AIP | The Journal of Chemical Physics

A Summary of the Entropies of Aqueous Ions

Wendell M. Latimer, Philip W. Schutz, and J. F. G. Hicks Jr.

Citation: The Journal of Chemical Physics **2**, 82 (1934); doi: 10.1063/1.1749424
View online: http://dx.doi.org/10.1063/1.1749424
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/2/2?ver=pdfcov
Published by the AIP Publishing

FEBRUARY, 1934 JOURNAL OF CHEMICAL PHYSICS VOLUME 2

A Summary of the Entropies of Aqueous Ions

WENDELL M. LATIMER, PHILIP W. SCHUTZ AND J. F. G. HICKS, JR., *Chemical Laboratory, University of California*

(Received November 17, 1933)

A critical survey has been made of existing data on the heats, free energies and entropies of reactions involving aqueous ions. These data lead to remarkably consistent values for the ionic entropies. The entropies of 20 positive ions and 12 negative ions have been tabulated.

LATIMER and Buffington[1] in 1926 published a list of ionic entropies which included many of the positive ions and a few of the more common negative ions. These values were based on rather meager data and consequently an accuracy of only two units could be claimed even in the cases where the data were most complete. Since the appearance of this initial article, an intensive program has been in progress in this laboratory with the primary object of establishing these values more definitely. It is felt that the work has progressed to such an extent as to warrant a review of the ionic entropy values now available.

In the initial paper many of the values were based on entropies for the solid salts which had been calculated by the approximate equation given by Latimer[2] or obtained by comparison with similar salts. This uncertainty has since been largely eliminated as a result of the specific heat measurements made in this laboratory.[3] Errors in the heats of solution and activities of salt solutions are still large in certain cases, but recent work by many investigators has reduced these uncertainties also.

The standard state, as in all previous work, of the ionic entropies is the hypothetical one molal solution, that is, a one molal solution of the ion obeying the perfect solution laws and the ions possessing the same partial molal heat content that they have at infinite dilution. $S°_{298.1}$ of H^+ is taken to be zero. The ionic entropies are of course partial molal quantities.

The calculations and the data used have been summarized in Tables I and II.

We have given in Table III the values for the entropies of the aqueous ions which appear to be the most probable. In general we have not taken the simple average of the various determinations summarized in Table I but have given weight to the data which appear to be the most reliable. In addition, we have included the value for fluoride given by Latimer and Buffington,[1] although the complete lack of data on the activity coefficients of fluorides renders this value only a rough approximation.

In earlier papers the theoretical significance and practical importance of the ionic entropies have been pointed out: we wish to call attention in this paper merely to the consistency which now exists in the values determined by wide varieties of methods. It should be noted that the checks obtained in Table I are, for almost every ion, more numerous than the cases listed under that ion. Thus, for example, if we use our accepted values for iodide, iodate, ferrous, ferric and sulfate, 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. It is also obvious from the data here presented that the third law of thermodynamics 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.

---

[1] Latimer and Buffington, J. Am. Chem. Soc. **48**, 2297 (1926).

[2] Latimer, J. Am. Chem. Soc. **43**, 818 (1921).

[3] See references to entropies listed in Table II.

TABLE I. *Summary of entropy calculations: ΔH° and ΔF° in calories per mole. ΔS° in calories per degree per mole.* (*The entropy data for the elements and compounds used in these calculations are summarized in Table II.*)

Reaction	$\Delta H^\circ_{298.1}$	$\Delta F^\circ_{298.1}$	$\Delta S^\circ_{298.1}$	
				$S^\circ_{Cl^-}$
$\frac{1}{2}H_2+AgCl(s) = H^++Cl^-+Ag(s)$	−9600[4]	−5125[5]	−15.01	13.49
$HCl(g)=H^++Cl^-$	−17880[4d]	−8598[4d]	−31.14	13.52
$\frac{1}{2}H_2+\frac{1}{2}Cl_2(g)=H^++Cl^-$	−39940[4d]	−31373[4d]	−28.75	13.52
	−39940	−31367[6]	−28.77	13.50
				$S^\circ_{Ag^+}$
$AgCl(s)=Ag^++Cl^-$	15980[7]	13297[8]	9.0	18.5
	15980	13329[9]	8.9	18.4
$Ag+\frac{1}{2}Cl_2(g)=Ag^++Cl^-$	−14330[8a]	−12890[8a]	−4.8	18.4
$Ag+H^+=Ag^++\frac{1}{2}H_2$	25540[10]	18448[6]	23.8	18.3
				$S^\circ_{Hg_2^{++}}$
$2Hg(1)+2H^+=Hg_2^{++}+H_2$	40160[11]	36854[6]	11.1	16.5
$Hg_2Cl_2(s)=Hg_2^{++}+2Cl^-$	23740[12]	24446[11]	−2.4	16.2
				$S^\circ_{Br^-}$
$\frac{1}{2}Br_2+\frac{1}{2}H_2=Br^-+H^+$	−28945[11]	−24577[8a]	−14.65	19.3
$AgCl(s)+Br^- =AgBr(s)+Cl^-$	−4457[8a]	−3461[8a]	−3.3	19.4
$AgBr(s)+\frac{1}{2}H_2 =Ag(s)+H^++Br^-$	−5135[11]	−1673[6]	−11.6	19.5
				$S^\circ_{I^-}$
$AgI(s)=Ag^++I^-$	26710[13]	21889[14]	16.2	25.4
$\frac{1}{2}H_2+\frac{1}{2}I_2=H^++I^-$	−13660[15]	−12361[6]	−4.3	25.2
$HI(g)=H^++I^-$	−19550[15]	−12676[6]	−23.0	26.5
$Ag(s)+\frac{1}{2}I_2(s)=Ag^++I^-$	11870[8a, 13]	6087[6]	19.4	24.9
				$S^\circ_{Tl^+}$
$Tl+H^+=Tl^++\frac{1}{2}H_2$	935[15]	−7760[6]	29.2	28.5
$Tl+\frac{1}{2}Cl_2(g)=Tl^++Cl^-$	−38790[15]	−39105[7]	1.0	29.1
	−38930[16]	−39105	0.6	28.7
$TlCl=Tl^++Cl^-$	10125[17]	5086[11]	16.9	29.2
$Tl+\frac{1}{2}Br_2(1)=Tl^++Br^-$	−27990[11]	−32337[11]	14.5	28.4
$Tl+\frac{1}{2}I_2(s)=Tl^++I^-$	−12720[11]	−20082[11]	24.7	28.0
$TlI=Tl^++I^-$	17530[11]	9938[11]	25.5	28.6
				$S^\circ_{NO_3^-}$
$TlNO_3=Tl^++NO_3^-$	9970[18]	1790[18]	27.4	36.9
				$S^\circ_{Ba^{++}}$
$Ba(NO_3)_2=Ba^{++}+2NO_3^-$	10200[19]	3200[19]	23.5	0.8
				$S^\circ_{OH^-}$
$H_2O=H^++OH^-$	13329[20]	19122[11]	−19.4	−2.5
				$S^\circ_{Ca^{++}}$
$Ca(OH)_2=Ca^{++}+2OH^-$	−3385[21]	6960[21]	−34.7	−11.4
				$S^\circ_{Mg^{++}}$
$Mg(OH)_2=Mg^{++}+2OH^-$	−1180[15]	15410[22]	−55.6	−35.5
				$S^\circ_{K^+}$
$KCl=K^++Cl^-$	4119[23]	−1207[24]	17.9	24.3
$KBr=K^++Br^-$	4910[25]	−1546[26]	21.7	24.8
$K+H^+=K^++\frac{1}{2}H_2$	−60340[11]	−67431[11]	23.8	24.7
				$S^\circ_{S^=}$
$H_2+S(s)=2H^++S^=$	10040[11]	23450[11]	−45.0	−6.2
$H_2S(g)=2H^++S^=$	15300[11]	31290[11]	−53.6	−5.4
				$S^\circ_{SO_4^=}$
$Ag_2SO_4=2Ag^++SO_4^=$	4210[41]	6722[41]	−8.4	2.8
$BaSO_4=Ba^{++}+SO_4^=$	5455[42]	13718[42]	−27.7	3.0
$CaSO_4\cdot 2H_2O =Ca^{++}+SO_4^=+2H_2O$	270[42]	6308[42]	−20.2	3.8
				$S^\circ_{Na^+}$
$NaCl=Na^++Cl^-$	1019[27]	−2524[24]	11.9	15.7
	1019	−2161[28]	10.7	14.4
$NaBr=Na^++Br^-$	0[27]	−4231[24]	14.2	14.9
$Na+H^+=Na^++\frac{1}{2}H_2$	−57520[15]	−62588[11]	17.0	13.9
				$S^\circ_{Pb^{++}}$
$Pb+2H^+=Pb^{++}+H_2$	−600[11]	−5877[29]	17.7	2.1
$Pb+Cl_2(g)=Pb^{++}+2Cl^-$	−80330[11]	−68567[11]	−39.5	2.4
$PbCl_2=Pb^{++}+2Cl^-$	5060[11]	6483[30]	−4.8	2.1
				$S^\circ_{Fe^{++}}$
$Fe+Hg_2Cl_2(s) =Fe^{++}+2Cl^-+2Hg(1)$	−37500[11]	−32585[11]	−16.5	−28.0
$Fe+2TlCl(s) =Fe^{++}+2Cl^-+2Tl$	−3170[11]	5455[11]	−28.9	−27.6
$Fe+2H^+=Fe^{++}+H_2$	−20800[11]	−20240[11]	−1.9	−26.6
				$S^\circ_{Fe^{+++}}$
$Fe^{++}+H^+=Fe^{+++}+\frac{1}{2}H_2$	11240[11]	17230[11]	−20.1	−63.1
$Fe^{+++}+Ag=Ag^++Fe^{++}$	14300[11]	1218[31]	43.9	−63.0
				$S^\circ_{Al^{+++}}$
$CsAl(SO_4)_2\cdot 12H_2O =Cs^++Al^{+++} +2SO_4^=+12H_2O$	13560[32]	12910[32]	2.18	−71.7
				$S^\circ_{Li^+}$
$Li+H^+=Li^++\frac{1}{2}H_2$	−66380[33]	−68248[33]	6.2	1.8
				$S^\circ_{Rb^+}$
$Rb+H^+=Rb^++\frac{1}{2}H_2$	−61210[33]	−67473[33]	21.0	22.8
				$S^\circ_{Cu^{++}}$
$Cu+2H^+=Cu^{++}+H_2$	16640[33]	15912[33]	2.4	−21.0
				$S^\circ_{Cd^{++}}$
$Cd+2H^+=Cd^{++}+H_2$	−16510[33]	−18348[33]	6.2	−12.7
				$S^\circ_{Sn^{++}}$
$Sn+2H^+=Sn^{++}+H_2$	−2390[33]	−6276[33]	13.0	−5.9
				$S^\circ_{Hg^{++}}$
$Hg+2H^+=Hg^{++}+H_2$	41590[33]	39679[33]	6.4	−6.5
				$S^\circ_{Zn^{++}}$
$Zn+2H^+=Zn^{++}+H_2$	−36720[33]	−34984[33]	−5.8	−27.2
				$S^\circ_{ClO_3^-}$
$KClO_3=K^++ClO_3^-$	10120[34]	1277[34]	29.7	39.3
				$S^\circ_{BrO_3^-}$
$Ba(BrO_3)_2\cdot H_2O =Ba^{++}+2BrO_3^-+H_2O$	15360[35]	7170[35]	26.5	38.7
$KBrO_3=K^++BrO_3^-$	9540[36]	1690[36]	26.3	37.4
				$S^\circ_{IO_3^-}$
$AgIO_3=Ag^++IO_3^-$	13200[37]	10200[37]	10.1	27.7
$KIO_3=K^++IO_3^-$	6340[36]	1770[36]	15.3	26.9
				$S^\circ_{ClO_4^-}$
$KClO_4=K^++ClO_4^-$	12115[38]	2690[38]	31.6	43.1
				$S^\circ_{C_2O_4^=}$
$CaC_2O_4\cdot H_2O =Ca^{++}+C_2O_4^=+H_2O$	5090[39]	11790[39]	−22.5	9.3
				$S^\circ_{CO_3^=}$
$CaCO_3+C_2O_4^=+H_2O =CaC_2O_4\cdot H_2O+CO_3^=$	−7460[11]	−306[11]	−24.0	−13.1
$C+{}^3/_2O_2+H_2 =2H^++CO_3^=$	−161100[11]	−125760[11]	−118.5	−12.5
$CaCO_3=Ca^{++}+CO_3^=$	−278[40]	10922[40]	−46.0	−12.6

---

[4] (a) Noyes and Ellis, J. Am. Chem. Soc. **36**, 1969 (1914); (b) Harned and Brumbaugh, J. Am. Chem. Soc. **44**, 2729 (1922); (c) Butler and Robertson, Proc. Roy. Soc. **A125**, 694 (1929); (d) Rossini, Bur. Standards J. Research **9**, 679 (1932). The average of these values is −9600 with a maximum deviation of 48 cal.

[5] Randall and Young, J. Am. Chem. Soc. **50**, 989 (1928).

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

[7] Lange and Fuoss, Zeits. f. physik. Chemie **125**, 431 (1927).

[8] (a) Randall and Spencer, unpublished data; (b) Gerke's value for Ag−Ag⁺ electrode, reference 6.

[9] Randall and Young, reference 5, data for silver chloride electrode with reference (8b).

[10] Combination of data from reference 8(a) and Rossini, reference 4(d).

[11] *International Critical Tables.*

[12] Kohlrausch, Zeits. f. physik. Chemie **64**, 129 (1908), temperature coefficient of solubility data.

[13] Lange and Shibata, Zeits. f. physik. Chemie **A149**, 465 (1930).

[14] The solubility of AgI has been taken as $1.05\times 10^{-8}M$ from a survey of various values in the literature. The potential of the silver-silver iodide electrode by Jones and

TABLE II. *Summary of entropy values used in the calculation of Table I. Values in calories per degree per mole.*

Substance	$S°_{298.1}$	Substance	$S°_{298.1}$
$Ba(BrO_3)_2 \cdot H_2O$	68.7[35]	O_2	49.0[51]
$Ba(NO_3)_2$	51.1[19]	K	16.5[11]
$BaSO_4$	31.5[42]	KBr	22.5[11]
Br_2	36.8[43]	$KBrO_3$	35.6[36]
Cd	12.3[11]	KCl	19.9[52]
$CaCO_3$	22.1[11]	$KClO_3$	34.2[34]
$Ca(OH)_2$	18.2[39]	$KClO_4$	36.1[38]
$CaC_2O_4 \cdot H_2O$	37.3[39]	KIO_3	36.2[36]
$CaSO_4 \cdot 2H_2O$	46.4[42]	Rb	17.4[11]
C	1.4[11]	Ag	10.0[53]
$CsAl(SO_4)_2 \cdot 12H_2O$	163.8[32]	AgBr	25.6[54]
Cl_2	53.3[44]	AgCl	23.0[54]
Cu	7.8[11]	AgI	27.6[49]
H_2	31.2[45]	$AgIO_3$	36.0[37]
HCl	44.7[46]	Ag_2SO_4	47.8[41]
HI	49.5[47]	NaCl	17.2[30]
H_2O	16.9[48]	NaBr	20.1[2]
H_2S	48.2[49]	Na	12.5[11]
I_2	27.9[11]	S	7.6[11]
Fe	6.5[11]	Tl	14.9[11]
Pb	15.6[11]	TlBr	28.9[11]
$PbCl_2$	33.9[11]	TlCl	25.8[11]
Li	7.6[11]	TlI	28.6[11]
$Mg(OH)_2$	15.1[50]	$TlNO_3$	38.1[18]
Hg	18.3[11]	Sn	12.3[11]
Hg_2Cl_2	45.6[11]	Zn	9.8[11]

TABLE III. *Entropies of aqueous ions at 298.1°K. Values in calories per degree per mole.*

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

Kasplan, J. Am. Chem. Soc. **50**, 1863 (1928) gives a value of 21,887 for this free energy.

[15] *International Critical Tables*, corrected to 25°C.

[16] *International Critical Tables*, using the sum of the heats of formation instead of the direct determination.

[17] (a) Thomsen, *Thermochemistry*, p. 52, Longmans Green and Co., N. Y., 1908. (b) Butler and Hiscocks, J. Chem. Soc. 2554 (1926). We have used a mean of these values after correcting for dilution and temperature effects.

[18] Latimer and Ahlberg, J. Am. Chem. Soc. **54**, 1903 (1932).

[19] Latimer and Ahlberg, Zeits. f. physik. Chemie **A148**, 468 (1930).

[20] Rossini, Bur. Standards J. Research **6**, 847 (1931).

[21] Latimer, Schutz and Hicks, J. Am. Chem. Soc. **55**, 971 (1933).

[22] Kline, J. Am. Chem. Soc. **51**, 2093 (1929), gives 5×10^{-12} as the solubility product of $Mg(OH)_2$.

[23] Lange and Monheim, Zeits. f. physik. Chemie **A150**, 349 (1930).

[24] Pearce and Nelson, J. Am. Chem. Soc. **54**, 3544 (1932) give $\gamma \pm = 0.576$ at saturation, $4.81M$ KCl.

[25] *Landolt Börnstein Tabellen*, corrected to 25°C.

[26] (a) Seidell, *Solubility of Inorganic and Organic Compounds*, D. Van Nostrand Co., N. Y. (1919). (b) *Landolt Börnstein, Tabellen*, II Ergänzungband gives $\gamma \pm$ as 0.627 for $4M$ KCl. Extrapolating to saturated solution we find $\gamma \pm 0.65$.

[27] Wüst and Lange, Zeits. f. physik. Chemie **A116**, 190 (1925).

[28] Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, N. Y. (1923).

[29] Fromherz, Zeits. f. physik. Chemie **A153**, 376 (1931).

[30] *Landolt Börnstein Tabellen.*

[31] Noyes and Beam, J. Am. Chem. Soc. **34**, 1016 (1912).

[32] Latimer and Greensfelder, J. Am. Chem. Soc. **50**, 2202 (1928).

[33] These data have been obtained from various sources including the *International Critical Tables* and *Landolt Börnstein Tabellen*. Special reference should also be made to the work of Richards and co-workers.

[34] Latimer, Schutz and Hicks, J. Am. Chem. Soc. (in press).

[35] Greensfelder and Latimer, J. Am. Chem. Soc. **50**, 3286 (1928). These values have been recalculated and a large error in the graphical integration of the entropy of $Ba(BrO_3)_2 \cdot H_2O$ has been corrected. The correct value is 68.7.

[36] Ahlberg and Latimer, J. Am. Chem. Soc. (in press).

[37] Greensfelder and Latimer, J. Am. Chem. Soc. **53**, 3813 (1931). The ΔH value given in this paper has been recalculated from the solubility data.

[38] Latimer and Ahlberg, J. Am. Chem. Soc. **52**, 549 (1930).

[39] Latimer, Schutz and Hicks, J. Am. Chem. Soc. **55**, 971 (1933).

[40] Backström, J. Am. Chem. Soc. **47**, 2432 (1925).

[41] Latimer, Hicks and Schutz, J. Chem. Phys. **1**, 424 (1933).

[42] Latimer, Hicks and Schutz, J. Chem. Phys. **1**, 620 (1933).

[43] Latimer and Hoenshel, J. Am. Chem. Soc. **48**, 19 (1926).

[44] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1741 (1932).

[45] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

[46] Giauque and Wiebe, J. Am. Chem. Soc. **50**, 101 (1928).

[47] Giauque and Wiebe, J. Am. Chem. Soc. **51**, 1441 (1929).

[48] Giauque and Ashley, Phys. Rev. **43**, 1 (1933).

[49] Kelley, U. S. Bureau of Mines Bull. 350 (1932).

[50] Giauque and Archibald, unpublished data.

[51] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

[52] Nernst, Ann. d. Physik **36**, 395 (1911).

[53] Giauque and Meads, unpublished data.

[54] Eastman and Milner, J. Chem. Phys. **1**, 444 (1933).