

5g. Electrochemical Information

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Editor's note. The symbols used in this section are essentially those recommended by the International Union of Pure and Applied Chemistry (cf. Christiansen, 1960).

Conductance data and transference numbers are taken from Harned and Owen (1958), Kortüm, and Robinson and Stokes (1959). Additional data can be found in these books, in Conway (1952) and in Parsons (1955).

Much information concerning a wide variety of electrochemical phenomena including conductance can be found in the general tables: "International Critical Tables," 1926-1933; "International Annual Tables," 1950—; and Landolt-Börnstein 1950—.

Additional information may be derived from tables of polarographic data compiled by Kolthoff and Lingane (1952) and by von Stackelberg (1950).

Standard electromotive forces of half cells were taken from Latimer (1952). Many additional data are available in his tables. Note especially his table on page 345 for alkaline solutions. Other values of E° may be calculated from the free-energy data of Rossini et al. (1952).

Activity coefficients were selected from extensive tables in Harned and Owen (1958), Kortüm and Bockris (1951), and Robinson and Stokes (1959). Additional data can be found in these sources and in Robinson and Stokes (1949) and in Conway (1952).

Dissociation constants are from Harned and Owen (1958) and Hood, Redlich, and Reilly (1954). Constants for many other equilibria can be found in Harned and Owen

(1958), Redlich (1946), Bjerrum et al. (1957), Scudder (1914), and can be derived from thermodynamic data of Rossini et al. (1952) and of Latimer (1952).

The molal heat content (enthalpy) data were taken from Harned and Owen (1958).

Standard entropies of ions were taken from Latimer (1952) and from Powell and Latimer (1951). Additional values can be found in those sources and in Robinson and Stokes (1959) and in Kortüm and Bockris (1951).

Electrochemical data of many other kinds have been tabulated by Robinson and Stokes (1959), Harned and Owen (1958), and Kortüm and Bockris (1951). Information especially useful for the electrometric determination of pH has been assembled by Bates (1954). Polarographic data have been collected by Kolthoff and Lingane (1952) and by von Stackelberg (1950).

Further data on the rates of fast equilibria can be found in Caldin (1963) and Stuehr and Yeager (1965).

Notes on Abbreviations, Symbols, and Terminology Used in Table 5g-3 and in the Discussion Which Follows. The letters (g), (l), (s), and (aq) denote *gas*, *liquid*, *solid*, and *aqueous solution*, respectively. These symbols are often omitted for substances which are in their most familiar states.

Pt. Many authors writing symbols for electrodes include the symbol "Pt" whenever no solid conducting element appears elsewhere in the formulation of the electrode. Its purpose is to remind the reader that some connection (not necessarily platinum) to the external portion of the circuit must be provided. The symbol is not essential and has been omitted in Table 5g-3.

Cathode and Anode. The words *cathode* and *anode* are not essential for a discussion of electrochemical cells. They are not used in the explanation which follows. Because some writers use the words frequently, their meanings must be understood. At the cathode reduction occurs; at the anode oxidation occurs. In the external portion of the circuit electrons flow from anode to cathode, whereas the "positive current" is said to flow in the external conductor from cathode to anode. Within the cell the "positive current" flows from anode to cathode, thus completing the circuit. The current within the cell consists of both positive ions moving from anode to cathode and negative ions moving from cathode to anode. Note that in an electrochemical cell operating spontaneously the anode is the negative pole and the cathode is the positive pole. For a somewhat more detailed discussion of the words, see Daniels and Alberty (1955).

E denotes the electromotive force (emf) of a cell or half cell.

E° denotes the standard emf defined below.

ΔG denotes the increase in Gibbs free energy for the reaction specified.

ΔG° denotes the standard increase in free energy. It is related to E° by an equation similar to Eq. (5g-1).

TABLE 5g-1. EQUIVALENT CONDUCTANCES AND CATION TRANSFERENCE
 NUMBERS OF ELECTROLYTES IN AQUEOUS SOLUTIONS AT 25°C
 (Λ in $\text{cm}^2 \text{ ohm}^{-1} \text{ equivalent}^{-1}$; N in equivalent liter $^{-1}$)

	N	0	0.001	0.01	0.02	0.05	0.1
HCl	Λ	426.16	421.36	412.00	407.24	399.09	391.32
	t_+	0.8209	0.8251	0.8266	0.8292	0.8314
LiCl	Λ	115.03	112.40	107.32	104.65	100.11	95.86
	t_+	0.3364	0.3289	0.3261	0.3211	0.3168
NaCl	Λ	126.45	123.74	118.51	115.76	111.06	106.74
	t_+	0.3963	0.3918	0.3902	0.3876	0.3854
KCl	Λ	149.86	146.95	141.27	138.34	133.37	128.96
	t_+	0.4906	0.4902	0.4901	0.4899	0.4898
NH ₄ Cl	Λ	149.7	141.28	138.33	133.29	128.75
	t_+	0.4909	0.4907	0.4906	0.4905	0.4907
KBr	Λ	151.9	143.43	140.48	135.68	131.39
	t_+	0.4849	0.4833	0.4832	0.4831	0.4833
NaI	Λ	126.94	124.25	119.24	116.70	112.79	108.78
KI	Λ	150.38	142.18	139.45	134.97	131.11
	t_+	0.4892	0.4884	0.4883	0.4882	0.4883
KNO ₃	Λ	144.96	141.84	132.82	132.41	126.31	120.40
	t_+	0.5072	0.5084	0.5087	0.5093	0.5103
KHCO ₃	Λ	118.00	115.34	110.08	107.22		
NaO ₂ C ₂ H ₃	Λ	91.0	88.5	83.76	81.24	76.92	72.80
	t_+	0.5507	0.5537	0.5550	0.5573	0.5594
NaO ₂ C(CH ₃) ₂ CH ₃	Λ	82.70	80.31	75.76	73.39	69.32	65.27
NaOH	Λ	247.8	244.7	238.0			
AgNO ₃	Λ	133.36	130.51	124.76	121.41	115.24	109.14
	t_+	0.4643	0.4648	0.4652	0.4664	0.4682
$\frac{1}{2}$ MgCl ₂	Λ	129.40	124.11	114.55	110.04	103.08	97.10
$\frac{1}{2}$ CaCl ₂	Λ	135.84	130.36	120.36	115.65	108.47	102.46
	t_+	0.4380	0.4264	0.4220	0.4140	0.4060
$\frac{1}{2}$ SrCl ₂	Λ	135.80	130.33	120.29	115.54	108.25	102.19
$\frac{1}{2}$ BaCl ₂	Λ	139.98	134.34	123.94	119.09	111.48	105.19
$\frac{1}{2}$ Na ₂ SO ₄	Λ	129.9	124.15	112.44	106.78	97.75	89.98
	t_+	0.386	0.3848	0.3836	0.3829	0.3828
$\frac{1}{2}$ CuSO ₄	Λ	133.6	115.26	83.12	72.20	59.05	50.58
$\frac{1}{2}$ ZnSO ₄	Λ	132.8	115.53	84.91	74.24	61.20	52.64
$\frac{1}{2}$ LaCl ₃	Λ	145.8	137.0	121.8	115.3	106.2	99.1
	t_+	0.477	0.4625	0.4576	0.4482	0.4375
$\frac{1}{2}$ K ₃ Fe(CN) ₆	Λ	174.5	163.1				
$\frac{1}{2}$ K ₄ Fe(CN) ₆	Λ	184.5	167.24	134.83	122.82	107.70	97.87

TABLE 5g-2. LIMITING EQUIVALENT CONDUCTANCES OF IONS IN WATER IN INFINITELY DILUTE SOLUTION
($\text{cm}^2 \text{ohm}^{-1} \text{equivalent}^{-1}$)

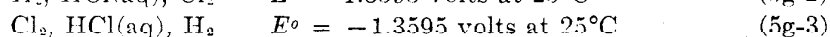
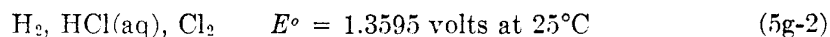
Ion	$t^\circ\text{C}$	Λ_0	Ion	$t^\circ\text{C}$	Λ_0
H ⁺	15	300.6	OH ⁻	25	197.6
	25	349.8	Cl ⁻	15	61.42
	35	397.0		25	76.34
Li ⁺	25	38.69		35	92.21
Na ⁺	15	39.75	Br ⁻	15	63.3
	25	50.11		25	78.3
	35	61.53		35	94.2
K ⁺	15	59.66	I ⁻	25	76.8
	25	73.50	NO ₃ ⁻	25	71.4
	35	88.21	ClO ₄ ⁻	25	68.0
NH ₄ ⁺	25	73.4	HCO ₃ ⁻	25	44.5
Ag ⁺	25	61.92	CH ₃ CO ₂ ⁻	25	40.9
Tl ⁺	25	74.7	ClCH ₂ CO ₂ ⁻	25	39.8
$\frac{1}{2}$ Mg ⁺⁺	25	53.06	CH ₃ CH ₂ CO ₂ ⁻	25	35.8
$\frac{1}{2}$ Ca ⁺⁺	25	59.50	CH ₃ (CH ₂) ₂ CO ₂ ⁻	25	32.6
$\frac{1}{2}$ Sr ⁺⁺	25	59.46	C ₆ H ₅ CO ₂ ⁻	25	32.3
$\frac{1}{2}$ Ba ⁺⁺	25	63.64	HC ₂ O ₄ ⁻	25	40.2
$\frac{1}{2}$ Cu ⁺⁺	25	54	$\frac{1}{2}$ C ₂ O ₄ ⁼⁼	25	74.2
$\frac{1}{2}$ Zn ⁺⁺	25	53	$\frac{1}{2}$ SO ₄ ⁼⁼	25	80
$\frac{1}{3}$ La ³⁺	25	69.5	$\frac{1}{3}$ Fe(CN) ₆ ³⁻	25	101
$\frac{1}{3}$ Co(NH ₃) ₆ ³⁺	25	102	$\frac{1}{4}$ Fe(CN) ₆ ⁴⁻	25	111

N denotes the number of Faradays (F) of electricity. N may have any positive value. For simplicity it is arbitrarily chosen as unity for all of Table 5g-3 and for each example of its use.

Significance of Table 5g-3 and Conventions. When current passes through a reversible electrolytic cell, oxidation occurs at one electrode and reduction at the other. When the direction of the current is reversed, the chemical reaction is reversed and oxidation and reduction exchange places. While no current is passing through the cell, a reversible emf can be measured with a potentiometer. Electromotive forces of cells are important thermodynamic data since

$$\Delta G = -NFE \quad (5g-1)$$

It is conventional to associate ΔG with the reaction which occurs when N Faradays, i.e., *ca.* N 96,500 coulombs, of positive electricity is passed through the cell from left to right. It is conventional to write E as positive if this current flows spontaneously from left to right through the cell, i.e., if electrons are caused by the cell reaction to move in the external part of the circuit from left to right. According to this convention E of the cell is positive if the right-hand electrode is positive with respect to the left-hand electrode. If the cell is rewritten in the reverse order, the algebraic sign of its emf is changed. [The negative sign in Eq. (5g-1) is a consequence of these two conventions.] Examples:

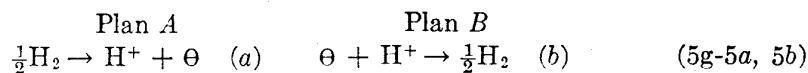


In these equations the symbol $^\circ$ (read "standard") indicates that all the cell reactants and products are in their standard states, i.e., each is at unit activity. Actually there are no criteria for the decision that the activity of any single ion (a_+ of H^+ or a_- of Cl^- , in this example) is unity. The emf of the cell is completely determined, however, by a product of ion activities, in this example by

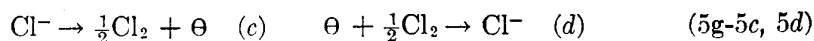
$$a_+a_- = a_2 \quad (5g-4)$$

The activity a_2 of the solute, e.g., HCl , can be measured and is known for many electrolytes as functions of their concentration.

The emf of a cell may be regarded as the net result of two opposing half-cell reactions, one at each electrode. Each of these two half reactions may be thought of as having a tendency to liberate electrons, or each may be considered to possess a tendency to consume electrons. The half reaction having the greater tendency to acquire electrons forces the other half reaction to surrender them, or according to the alternative point of view, the half reaction having the greater tendency to liberate electrons forces the other to accept them. These two points of view are designated below as plan *A* and plan *B*, respectively. Either plan is quite correct and general. Example: Consider the cell of Eq. (5g-2), $\text{H}_2, \text{HCl(aq)}, \text{Cl}_2$. At the left-hand electrode the half reaction, for $N = 1$, may be considered to be either (a) or (b); thus



The opposing half-cell reaction (at the other electrode) is written



Since E° of cell (2) is positive it is obvious that half reaction (c) has less tendency to proceed than half reaction (a), and that (d) has more tendency to proceed than (b). The difference in each case is 1.3595 volts.

TABLE 5g-3. STANDARD ELECTROMOTIVE FORCES OF HALF CELLS IN WATER AT 25°C
(E° in absolute volts relative to the standard hydrogen electrode)

Half-cell reaction	Electrode	E° electrode potential	Half-cell reaction	Electrode	E° electrode potential
Acid solution					
$\text{O} + \text{Li}^+ \rightarrow \text{Li}$	Li^+, Li	-3.045	$\text{O} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}^-$	$\text{Cl}^-, \text{Cl}_2(\text{g})$	1.3595
$\text{O} + \text{K}^+ \rightarrow \text{K}$	K^+, K	-2.925	$\text{O} + \frac{1}{3}\text{Al}^{3+} \rightarrow \frac{1}{3}\text{Al}$	$\text{Al}^{3+}, \text{Al}$	1.50
$\text{O} + \text{Rb}^+ \rightarrow \text{Rb}$	Rb^+, Rb	-2.925	$\text{O} + \frac{1}{2}\text{H}^+ + \frac{1}{2}\text{MnO}_4^- \rightarrow \frac{1}{2}\text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{Mn}^{++}$	$\text{H}^+, \text{MnO}_4^-, \text{Mn}^{++}$	1.51
$\text{O} + \frac{1}{2}\text{Ba}^{++} \rightarrow \frac{1}{2}\text{Ba}$	$\text{Ba}^{++}, \text{Ba}$	-2.90	$\text{O} + \text{Bk}^{4+} \rightarrow \text{Bk}^{3+}$	$\text{Bk}^{4+}, \text{Bk}^{3+}$	1.6
$\text{O} + \frac{1}{2}\text{Sr}^{++} \rightarrow \frac{1}{2}\text{Sr}$	$\text{Sr}^{++}, \text{Sr}$	-2.89	$\text{O} + \text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$	$\text{Ce}^{4+}, \text{Ce}^{3+}$	1.61
$\text{O} + \frac{1}{2}\text{Ca}^{++} \rightarrow \frac{1}{2}\text{Ca}$	$\text{Ca}^{++}, \text{Ca}$	-2.87	$\text{O} + \text{AmO}_2^{++} \rightarrow \text{AmO}_2^+$	$\text{AmO}_2^{++}, \text{AmO}_2^+$	1.64
$\text{O} + \text{Na}^+ \rightarrow \text{Na}$	Na^+, Na	-2.714	$\text{O} + \text{Au}^+ \rightarrow \text{Au}$	Au^+, Au	1.68
$\text{O} + \frac{1}{2}\text{Mg}^{++} \rightarrow \frac{1}{2}\text{Mg}$	$\text{Mg}^{++}, \text{Mg}$	-2.37	$\text{O} + \text{Am}^{4+} \rightarrow \text{Am}^{3+}$	$\text{Am}^{4+}, \text{Am}^{3+}$	2.18
$\text{O} + \frac{1}{2}\text{Am}^{3+} \rightarrow \frac{1}{2}\text{Am}$	$\text{Am}^{3+}, \text{Am}$	-2.32	$\text{O} + \text{H}^+ + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{HF}(\text{aq})$	$\text{H}^+, \text{HF}(\text{aq}), \text{F}_2(\text{g})$	3.06
Basic solution					
$\text{O} + \frac{1}{2}\text{Pu}^{3+} \rightarrow \frac{1}{2}\text{Pu}$	$\text{Pu}^{3+}, \text{Pu}$	-2.07	Basic solution		
$\text{O} + \frac{1}{2}\text{Th}^{4+} \rightarrow \frac{1}{2}\text{Th}$	$\text{Th}^{4+}, \text{Th}$	-1.90	$\text{O} + \frac{1}{2}\text{Ca}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Ca} + \text{OH}^-$	$\text{Ca}(\text{OH})_2, \text{Ca}$	-3.03
$\text{O} + \frac{1}{2}\text{Np}^{3+} \rightarrow \frac{1}{2}\text{Np}$	$\text{Np}^{3+}, \text{Np}$	-1.86	$\text{O} + \frac{1}{2}\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Sr} + \text{HO}^- + 4\text{H}_2\text{O}$	$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}, \text{Sr}$	-2.99
$\text{O} + \frac{1}{2}\text{Be}^{++} \rightarrow \frac{1}{2}\text{Be}$	$\text{Be}^{++}, \text{Be}$	-1.85	$\text{O} + \frac{1}{2}\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Ba} + \text{OH}^- + 4\text{H}_2\text{O}$	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}, \text{Ba}$	-2.97
$\text{O} + \frac{1}{2}\text{U}^{3+} \rightarrow \frac{1}{2}\text{U}$	U^{3+}, U	-1.80	$\text{O} + \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{H}_2(\text{g}) + \text{OH}^-$	$\text{H}_2\text{O}, \text{H}_2(\text{g})$	-2.93
$\text{O} + \frac{1}{2}\text{Al}^{3+} \rightarrow \frac{1}{2}\text{Al}$	$\text{Al}^{3+}, \text{Al}$	-1.66	$\text{O} + \frac{1}{4}\text{La}(\text{OH})_3 \rightarrow \frac{1}{4}\text{La} + \text{OH}^-$	$\text{La}(\text{OH})_3, \text{La}$	-2.90
$\text{O} + \frac{1}{2}\text{Ti}^{3+} \rightarrow \frac{1}{2}\text{Ti}$	$\text{Ti}^{3+}, \text{Ti}$	-1.63	$\text{O} + \frac{1}{2}\text{Mg}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Mg} + \text{OH}^-$	$\text{Mg}(\text{OH})_2, \text{Mg}$	-2.69
$\text{O} + \frac{1}{2}\text{Zn}^{++} \rightarrow \frac{1}{2}\text{Zn}$	$\text{Zn}^{++}, \text{Zn}$	-0.763	$\text{O} + \frac{1}{4}\text{Be}_2\text{O}_3^{--} + \frac{3}{4}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Be} + \frac{3}{2}\text{OH}^-$	$\text{Be}_2\text{O}_3^{--}, \text{Be}$	-2.62
$\text{O} + \text{U}^{4+} \rightarrow \text{U}^{3+}$	$\text{U}^{4+}, \text{U}^{3+}$	-0.61	$\text{O} + \frac{1}{4}\text{Th}_2(\text{OH})_4 \rightarrow \frac{1}{4}\text{Th} + \text{OH}^-$	$\text{Th}_2(\text{OH})_4, \text{Th}$	-2.48
$\text{O} + \frac{1}{2}\text{Fe}^{++} \rightarrow \frac{1}{2}\text{Fe}$	$\text{Fe}^{++}, \text{Fe}$	-0.440	$\text{O} + \frac{1}{3}\text{H}_2\text{AlO}_3 + \frac{1}{3}\text{H}_2\text{O} \rightarrow \frac{1}{3}\text{Al} + \frac{1}{3}\text{OH}^-$	$\text{H}_2\text{AlO}_3, \text{Al}$	-2.35
$\text{O} + \text{Eu}^{3+} \rightarrow \text{Eu}^{++}$	$\text{Eu}^{3+}, \text{Eu}^{++}$	-0.43	$\text{O} + \frac{1}{4}\text{SiO}_3^{--} + \frac{3}{4}\text{H}_2\text{O} \rightarrow \frac{1}{4}\text{Si} + \frac{3}{4}\text{OH}^-$	$\text{SiO}_3^{--}, \text{Si}$	-1.70
$\text{O} + \frac{1}{2}\text{Cd}^{++} \rightarrow \frac{1}{2}\text{Cd}$	$\text{Cd}^{++}, \text{Cd}$	-0.403	$\text{O} + \frac{1}{2}\text{Mn}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Mn} + \text{OH}^-$	$\text{Mn}(\text{OH})_2, \text{Mn}$	-1.55
$\text{O} + \text{Ti}^{3+} \rightarrow \text{Ti}$	$\text{Ti}^{3+}, \text{Ti}$	-0.3363	$\text{O} + \frac{1}{3}\text{Cr}(\text{OH})_3 \rightarrow \frac{1}{3}\text{Cr} + \text{OH}^-$	$\text{Cr}(\text{OH})_3, \text{Cr}$	-1.3
$\text{O} + \frac{1}{2}\text{Ni}^{++} \rightarrow \frac{1}{2}\text{Ni}$	$\text{Ni}^{++}, \text{Ni}$	-0.250			
$\text{O} + \text{AgI} \rightarrow \text{Ag} + \text{I}^-$	$\text{I}^-, \text{AgI}, \text{Ag}$	-0.151			

$\Theta + \frac{1}{2}\text{Sn}^{++} \rightarrow \frac{1}{2}\text{Sn}$	$\text{Sn}^{++}, \text{Sn}$	-0.136	$\Theta + \frac{1}{2}\text{Zr}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Zn} + \text{OH}^-$	$\text{Zn}(\text{OH})_2, \text{Zn}$	-1.245
$\Theta + \frac{1}{2}\text{Pb}^{++} \rightarrow \frac{1}{2}\text{Pb}$	$\text{Pb}^{++}, \text{Pb}$	-0.126	$\Theta + \frac{1}{2}\text{ZrO}_2 + \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Zn} + 2\text{OH}^-$	ZnO_2, Zn	-1.216
$\Theta + \text{H}^+ \rightarrow \frac{1}{2}\text{H}_2(\text{g})$	$\text{H}^+, \text{H}_2(\text{g})$	±0.0000	$\Theta + \frac{1}{2}\text{Te} \rightarrow \frac{1}{2}\text{Te}^{--}$	$\text{Te}, \text{Te}^{--}$	-1.14
$\Theta + \text{UO}_2^{++} \rightarrow \text{UO}_2^+$	$\text{UO}_2^{++}, \text{UO}_2^+$	0.05	$\Theta + \text{SO}_3^{--} + \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{SO}_4^{--} + 2\text{OH}^-$	$\text{SO}_3^{--}, \text{SO}_4^{--}$	-1.12
$\Theta + \text{AgBr} \rightarrow \text{Ag} + \text{Br}^-$	$\text{Br}^-, \text{AgBr}, \text{Ag}$	0.095	$\Theta + \frac{1}{2}\text{In}(\text{OH})_3 \rightarrow \frac{1}{2}\text{In} + \text{OH}^-$	$\text{In}(\text{OH})_3, \text{In}$	-1.0
$\Theta + \text{Np}^{3+} \rightarrow \text{Np}^{3+}$	$\text{Np}^{3+}, \text{Np}^{3+}$	0.147	$\Theta + \frac{1}{2}\text{SCl}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{SO}_3^{--} + \text{OH}^-$	$\text{SO}_3^{--}, \text{SO}_2^{--}$	-0.93
$\Theta + \frac{1}{2}\text{Sn}^{++} \rightarrow \frac{1}{2}\text{Sn}^{++}$	$\text{Sn}^{++}, \text{Sn}^{++}$	0.15	$\Theta + \frac{1}{2}\text{Se} \rightarrow \frac{1}{2}\text{Se}^{--}$	$\text{Se}, \text{Se}^{--}$	-0.92
$\Theta + \text{Cu}^{++} \rightarrow \text{Cu}^+$	$\text{Cu}^{++}, \text{Cu}^+$	0.153	$\Theta + \frac{1}{2}\text{P} + \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{PH}_3(\text{g}) + \text{OH}^-$	$\text{P}, \text{PH}_3(\text{g})$	-0.89
$\Theta + \text{AgCl} \rightarrow \text{Ag} + \text{Cl}^-$	$\text{Cl}^-, \text{AgCl}, \text{Ag}$	0.2223	$\Theta + \frac{1}{2}\text{Fe}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Fe} + \text{OH}^-$	$\text{Fe}(\text{OH})_2, \text{Fe}$	-0.877
$\Theta + \frac{1}{2}\text{Cu}^{++} \rightarrow \frac{1}{2}\text{Cu}$	$\text{Cu}^{++}, \text{Cu}$	0.337	$\Theta + \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{H}_2(\text{g}) + \text{OH}^-$	$\text{H}_2\text{O}, \text{H}_2(\text{g})$	-0.828
$\Theta + \text{H}^+ + \frac{1}{2}\text{C}_2\text{H}_4(\text{g}) \rightarrow \frac{1}{2}\text{C}_2\text{H}_6(\text{g})$	$\text{H}^+, \text{C}_2\text{H}_4(\text{g}), \text{C}_2\text{H}_6(\text{g})$	0.52	$\Theta + \frac{1}{2}\text{Cd}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Cd} + \text{OH}^-$	$\text{Cd}(\text{OH})_2, \text{Cd}$	-0.809
$\Theta + \text{Cu}^+ \rightarrow \text{Cu}$	Cu^+, Cu	0.521	$\Theta + \frac{1}{2}\text{Co}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Co} + \text{OH}^-$	$\text{Co}(\text{OH})_2, \text{Co}$	-0.73
$\Theta + \frac{1}{2}\text{I}_2 \rightarrow \text{I}^-$	I^-, I_2	0.5355	$\Theta + \text{Ni}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Ni} + \text{OH}^-$	$\text{Ni}(\text{OH})_2, \text{Ni}$	-0.72
$\Theta + \frac{1}{2}\text{I}_3^- \rightarrow \frac{3}{2}\text{I}^-$	I^-, I_3^-	0.536	$\Theta + \frac{1}{2}\text{SO}_3^{--} + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{SO}_3^{--} + \frac{3}{2}\text{OH}^-$	$\text{SO}_3^{--}, \text{SO}_2^{--}$	-0.58
$\Theta + 2\text{H}^+ + \frac{1}{2}\text{UO}_2^{++} \rightarrow \frac{1}{2}\text{U}^{4+} + \text{H}_2\text{O}(\text{l})$	$\text{H}^+, \text{UO}_2^{++}, \text{U}^{4+}$	0.62	$\Theta + \text{Fe}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2 + \text{OH}^-$	$\text{Fe}(\text{OH})_2, \text{Fe}(\text{OH})_2$	-0.56
$\Theta + 4\text{H}^+ + \text{NpO}_2^+ \rightarrow \text{Np}^{3+} + 2\text{H}_2\text{O}(\text{l})$	$\text{H}^+, \text{NpO}_2^+, \text{Np}^{3+}$	0.75	$\Theta + \text{O}_2(\text{g}) \rightarrow \text{O}_2^-$	$\text{O}_2(\text{g}), \text{O}_2^-$	-0.56
$\Theta + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	$\text{Fe}^{3+}, \text{Fe}^{2+}$	0.771	$\Theta + \frac{1}{2}\text{S} \rightarrow \frac{1}{2}\text{S}^{--}$	S, S^{--}	-0.48
$\Theta + \frac{1}{2}\text{Hg}_2^{++} \rightarrow \text{Hg}(\text{l})$	$\text{Hg}_2^{++}, \text{Hg}(\text{l})$	0.789	$\Theta + \frac{1}{2}\text{Bi}_2\text{O}_3 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Bi} + \text{OH}^-$	$\text{Bi}_2\text{O}_3, \text{Bi}$	-0.44
$\Theta + \text{Ag}^+ \rightarrow \text{Ag}$	Ag^+, Ag	0.7991	$\Theta + \frac{1}{2}\text{Cu}_2\text{O} + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Cu} + \text{OH}^-$	$\text{Cu}_2\text{O}, \text{Cu}$	-0.358
$\Theta + \text{Hg}_2^{++} \rightarrow \frac{1}{2}\text{Hg}_2^{++}$	$\text{Hg}_2^{++}, \text{Hg}_2^{++}$	0.920	$\Theta + \text{TiOH} \rightarrow \text{Ti} + \text{OH}^-$	TiOH, Ti	-0.345
$\Theta + \text{PuO}_2^{++} \rightarrow \text{PuO}_2^+$	$\text{PuO}_2^{++}, \text{PuO}_2^+$	0.93	$\Theta + \text{HO}_2^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + 2\text{OH}^-$	HO_2^-, OH	-0.24
$\Theta + \text{Pu}^{4+} \rightarrow \text{Pu}^{3+}$	$\text{Pu}^{4+}, \text{Pu}^{3+}$	0.97	$\Theta + \frac{1}{2}\text{CrO}_4^{--} + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Cr}(\text{OH})_3 + \frac{3}{2}\text{OH}^-$	$\text{CrO}_4^{--}, \text{Cr}(\text{OH})_3$	-0.13
$\Theta + \frac{1}{2}\text{Pd}^{++} \rightarrow \frac{1}{2}\text{Pd}$	$\text{Pd}^{++}, \text{Pd}$	0.987	$\Theta + \text{Cu}(\text{OH})_2 \rightarrow \frac{1}{2}\text{Cu}_2\text{O} + \text{OH}^-$	$\text{Cu}(\text{OH})_2, \text{Cu}_2\text{O}$	-0.080
$\Theta + \frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{Br}^-$	$\text{Br}^-, \text{Br}_2(\text{l})$	1.0652	$\Theta + \frac{1}{2}\text{O}_2(\text{g}) + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{HO}_2^- + \frac{1}{2}\text{OH}^-$	$\text{O}_2(\text{g}), \text{HO}_2^-$	-0.076
$\Theta + \text{NpO}_2^{++} + \text{NpO}_2^+$	$\text{NpO}_2^{++}, \text{NpO}_2^+$	1.15	$\Theta + \frac{1}{2}\text{Ti}(\text{OH})_3 \rightarrow \frac{1}{2}\text{Ti}(\text{OH}) + \text{OH}^-$	$\text{Ti}(\text{OH})_3, \text{TiOH}$	-0.05
$\Theta + 4\text{H}^+ + \text{PuO}_2^+ \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{Pu}^{4+}$	$\text{H}^+, \text{PuO}_2^+, \text{Pu}^{4+}$	1.15	$\Theta + \frac{1}{2}\text{MnO}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Mn}(\text{OH})_2 + \text{OH}^-$	$\text{MnO}_2, \text{Mn}(\text{OH})_2$	-0.05
$\Theta + \text{H}^+ + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \frac{1}{2}\text{H}_2\text{O}(\text{l})$	$\text{H}^+, \text{O}_2(\text{g})$	1.229	$\Theta + \frac{1}{2}\text{NO}_3^- + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{NO}_2^- + \text{OH}^-$	$\text{NO}_3^-, \text{NO}_2^-$	0.01
$\Theta + \frac{1}{2}\text{H}^+ + \frac{1}{6}\text{Cr}_2\text{O}_7^{--} \rightarrow \frac{1}{6}\text{H}_2\text{O}(\text{l}) + \frac{1}{3}\text{Cr}^{3+}$	$\text{H}^+, \text{Cr}_2\text{O}_7^{--}, \text{Cr}^{3+}$	1.33			

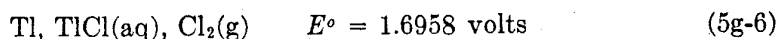
TABLE 5g-3. STANDARD ELECTROMOTIVE FORCES OF HALF CELLS IN WATER AT 25°C (Continued)
 (E° in absolute volts relative to the standard hydrogen electrode)

Half-cell reaction	Electrode	E° electrode potential	Half-cell reaction	Electrode	E° electrode potential
Basic solution					
$\theta + \frac{1}{2}\text{SeO}_4^{--} + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{SeO}_3^{--} + \text{OH}^-$	$\text{SeO}_4^{--}, \text{SeO}_3^{--}$	0.05	$\theta + \frac{1}{2}\text{O}_2(\text{g}) + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{OH}^-$	$\text{O}_2(\text{g}), \text{OH}^-$	0.401
$\theta + \frac{1}{2}\text{HgO}(\text{r}) + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Hg} + \text{OH}^-$	$\text{HgO}(\text{r}), \text{Hg}$	0.098	$\theta + \frac{1}{2}\text{NiO}_2 + \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Ni}(\text{OH})_2 + \text{OH}^-$	$\text{NiO}_2, \text{Ni}(\text{OH})_2$	0.49
$\theta + \text{Mn}(\text{OH})_3 \rightarrow \text{Mn}(\text{OH})_2 + \text{OH}^-$	$\text{Mn}(\text{OH})_3, \text{Mn}(\text{OH})_2$	0.1	$\theta + \text{Ag}_2\text{O} + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Ag}_2\text{O} + \text{OH}^-$	$\text{Ag}_2\text{O}, \text{Ag}_2\text{O}$	0.57
$\theta + \text{Co}(\text{OH})_3 \rightarrow \text{Co}(\text{OH})_2 + \text{OH}^-$	$\text{Co}(\text{OH})_3, \text{Co}(\text{OH})_2$	0.17	$\theta + \frac{1}{2}\text{MnO}_4^{--} - \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{MnO}_2 + 2\text{OH}^-$	$\text{MnO}_4^{--}, \text{MnO}_2$	0.60
$\theta + \frac{1}{2}\text{PbO}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{PbO}(\text{r}) + \text{OH}^-$	$\text{PbO}_2, \text{PbO}(\text{r})$	0.248	$\theta + \frac{1}{2}\text{CO}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{CO}_3^{--} + \text{OH}^-$	$\text{CO}_3^{--}, \text{ClO}^-$	0.66
$\theta + \frac{1}{2}\text{ClO}_3^- + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{ClO}_2^- + \text{OH}^-$	$\text{ClO}_3^-, \text{ClO}_2^-$	0.33	$\theta + \frac{1}{2}\text{HO}_2^- + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{OH}^-$	$\text{HO}_2^-, \text{OH}^-$	0.88
$\theta + \frac{1}{2}\text{Ag}_2\text{O} + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Ag} + \text{OH}^-$	$\text{Ag}_2\text{O}, \text{Ag}$	0.344	$\theta + \frac{1}{2}\text{ClO}^- + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Cl}^- + \text{OH}^-$	$\text{ClO}^-, \text{Cl}^-$	0.89
			$\theta + \frac{1}{2}\text{O}_3(\text{g}) + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2(\text{g}) + \text{OH}^-$	$\text{O}_3(\text{g}), \text{O}_2(\text{g})$	1.24

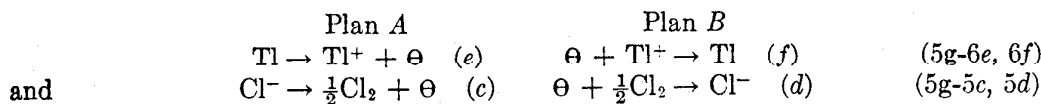
TABLE 5g-4. THEORETICAL VOLTAGES FOR BATTERY REACTIONS AT 25° IN H₂O

Reaction	ΔG° , kcal	E° , volts
$\text{MnO}_2(\text{s}) + \text{Zn}(\text{s}) + 4\text{H}^+ \rightarrow \text{Mn}^{++} + \text{Zn}^{++} + 2\text{H}_2\text{O}$	-92.054	1.996
$\text{HgO}(\text{s}) + \text{Zn}(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{Hg}(\text{l})$	-62.100	1.346
$\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	-94.204	2.042
$\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 4\text{H}^+ \rightarrow 2\text{Pb}^{++} + 2\text{H}_2\text{O}$	-73.084	1.584
$\text{Mg}(\text{s}) + 2\text{AgCl}(\text{s}) \rightarrow \text{Mg}^{++} + 2\text{Cl}^-$	-119.246	2.585
$\text{Pb}(\text{s}) + \text{Ag}_2\text{O}(\text{s}) \rightarrow \text{PbO}(\text{s}) + 2\text{Ag}(\text{s})$	-42.230	0.916
$2\text{NiOOH}(\text{s}) + \text{Cd}(\text{s}) + 2\text{H}_2\text{O} \rightarrow 2\text{Ni}(\text{OH})_2(\text{s}) + \text{Cd}(\text{OH})_2(\text{s})$	-60.056	1.302
$\text{H}_2(\text{g}) + \text{O}_2(\text{g}) + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$	-35.193	0.763
$\text{Zn}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{Zn}^{++} + 2\text{Cl}^-$	-97.884	2.122
$2\text{AgO}(\text{s}) + \text{Zn}(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{Ag}_2\text{O}(\text{s})$	-85.500	1.854
$\text{Zn}(\text{s}) + 2\text{AgCl}(\text{s}) \rightarrow \text{Zn}^{++} + 2\text{Cl}^- + 2\text{Ag}(\text{s})$	-45.396	0.984
$2\text{MnO}_2(\text{s}) + \text{Zn}(\text{s}) + 3\text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{ZnO}(\text{s}) + 2\text{Mn}(\text{OH})_4^-$	-52.531	1.139

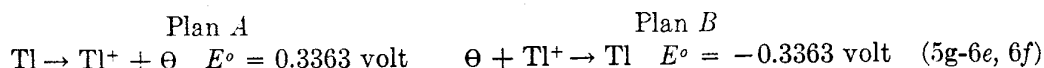
Similarly the cell



involves two opposing half reactions which are



Since E° of the cell is 1.6958 volts, the tendency of (e) is 1.6958 *greater* than that of (c) and the tendency of (f) is 1.6958 volts *less* than that of (d). To simplify the tabulation of relative half-cell emfs it has long been the custom to compare all reactions with (a) in plan A or (b) in plan B. In the same sense that the altitude of sea level is arbitrarily set equal to zero, the half-cell emfs of (a) and (b) are called zero and the emfs of all other half cells are listed relatively to (a) or to (b) depending upon the "plan" used by an author. Since the tendency of (e) is 1.6958 volts greater than that of (c), which, in turn, is 1.3595 volts less than that of (a), the appropriate entries for the table are, respectively,



It should be clearly understood that all the standard emfs of Table 5g-3 are equilibrium values and are valid strictly only when no current is passing or when the current passing is so small that resulting changes in the cell are negligible. The reversal of such a current would not affect the magnitude and, of course, could not alter the algebraic sign of the emf of a cell or half cell. The choice of plan A or plan B is an arbitrary one and has nothing to do with the direction in which current is actually passed through a given cell.

Only plan B emfs are listed here. Most electrochemists have preferred this approach, and it has been overwhelmingly recommended by the international commissions concerned with such matters. It has also been adopted in many of the most recent physical chemistry texts. In the past American physical chemists have preferred plan A and it was promoted by the extensive treatise of Professor W. B. Latimer. To use his tables one must note that Latimer's standard half-cell emfs are the negatives of the respective "electrode potentials" and that his equations must be written

TABLE 5g-6. MEAN-ACTIVITY COEFFICIENTS γ_{\pm} OF HCl IN AQUEOUS SOLUTION
(m in mole kg^{-1})

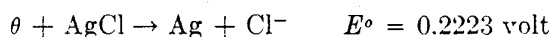
m	0°	10°	20°	25°	40°	50°	60°
0.0001	0.9890	0.9890	0.9892	0.9891	0.9885	0.9879	0.9879
0.0002	0.9848	0.9846	0.9844	0.9842	0.9833	0.9831	0.9831
0.0005	0.9756	0.9756	0.9759	0.9752	0.9741	0.9738	0.9734
0.001	0.9668	0.9666	0.9661	0.9656	0.9643	0.9639	0.9632
0.002	0.9541	0.9544	0.9527	0.9521	0.9505	0.9500	0.9491
0.005	0.9303	0.9300	0.9294	0.9285	0.9265	0.9250	0.9235
0.01	0.9065	0.9055	0.9052	0.9048	0.9016	0.9000	0.8987
0.02	0.8774	0.8773	0.8768	0.8755	0.8715	0.8690	0.8666
0.05	0.8346	0.8338	0.8317	0.8304	0.8246	0.8211	0.8168
0.1	0.8027	0.8016	0.7985	0.7964	0.7891	0.7850	0.7813
0.2	0.7756	0.7740	0.7694	0.7667	0.7569	0.7508	0.7437
0.5	0.7761	0.7694	0.7616	0.7571	0.7432	0.7344	0.7237
1.0	0.8419	0.8295	0.8162	0.8090	0.7865	0.7697	0.7541
2.0	1.078	1.053	1.024	1.009	0.9602	0.9327	0.9072
4.0	2.006	1.911	1.812	1.762			

in the reverse direction to fit plan *B*. It should also be noted that his equations are written for integral values of N but not necessarily for $N = 1$.

The Use of Table 5g-3. To calculate E° of any cell, e.g.,



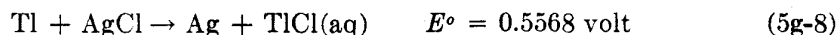
write the half-cell reaction and E° for the *right-hand* electrode



Subtract both the half-cell reaction of E° of the *left-hand* electrode



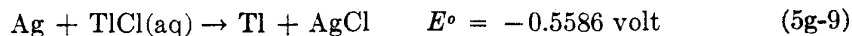
to give



or the completely equivalent form



Since E° is positive, ΔG° is negative for the reaction. Equation (5g-8) is therefore the equation for the reaction actually taking place in the cell when all activities are unity. If the cell had been written Ag, AgCl, TlCl(aq), Tl the indicated reaction would have been



The conclusions about the actual reaction and the absolute values of E° and ΔG° are unchanged.

TABLE 5g-7. DISSOCIATION CONSTANTS OF WATER AND OF ELECTROLYTES IN AQUEOUS SOLUTIONS
(Constants* are on the molality scale. *Italics* indicate maximum values)

Material	°C	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
Water.....	$K \times 10^{14}$	0.1139	0.1846	0.2920	0.4505	0.6809	1.008	1.469	2.089	2.919	4.018	5.474
Formic acid.....	$K_A \times 10^4$	1.638	1.691	1.728	1.749	1.765	<i>1.772</i>	1.768	1.747	1.716	1.685	1.650
Acetic acid.....	$K_A \times 10^5$	1.657	1.700	1.729	1.745	1.753	<i>1.754</i>	1.750	1.728	1.703	1.670	1.633
Propionic acid.....	$K_A \times 10^5$	1.274	1.305	1.326	1.336	<i>1.338</i>	1.336	1.326	1.310	1.280	1.257	1.229
n-Butyric acid.....	$K_A \times 10^5$	1.563	1.574	<i>1.576</i>	1.569	1.542	1.515	1.484	1.439	1.395	1.347	1.302
Chloroacetic acid.....	$K_A \times 10^3$	1.528	1.488	1.379	1.230
Lactic acid.....	$K_A \times 10^4$	1.287	<i>1.374</i>	1.270
Glycolic acid.....	$K_A \times 10^4$	1.334	<i>1.475</i>	1.415
Sulfuric acid.....	$K_{2A} \times 10^2$	1.80	1.36	1.01	0.75	0.56
Carbonic acid.....	$K_{1A} \times 10^7$ $K_{2A} \times 10^{11}$	2.64 2.36	3.0 [†] 2.77	3.44 3.24	3.81 3.71	4.16 4.20	4.45 4.69	4.71 5.13	4.90 5.62	5.04 6.03	5.13 6.38	5.19 6.73
Phosphoric acid.....	$K_{1A} \times 10^3$ $K_{2A} \times 10^8$	8.97 4.85 5.2 [†] 5.57 5.89 6.12	7.52 6.34 6.46 6.53 6.58 6.59	5.50 6.55
Nitric acid.....	K_A	21
Glycine.....	$K_A \times 10^3$ $K_B \times 10^5$	3.94 4.68 5.12	4.31 5.57	4.47 6.04	4.59 6.52 6.98	4.81 7.43	7.87
Alanine.....	$K_A \times 10^3$ $K_B \times 10^5$	4.47 6.90	4.57 7.47	4.66 8.08	4.71 8.61	4.74 9.10	4.76 9.60

* Letter subscripts on K indicate dissociation as acid or base, respectively; number subscripts indicate first or second dissociation. -

TABLE 5g-8. RATE CONSTANTS FOR PROTON TRANSFER REACTIONS IN H₂O AT 25°

Reaction: $A + B \xrightleftharpoons[k_b]{k_f} C + D$	$k_f, M^{-1} \text{ sec}^{-1}$	$k_b, \text{ sec}^{-1}$
$H^+ + OH^- \rightleftharpoons H_2O$	1.4×10^{11}	2.5×10^{-5}
$D^+ + OD^- \rightleftharpoons D_2O$	8.4×10^{10}	2.5×10^{-6}
$H^+ + SO_4^{--} \rightleftharpoons HSO_4^-$	1×10^{11}	1×10^9
$H^+ + F^- \rightleftharpoons HF$	1.0×10^{11}	7×10^7
$H^+ + HS^- \rightleftharpoons H_2S$	7.5×10^{10}	4.3×10^3
$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$	4.7×10^{10}	8×10^6
$H^+ + HCOO^- \rightleftharpoons HCOOH$	5×10^{10}	8.6×10^6
$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$	4.5×10^{10}	7.8×10^5
$OH^- + NH_4^+ \rightleftharpoons NH_3 \cdot H_2O$	3.4×10^{10}	6×10^5
$OH^- + C_6H_5OH \rightleftharpoons H_2O + C_6H_5O^-$	1.4×10^{10}	1.3×10^6
$OH^- + HCN \rightleftharpoons H_2O + CN^-$	3.7×10^9	5.2×10^4
$OH^- + HPO_4^{--} \rightleftharpoons H_2O + PO_4^{3-}$	2×10^9	2×10^7

TABLE 5g-9. RELATIVE APPARENT MOLAL HEAT CONTENT φL AND PARTIAL MOLAL HEAT CONTENT \bar{L}_2 OF SOLUTES IN DILUTE AQUEOUS SOLUTIONS AT 25°C (cal mole⁻¹)

m		0.0001	0.0004	0.0016	0.0064	0.0100	0.0400	0.0900
NaCl	φL	4.5	8.5	17.0	33	40	67	83
	\bar{L}_2	6.5	12.5	24.0	46	57	92	104
NaIO ₃	φL	4.0	7.5	14.0	21	21	0	
	\bar{L}_2	5.8	11.0	19.8	24	20	-41	
KCl	φL	4.5	8.5	16.0	31	38	65	77
	\bar{L}_2	6.5	12.5	24.0	46	55	82	91
KClO ₄	φL	4.3	8.0	13.0	16	14	-28	
	\bar{L}_2	6.2	11.3	16.6	13	4	-86	
Li ₂ SO ₄	φL	24	47	91	177	218	377	488
	\bar{L}_2	35	69	135	260	317	508	620
Cs ₂ SO ₄	φL	20	39	71	121	139	161	137
	\bar{L}_2	29	57	102	161	176	152	87
SrCl ₂	φL	23	46	86	161	195	332	420
	\bar{L}_2	34	66	125	232	277	443	528
SrBr ₂	φL	23	44	82	152	182	293	366
	\bar{L}_2	33	64	119	216	254	383	452
Ba(NO ₃) ₂	φL	19	36	59	72	66	-46	-223
	\bar{L}_2	27	51	75	68	37	-195	-528

TABLE 5g-10. STANDARD ENTROPIES OF MONATOMIC IONS
IN AQUEOUS SOLUTIONS AT 25°C
(Referred* to $H_2 \rightarrow 2H^+ + 2\theta$; $\Delta S^\circ = 0$; cal mole⁻¹ deg⁻¹)

Ion	\bar{S}°	Ion	\bar{S}°	Ion	\bar{S}°
Cs ⁺	31.8	Ca ⁺⁺	-13.2	Cr ³⁺	-73.5
Tl ⁺	30.4	Cd ⁺⁺	-14.6	Al ³⁺	-71.9
Rb ⁺	29.7	Mn ⁺⁺	-20	Ga ³⁺	-83
K ⁺	24.5	Cu ⁺⁺	-23.6	U ⁴⁺	-78
Ag ⁺	17.67	Zn ⁺⁺	-25.45	Pu ⁴⁺	-87
Na ⁺	14.4	Fe ⁺⁺	-27.1	I ⁻	26.14
Li ⁺	3.4	Mg ⁺⁺	-28.2	Br ⁻	19.25
Pb ⁺⁺	5.1	U ³⁺	-36	Cl ⁻	13.17
Ba ⁺⁺	3.0	Pu ³⁺	-39	F ⁻	-2.3
Hg ⁺⁺	-5.4	Gd ³⁺	-43	S ⁻	-6.4
Su ⁺⁺	-5.9	In ³⁺	-62		
Sr ⁺⁺	-9.4	Fe ³⁺	-70.1		

* This is not equivalent to the setting of S° of H^+ equal to zero; cf. Klotz (1950).

TABLE 5g-11. STANDARD ENTROPIES OF POLYATOMIC IONS
IN AQUEOUS SOLUTIONS AT 25°C
(Referred* to $H_2 \rightarrow 2H^+ + 2\theta$; $\Delta S^\circ = 0$; cal mole⁻¹ deg⁻¹)

Ion	\bar{S}°	Ion	\bar{S}°	Ion	\bar{S}°
OH ⁻	-2.5	HSO ₄ ⁻	30.3	PO ₄ ³⁻	-52
ClO ⁻	10.0	H ₂ AsO ₄ ⁻	28	AsO ₄ ³⁻	-34.6
HCO ₂ ⁻	21.9	H ₂ PO ₄ ⁻	21.3	HF ₂ ⁻	0.5
ClO ₂ ⁻	24.1	HN ₂ O ₄ ⁻	34	BF ₄ ⁻	40
NO ₂ ⁻	20.0	BeO ₂ ⁻	-27	SiF ₆ ⁻	-12
NO ₃ ⁻	35.0	CO ₃ ⁻	-12.7	CuCl ₂ ⁻	49.2
ClO ₃ ⁻	39.0	SO ₃ ⁻	-7	AuCl ₄ ⁻	61
BrO ₃ ⁻	38.5	SO ₄ ⁻	4.1	PdCl ₄ ⁻	36
IO ₃ ⁻	28.0	SeO ₄ ⁻	5.7	PtCl ₄ ⁻	42
ClO ₄ ⁻	43.2	N ₂ O ₂ ⁻	6.6	PtCl ₆ ⁻	52.6
MnO ₄ ⁻	45.4	C ₂ O ₄ ⁻	10.6	I ₃ ⁻	41.5
HCO ₃ ⁻	22.7	Cr ₂ O ₇ ⁻	51.1	Ag(CN) ₂ ⁻	49
HSO ₃ ⁻	26	HPO ₄ ⁻	-8.6	Ni(CN) ₄ ⁻	33
SH ⁻	14.9	HAsO ₄ ⁻	0.9	FeCl ⁺⁺	-22

* This is not equivalent to the setting of S° of H^+ equal to zero; cf. Klotz (1950).

Effect of Concentration. For the case where the reactants are not at unit activity, the Nernst equation is used:

$$E = E^\circ - \frac{RT}{NF} \log \pi a_i^{v_i} \quad (5g-10)$$

For the example above ($N = 1$, 25°C) this reduces to

$$E = 0.5586 - 0.059 \log \frac{a_{Ag} a_{TlCl}}{a_{Tl} a_{AgCl}} \quad (5g-11)$$

The activities of pure solids and liquids are conventionally taken as unity so that

$$a_{\text{Ag}} = a_{\text{AgCl}} = a_{\text{Tl}} = 1$$

and

$$E = 0.5586 - 0.05915 \log a_{\text{TlCl}}$$

In many cases the activities of the dissolved species (e.g., TlCl above) are approximated by their molar concentrations.

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