY WENDELL M. LATIMER AND RALPH M. BUFFINGTON

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A knowledge of the values of the entropies of aqueous ions would place at our command a powerful tool for the direct solution of a large number of thermodynamical problems, many of which otherwise are open only to the most roundabout methods of attack. The treatment of these fundamental entropies has long been deferred by workers in the field of thermodynamics, in part because of the large discrepancies existing in the experimental reaction heats that are involved in their calculation, and in part because of the general lack of information in regard to the entropies of compounds. It would seem, however, that a profitable start may now be made, using as a guide the approximate proportionality pointed out by Latimer[1] between the entropy of solution and the heat of solution of gaseous ions. It is the purpose of this paper to investigate this relation and to give from a survey of existing data a table of values for the entropies of the more important ions. A few typical examples will be given to illustrate the tremendous value of such a table of entropies in the simplification of the thermodynamics of solutions.

As a standard state for comparison we will adopt the hypothetical one molal solution, and define it as a one molal solution of the ions obeying the laws of the perfect dilute solution and the ions possessing the same partial molal heat content that they have at infinite dilution.

In our initial calculations we have no means of obtaining absolute values for the entropies of the individual ions, but must calculate the values as the sum of the entropies of equivalent weights of two ions of unlike charge, or the difference in the entropies of equivalent weights of two ions of like charge.

The sum of the entropies of two ions is most accurately determined from a knowledge of the entropy of a compound and the entropy change for the reaction; compound equals ions in hypothetical one molal aqueous solution. For example, the sum of the entropies of H^+ and Cl^- is equal to the entropy of hydrogen chloride plus the entropy of solution of hydrogen chloride. This latter quantity is obtained from the relation $\Delta S = (\Delta H - \Delta F)T$, where ΔH is the heat of solution of hydrogen chloride in an infinitely dilute

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[1] Latimer, THIS JOURNAL, **48**, 1234 (1926).

solution, ΔF is the free energy of solution at a concentration of hypothetical one molal hydrogen and chloride ions, and T is the absolute temperature. The data and results of a large number of such calculations have been summarized in Table I.

The sum of the entropies of two ions may also be obtained from the value for the entropy of formation of the ions at hypothetical one molal concentration from their elements, together with the values for the entropies of the elements. In general, the heats of these reactions are large, and are not known with great accuracy. As a consequence the method is not so reliable as the first outlined, and has been employed only in cases where no other data exist, or where the data seemed unusually good. The results are given in Table II.

The difference of the entropies of two ions may be obtained from many types of replacement reactions. Thus the entropy change in the reaction $Na + H^+ = Na^+ + {}^1/_2H_2$, is again equal to $(\Delta H - \Delta F)/T$, where ΔH is the heat of solution of sodium in a dilute solution of hydrogen ion, and ΔF in calories is 23,074 times the difference in the normal electropotential of sodium and hydrogen. This value of ΔS plus the difference in entropy between half a mole of hydrogen gas and sodium metal then gives the difference between sodium and hydrogen ions. The data and results for

TABLE I

THE SUM OF THE ENTROPIES OF PAIRS OF IONS FROM THE ENTROPY OF THEIR COMPOUND AND THE ENTROPY OF SOLUTION AT 25°

	Entropy of subs.	ΔH of soln.	$\Delta F°$ of soln.	$\Delta S°$ of soln.	Sum of entropies of ions
HCl	+44.5	−17.3	− 8.7	−28.9	+15.6
HBr	47.0	−19.9	−12.0	−26.4	20.6
HI	49.0	−19.2	−12.7	−21.9	27.1
$NaCl$	18.5	+ 1.0	− 2.2	+10.6	29.1
KCl	19.7	4.4	− 0.9	18.0	37.7
$AgCl$	24.0	16.0	+13.3	9.0	33.0
$AgBr$	25.0	20.1	16.6	11.8	36.8
AgI	26.8	26.4	21.8	15.6	42.4
$TlCl$	24.6	10.1	5.0	17.2	41.8
$TlBr$	27.0	13.7	7.4	21.2	48.2
TlI	28.5	17.3	9.9	24.7	53.2
$PbCl_2$	34.4	6.8	7.0	− 0.7	33.7
$PbBr_2$	39.7	10.0	7.7	7.7	47.4
PbI_2	41.3	15.9	11.6	14.3	55.5
MgF_2	15.7	− 2.8	10.7	−45.0	−29.3
CaF_2	17.2	+ 2.7	13.9	−37.3	−20.1
PbF_2	22.0	+ 2.2	10.1	−26.3	− 4.3
Tl_2SO_4	52.5	8.3	5.2	+10.3	+67.8
Ag_2SO_4	49.7	4.5	7.3	− 9.3	40.4
$BaSO_4$	38.0	5.6	13.1	−25.0	13.0
$CaCO_3$	22.0	− 2.0	11.0	−43.3	−23.3
H_2O	16.8	+13.4	19.1	−19.0	− 2.2

this and similar calculations are given in Table III. In all of these tables, free energies and heats are given in kilogram calories, and entropies in small calories per degree.

TABLE II

THE SUM OF THE ENTROPIES OF PAIRS OF IONS CALCULATED FROM THE ENTROPY OF FORMATION FROM THEIR ELEMENTS AT 25°

	ΔH	ΔF	ΔS	S_{elements}		$S_{M^{n+}} + nS_{X^-}$
$Cu + Cl_2$	− 62.6	−46.9	− 52	8	51	7
$Cu + Br_2$	− 40.6	−33.2	− 25	8	36	19
$Fe + 3/2Cl_2$	−127.7	−96.8	−104	7	76	−21
$Fe + 3/2Br_2$	− 95.5	−76.0	− 65	7	55	− 3
$Tl + 3/2Br_2$	− 56.4	−27.3	− 98	18	55	−25

TABLE III

ENTROPY CHANGES IN THE REPLACEMENT OF H^+ BY OTHER IONS AT 25°

Ion	ΔH of reaction	ΔF of reaction	ΔS of reaction	S of element	$S_{M^{n+}} - nS_{H^+}$
Li	−66.0	−68.3	7.7	7.6	0.5
Na	−56.8	−62.6	19.3	12.3	16.8
K	−61.5	−67.4	19.9	16.6	21.8
Rb	−60.8	−67.5	22.4	17.4	25.1
Cu	−129.0	−131.9	9.7	10.6	− 9.1
Zn	−36.3	−35.0	− 4.3	9.8	−23.9
Cd	−17.1	−18.3	4.0	11.8	−13.6
Fe	−20.7	−20.3	− 0.1	7.7	−21.8
Sn	− 4.5	− 6.3	6.0	11.2	−12.2

The space allowed does not permit a detailed discussion of the very large number of sources of data utilized in these calculations. A critical study has been made of many of the original articles. The general references used are Landolt-Börnstein, "Tabellen;" Thomsen, "Thermochemistry;"[2] Lewis and Randall, "Thermodynamics."[3] Special reference should be made to Richards[4] and co-workers' careful work upon the heats of solution of metals in hydrochloric acid. We are indebted to Mr. T. F. McCormick of this Laboratory for experimental data enabling us to correct Richards' values to infinite dilution. Latimer's[5] expression for the entropy of solids has been used in estimating the entropies of certain of the salts. The entropies of hydrogen chloride, hydrogen bromide, hydrogen iodide and chlorine have been taken in general agreement with the Tetrode[6] equation. The value of Latimer and Hoenshel[7] for the

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[2] Thomsen, "Thermochemistry," Longmans, Green and Co., New York, **1908**.

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**.

[4] (a) Richards and Burgess, THIS JOURNAL, **32,** 431 (1910). (b) Richards and Tamaru, *ibid.*, **44,** 1060 (1922).

[5] Latimer, *ibid.*, **43,** 818 (1921).

[6] Tetrode, *Ann. Physik,* **33,** 434 (1912).

[7] Latimer and Hoenshel, THIS JOURNAL, **48,** 19 (1926).

entropy of liquid bromine has been used. Reference should also be made to the "Summary of Electrode Potentials," by Gerke.[8]

Calculation of Relative Ionic Entropies

We may now proceed to use the results of Tables I, II and III to obtain a set of very useful values, namely, the relative entropies of the ions. In so far as the use of the ionic entropies is confined to chemical reactions the absolute values are entirely unnecessary, just as the absolute electrode potentials are quite unnecessary in calculating free energies of reaction. In agreement with the usage of choosing the ionic free energy of hydrogen ion equal to zero in the standard state, we will also take the entropy of hydrogen ion in hypothetical one molal solution equal to zero. The first column of Table IV gives the values of the aqueous entropies in terms of $S_{\mathrm{H}^+} = 0$. The second column gives the corresponding values for the ions as monatomic gases calculated from the Sackur equation.[9] Now differences in the entropies of the ions as gases are due entirely to differences in mass and, moreover, it is obvious from the fact that the Trouton constant is independent of mass, that the mass function must be the same

Table IV

Relative Entropies of Aqueous Ions at 25° and a Comparison of ΔS and ΔE of Solution of Gaseous Ions

	$S_{\mathrm{H}^+} = 0$	S of gas ion	ΔS of solution of gas ion	ΔE of solution of gas ion
Li^+	0.5	31.5	31	119
Ag^+	17.4, 16.2, 15.3	39.7	24	107
Na^+	13.5, 16.8	35.1	20	96
Tl^+	26.2, 27.6, 26.1	41.6	15	78
K^+	22.1, 21.8	36.6	15	77
Rb^+	25.1	39.0	14	72
F^-	−6.0, −4.0	34.5	39	250
Cl^-	15.6	36.4	21	161
Br^-	20.6	38.8	19	140
I^-	27.1	40.1	13	122
Zn^{++}	−23.9	38.3	62	494
Cu^{++}	−24.2, −22.2	38.2	61	475
Fe^{++}	−21.8	37.7	59	465
Sn^{++}	−12.2	39.9	52	465
Mg^{++}	−19.0	35.2	54	450
Cd^{++}	−13.6	39.8	53	440
Ca^{++}	−9.0	36.7	46	379
Pb^{++}	2.4, 6.2, 1.3	41.7	39	345
Ba^{++}	4.0	40.4	36	290
Fe^{+++}	−68, −65	37.7	105	1010
Tl^{+++}	−87	41.6	128	700

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[8] Gerke, *Chem. Rev.*, **1**, 377 (1925).

[9] Lewis, Gibson and Latimer, This Journal, **44**, 1008 (1922).

for both liquids and gases. It therefore follows that the entropy of solution of the gaseous ions should be independent of any mass effect and depend only upon the force of attraction between the ions and the water molecules. We should then expect to find a proportionality between the entropy of solution and the energy of solution of the gaseous ions. A comparison of these two values is given in Cols. 3 and 4. The values for the energy of solution are those calculated by Latimer.[1]

A survey of Table IV shows the remarkable parallelism that exists between the entropy of solution and energy of solution, and since it has been shown by the senior author that the energy of solution depends almost entirely upon the size and charge of the ion, we may state that *the entropy of solution of the gaseous ions is also to a high degree a function solely of the size and charge of the ion.* The parallelism is so close that we feel confident that if we had the absolute values for the entropies of the aqueous ions a general relation would be obtained covering all the different ion types. We might now proceed to estimate the absolute values of the ions by choosing a value that would make ΔS and ΔE proportional for both the positive and negative univalent ions. This was done by Latimer[1] in order to obtain roughly the absolute values for the entropies of the electrode reactions. However, since we have no check at present upon the ΔE values for the negative ions it seems more desirable for the purpose of this paper to keep the ΔS in terms of $S_{\mathrm{H}^+} = 0$ and consider the different types of ions separately.

In Figs. 1 and 2 we have plotted the ΔS of solution against the reciprocal of the atomic radii in Ångström units as given by Bragg and Bragg.[10] These curves may be used to estimate the entropy of solution of any uni- or bivalent positive ion whose atomic radius is known, and hence by means of the Sackur equation to obtain the entropy of the aqueous ion; thus, $S_{\text{aq. ion, 298°K.}} = 3/2R\ ln$ at. wt. $+ 25.7 - \Delta S_{\text{solution}}$, where ΔS has the value from Curves I and II, $\Delta S_{M^+} = -12.6 + 58.6(1/r)$ and $\Delta S_{M^{++}} = -9.5 + 94.5(1/r)$.

Hydrogen ion, $\Delta S = 26$ and $\Delta E = 240$, is not in good agreement with the other univalent ions, the value for the entropy of hydrogen ion being proportionally too high. The experimental data used in calculating the entropy of lithium ion are not very reliable, and this value may be several units too low. If more weight were given to hydrogen ion and less to lithium ion the slope of the curve for the univalent ions would be more nearly half that of the bivalent ions, although it is not obvious from a theoretical standpoint what this ratio should be. Of the two values for the tervalent positive ions, that for ferric should be more reliable than the one for thallic, since we obtain a good check between the reactions with iron and both chlorine and bromine carried out by different observers.

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[10] Bragg and Bragg, "X-Rays and Crystal Structure," Bell and Sons, London, 1924.

However, we do not feel warranted in drawing any definite conclusions in regard to the tervalent ions, especially since we have very little information regarding the size of ferric and thallic ions in their compounds. The dependence of the entropy on the ionic radius, as shown by Curves 1 and 2, is in general so remarkable that much added weight is given to the belief that in dilute solutions specific hydration effects do not exist, and that the chemical properties of these solutions are those simply of a charged sphere of a given size in a medium of a certain dielectric constant.

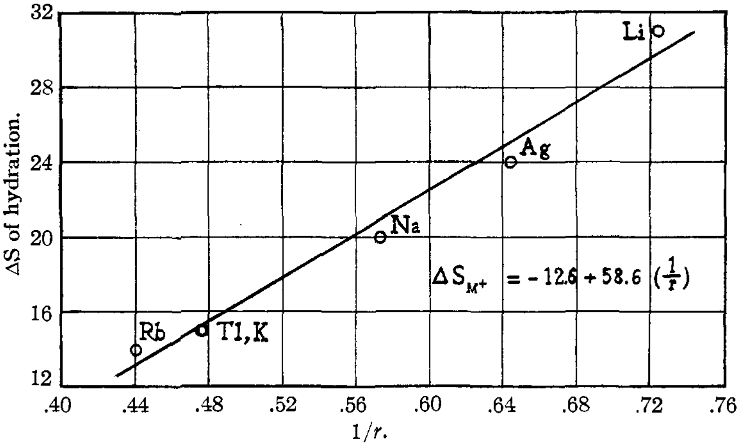

Fig. 1.—Entropy of hydration of univalent gas ions.

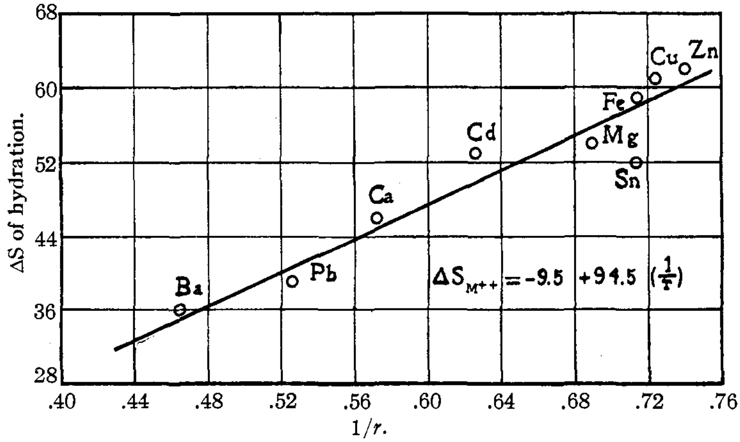

Fig. 2.—Entropy of hydration of bivalent gas ions.

Entropy of Sulfate, Carbonate and Hydroxide Ions

From the data contained in Table I, together with the values for the relative entropies given in Table IV, we may calculate the values referred to hydrogen for sulfate, carbonate and hydroxide ions. Thus for $S_{SO_4^{--}}$ we find 10 entropy units from the data on thallous sulfate and 9 from silver sulfate. This value we have used to obtain the entropy of barium from barium sulfate. From the sum of the carbonate and calcium ions equal to —23, we find for the carbonate ion —14, and from the data on the dissociation of water the entropy of hydroxide ion is —2.

The Use of Ionic Entropies in Thermodynamical Calculations

A large number of thermodynamical calculations using the values of the ionic entropies at once suggest themselves, and a few will be given as typical examples.

The Potential of the Normal Magnesium Electrode.—Richards[11] gives for the heat of solution of "a mole of magnesium in dilute hydrochloric acid, and 200 moles of water at 20°," 110.2 kg. cal. This value probably does not differ from the heat of solution at 25° in infinitely dilute hydrochloric acid by more than 0.2 kg. cal. For the ΔS of the reaction we find 2.1, using for the entropies of the substances: magnesium, 8.3; hydrogen ion, 0; magnesium ion, —19; hydrogen, 29.4. ΔF is then —110.8 kg. cal., and the hypothetical normal electrode potential, —2.40 volts referred to hydrogen. This value is in approximate agreement with that calculated from thermal data on the fluoride and carbonate. Here we have a case where Thomsen's rule is very nearly true, but only, of course, through the merest chance of the entropies of the products being equal to those of the initial substances.

The Heat of Solution of Cuprous Chloride.—We find no value in the literature for the heat of solution of cuprous chloride. This may be calculated, however, using for the entropies: cuprous chloride, 21.1; cuprous ion, 8; chloride ion, 15.5, and for the solubility product 1×10^{-6}. These give ΔS 2.4, ΔF 8.2 and ΔH of solution 8.9 kg. cal. The value for the entropy of cuprous ion was calculated using 1.38 as the radius of the ion.

The Entropy of Solid Magnesium Hydroxide.—As the values for the entropies of the ions become established with greater accuracy, we may reverse the calculations of Table I and calculate the entropies of compounds with considerable assurance, thus avoiding the difficulties of the determinations of heat capacities at very low temperatures. Very little is known regarding the entropy of solid hydroxides, but we can calculate values that appear very reasonable. Thus for magnesium hydroxide we find ΔH of solution equal to zero from Thomsen and ΔF equal to 14.6, using the solubility product 2×10^{-11}. ΔS then is 49.0, and using S_{OH^-} —2 and $S_{Mg^{++}}$ —19, we find S_{298} for magnesium hydroxide to be 26.0 cal. per degree per mole.

The Free Energy of Solution of Zinc Chloride.—One of the most difficult experimental problems is the determination of the free energy change for a very soluble salt going from the solid to hypothetical one molal solu-

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[11] Richards, THIS JOURNAL, **32,** 431, 1176 (1910).

tion. In many cases it is possible neither to set up a cell capable of giving the free-energy change nor to use the Duhem equation applied to the lowering of the freezing point of the solution, because of the inability to obtain equilibrium between the anhydrous salt and solution. However, a knowledge of the entropy of the ions and the heat of solution of the salt at a low concentration permits an immediate calculation of the free-energy change. Thus for zinc chloride, using the values of the entropies zinc chloride, 31; chloride ion, 15.5^-, zinc ion, —24, we find ΔS to be —24. ΔH is —15.6 kg. cal., so that ΔF of solution at a hypothetical one molal concentration is —22.8 kg. cal.

Reliability of Values for the Ionic Entropies

Attention should be called to the large number of checks that we have obtained upon the values given in Table IV. Thus we have calculated the entropies of sodium and potassium ions both from the solution of the metals in acid and from the solution of their chlorides in water. The former involves the heats of the reactions and the potentials of the sodium and potassium electrodes. The latter involves the determination of the activity of the water from freezing-point lowerings and the use of the Duhem equation for obtaining the activities of the salts, together with data for heats of dilution and partial molal specific heats of the solution. In these cases the agreement that we find between two such different methods, of approach and involving data of great experimental difficulties argues well for the reliability of the values obtained for other ions under far more favorable experimental conditions. The data for chloride, bromide and iodide from the corresponding halogen acids seem especially good. Checks are also obtained upon these values through the concordant results secured when those values are used to calculate the entropies of silver and thallous ions from data on their halides. In general, the values obtained by the method in Table I should be more reliable than those by the other methods, as the heats of the reaction are as a rule very much less. When possible, the calorimetric heats of solution of the sparingly soluble salts have been checked against those calculated from the change in solubility with temperature. Of the values obtained from Table III, the entropies of zinc, cadmium and ferrous ions should be the most accurate, as they are obtained from the heats of solution of the metals in acid by Richards, and well established electrode potentials. We believe that the majority of the values are correct to within two entropy units, that is, approximately 600 cal. or 0.026 volt equivalents at 298°K. This belief seems to be substantiated by the curves of Figs. 1 and 2.

Summary

We have collected in Table V the values that we obtain for the relative entropies of the ions referred to hydrogen at hypothetical one molal con-

TABLE V

IONIC ENTROPIES REFERRED TO $H^+ = 0$ AT HYPOTHETICAL ONE MOLAL CONCENTRATION AND 298°K.

	$S_{1\ M,\ 298°}$		$S_{1\ M,\ 298°}$		$S_{1\ M,\ 298°}$
Li^+	1	Fe^{+++}	−67	I^-	27
F^-	− 5	Cu^{++}	−23	Ba^{++}	4
Na^+	15	Zn^{++}	−24	Tl^+	26.5
Mg^{++}	−19	Br^-	20.5	Tl^{+++}	−87
Cl^-	15.5	Rb^+	25	Pb^{++}	2
K^+	22	Ag^+	16	OH^-	−2
Ca^{++}	− 9	Cd^{++}	−14	CO_3^{--}	−14
Fe^{++}	−22	Sn^{++}	−12	SO_4^{--}	9

centration and 298°K. To these might be added many more estimated from the relation found between the entropy of solution and the ionic radii.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MEASUREMENT OF COEFFICIENTS OF EXPANSION AT LOW TEMPERATURES

SOME THERMODYNAMIC APPLICATIONS OF EXPANSION DATA

BY RALPH M. BUFFINGTON[1] AND WENDELL M. LATIMER

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This research was undertaken with the purpose of obtaining data on coefficients of thermal expansion of solids at low temperatures which are required for testing theories of the solid state. The mathematical development of such theories involves certain differential coefficients, for example, the various elastic moduli, the specific heat and the coefficient of expansion. The functional relations of these quantities are, therefore, important topics for experimental investigation. While most of the important coefficients have been studied at ordinary temperatures, the experimental difficulties have practically limited quantitative work at low temperatures to measurements of specific heats and of coefficients of expansion, and of a few other properties, such as electrical conductivity, whose relations to the main problem are still obscure.

We have three important principles that indicate the method of attack: the third law of thermodynamics,[2] the quantum theory of specific heats[3] and the approximate constancy of the ratio of the specific heat of a substance to its coefficient of expansion which was discovered by Grüneisen.[4]

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[1] National Research Fellow while a part of this work was done.

[2] Lewis and Gibson, THIS JOURNAL, **42,** 1542 (1920).

[3] (a) Einstein, *Ann. Physik,* [4] **22,** 180 (1907). (b) Debye, *ibid.,* [4] **39,** 789 (1912). (c) Born and Kármán, *Physik. Z.,* **13,** 297 (1913); **14,** 15 (1913).

[4] Grüneisen, *Ann. Physik,* [4] **26,** 211 (1908).