Electromotive Force Series in Molten Salts

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Literature values of standard potentials of cells employing a molten salt electrolyte have been critically reviewed and are reported in tabular e.m.f. series form.

THIS REVIEW is a selective compilation of electromotive force series determined in molten salts. The number of reliable, systematic experimental determinations of such series is comparatively small. Although a considerable body of e.m.f. data has been accumulated, much is unreliable or taken under conditions which do not permit its reduction to series and is not included, but can be obtained by referring to recent reviews (*8, 31, 38, 43*).

The series reported here, unless otherwise stated, have been established by equilibrium e.m.f. measurements using compartmented cells, which is probably the most accurate method of determining potentials. In this type of cell, porous plugs or frits are used to prevent mixing of the contents of the various compartments in a manner analogous to aqueous salt bridges. When the solvent salt is the same in all compartments and the concentrations of solutes are low, the liquid junction potentials across the compartment separators are at most one or two millivolts and can be neglected. Concentrations of solutes below about 0.1 molal have been used in the molten salt e.m.f. measurements reported here, and liquid junction potentials are negligible at these low concentrations. Glass membranes can be used to maintain large differences in melt level and/or composition between different compartments. Although they are better than porous plugs in this respect, they invariably introduce unknown, but probably not negligible, junction potentials at the melt-membrane interfaces, and for this reason should be used only as secondary reference electrodes. Except for the LiCl-KCl eutectic where specifically noted, such data are not included.

No generally accepted reference electrode is available for molten salt studies; the subject has been reviewed (*2, 8, 35*). Although workers in the same solvent salt do not necessarily employ the same reference electrode, each usually measures the e.m.f. of the reference electrodes employed by others with respect to his own, permitting the combination of e.m.f. data obtained by several workers into a single series. No standard temperature for electromotive force series in molten salts has been established and, owing to the wide range of melting points of the solvent salts used, it is unlikely that this will be possible. However, different investigators employing the same solvent have generally taken pains to obtain data at the same temperature.

The tables list half-cell potentials which have been experimentally determined or which have been calculated from experimentally determined values by addition or subtraction of the appropriate free energies. The standard potentials in the tables are given for different concentration scales; the notations E^0_M, E^0_m, and E^0_X refer to the molarity, molality, and mole fraction scales, respectively. In some cases, the available data are insufficient to permit the calculation of standard potentials on all three scales. The values for the precision of these potentials are, unless otherwise stated, those given by the original authors. The precision of potentials calculated by the present author is the square root of the sum of squares of the reported errors in the experimental data. The potentials are given in volts and the sign is appropriate for the half-reaction written as a reduction, as required by the I.U.P.A.C. Stockholm convention (*36*).

The soluble species is generally identifiable only by its oxidation state. In dilute solutions of metal ions in pure molten salts the probable nature of the solute species is a metal ion of the appropriate charge coordinated to four or six anions. Spectrophotometric studies (*21*) have indicated the probable nature of these species, but such data are considered beyond the scope of this article.

The choice of standard states for the establishment of standard electromotive force series in molten salts is to a large extent determined by the manner in which the measurements are made. The usual thermodynamic standard state of the pure substance in its most stable form under one atmosphere pressure at the temperature of measurement can be employed for metals and gases. However, the choice of a standard state for any species which is included in the solvent or is linked to the solvent by a chemical equilibrium—e.g., chloride ions in molten alkali chlorides—cannot be independent of the choice of the solvent itself; thus the standard state for such a species is chosen as the actual state of the species in the specific solvent molten salt under one atmosphere pressure at the temperature of measurement. The definition of standard state with regard to solute ionic species, such as Fe(II), is more complex. The partial free energy of such a species, μ_+, is given by $\mu_+ = RT \ln C_+ + RT \ln \gamma_+ + \mu^0_+$ where C_+ is the concentration of the $M(n)$ ionic species of oxidation state n, γ_+ is its activity coefficient, and μ^0_+ is its standard partial free energy. Since $\mu = -nFE$, this equation becomes $E^0_+ = E_+ - RT/nF \ln C_+ - RT/nF \ln \gamma_+$. If the other species taking part in the half-reaction for the couple are included, this equation is the well-known Nernst equation. The cell generally is constructed so that these other species are present in their standard states, so that $E_+ = E$ and $E^0_+ = E^0$. If γ_+ is defined such that γ_+ approaches zero as C_+ approaches unity, then $E^0 = E - RT/nF \ln C_+$. A linear relationship between the measured values of E and $\ln C_+$ is generally observed, within experimental error, whenever C_+ is less than approximately 0.1 molal; this indicates that γ_+ remains unity over this concentration range. The calculation of E^0 from this relationship, however, requires that $E = E^0$ when C_+ is unity on the concentration scale chosen. Thus, the standard state of an ionic species is one which is physically unreal, for it is a solution of unit concentration—e.g., mole fraction—which has certain of the thermodynamic properties of an infinitely dilute solution. The value of E^0 is usually calculated from several sets of $E - \ln C_+$ data, and the error assigned is usually the standard deviation in E^0. These E^0 values are experimentally significant only in solutions of concentrations below about 0.1 molal, since γ_+ does not remain unity at higher concentrations.

DATA

The most extensive electromotive force series compiled to date is in the lithium chloride–potassium chloride eutectic—59 mole % LiCl, m.p. 352° C.—at 450° C. (Table I). The useful potential range of this melt is about 3.6 volts. The U(III)-U(0) couple has probably been the most extensively studied; the value listed is that of Gruen and Osteryoung (*22*) which is in good agreement with the final

Table I. Electromotive Force Series LiCl–KCl Eutectic, 450° C.

Couple	E^0_M	E^0_m	E^0_X	Precision	Reference
Li(I)-Li(0)	−3.304	−3.320	−3.410	0.002	*(30)*
La(III)-La(0)	−2.877	−2.882	−2.912	0.005	*(59)*^{a}
Y(III)-Y(0)	−2.859	−2.864	−2.894	0.005	*(59)*^{a}
Nd(III)-Nd(0)	−2.819	−2.824	−2.854	0.005	*(59)*^{a}
Gd(III)-Gd(0)	−2.788	−2.793	−2.823	0.005	*(59)*^{a}
H_2(g)-H-	−2.80	−2.98	−3.11	0.06	text
Mg(II)-Mg(0)	−2.580	−2.580	−2.580	0.002	*(30)*
Pu(III)-Pu(0)	−2.535	−2.540	−2.570	0.002	*(6)*
Th(IV)-Th(0)	−2.359	−2.366	−2.411	0.004	*(58)*^{a}
U(III)-U(0)	−2.218	−2.223	−2.253	0.005	*(22)*
Zr(IV)-Zr(II)	−1.864	−1.880	−1.970	0.01	*(4)*^{b}
Mn(II)-Mn(0)	−1.849	−1.849	−1.849	0.008	*(30)*
Hf(IV)-Hf(0)	−1.827	−1.835	−1.880	0.01	*(4)*
Zr(IV)-Zr(0)	−1.807	−1.815	−1.860	0.01	*(4)*
Al(III)-Al(0)	−1.762	−1.767	−1.797	0.009	*(30)*
Zr(II)-Zr(0)	−1.75	−1.75	−1.75	0.01	*(4)*^{a}
Ti(II)-Ti(0)	−1.74	−1.74	−1.74	0.01	*(3)*
Ti(III)-Ti(0)	−1.60	−1.61	−1.64	0.02	*(3)*^{b}
Zn(II)-Zn(0)	−1.566	−1.566	−1.566	0.002	*(30)*
V(II)-V(0)	−1.533	−1.533	−1.533	0.01	*(32)*
Tl(I)-Tl(0)	−1.476	−1.460	−1.370	0.002	*(30)*
Ti(III)-Ti(II)	−1.32	−1.34	−1.43	0.02	*(3)*
Cr(II)-Cr(0)	−1.425	−1.425	−1.425	0.003	*(30)*
Cd(II)-Cd(0)	−1.316	−1.316	−1.316	0.002	*(30)*
Fe(II)-Fe(0)	−1.172	−1.172	−1.172	0.005	*(30)*
U(IV)-U(0)	−1.121	−1.128	−1.190	0.011	*(22)*^{b}
U(IV)-U(III)	−1.144	−1.160	−1.250	0.01	*(24)*
Pb(II)-Pb(0)	−1.101	−1.101	−1.101	0.002	*(30)*
Sn(II)-Sn(0)	−1.082	−1.082	−1.082	0.002	*(30)*
Co(II)-Co(0)	−0.991	−0.991	−0.991	0.003	*(30)*
Cu(I)-Cu(0)	−0.957	−0.941	−0.851	0.004	*(30)*
Ga(III)-Ga(0)	−0.84	−0.84	−0.88	0.02	*(30)*
In(III)-In(0)	−0.800	−0.805	−0.835	0.009	*(30)*
Ni(II)-Ni(0)	−0.795	−0.795	−0.795	0.002	*(30)*
V(III)-V(0)	−0.760	−0.766	−0.796	0.01	*(32)*^{b}
V(III)-V(II)	−0.748	−0.764	−0.854	0.002	(32)
Ag(I)-Ag(0)	−0.743	−0.727	−0.637	0.002	*(30)*
HCl(g)-H_2(g)	−0.694	−0.710	−0.800	0.005	*(33)*
Cr(III)-Cr(0)	−0.650	−0.655	−0.685	0.01	*(30)*^{b}
Sb(III)-Sb(0)	−0.635	−0.640	−0.670	0.002	*(30)*
Bi(III)-Bi(0)	−0.635	−0.640	−0.670	0.01	*(29, 34)*
Mo(III)-Mo(0)	−0.603	−0.608	−0.638	0.002	*(44)*^{a}
Cr(III)-Cr(II)	−0.525	−0.541	−0.631	0.01	*(30)*
Hg(II)-Hg(0)	−0.5	−0.5	−0.5	estimated	*(30)*
Cu(II)-Cu(0)	−0.448	−0.448	−0.448	0.003	*(30)*^{b}
Fe(III)-Fe(0)	−0.362	−0.367	−0.397	0.006	*(32)*^{b}
UO_2(VI)-UO_2(IV)	−0.285	−0.285	−0.285	0.005	*(24)*
Pd(II)-Pd(0)	−0.214	−0.214	−0.214	0.002	*(30)*
I_2-I^-	−0.207	−0.254	−0.525	0.008	*(30)*
Rh(III)-Rh(0)	−0.196	−0.201	−0.231	0.004	*(33)*
Ir(III)-Ir(0)	−0.057	−0.062	−0.092	0.002	*(33)*
Pt(II)-Pt(0)	0.000	0.000	0.000	defined	*(30)*
Cu(II)-Cu(I)	+0.061	+0.045	−0.045	0.002	*(30)*
Fe(III)-Fe(II)	+0.086	+0.070	−0.020	0.003	*(32)*
Br_2-Br^-	+0.177	+0.130	−0.141	0.002	*(32)*
Au(I)-Au(0)	+0.205	+0.221	+0.311	0.008	*(30)*
Cl_2-Cl^-	+0.322	+0.306	+0.216	0.002	*(32)*

^{a}Extrapolated from values measured over a range of higher temperatures. ^{b}Value calculated from experimental free energies.

value accepted by Inman and Bockris *(25)*. These values and those of Inman *et al.* *(26)* have been critically discussed by Partridge *(42)*. The Pu(III)-Pu(0) potential is calculated by the present author from the data of Campbell and Leary *(6)*, and replaces the estimate of Gruen and Osteryoung *(22)*. The values of Baboian, Hill, and Bailey *(3)* for titanium are the authors' extrapolations from data taken at 500° to 600° C. to resolve a discrepancy between earlier studies of Menzies *et al.* *(40)* and Smirnov, Ivanovskii, and Logenov *(48)* in this eutectic. The potential of the Zr(IV)-Zr(0) couple given is that of Baboian, Hill, and Bailey *(4)*, which is in agreement with the value calculated by the present author from the earlier data of Yang *et al.* *(57-59)*, $E^0_m = -1.807 \pm 0.031$ v. However, the study of zirconium potentials is complicated by temperature-dependent equilibria between Zr(IV), Zr(II), and Zr(0) which give rise to mixed potentials. The work of Smirnov and coworkers *(28, 45)* on zirconium, both in this melt and in NaCl-KCl, appears particularly suspect in this regard. An additional source of error for the Zr(IV) couples could be volatilization of $ZrCl_4$ from the melts. Very similar arguments hold for hafnium. The value of Baboian, Hill, and Bailey (*4*) is given. Their value is about 60 mv. less negative than that calculated by the present author from the data of Yang and Hudson (*59*), and is preferred since no temperature correction is necessary.

The data of Yang and Hudson (*59*) and Smirnov and Chukreev (*46, 47*) on beryllium in this melt appears to involve mixed potentials, and hence these potentials are not included. Caton and Freund (*7*) have redetermined the standard potentials of Cr(III)-Cr(II) and V(III)-V(II) by a controlled-potential coulometric technique and give values of -0.539 ± 0.001 and -0.740 ± 0.001 v., respectively, in good agreement with the values given in Table I. These authors were unable to determine a standard potential for a niobium couple, apparently because anodization of the metal produced a mixture of oxidation states. Less precise data obtained from pill cells by Panzer (*41*) are generally in agreement with the values reported in Table I. The reported data of Yang *et al.* (*58, 59*) were corrected by the present author for temperature, chlorine pressure, reference electrode, and solute concentration. Inasmuch as these calculations assume that the experimental temperature coefficients of the cell potentials are valid 50° below the lowest temperature at which measurements were made and only a few points are given for each couple, the actual error may be considerably greater than that assigned. Another significant source of error in these particular cases could be the use of borosilicate glass membranes to separate the electrode compartments; the authors (*30*) claim, however, that this error should not exceed 5 mv. The value for the $H_2(g)$-H^- couple is estimated by the present author from unpublished data of Plambeck and Elder and of C.F. Johnson obtained at Argonne National Laboratory.

A standard potential series has been established, primarily by Flengas and coworkers (*11*), in equimolar NaCl-KCl [m.p. approx. 658° C. (*1*)] over the temperature range 700° to 900° C. (Table II). The useful potential range of this melt has not been determined but is probably very similar to that of the LiCl-KCl eutectic. These potentials, extrapolated to 450° C., are in substantial agreement with those presented in Table I (*17*). The zirconium work of Smirnov *et al.* (*28, 45*) has been discussed by Swaroop and Flengas (*52*). There is a significant discrepancy between the uranium potentials determined by Smirnov and Skiba (*49*) and Flengas (*10*).

An electromotive force series has been established in sodium fluoride-potassium fluoride eutectic—40 mole % NaF—at 850° C. by Grjotheim (*20*). Although these values were originally given with respect to Ni(II)-Ni(0), they are given with respect to Ag(I)-Ag(0) in Table III. The precision is less than that of the other series given here; this is due partly to the disintegration of the porous plug used in the presence of the fluoride, reducing the time during which measurements could be made to one to two hours at most. The useful potential range of this melt is not known but is probably about three volts.

Gaur and Behl (*5, 18, 19*) have established an e.m.f. series in molten magnesium chloride-sodium chloride-potassium chloride eutectic—50 mole % $MgCl_2$, 20 mole % KCl, m.p. 396° C.—at 475° C. (Table IV). The useful potential range of this melt is about three volts.

One of the methods used to determine decomposition and deposition potentials in molten salts is the method of current-voltage curves, in which the cell potential is studied as a function of the applied current. At low currents the cell potential shifts rapidly with increasing current; eventually a region is reached in which the potential in-

Table II. Electromotive Force Series Equimolar NaCl–KCl, 700° to 900° C.

Couple	E^0_X, 700° C.	E^0_X, 800° C.	E^0_X, 900° C.	Precision[a]	Reference
Th(IV)-Th(0)	−1.642	−1.598	. . .	0.002	(*51*)
U(III)-U(0)	−1.554	−1.519	. . .	0.002	(*10*)
Zr(II)-Zr(0)	−1.355	. . .	. . .	0.008	(*52*)
U(IV)-U(0)	−1.285	−1.252	. . .	0.003	(*10*)[b]
Zr(III)-Zr(0)	−1.226	. . .	. . .	0.012	(*52*)
Mn(II)-Zr(0)	−1.206	−1.190	−1.172	not given	(*16, 17*)
Ti(II)-Ti(0)	−1.106	−1.076	. . .	0.001	(*9*)
Ti(III)-Ti(0)	−1.046	. . .	. . .	0.015	(*9*)[c]
Zr(IV)-Zr(0)	−1.018	. . .	. . .	0.012	(*52*)[b]
Zr(III)-Zr(II)	−0.968	. . .	. . .	0.020	(*52*)
Ti(III)-Ti(II)	−0.910	. . .	. . .	0.015	(*9*)[c]
Zn(II)-Zn(0)	−0.860	−0.835	−0.810	not given	(*13, 17*)
Cr(II)-Cr(0)	−0.758	−0.740	−0.728	not given	(*15, 17*)
Ti(IV)-Ti(0)	−0.697	. . .	. . .	0.033	(*9*)[c]
Tl(I)-Tl(0)	−0.665	. . .	. . .	not given	(*15, 17*)
Cd(II)-Cd(0)	−0.620	−0.580	. . .	not given	(*14, 17*)
Fe(II)-Fe(0)	−0.520	−0.510	−0.498	not given	(*15, 17*)
U(IV)-U(III)	−0.483	−0.459	. . .	0.002	(*10*)
Cr(III)-Cr(0)	−0.425	−0.385	−0.345	not given	(*15, 17*)
Pb(II)-Pb(0)	−0.390	−0.376	−0.355	not given	(*13, 17*)
Sn(II)-Sn(0)	−0.370	−0.354	−0.340	not given	(*15, 17*)
Co(II)-Co(0)	−0.324	−0.300	−0.275	not given	(*12, 17*)
Cu(I)-Cu(0)	−0.260	−0.256	−0.260	not given	(*15, 17*)
Cr(III)-Cr(II)	−0.241	−0.325	−0.421	not given	(*15, 17*)
Ni(II)-Ni(0)	−0.140	. . .	. . .	not given	(*13, 17*)
Ag(I)-Ag(0)	0.0	0.0	0.0	defined	(*12, 17*)
Cu(II)-Cu(0)	+0.170	+0.180	+0.192	not given	(*15, 17*)[b]
Ti(IV)-Ti(III)	+0.350	. . .	. . .	0.030	(*9*)
UO_2^{++}-UO_2	+0.468	+0.500	+0.553	0.004	(*50*)
Cu(II)-Cu(I)	+0.600	+0.616	+0.644	not given	(*15, 17*)
Cl_2-Cl^-	+0.845	+0.820	+0.795	not given	(*12, 17*)

[a] Precision where not given probably 2 to 3 mv. [b] Value calculated from experimental free energies. [c] Value at 670° C.

Table III. Electromotive Force Series NaF–KF Eutectic, 850° C.

Couple	E^0_x	Precision
Al(III)-Al(0)	−2.14	0.10
Mn(II)-Mn(0)	−1.68	0.03
Cr(III)-Cr(0)	−1.34	0.03
Co(II)-Co(0)	−0.71	0.03
Ni(II)-Ni(0)	−0.64	0.03
Fe(III)-Fe(0)	−0.52	0.03
Cu(I)-Cu(0)	−0.16	0.03
Ag(I)-Ag(0)	0.0	defined

creases linearly with applied current. The line is extrapolated back to zero current and the potential at zero current is taken as the decomposition or deposition potential. Deposition potentials measured in a two-electrode cell are open to question since the amount of current applied to the cell may be sufficient to polarize the reference electrode. Deposition potentials measured in a three-electrode cell, in which current flows between an indicator electrode and a counterelectrode while the cell potential is measured between the indicator electrode and a reference electrode from which essentially no current is being drawn, are not open to this objection. A considerable body of data on decomposition and deposition potentials has been reviewed (*8*); in most cases, however, it is difficult if not impossible to utilize these data to construct electromotive force series since the experimental conditions have varied widely. Emphasis has been placed upon the decomposition potentials of pure fused salts. Hamer, Malmberg, and Rubin (*23*) have calculated the e.m.f. values of reversible galvanic cells of the type $M/MX_n/X_2$ from thermodynamic data as functions of temperature, and certain experimental decomposition potentials of pure halides are in good agreement with their calculations.

The data of Yntema and coworkers (*39, 53-56*) on the deposition and decomposition potentials of metals in aluminum halide–alkali halide solvents can be used to establish e.m.f. series in these solvents, whose useful potential range is two volts or less. Since these studies were made by the method of current-voltage curves in three-electrode cells the potentials reported are comparable to equilibrium potential measurements. The experiments were carried out in 1.0 mole % solutions of metal compound in the solvent; these solutions are probably sufficiently dilute to permit the calculation of E^0 values on the mole fraction scale. The precision assigned is that given for the original measured potentials and does not include any error introduced in the extrapolation to E^0_X.

In some cases, the nature of the electrochemically active species was not established; the same potentials were observed for WO_3 and $K_3W_2Cl_9$, and for MoO_3 and K_3MoCl_6, solutions. The gallium, tellurium, bismuth, and antimony potentials were determined using only solutions of oxygenated species, and these electrochemical reactions are unlikely to involve only chloride-solvated metal ions. In some cases, the authors were not certain as to the oxidation state of a species involved in the electrochemical reaction—indicated by a question mark in the tables. Thallium, vanadium, manganese, titanium, tantalum, germanium, and niobium could not be deposited at potentials lower than that of aluminum. The hydrogen potentials reported are those for hydrogen evolution from a solution of one mole % water in the solvent and probably correspond to the half-reaction $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$; they are not comparable with the hydrogen–hydrogen chloride potential determined in anhydrous LiCl-KCl eutectic (*33*).

The most extensive series established by these authors was in an aluminum–sodium–potassium chloride mixture—66 mole % $AlCl_3$, 20 mole % NaCl—at 218° C. (Table V). The potential of the Al(III)–Al(0) couple is that of an aluminum bar immersed in the solvent; the standard and observed potentials are the same for this couple since the activity of aluminum ion is fixed by the choice of solvent. For ease in comparison with other series, the potentials are given with reference to the chlorine-chloride couple rather than the aluminum reference actually used. The data can be reconverted to the original Al(III)–Al(0) reference for comparison with the data in Table VI, which

Table IV. Electromotive Force Series $MgCl_2$–NaCl–KCl Eutectic, 475° C.

Couple	E^0_m	E^0_x	Precision	Reference
Mg(II)-Mg(0)	−2.646	−2.646	not given	(*40*)
U(III)-U(0)[a]	−2.22	−2.25	0.01	(*14*)
U(IV)-U(0)[a]	−1.97	−2.01	0.01	(*14*)[b]
Al(III)-Al(0)	−1.886	−1.914	0.008	(*40*)
Mn(II)-Mn(0)	−1.794	−1.794	0.007	(*40*)
Zn(II)-Zn(0)	−1.550	−1.550	0.002	(*40*)
Cr(II)-Cr(0)	−1.396	−1.396	0.004	(*39*)
Cd(II)-Cd(0)	−1.312	−1.312	not given	(*40*)
U(IV)-U(III)[a]	−1.21	−1.30	0.01	(*14*)
Fe(II)-Fe(0)	−1.183	−1.183	0.002	(*39*)
Pb(II)-Pb(0)	−1.171	−1.171	0.001	(*40*)
Sn(II)-Sn(0)	−1.147	−1.147	0.001	(*40*)
Cr(III)-Cr(0)	−1.131	−1.159	0.005	(*39*)[b]
Co(II)-Co(0)	−0.970	−0.970	0.004	(*40*)
Cu(I)-Cu(0)	−0.947	−0.863	0.001	(*39*)
Fe(III)-Fe(0)	−0.852	−0.880	0.004	(*39*)[b]
Ni(II)-Ni(0)	−0.792	−0.792	0.001	(*40*)
Ag(I)-Ag(0)	−0.763	−0.680	0.004	(*40*)
Sb(III)-Sb(0)	−0.745	−0.773	0.01	(*40*)
Bi(III)-Bi(0)	−0.626	−0.654	0.003	(*40*)
Cr(III)-Cr(II)	−0.602	−0.685	0.003	(*39*)
Cu(II)-Cu(0)	−0.519	−0.519	0.001	(*39*)[b]
Fe(III)-Fe(II)	−0.190	−0.274	0.004	(*39*)
Cu(II)-Cu(I)	−0.091	−0.175	0.001	(*39*)
Pt(II)-Pt(0)	0.000	0.000	defined	(*38-40*)
Au(I)-Au(0)	+0.193	+0.277	0.003	(*40*)

[a] Value at 450° C. [b] Value calculated from experimental free energies.

Table V. Electromotive Force Series $AlCl_3$–NaCl–KCl Mixture, 218° C.

Couple	$E,_{x=0.01}$	E^0_x	Precision
Al(III)-Al(0)	−2.09	−2.09	0.04
Cr(II)-Cr(0)	−1.93	−1.83	0.02
Ga(III)-Ga(0)[a]	−1.89	−1.83	0.04
Zn(II)-Zn(0)	−1.85	−1.75	0.03
Mo(III)-Mo(0)	−1.78	−1.72	0.04
Cd(II)-Cd(0)	−1.73	−1.63	0.02
Pb(II)-Pb(0)	−1.73	−1.63	0.02
W(III)-W(0)	−1.70	−1.64	0.04
Fe(II)-Fe(0)	−1.62	−1.52	0.04
Sn(II)-Sn(0)	−1.60	−1.50	0.03
Bi(III)-Bi(0)	−1.58	−1.52	0.03
Cu(I)-Cu(0)	−1.47	−1.28	0.03
Ag(I)-Ag(0)	−1.43	−1.24	0.03
Co(II)-Co(0)	−1.40	−1.30	0.02
Ni(II)-Ni(0)	−1.29	−1.19	0.02
Hg(I)-Hg(0)	−1.18	−0.99	0.02
Sb(III)-Sb(0)	−1.14	−1.08	0.02
As(III)-As(0)	−1.09	−1.03	0.04
H_2O-H_2	−1.04	−0.85	0.02
Te(II)[a]-Te(0)	−1.02	−0.92	0.02
Cl_2-Cl^-	0.00	0.00	defined

[a] Uncertainty as to oxidation state.

Table VI. Electromotive Force Series, Aluminum Halide–Alkali Halide Mixtures, 218° C.

Couple	$E,^a{}_{x=0.01}$	$E,^b{}_{x=0.01}$
Al(III)-Al(0)	0.00	0.00
Zn(II)-Zn(0)	+0.05	. . .
Pb(II)-Pb(0)	+0.17	. . .
Bi(III)[d]-Bi(0)	+0.31	. . .
Ag(I)-Ag(0)	+0.37	+0.58
Cu(I)-Cu(0)	+0.41	. . .
Hg(I)-Hg(0)[d]	+0.66	+0.85
Hg(II)-Hg(I)[d]	+1.02	+1.04
H_2O-H_2	+1.05	. . .
Br_2-Br^-	+1.61	+1.71[c]

[a] $AlBr_3$ (66 mole %), NaBr (20 mole %), KBr (14 mole %). [b] $AlCl_3$ (66 mole %), NaBr (20 mole %), KBr (14 mole %). [c] Probably a mixed chlorine-bromine evolution potential. [d] Uncertainty as to oxidation state.

contains the series established in other aluminum halide-alkali halide melts at this temperature, by subtraction of the values given from that of Al(III)-Al(0).

Two electromotive force series have been established in molten sulfates. A series has been established by Liu (*37*) in lithium sulfate-potassium sulfate eutectic—80 mole % Li_2SO_4, m.p. 535° C.—at 625° C. (Table VII). A second series was established in molten lithium sulfate-sodium sulfate-potassium sulfate eutectic—78 mole % Li_2SO_4, 8.5 mole % Na_2SO_4, m.p. 512° C.—at 575° C. by Johnson and Laitinen (*27*) (Table VIII). The limiting anodic and cathodic processes in sulfate melts are the oxidation and reduction of sulfate ions, respectively, and the useful range of potentials is less than three volts.

Table VII. Electromotive Force Series, Li_2SO_4–K_2SO_4, 625° C.

Couple	E^0_m, Volts	Precision
Cu(I)-Cu(0)	−0.202	0.003
Cu(II)-Cu(0)	−0.075	0.004[a]
Ag(I)-Ag(0)	0.00	defined
Cu(II)-Cu(I)	+0.051	0.003
Rh(III)-Rh(0)	+0.387	0.003
Pd(II)-Pd(0)	+0.541	0.003

[a] Value calculated from experimental free energies.

Table VIII. Electromotive Force Series, Li_2SO_4–Na_2SO_4–K_2SO_4 Eutectic, 575° C.

Couple	E^0_M	E^0_m	E^0_X	Precision
Co(II)-Co(0)[a]	−0.662	−0.689	−0.764	0.017
Cu(I)-Cu(0)	−0.220	−0.220	−0.220	0.004
Cu(II)-Cu(0)	−0.055	−0.082	−0.060	0.006[b]
Ag(I)-Ag(0)	0.0	0.0	0.0	defined
Cu(II)-Cu(I)	+0.110	+0.055	−0.099	0.004
Rh(III)-Rh(0)	+0.407	+0.370	+0.267	0.004
Pd(II)-Pd(0)	+0.546	+0.518	+0.441	0.004

[a] Value measured at 550° C. [b] Value calculated from experimental free energies.

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Entropies of the Aqueous Zn^{+2}, Cd^{+2}, Hg^{+2}, and Hg_2^{+2} Ions

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Thermochemical and equilibrium data in the literature were used to calculate partial molal entropies for the aqueous Zn^{+2}, Cd^{+2}, Hg^{+2}, and Hg_2^{+2} ions. Several paths were considered in calculating each entropy value. Average values are: $\bar{S}^\circ_2 = -26.0 \pm 1.4, -18.9 \pm 1.8, -5.4 \pm 1.5$, and 18.8 ± 2.0 cal. deg.$^{-1}$ mole^{-1} for the aqueous Zn^{+2}, Cd^{+2}, Hg^{+2}, and Hg_2^{+2} ions, respectively. The value for the Cd^{+2} ion is slightly lower than previous literature values. Those for the other ions substantiate values in the literature. "Best" values were chosen for the entropies of the aqueous ions and were combined with free energy data to calculate $\Delta H^\circ_f = -36.6, -18.3, 41.3$, and 40.1 kcal. mole^{-1} for the aqueous Zn^{+2}, Cd^{+2}, Hg^{+2}, and Hg_2^{+2} ions, respectively.

FOR a forthcoming review (*6*) of the thermodynamics and thermochemistry of the transition metal ions and their compounds we have reviewed literature data for the aqueous Zn^{+2}, Cd^{+2}, Hg_2^{+2}, and Hg^{+2} ions. Accurate heats and free energies of formation, and partial molal entropies for these species are necessary if the many solution equilibria and thermochemical studies, extant in the literature, are to be useful in calculating the thermodynamic properties for compounds and aqueous species involving these ions.

The partial molal entropies are of particular interest, since many such compounds, particularly of Zn^{+2} and Cd^{+2}, crystallize from their saturated solutions as hydrates—e.g., $CdBr_2 \cdot 4H_2O$ (c). "Third-law" entropies, based on low-temperature calorimetric studies, have been determined for only a few such hydrates (*12*), and the remaining entropies must be derived by "second-law" methods or be estimated. Of the estimation procedures available, that of Latimer (*14*) is deservedly popular and produces entropies that are generally within 2 to 3 cal. deg.$^{-1}$ mole^{-1} of experimental values. In compiling data tables for many compounds of a single element, there is no way of determining the internal consistency of such estimated entropies. "Second-law" entropies, based on a common partial molal entropy, have a built-in consistency, and are perhaps more useful for such tabulations. An example of such a "second-law" determination is indicated below for $ZnSO_4 \cdot 7H_2O$ (c).

Stephenson (*29*) has reviewed literature equilibrium and thermochemical data, and concludes that $\Delta S^\circ_1 = 2.3$ cal. deg.$^{-1}$ mole^{-1}.

$$ZnSO_4 \cdot 7H_2O = Zn^{+2} + SO_4^{-2} + 7H_2O \qquad (1)$$

This datum, the partial molal entropies of Zn^{+2} and SO_4^{-2} ions (*12*) and the entropy of H_2O permit a calculation of $S^\circ = 93.4$ cal. deg.$^{-1}$ mole^{-1} for the heptahydrate. The "third-law" value (*12*) is 92.9 cal. deg.$^{-1}$ mole^{-1}.

Partial molal entropies are generally derived by one of two methods. The first is to derive an entropy increment from equilibrium and thermochemical data at a single temperature, $\Delta S^\circ_T = (\Delta H^\circ_T - \Delta G^\circ_T)/T$, and then a partial molal entropy (or more properly the sum of two partial molal entropies) by reversal of the procedure used for $ZnSO_4 \cdot 7H_2O$. The second method depends on evaluating an entropy increment from the temperature dependence of equilibrium data alone. This is most often achieved from e.m.f. studies, at several temperatures, for a cell reacting, in the case of Zn^{+2}, as $Zn + 2H^+ = Zn^{+2} + H_2$. The entropy increment, $\Delta S^\circ = nF\ (dE^\circ/dT)$, the entropies of Zn and H_2, and that of H^+ (assigned as zero