

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

**STANDARD POTENTIALS OF AMALGAM
ELECTRODES IN AQUEOUS SOLUTIONS,
TEMPERATURE COEFFICIENTS AND
ACTIVITY COEFFICIENTS OF METALS
IN MERCURY**

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*Membership of the Commission during the preparation of this report (1981–83) was as follows:

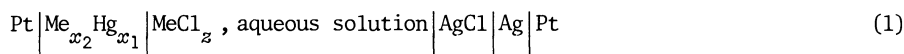
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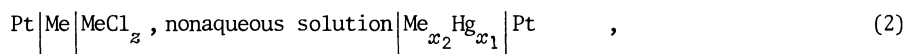
Standard potentials of amalgam electrodes in aqueous solutions, temperature coefficients, and activity coefficients of metals in mercury

1. INTRODUCTION

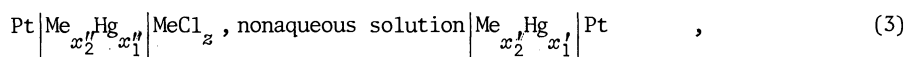
The sparse, pioneering data on standard potentials and activity coefficients of amalgams available before about 1970 (refs.1-10) have been supplemented, or redetermined, during the last decade through systematic research on dilute amalgams of the alkali metals (refs.11-17), the alkaline earth metals (refs.18-21), Group IIB metals (refs.22,23), and Group IIIA metals (refs. 24-26), based on reversible e.m.f. measurements on the general cell:



These measurements were frequently supplemented by reversible e.m.f. measurements on metal concentration cells of the types:



or



where $x_2 = 1 - x_1$, $x_2' > x_2$ and $x_1' < x_1$ (subscripts 1 and 2 will be used henceforth to denote the mercury and the metal Me in the amalgam, respectively).

For these amalgams the standard aqueous potentials, $E_{\text{Me}^{z+}/\text{Me+Hg}}^{\circ}$, and the corresponding temperature coefficients, $dE_{\text{Me}^{z+}/\text{Me+Hg}}^{\circ}/dT$, were determined, usually over the range 283 to 343 K (cf. Table 1). Standard thermodynamic functions for the amalgam species Me+Hg and for the amalgamation reactions were calculated from these data (cf. Table 1). In addition, the standard aqueous electrode potentials, $E_{\text{Me}^{z+}/\text{Me}}^{\circ}$, were redetermined for pure lithium (ref.12), sodium (ref.14), potassium (ref.15), indium (ref.24), thallium (ref.26), and calcium (ref.23)(cf. Table 2). The above comprehensive data made possible the present critical evaluation of $E_{\text{Me}^{z+}/\text{Me+Hg}}^{\circ}$, $dE_{\text{Me}^{z+}/\text{Me+Hg}}^{\circ}/dT$, and related thermodynamic functions. The appropriateness and use of amalgam electrodes for determinations of electrolyte activity coefficients in aqueous, and especially in nonaqueous solutions, has been examined by Bennetto and Willmott (ref.27).

2. DEFINITIONS AND STANDARD STATES

Since the chemical potential of the solute (Me = 2) in the solvent (Hg = 1) does not depend on the standard state used, the following holds:

$$\mu_2 = \mu_2^{01} + RT \ln (x_2 f_2^1) = \mu^{00} + RT \ln (x_2 f_2^0) \quad (4)$$

where

$$\mu_2^{01} = \lim_{x_2 \rightarrow 1} (\mu_2 - RT \ln x_2) \quad (5)$$

and

$$\mu_2^0 = \lim_{x_2 \rightarrow 0} (\mu_2 - RT \ln x_2) \quad (6)$$

Equations (5) and (6) define the standard chemical potentials and the activity coefficients for two scales (refs.10,28,29): that with superscript ¹ has the pure metal Me as the standard state ($f_2^1 = 1$ at $x_2 = 1$), and that with superscript ⁰ has the infinitely dilute solution of Me in Hg as the reference state, where $f_2^0 = 1$. The ratio of the activity coefficients on the two scales is a temperature-dependent constant:

$$f_2^1/f_2^0 = \exp\{(\mu_2^{00} - \mu_2^{01})/RT\} = \exp\{zF(E^{\bullet 1} - E^{\bullet 0})/RT\} = K_T \quad (7)$$

Here $E^{\bullet 1}$ (*i.e.*, $E_{\text{Me}^{z+}/\text{Me}}^0$) is the standard potential of the Me electrode, μ_2^{01} is the standard Gibbs energy of the metal (by convention zero at all temperatures where the metal is in its standard state), $E^{\bullet 0}$ is the standard potential of the amalgam electrode (*i.e.*, $E_{\text{Me}^{z+}/\text{Me+Hg}}^0$), while μ_2^{00} is the standard Gibbs energy of Me in amalgam and is equal to the standard Gibbs energy change of the amalgamation reaction:



where $q = (1-x_2)/x_2$. The ($E^{00} - E^{01}$) difference is simply the standard e.m.f. of the cell (2), which provides a precise and convenient experimental basis for the conversion factor for determining values of f_2^1 from f_2^0 values, and *vice versa*, at any x_2 . Let us take the case of cesium amalgams at 298 K (ref.17) to give an example of the different orders of magnitude of f_2^1 and f_2^0 values. With the standard state defined by equation (5) and implying $f_2^1 \rightarrow 1$ as $x_2 \rightarrow 1$, the pure cesium has obviously unit activity, a rather familiar concept, whereas a cesium amalgam of mole fraction 10^{-4} would have an activity as low as 3.6×10^{-21} which would be somewhat difficult to visualize on account of the quasi-ideal behaviour shown by dilute cesium amalgams (ref.17). Conversely, with the reference state implying $f_2^0 \rightarrow 1$ as $x_2 \rightarrow 0$ (cf. equation (6)), a cesium amalgam of mole fraction $x_2 = 10^{-4}$ is practically ideal in behaviour ($f_2^0 \approx 1$) and its activity is then $a_2^0 = 10^{-4}$, which is quite reasonable to conceive, but pure cesium, $x_2 = 1$, would have an activity $a_2^0 = 2.8 \times 10^{16}$.

It was found that the logarithm of the activity coefficient referred to $f_2^0 = 1$ at infinite dilution of Me in the amalgam varies linearly with the Me mole fraction, in dilute amalgams:

$$\lg f_2^0 = Q x_2 \quad (9)$$

where Q is a temperature-dependent constant which is specific to each Me (cf. Table 1). This is a characteristic feature of all the amalgam systems cited in this section.

3. DESCRIPTION OF DATA

The data in Tables 1 and 2 are from the original referenced sources, with a few minor corrections for occasional misprints and conversion from calories to joules (1 cal = 8.18400 J). Standard potentials $E_{\text{Me}^{z+}/\text{Me+Hg}}^0$ (henceforth abbreviated to $E_{\text{Me+Hg}}^0$) and their temperature coefficients $dE_{\text{Me}^{z+}/\text{Me+Hg}}^0/dT$ (henceforth abbreviated to $dE_{\text{Me+Hg}}^0/dT$) are given in terms of the general scheme of Me amalgam electrode reaction:



under the reference conditions of infinite dilution (molality scale) for the metal ion Me^{z+} and of infinite dilution (mole fraction scale) for the metal Me in the amalgam $\{\text{Me}+q\text{Hg}\}$.

[It is worthwhile noting that the temperature coefficients reported here correspond to tho-

TABLE 1 - Observed standard aqueous electrode potentials E_{Me+Hg}° (with constants for the interpolation polynomials $E_{Me+Hg}^{\circ} = A + BT + CT^2$) over a range of temperatures T for amalgams Me+Hg of metals Me; values at 298.15 K of the temperature coefficients dE_{Me+Hg}°/dT ; values at 298.15 K of the standard thermodynamic functions $\Delta G^{\circ}, \Delta H^{\circ}$ and ΔS° for the amalgamation reaction (9) and μ°, H° and S° for the amalgam species Me+Hg; values at 298.15 K of the Q parameters in equation (9) for the determination of activity coefficients f_2 of Me in dilute amalgams) with the constants for the interpolation polynomials $Q = a + bT + cT^2$. The respective standard errors (refs. 54,55) for the above quantities are quoted whenever applicable. All the E_{Me+Hg}° values quoted are referred to $E_{H^+/H_2}^{\circ} = 0$ at all temperatures.

	T/K	Li+Hg	Na+Hg	K+Hg	Rb+Hg	Cs+Hg	In+Hg *	Tl+Hg \square
E_{Me+Hg}° / mV	283.15	-2184.1±0.3	-1941.81±0.36	-1950.32±0.40	-1943.47±0.28	-1919.65±0.34	-	-273.09±0.19
	298.15	-2195.1±0.3	-1958.92±0.23	-1975.47±0.27	-1969.94±0.28	-1950.18±0.34	-313±4	-293.67±0.09
	313.15	-2205.2±0.3	-1976.21±0.14	-1998.69±0.66	-1996.91±0.41	-1979.22±0.42	-	-314.56±0.16
	328.15	-	-1992.55±0.34	-2020.29±0.55	-2022.57±0.44	-2006.71±0.19	-	-333.60±0.17
	343.15	-	-2008.78±0.52	-2038.53±0.88	-2049.01±0.28	-2035.48±0.55	-	-
A/mV		-1788.22	-1541.877	-1053.755	-1403.371	-1217.808	-	262.1201
B/mV K ⁻¹		-2.02625	-1.65575	-4.561286	-2.030565	-2.94012	-	-2.356183
1000C/mV K ⁻²		+2.21850	+0.86000	+4.927894	+0.435092	+1.62677	-	+1.646874
$(dE_{Me+Hg}^{\circ}/dT)/\mu V K^{-1}$	298.15	-703.4±0.1	-1142.9±0.2	-1622.8±0.4	-1771.1±0.3	-1970.1±0.3	-	-1374.2±0.4
$(\mu_{Me+Hg}^{\circ} \equiv \Delta G_{amalgamation}^{\circ})/kJ mol^{-1}$	298.15	-82.13±0.08	-72.864±0.029	-91.584±0.029	-92.13±0.04	-93.85±0.04	-7.1±1.3	-3.1995±0.0008
$(H_{Me+Hg}^{\circ} \equiv \Delta H_{amalgamation}^{\circ})/kJ mol^{-1}$	298.15	-87.450±0.038	-83.529±0.054	-107.65±0.08	-107.1±0.4	-116.3±0.4	-	-2.7020±0.0008
$\Delta S_{amalgamation}^{\circ}/J K^{-1} mol^{-1}$	298.15	-17.95±0.29	-35.9±0.4	-54.0±1.3	-50.2±0.4	-74.4±0.4	-	1.6673±0.0004
$S_{Me+Hg}^{\circ}/J K^{-1} mol^{-1}$	298.15	10.08±0.29	15.1±0.4	10.0±1.2	18.8±0.4	8.4±0.4	-	65.86±0.08
Q	298.15	9.5±1.1	16.33±0.01	29.90±0.42	37.21±0.44	40.59±0.47	3.08±0.10	14.19±0.23
a		18.48	18.720	61.1122	76.100	104.151	-	33.976
100b		-3.00	-0.800	-10.3734	-13.088	-21.133	-	-6.6533
1000c		-	-	-	-	-	-	-
Reference Nos.		11	13	15	16	17	24	26

* In the electrode reaction (10) the metal ion is In^{3+} . \square In the electrode reaction (10) the metal ion is Tl^{+} .

Table 1 contd. from p. 172

	T/K	Mg+Hg	Ca+Hg	Sr+Hg	Ba+Hg	Zn+Hg	Cd+Hg
$E_{\text{Me+Hg}}^{\ominus}$ / mV	283.15	-	-1995.32±0.12	-1889.33±0.21	-1700.22±0.13	-802.86±0.17	-
	288.15	-	-	-	-	-	-379.92±0.02
	293.15	-	-	-	-	-	-379.64±0.03
	298.15	-1980.1±0.5	-2003.38±0.23	-1900.74±0.21	-1717.15±0.07	-801.98±0.06	-379.78±0.02
	303.15	-	-	-	-	-800.59±0.10	-380.27±0.02
	308.15	-	-	-	-	-	-380.13±0.02
	313.15	-	-2011.46±0.04	-1911.96±0.33	-1728.81±0.09	-789.69±0.12	-
	328.15	-	-2018.21±0.05	-1921.18±0.37	-1741.74±0.16	-	-
	343.15	-	-2024.35±0.19	-1929.52±0.36	-1753.27±0.06	-	-
A/mV B/mV K ⁻¹ 1000C/mV K ⁻²	-	-	-1727.256	-1448.013	-1160.117	-609.533	-373.6907
	-	-	-1.321118	-2.289353	-2.765854	-1.42574	-0.02099557
	-	-	1.322877	2.582182	3.025048	2.62404	-
$(dE_{\text{Me+Hg}}^{\ominus}/dT)/\mu\text{V K}^{-1}$	298.15	-	-532.33±0.06	-749.60±0.08	-962.02±0.6	138.95±0.02	-20.996±0.001
$(\mu_{\text{Me+Hg}}^{\ominus} \equiv \Delta G_{\text{amalgamation}}^{\ominus})/$ $/\text{kJ mol}^{-1}$	298.15	-73.93±0.04	-166.44±0.04	-190.50±0.04	-229.3±0.4	7.61±0.08	-4.276±0.042
$(H_{\text{Me+Hg}}^{\ominus} \equiv \Delta H_{\text{amalgamation}}^{\ominus})/$ $/\text{kJ mol}^{-1}$	298.15	-	-186.98±0.04	-221.84±0.04	-262.34±0.04	8.62±0.08	-1.427±0.042
$\Delta S_{\text{amalgamation}}^{\ominus}/\text{J K}^{-1} \text{ mol}^{-1}$	298.15	-	-68.91±0.04	-105.10±0.04	-109±4	-3.39±0.08	9.565±0.025
$S_{\text{Me+Hg}}^{\ominus}/\text{J K}^{-1} \text{ mol}^{-1}$	298.15	-	-27.6±0.4	-53.6±0.4	-42±4	45.2±0.8	61.34±0.08
φ	298.15	22.6±0.8	38.3±0.2	47.2±0.6	54.2±0.8	-2.00±0.11	0.290±0.006
a 100b 1000c	-	-	613.919	541.347	767.43	162.929	0.039362
	-	-	-342.341	-283.05	-417.93	-109.673	0.083999
	-	-	4.99400	3.95021	6.0068	1.82329	-
Reference Nos.		19	19	20	21	22	23

TABLE 2 - Observed standard aqueous potentials E_{Me}^0 (with constants for the interpolation polynomials $E_{Me}^0 = A + B T + C T^2$), over a range of temperatures, of some metal Me electrodes whose determination or redetermination is linked with that of the parallel E_{Me+Hg}^0 for the amalgam electrode; values at 298.15 K of the standard thermodynamic functions μ^0 , H^0 and S^0 for the aqueous metal ion Me^{z+} ; the respective standard errors (refs. 54, 55) for the above quantities are reported whenever applicable. All the E_{Me}^0 's quoted are referred to $E_{H^+/H_2}^0 = 0$ at all temperatures, as also are the temperature coefficients dE_{Me}^0/dT .

	T/K	Li	Na	K	In *	Tl μ	Cd
E_{Me}^0 / mV	283.15	-3034.2±0.5	-	-	-340.3±0.8	-313.05±0.15	-401.21±0.05
	288.15	-	-	-	-	-320.14±0.15	-401.71±0.05
	293.15	-	-	-	-339.2±1.0	-327.14±0.15	-402.12±0.05
	298.15	-3042.2±0.5	-2717.32±0.34	-2928.4±0.4	-	-334.05±0.15	-402.42±0.05
	303.15	-	-	-	-339.1±1.2	-340.89±0.15	-402.62±0.05
	308.15	-	-	-	-	-	-
	313.15	-3049.2±0.5	-	-	-339.4±1.0	-	-
	318.15	-	-	-	-339.0±0.9	-	-
333.15	-	-	-	-	-	-	
A / mV		-2629.57	-	-	-345.988	194.9595	-199.1361
B / mV K ⁻¹		-2.26862	-	-	0.021311	-2.110302	-1.29106
1000 C / mV K ⁻²		2.96585	-	-	-	1.204957	2.04681
$(dE_{Me}^0/dT)/\mu V K^{-1}$	298.15	-500.1±0.1	-	-	21.3±0.1	-1391.8±0.7	-70.547±0.009
$\mu_{Me^{z+}}^0/kJ mol^{-1}$	298.15	-293.53±0.05	-262.186±0.033	-282.55±0.04	-98.30±0.29	-31.562±0.014	-77.599±0.010
$H_{Me^{z+}}^0/kJ mol^{-1}$	298.15	-279.14±0.05	-	-	-100.14±0.29	8.477±0.025	-73.540±0.010
$S_{Me^{z+}}^0/J K^{-1} mol^{-1}$	298.15	76.27±0.08	-	-	-144.20±0.03	133.18±0.08	-65.21±0.04
Reference Nos.		12	14	15	24, 33	26	23

* In the electrode reaction (17) the metal ion is In^{3+} . μ In the electrode reaction (17) the metal ion is Tl^+ .

se in De Bethune's extended compilation (ref.30) of E° 's and dE^\bullet/dT 's and called *isothermal* temperature coefficients — that is, they are based on e.m.f.'s of *isothermal cells* — and are not the same as *thermal* temperature coefficients — *i.e.* based on e.m.f.'s of non-isothermal cells J . Reaction (10) must be combined with the silver/silver-chloride electrode reaction in order to obtain the overall reaction of the cell (1), which was customarily used to determine the $E_{\text{Me+Hg}}^\circ$ data in Table 1. This cell has a general e.m.f. expression of the type:

$$E = E_{\text{AgCl}}^\circ - E_{\text{Me+Hg}}^\circ - rk \lg (\sqrt[2r]{z m \gamma_{\pm}} / m^\circ) + (k/z) \lg (x_2 f_2^0) \quad (11)$$

where E_{AgCl}° is the standard potential of the silver/silver-chloride electrode (whose value was redetermined by Bates and Bower (ref.31)), $k = (RT \ln 10)/F$, $m^\circ = 1 \text{ mol kg}^{-1}$, z is the charge on the metal ion Me^{z+} , and $r = (1+z)/z$. From equations (11) and (9), together with the Debye-Hückel extended equation (ref.32) for the mean activity coefficients (molality scale) γ_{\pm} of the MeCl_z electrolyte, one can define the extrapolation function:

$$\begin{aligned} \phi = E - E_{\text{AgCl}}^\circ + rk \ln (\sqrt[2r]{z m / m^\circ}) - (1+z)kA\sqrt{I}/(1+\alpha_0 B\sqrt{I}) - rk \ln \{1+(1+z)mM\} = \\ -E_{\text{Me+Hg}}^\circ + (k/z)(\lg x_2 + Qx_2) - rkbI \end{aligned} \quad (12)$$

where I is the ionic strength of the MeCl_z electrolyte of molality m , M is the molar mass of the solvent, A and B are the Debye-Hückel constants, and α_0 and b are the ion-size and the interaction parameter respectively. From equation (12), $E_{\text{Me+Hg}}^\circ$ can be obtained from values of E measured as a function of m and of x_2 by two linear extrapolations. The first is from a plot of ϕ versus I giving (as intercept at $I = 0$) the quantity:

$$\phi^0 = -E_{\text{Me+Hg}}^\circ + (k/z)(\lg x_2 + Qx_2) \quad (13)$$

where ϕ^0 still depends on x_2 . Rearranging terms in equation (13) to define the function ψ , one obtains:

$$\psi = -\phi^0 + (k/z) \lg x_2 = E_{\text{Me+Hg}}^\circ + (k/z)Qx_2 \quad (14)$$

It is clear that a plot of ψ versus x_2 yields $E_{\text{Me+Hg}}^\circ$ as intercept at $x_2 = 0$ (second extrapolation). The slope gives the parameter Q in equation (9) for the calculation of the activity coefficients f_2^0 . The coefficients f_2^1 can be calculated, if necessary, from the f_2^0 values in terms of equation (7).

The original $E_{\text{Me+Hg}}^\bullet$ data, with standard errors (refs.54,55), are given in the Table 1 at the temperatures of experiments. The related $dE_{\text{Me+Hg}}^\bullet/dT$ and Q data are reported only at 298.15 K. For both $E_{\text{Me+Hg}}^\bullet$ and Q the constants for the least-squares polynomials:

$$E_{\text{Me+Hg}}^\bullet = A + BT + CT^2 \quad (15)$$

and:

$$Q = a + bT + cT^2 \quad (16)$$

are included for interpolation purposes. The values at 298.15 K of the related thermodynamic functions ΔG° , ΔH^\bullet , and ΔS^\bullet for the amalgamation reaction (8) as well as G° , H° , and S^\bullet for the amalgam species $\{\text{Me}+q\text{Hg}\}$ are also given.

Table 2 reports values of the standard potentials, $E_{\text{Me}^{z+}/\text{Me}}^\circ$, and related temperature coefficients $dE_{\text{Me}^{z+}/\text{Me}}^\bullet/dT$, of pure metal Me electrodes whose determination or redetermination was linked with that of the related Me amalgam electrodes in Table 1. These standard potentials and temperature coefficients, henceforth denoted respectively as E_{Me}° and $dE_{\text{Me}}^\bullet/dT$ for simplification, are for lithium (ref.12), sodium (ref.14), potassium (ref.15), indium (refs.24,33), thallium (ref.26), and cadmium (ref.23) electrodes. They refer to the general Me electrode

reaction scheme:



under the reference conditions of infinite dilution for the metal ion Me^{z+} . Of course, the operative cell involved is mainly (2) for which the e.m.f., expressed by the equation:

$$E = E_{\text{Me+Hg}}^0 - E_{\text{Me}}^0 - (k/z) \lg(x_2 f_2^0) \quad (18)$$

is measured at the same value of x_2 of, and added to the e.m.f. of cell (1), the e.m.f. of which is given by equation (11). However, different cell schemes can also be used, as was done *e.g.* in the case of indium electrodes (refs.24,33). Analogously to the $E_{\text{Me+Hg}}^0$ data in Table 1, in Table 2 are reported the available least-squares constants for the interpolation polynomials:

$$E_{\text{Me}}^0 = A + BT + CT^2 \quad (19)$$

The related standard thermodynamic functions G^0 , H^0 , and S^0 for the aqueous metal ion Me^{z+} are also reported. In particular, to facilitate comparison with the literature, the $S_{\text{Me}^{z+}}^0$ data are quoted relative to the convention $S_{\text{Me}^{z+}}^0 = 0$, which is, however, inconsistent (refs.34, 35) with the universally accepted convention (refs.35-43):

$$E_{\text{H}^+/\text{H}_2}^0 = 0 \quad \text{at all temperatures} \quad (20)$$

Indeed, convention (20) would imply (refs.34,35,43) that, at 298.15 K :

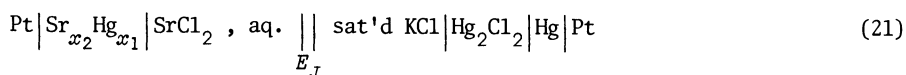
$$S_{\text{H}^+, \text{aq}}^0 = \frac{1}{2} S_{\text{H}_2}^0 = 65.287 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad (20a)$$

Thus, for practical consistency with (20) and (20a), the $S_{\text{Me}^{z+}}^0$ values quoted relative to $S_{\text{H}^+, \text{aq}}^0 = 0$ should be corrected by addition of the quantity $65.287 z^+ \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The activity coefficients f_{Me}^0 for the metal Me at mole fraction x_{Me} in amalgams can be easily computed from equation (9) by using the appropriate values for Q . It is recommended that Q values be interpolated using the polynomial (16) with the relevant least-squares constants reported in Table 1. These Q values are only applicable within the x_{Me} range of linear extrapolation of the function ψ (equation (14)): at higher values of x_{Me} the f_{Me}^0 values are best calculated from the original E data through equations (11) or (18), once the required values of standard potentials have been determined by linear or even non-linear extrapolation. This procedure was used by Salomon (ref.44) in studying dilute thallium amalgams by cell (2). Any extension of the x_{Me} range should, therefore, be considered with caution and with appropriate reference to phase diagrams for the Me+Hg systems.

4. COMPARISON OF DATA

A large number of the initial determinations and redeterminations of $E_{\text{Me+Hg}}^0$ of amalgam electrodes was accomplished by one group of workers (refs.11-23,26) over a wide temperature range (283 to 343 K). Final correlations for the $E_{\text{Me+Hg}}^0$ values and the related thermodynamic functions were made by a rigorous procedure of double extrapolation using the relevant function (11) for the concentration dependence of the e.m.f. of the general reversible cell (1). Cells of this type were made up according to an appropriate design (ref.45). The resulting $E_{\text{Me+Hg}}^0$ and Q data are thus intrinsically more accurate and reliable than any corresponding previous data (which were invariably obtained at one single temperature – 298.15 K – and often based on a single concentration of non-electrolyte or electrolyte with assumed values of single-ion activity coefficients, and even with inclusion of liquid junction potentials in the relevant

cells). It is noteworthy that the redetermined $E_{\text{Me+Hg}}^{\circ}$ data substantiate most of the pioneering data, typically within ± 1 mV. Only three cases deserve discussion: they concern the Q values for the lithium and the strontium amalgams, and the $E_{\text{Sr+Hg}}^{\circ}$ of the strontium amalgam electrode. For $Q_{\text{Li+Hg}}$ at 298.15 K, Table 1 reports the value 9.5, redetermined recently by Longhi, Rondinini, Ardizzone and Mussini (ref.11). Previous literature data are at variance: 14.6 was obtained by Cogley and Butler (ref.46), 7.6 by Spiegel and Ulich (ref.6), and 11.5 by Wagner (ref.8) – the latter value being from studies on ternary amalgams. However, it is known that for both the alkali-metal and the alkaline-earth metal amalgams there exists a linear correlation (refs.11,16,17,19-21) between $Q_{\text{Me+Hg}}$ and r_{Me}^2 (r_{Me} being the atomic radius of the metal Me concerned), the slope of the straight line for the alkaline-earth metal amalgams being twice the slope of that for the alkali-metal amalgams (ref.19). This is a sound basis for selection of the above value, $Q_{\text{Li+Hg}} = 9.5$, reported in the Table 1, as the appropriate one. The same rationale applies to $Q_{\text{Sr+Hg}}$, for which Table 1 at 298.15 K reports the value of 47.2, as obtained by Longhi, Mussini and Vaghi (ref.20) from both the cells (1) and (3), in contrast to the value of 39 found by Khlystova and Korshunov (ref.47) from the e.m.f. of a cell with liquid junction. The aforementioned $Q_{\text{Me+Hg}}$ vs. r_{Me}^2 linear relationship confirms the value $Q_{\text{Sr+Hg}} = 47.2$. $E_{\text{Sr+Hg}}^{\circ}$ of the strontium amalgam electrode was determined over the temperature range from 283 to 343 K from the general cell (1) by Longhi, Mussini and Vaghi (ref. 20) using the procedure describe above. The value, $E_{\text{Sr+Hg}}^{\circ} = -1.90074$ V at 298.15 K, in Table 1, is in contrast to that, -1.893 V, obtained by Khlystova and Korshunov (ref.47) from the cell:



The latter value is, however, not comparable to the former, on account of the following points: (i) the liquid junction potential E_J cannot be precisely evaluated or reduced to zero exactly; (ii) the single-ion activity coefficient $\gamma_{\text{Sr}^{2+}}$ is a thermodynamically undefinable quantity, making the claimed attainment (ref.47) of the experimental condition of $a_{\text{Sr}^{2+}} = 1$ unreliable. No $E_{\text{Me+Hg}}^{\circ}$ data are available for comparison at temperatures other than 298.15 K.

5. RECENT DATA

Recently, Udris and Korshunov (ref.48) reported the standard potential of the europium amalgam electrode at 298.15 K as $E_{\text{Eu+Hg}}^{\circ} = -1.77 \pm 0.01$ V (the metal ion in the relevant electrode reaction (10) being Eu^{2+}) and, correspondingly, $Q = 40 \pm 5$. However, no e.m.f. measurements or details of the cell were quoted, although it may be reasonably inferred that the cell used was of type (21). It is important to note that the observed Q value satisfactorily fits the linear Q vs. r_{Me}^2 relationship obeyed by the alkaline-earth metal amalgams, which suggests that the $E_{\text{Eu+Hg}}^{\circ}$ value obtained is correct. The latter value was also confirmed by polarographic studies (see Sect. 7). However, the large uncertainty in the above Q value precludes its use for calculations of activity coefficients f_{Eu}° through equation (9).

6. EXPRESSION OF THERMODYNAMIC QUANTITIES OF AMALGAMS ON DIFFERENT CONCENTRATION SCALES

According to common practice, in the present report the mole fraction scale has been used for the standard states for metal Me solutes (cf. definitional equations (5) and (6), respectively). Concentration scales other than the mole fraction, *e.g.* the molality (m) and the amount-of-substance concentration (c) (or, molarity), have been seldom used (refs.49,50). Interconversion formulae for standard potentials, activity coefficients and related thermodynamic functions, are available in electrochemical textbooks (ref.51).

7. KINETIC STUDIES DEALING WITH STANDARD POTENTIALS OF AMALGAM ELECTRODES
 IN AQUEOUS SOLUTIONS

Kinetic investigations having relevancy to determinations of standard potentials of amalgam electrodes in aqueous solutions are quite recent and concern the ammonium, magnesium, and europium amalgam electrodes. Stromberg and Konkova (ref.52) have studied the dependence of the radius of the drop of ammonium amalgam foam (which is generated at a stationary mercury drop cathode in aqueous NH_4Cl) on the electrolysis time at various electrolysis potentials, together with polarisation curves and a correction for joint discharge of H^+ ions. They give $E_{\text{NH}_4+\text{Hg}}^{\circ} = -1.7$ V for the standard potential of the ammonium amalgam electrode. This estimated value should be viewed with extreme caution; in fact, considering the values of standard potentials for the lithium, sodium, potassium, rubidium, and cesium amalgams (cf. Table 1), there is the possibility that the above value be affected by some mixed potential condition. Korshunov and Udris (ref.53), having ascertained that the polarographic reduction of Ca^{2+} , Sr^{2+} and Ba^{2+} ions on dropping mercury cathodes to the respective amalgams proceeds fairly reversibly, carried out an analysis of the mechanism of the reduction of Mg^{2+} . Taking into account theoretical evaluations based on amalgam models and on e.m.f. data of magnesium amalgams in ether, they concluded that $E_{\text{Mg}+\text{Hg}}^{\circ}$ was "possibly close to -2.10 V". This provides qualitative confirmation of the value of -1.9801 ± 0.0005 V, redetermined for $E_{\text{Mg}+\text{Hg}}^{\circ}$ from equation (14) by Ardizzone *et al.* (ref.18), who worked with forty-nine cells of the type (1) covering a large range of x_{Mg} in dilute amalgams. Finally, Udris and Korshunov (ref.48), from the polarographic half-wave potential $E_{\frac{1}{2}}$ of Eu^{2+} reduction to $\text{Eu}+\text{Hg}$ at a dropping mercury cathode, calculated the standard potential $E_{\text{Eu}+\text{Hg}}^{\circ}$ of the europium amalgam electrode using the equation:

$$E_{\frac{1}{2}} = E_{\text{Eu}+\text{Hg}}^{\circ} + (k/2) \lg (D_{\text{Red}}/D_{\text{Ox}}) \quad (22)$$

where D_{Ox} and D_{Red} are the diffusion coefficients of the oxidised and reduced form, respectively, which were apparently taken as identical. They found an $E_{\text{Eu}+\text{Hg}}^{\circ}$ value on the mole fraction scale of -1.76 to -1.77 V confirming the value, $E_{\text{Eu}+\text{Hg}}^{\circ} = -1.77 \pm 0.01$ V, determined by potentiometry (cf. Sect. 5).

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