4.45, 5.25, 4.00 and 3.90 cal. with an average of 4.4 ± 0.4 cal. The heat absorbed in the dilution of 10 ml. of 0.5 molal lead nitrate solution with 875 ml. of water was also measured, with the results: 8.40, 8.30, 9.45, and 9.00 cal., average 8.8 ± 0.4 cal. Combining this value with the data of Plake,[3] the heat absorbed in the dilution to zero concentration of the lead nitrate solution was found to be 9.3 cal. With the aid of the Debye–Hückel theory, the increase in heat content with dilution was estimated to be 0.8 cal. greater for the final solution than for the initial phosphate solution. Combining these quantities, one finds $\Delta H^0 = -2460 \pm 360$ cal. for the above equation.

(3) Plake, *Z. physik. Chem.*, **A162**, 257 (1932).

Making use of the heats of ionization of phosphoric acid recently published by the writer,[1] one obtains also the following results

$$Pb_3(PO_4)_2 + 2H^+ = 3Pb^{++} + 2HPO_4^{--}; \quad \Delta H^0 = 860 \pm 400 \text{ cal.}$$

$$Pb_3(PO_4)_2 = 3Pb^{++} + 2PO_4^{---}; \quad \Delta H^0 = 7860 \pm 1000 \text{ cal.}$$

All values given are for 25°.

Summary

Values have been obtained for the heats of solution at infinite dilution and 25° of the following substances: $CsClO_4$, $\Delta H^0 = 13{,}260 \pm 100$ cal.; $RbClO_4$, $\Delta H^0 = 13{,}570 \pm 60$ cal.; $RbClO_3$, $\Delta H^0 = 11{,}410 \pm 60$ cal.; $Pb_3(PO_4)_2$, $\Delta H^0 = 7860 \pm 1000$ cal.

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

The Entropies of Aqueous Ions

BY WENDELL M. LATIMER, KENNETH S. PITZER AND WENDELL V. SMITH

In the course of the research program for the evaluation of the entropies of aqueous ions, in progress for some time in this Laboratory, a considerable body of data has accumulated which makes possible the calculation of the entropies of eleven additional ions. Because in most cases the entropy values depend on those for other ions, an extensive revision would be necessary in order to make these new values the best possible. Consequently it seemed best to make a complete revision of all ionic entropies and to include the new ions at the same time.

In order to avoid unnecessary length, specific references have been given only where the data are not included in some summary publication. Most of the new calculations are based upon data taken from recent publications in this research series[1] and from the references cited in the earlier summary paper.[2] In general entropies have been taken from the excellent summaries of Kelley,[3] heats of reaction from Bichowsky and Rossini,[4] and activity coefficients and other free energy data from the Landolt–Börnstein Tabellen.[5]

The calculations are summarized in Table I and the best values of the ionic entropies collected in Table II. Different methods of obtaining a given entropy are included only if they are independent in the least accurate step. An attempt has been made to include all sources of error in estimating the uncertainty in the final values. For this reason the uncertainty given for a final value is often much larger than the difference between the various values for that quantity would indicate.

The standard state for ionic entropies has been defined in several earlier papers, wherein the theoretical significance and practical importance of ionic entropies also have been discussed. As the body of data becomes larger, however, its consistency becomes more notable, and offers more and more evidence of the validity of the third law of thermodynamics when applied to crystalline inorganic salts. The possibility of difficulties in the case of hydrated crystals has arisen recently and has been discussed elsewhere.[1b] It is felt that errors from this source cannot have any serious effect on the values obtained in this paper.

(1) (a) Pitzer, Smith and Latimer, THIS JOURNAL, **60**, 1826 (1938); (b) Pitzer and Coulter, *ibid.*, **60**, 1310 (1938), (c) Pitzer, *ibid.*, **60**, 1828 (1938); **59**, 2365 (1937); (d) Smith, Pitzer and Latimer, *ibid.*, **59**, 2640, 2642 (1937); (e) Pitzer and Smith, *ibid.*, **59**, 2633 (1937); (f) Smith, Brown and Pitzer, *ibid.*, **59**, 1213 (1937); (g) Brown, Smith and Latimer, *ibid.*, **58**, 1728, 2144, 2228 (1936); **59**, 921 (1937).

(2) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

(3) Kelley, *Bur. Mines Bull.*, 350, 1932 and 394, 1936.

(4) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

(5) Landolt–Börnstein "Physikalisch-chemische Tabellen," including Supplements 1, 2 and 3, Verlag von Julius Springer, Berlin, 1923–1936.

TABLE I

SUMMARY OF ENTROPY CALCULATIONS

Units: cal. per degree per mole

Reaction	$\Delta S^\circ_{298.1}$	Ion	
$H_2O(l) = H^+ + OH^-$	−19.24[1c]	$S^\circ_{OH^-}$	− 2.49 ± 0.06
$HCl(g) = H^+ + Cl^-$	−31.14	$S^\circ_{Cl^-}$	13.52 ± .15
$AgCl(s) + {}^1/_2H_2 = H^+ + Cl^- + Ag$	−14.89		13.49 ± .15
$Ag_2O(s) + 2H^+ = 2Ag^+ + H_2O(l)$	22.58[1e]	$S^\circ_{Ag^+}$	17.46 ± .2
$AgCl(s) = Ag^+ + Cl^-$	8.15[1e]		17.62 ± .2
$AgBr(s) + Cl^- = AgCl(s) + Br^-$	3.69	$S^\circ_{Br^-}$	19.8 ± .2
$AgBr(s) + {}^1/_2H_2 = H^+ + Br^- + Ag$	−11.4[6]		19.6 ± .3
$0.5Br_2(l) + Cl^- = 0.5Cl_2(g) + Br^-$	14.3		19.5 ± .4
$AgI(s) + 0.5H_2 = H^+ + I^- + Ag$	− 7.6[13]	$S^\circ_{I^-}$	25.4 ± .5
$0.5I_2(s) + 0.5H_2(g) = H^+ + I^-$	− 4.3		25.2 ± .7
$KCl(s) = K^+ + Cl^-$	17.96	$S^\circ_{K^+}$	24.2 ± .2
$KBr(s) = K^+ + Br^-$	21.4		24.3 ± .8
$BaCl_2 \cdot 2H_2O(s) = Ba^{++} + 2Cl^- + 2H_2O(e)$	14.2[1g]	$S^\circ_{Ba^{++}}$	2.3 ± .3
$KNO_3(s) = K^+ + NO_3^-$	27.4	$S^\circ_{NO_3^-}$	35.0 ± .3
$Ba(NO_3)_2(s) = Ba^{++} + 2NO_3^-$	21.1[1g]		35.0 ± .3
$NaCl(s) = Na^+ + Cl^-$	10.4	$S^\circ_{Na^+}$	14.1 ± .5
$NaNO_3(s) = Na^+ + NO_3^-$	21.5		14.3 ± .5
$Na + H^+ = Na^+ + 0.5H_2(g)$	17.1		13.7 ± .5
$CaCO_3(s) + 2H^+ = Ca^{++} + H_2O(l) + CO_2(g)$	34.2	$S^\circ_{Ca^{++}}$	−11.4 ± .3
$SrCO_3(s) + 2H^+ = Sr^{++} + H_2O(l) + CO_2(g)$	37.4[7]	$S^\circ_{Sr^{++}}$	− 7.3 ± 1.5
$Na_2SO_4 \cdot 10H_2O(s) = 2Na^+ + SO_4^= + 10H_2O(l)$	57.7[1h]	$S^\circ_{SO_4^=}$	4.4 ± 1.0
$Ag_2SO_4(s) = 2Ag^+ + SO_4^=$	− 8.3		4.5 ± 2
$CaSO_4 \cdot 2H_2O(s) = Ca^{++} + SO_4^= + 2H_2O(l)$	−21.8		2.5 ± 2
$PbSO_4(s) + 2H_2O = H_2(g) + PbO_2(s) + SO_4^= + 2H^+$	−16.0[8]		3.2 ± 2
$Hg_2SO_4(s) + H_2(g) = 2Hg + 2H^+ + SO_4^=$	−37.0[9]		5.2 ± 2
$SO_4^= + H^+ = HSO_4^-$	26.3[1e]	$S^\circ_{HSO_4^-}$	30.6 ± 2
$CO_2(g) + H_2O(l) = H_2CO_3(aq)$	−22.7	$S^\circ_{H_2CO_3}$	45.1 ± 0.7
$H_2CO_3 = H^+ + HCO_3^-$	−22.9[1e]	$S^\circ_{HCO_3^-}$	22.2 ± .8
$HCO_3^- = H^+ + CO_3^=$	−35.2[1e]	$S^\circ_{CO_3^=}$	−13.0 ± 1.0
$H_2S(g) = H_2S(aq)$	−19.7	$S^\circ_{H_2S(aq)}$	29.4 ± 0.3
$H_2S(aq) = H^+ + HS^-$	−14.5	$S^\circ_{HS^-}$	14.9 ± 1.0
$HCN(g) = H^+ + CN^-$	−23	$S^\circ_{CN^-}$	25 ± 5
$NH_3(g) + H_2O(l) = NH_4OH(aq)$	−19.8	$S^\circ_{NH_4OH}$	42.8 ± 0.4
$NH_4OH = NH_4^+ + OH^-$	−18.9[1e]	$S^\circ_{NH_4^+}$	26.4 ± .5
$SO_2(g) + H_2O(l) = H_2SO_3(aq)$	−21.4	$S^\circ_{H_2SO_3}$	54.7 ± 1.0
$H_2SO_3 = H^+ + HSO_3^-$	−22.1	$S^\circ_{HSO_3^-}$	32.6 ± 1.5
$HSO_3^- = H^+ + SO_3^=$	−30	$S^\circ_{SO_3^=}$	3 ± 3
$Cl_2(g) + 2OH^- = H_2O + Cl^- + ClO^-$	− 8.1	$S^\circ_{ClO^-}$	10.0 ± 2.0
$Li_2CO_3 = 2Li^+ + CO_3^=$	−25.1[1g]	$S^\circ_{Li^+}$	4.7 ± 1.0
$KClO_3 = K^+ + ClO_3^-$	29.4	$S^\circ_{ClO_3^-}$	39.4 ± 0.5
$KClO_4 = K^+ + ClO_4^-$	31.7	$S^\circ_{ClO_4^-}$	43.6 ± .5
$RbClO_3 = Rb^+ + ClO_3^-$	32.0[10]	$S^\circ_{Rb^+}$	28.9 ± .8
$RbClO_4 = Rb^+ + ClO_4^-$	33.6[11]		28.5 ± 1.0
$CsClO_4 = Cs^+ + ClO_4^-$	33.5[1a]	$S^\circ_{Cs^+}$	31.8 ± 0.6
$TlNO_3 = Tl^+ + NO_3^-$	27.6[1g]	$S^\circ_{Tl^+}$	31.0 ± .5
$Tl + AgCl = Ag + Tl^+ + Cl^-$	15.3		30.1 ± .5
$AgNO_2 = Ag^+ + NO_2^-$	16.8	$S^\circ_{NO_2^-}$	29.9 ± 1.0
$Ag_2CrO_4 = 2Ag^+ + CrO_4^=$	− 6.2	$S^\circ_{CrO_4^=}$	10.5 ± 1.0
$AgClO_2 = Ag^+ + ClO_2^-$	9.5	$S^\circ_{ClO_2^-}$	24.1 ± 0.5
$KMnO_4 = K^+ + MnO_4^-$	29.9	$S^\circ_{MnO_4^-}$	46.7 ± .4
$KBrO_3 = K^+ + BrO_3^-$	27.2	$S^\circ_{BrO_3^-}$	38.7 ± 1
$Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O(l)$	26.5		38.1 ± 2
$KIO_3 = K^+ + IO_3^-$	15.9	$S^\circ_{IO_3^-}$	27.9 ± 1
$AgIO_3 = Ag^+ + IO_3^-$	10.1[12]		28.3 ± 3

TABLE I (*Concluded*)

Reaction	$\Delta S^\circ_{298.1}$	Ion	
$HF(g) = H^+ + F^-$	−43.9		− 2.4 ± 2
$BaF_2 = Ba^{++} + 2F^-$	−21.5[1a]	$S^\circ_{F^-}$	− 0.4 ± 2
$CaF_2 = Ca^{++} + 2F^-$	−36.2		− 4.2 ± 2
$Cu + 2H^+ = Cu^{++} + H_2$	− 2.7	$S^\circ_{Cu^{++}}$	−25.9 ± 3
$Cu + 2Ag^+ = Cu^{++} + 2Ag$	−49.2		−26.6 ± 1
$Zn + 2H^+ = Zn^{++} + H_2$	− 4.5	$S^\circ_{Zn^{++}}$	−25.7 ± 1
$Cd + 2H^+ = Cd^{++} + H_2$	2.5	$S^\circ_{Cd^{++}}$	−16.4 ± 1.5
$Fe + 2H^+ = Fe^{++} + H_2$	− 1.2	$S^\circ_{Fe^{++}}$	−25.9 ± 1
$Fe^{++} + H^+ = Fe^{+++} + 0.5H_2$	−19.8	$S^\circ_{Fe^{+++}}$	− 61 ± 5
$Sn + 2H^+ = Sn^{++} + H_2$	14.0	$S^\circ_{Sn^{++}}$	− 4.9 ± 1
$2Hg + 2H^+ = Hg_2^{++} + H_2$	11.9	$S^\circ_{Hg_2^{++}}$	17.7 ± 3
$PbCl_2 = Pb^{++} + 2Cl^-$	− 1.7	$S^\circ_{Pb^{++}}$	3.9 ± 0.9
$Mg(OH)_2 + 2H^+ + Mg^{++} + 2H_2O$	−13.3	$S^\circ_{Mg^{++}}$	31.6 ± 3
$CsAl(SO_4)_2 \cdot 12H_2O(s) = Cs^+ + Al^{+++} + 2SO_4^{=} + 12H_2O(l)$	2	$S^\circ_{Al^{+++}}$	−76 ± 10
$CaC_2O_4 \cdot H_2O = Ca^{++} + C_2O_4^{=} + H_2O(l)$	−22.5	$S^\circ_{C_2O_4^{=}}$	9.6 ± 1
$Ag^+ + 2NH_3(aq) = Ag(NH_3)_2^+$	−11.9[1f]	$S^\circ_{Ag(NH_3)_2^+}$	57.8 ± 1
$Pb_3(PO_4)_2 + 2H^+ = 3Pb^{++} + 2HPO_4^{=}$	−77.3[1a]	$S^\circ_{HPO_4^{=}}$	− 2.3 ± 1.5
$HPO_4^{=} + H^+ = H_2PO_4^-$	30.3	$S^\circ_{H_2PO_4^-}$	28.0 ± 1.5
$H_2PO_4^- + H^+ = H_3PO_4(aq)$	16.0	$S^\circ_{H_3PO_4}$	44.0 ± 1.5
$HPO_4^{=} = H^+ + PO_4^{\equiv}$	−43	$S^\circ_{PO_4^{\equiv}}$	−45 ± 2

TABLE II

ENTROPIES OF AQUEOUS IONS AT 298.1°K.

Units: cal. per degree per mole.

H^+	0.00	Cl^-	13.50 ± 0.10	Tl^+	30.5 ± .4	IO_3^-	28.0 ± 1.0
Li^+	4.7 ± 1.0	Br^-	19.7 ± .2	$Ag(NH_3)_2^+$	57.8 ± 1.0	HS^-	14.9 ± 1.0
Na^+	14.0 ± 0.4	I^-	25.3 ± .5	Mg^{++}	−31.6 ± 3	HSO_3^-	32.6 ± 1.5
K^+	24.2 ± .2	ClO^-	10.0 ± 2	Ca^{++}	−11.4 ± 0.3	SO_3^{--}	3 ± 3
Rb^+	28.7 ± .7	ClO_2^-	24.1 ± 0.5	Sr^{++}	− 7.3 ± 1.5	HSO_4^-	30.6 ± 2
Cs^+	31.8 ± .6	ClO_3^-	39.4 ± .5	Ba^{++}	2.3 ± 0.3	SO_4^{--}	4.4 ± 1.0
Ag^+	17.54 ± .15	ClO_4^-	43.6 ± .5	Fe^{++}	−25.9 ± 1.0	NO_2^-	29.9 ± 1.0
NH_4^+	26.4 ± .5	BrO_3^-	38.5 ± 1.0	Cu^{++}	−26.5 ± 1.0	NO_3^-	35.0 ± 0.2
				Zn^{++}	−25.7 ± 1.0	$H_2PO_4^-$	28.0 ± 1.5
				Cd^{++}	−16.4 ± 1.5	HPO_4^{--}	− 2.3 ± 1.5
				Hg_2^{++}	17.7 ± 3	PO_4^{---}	−45 ± 2
				Sn^{++}	− 4.9 ± 1.0	HCO_3^-	22.2 ± 0.8
				Pb^{++}	3.9 ± 0.9	CO_3^{--}	−13.0 ± 1
				Al^{+++}	−76 ± 10	$C_2O_4^{--}$	9.6 ± 1
				Fe^{+++}	−61 ± 5	CN^-	25 ± 5
				OH^-	− 2.49 ± 0.06	MnO_4^-	46.7 ± 0.4
				F^-	− 2.3 ± 2	CrO_4^{--}	10.5 ± 1.0

(6) Harned, Keston and Donelson, THIS JOURNAL, **58**, 989 (1936); **59**, 1280 (1937).

(7) Heat of solution: Zimmerman, private communication.

(8) Hamer, THIS JOURNAL, **57**, 9 (1935).

(9) (a) Harned and Hamer, *ibid.*, **57**, 27 (1935); (b) ($S^\circ_{Hg_2SO_4}$ = 48.0 cal. per degree per mole); Schutz, Ph.D. Dissertation, Univ. of California, 1933.

(10) ($S^\circ_{RbClO_3}$ = 36.3 cal. per degree per mole), Ahlberg, Ph.D. Dissertation, Univ. of California, 1930.

(11) ($S^\circ_{RbClO_4}$ = 38.5) estimated from values for $CsClO_4$,[1a] $KClO_4$, $RbClO_3$ and $KClO_3$, using the formula of Latimer, THIS JOURNAL, **43**, 818 (1921).

(12) (ΔF of soln. of $AgIO_3$), Kolthoff and Lingane, *J. Phys. Chem.*, **42**, 133 (1938).

(13) Owen, THIS JOURNAL, **57**, 1526 (1935).

Summary

The calculation of the entropies of aqueous ions have been completely revised and extended to include eleven additional ions.

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