

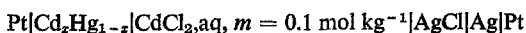
## Thermodynamics of the cadmium-amalgam electrode in aqueous medium

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From e.m.f. measurements of the cell:



over the temperature range from 288.15 to 308.15 K, the standard potential of the cadmium-amalgam electrode has been determined, which can be reproduced by the equation:

$$E_{\text{Cd}+\text{Hg}}^{\circ}/\text{V} = -0.3736907 - 2.099557 \times 10^{-5}(T/\text{K}).$$

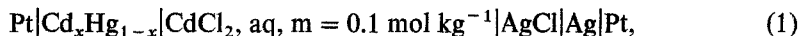
The parallel values of the standard potential of the cadmium electrode have also been recalculated from data in the literature and have been found to be representable by

$$E_{\text{Cd}}^{\circ}/\text{V} = -0.1991361 - 1.29106 \times 10^{-5}(T/\text{K}) + 2.04681 \times 10^{-9}(T/\text{K})^2.$$

From  $E_{\text{Cd}+\text{Hg}}^{\circ}$  and  $E_{\text{Cd}}^{\circ}$  have been determined the standard thermodynamic functions at 298.15 K for the cadmium amalgamation reaction and for the species: cadmium amalgam,  $\text{CdCl}_2(\text{aq})$  and  $\text{Cd}^{2+}(\text{aq})$ . Dilute cadmium amalgams behave as regular solutions as substantiated by the linear relation between the logarithm of the rational activity coefficient of cadmium in amalgam and the corresponding mole fraction:  $\log_{10} f_{\text{Cd}} = Qx$ , where in turn the parameter  $Q$  is a linear function of temperature:  $Q = 0.039362 + 8.3999 \times 10^{-4}(T/\text{K})$ .

### 1. Introduction

When compared with the groups of the alkali-metal amalgams or of the alkaline-earth amalgams—which were recently studied exhaustively<sup>(1-5)</sup>—the dilute cadmium amalgams are interesting both from the standpoint of the regular-solution features and of the electrode behaviour. The lack of data in the literature and the need for systematizing the matter prompted the present investigation, which is based on e.m.f. measurements of the cell:



over the temperature range from 288.15 to 308.15 K at various mole fractions  $x$  of Cd in amalgam.

The e.m.f. of cell (1) is expressed by

$$E_1 = E^{\circ}(\text{AgCl} + e^- = \text{Ag} + \text{Cl}^-, \text{aq}) - E^{\circ}\{\text{Cd}^{2+}(\text{aq}) + q\text{Hg} + 2e^- = (\text{Cd} + q\text{Hg})\} \\ + (k/2)\log_{10}(xf) - (k/2)\log_{10}\{4(m\gamma_{\pm}/m^{\circ})^3\}, \quad (2)$$

where  $q = (1-x)/x$ ;  $E^{\circ}\{\text{Cd}^{2+}(\text{aq}) + q\text{Hg} + 2e^- = (\text{Cd} + q\text{Hg})\}$  henceforth abbreviated to  $E_{\text{Cd}+\text{Hg}}^{\circ}$ , is the standard potential of the cadmium-amalgam electrode to be

determined;  $E^\circ(\text{AgCl} + e^- = \text{Ag} + \text{Cl}^-, \text{aq})$ , abbreviated to  $E_{\text{AgCl}}^\circ$ , is that of the silver|silver-chloride electrode as redetermined by Bates and Bower;<sup>(6)</sup>  $f$  is the rational activity coefficient of cadmium at the mole fraction  $x$  in the amalgam;  $\gamma_\pm$  is the activity coefficient of aqueous  $\text{CdCl}_2$  at the molality  $m$ ;  $m^\circ = 1 \text{ mol kg}^{-1}$ ;  $k = (RT/F)\ln 10$ , where  $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $F = 96487.0 \text{ C mol}^{-1}$ .<sup>(7)</sup>

The  $E_1$  values have been elaborated through equation (2) in terms of the equation:

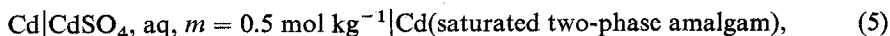
$$\log_{10} f = Qx, \quad (3)$$

implying regular-solution behaviour,<sup>(8)</sup> with the parameter  $Q$  constant at a given temperature, to determine  $E_{\text{Cd}+\text{Hg}}^\circ$  and  $Q$  simultaneously according to the procedure described later on. To specify the physical meaning of  $f$  in equation (3), it must be pointed out that the solute standard state chosen here<sup>(8,9)</sup> implies that  $f$  approaches unity in extremely dilute amalgams (Henry's law), that is to say  $f = a/x \rightarrow 1$  as  $x \rightarrow 0$ .

To attain the best accuracy for the values of the standard thermodynamic functions concerning the cadmium amalgamation reaction:



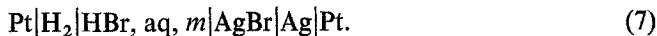
and of the species  $\text{CdCl}_2(\text{aq})$  and  $\text{Cd}^{2+}(\text{aq})$ , the present results have been combined with literature data of comparable accuracies. These data are essentially those by Parks and La Mer<sup>(10)</sup> concerning the standard e.m.f.  $E_5^\circ$  of the cell:



those by Bates<sup>(11)</sup> concerning the standard e.m.f.  $E_6^\circ$  of the cell:



and those by Hetzer, Robinson, and Bates<sup>(12)</sup> concerning the standard e.m.f.  $E_7^\circ$  of the cell:



The standard potential of the cadmium electrode,  $E^\circ\{\text{Cd}^{2+}(\text{aq}) + 2e^- = \text{Cd}\}$ , henceforth abbreviated to  $E_{\text{Cd}}^\circ$ , comes out as

$$E_{\text{Cd}}^\circ = -E_5^\circ - E_6^\circ + E_7^\circ. \quad (8)$$

As a result, a complete set of thermodynamic quantities is obtained and proposed both for completion and possible revision of earlier data in the literature.

## 2. Experimental

The cadmium amalgams required in the cell (1) were prepared by direct synthesis of weighed amounts of redistilled mercury and pro-analysi grade Merck cadmium under stirring by a hydrogen stream in an all-glass apparatus, described earlier,<sup>(13)</sup> which served also for the cadmium-amalgam electrode operation. A single stock of aqueous  $0.1 \text{ mol kg}^{-1} \text{ CdCl}_2$  solution enough for all the series of measurements to be done was prepared by weighing from triply distilled water and reagent-grade RP Carlo Erba  $\text{CdCl}_2$ . The silver|silver-chloride electrodes for completion of the cell (1) were of the electrolytic type,<sup>(14)</sup> as in previous works on amalgam electrodes.<sup>(1-5)</sup> The temperature of the cells was controlled to  $\pm 0.02 \text{ K}$  by means of a thermostat

described previously.<sup>(15)</sup> The type 602B Keithley electrometer used as a null-point detector in the potentiometer (a type K3 Leeds & Northrup one), enabled e.m.f. readings to be taken even with closed stopcocks in the cells, due to its input impedance of more than  $10^{16} \Omega$ . The e.m.f. measurements were made on triplicate cells: the averages are quoted in table 1, the e.m.f. deviations from the mean never exceeding  $\pm 0.03$  mV after equilibration.

### 3. Results and discussion

The measured values of the e.m.f.  $E_1$  of the cell (1) are collected in table 1. The values of the activity coefficient  $\gamma_{\pm}$  for aqueous  $\text{CdCl}_2$  at the fixed molality  $0.1 \text{ mol kg}^{-1}$  chosen here, which are required for use of equation (2), have been obtained from

TABLE 1. E.m.f.  $E_1$  of the cell (1) measured at various mole fractions  $x$  of Cd in amalgam and at various temperatures  $T$ , but with fixed molality of  $0.1 \text{ mol kg}^{-1}$  for aqueous  $\text{CdCl}_2$

T/K	288.15		293.15		298.15		303.15		308.15	
	$x$	$E_1/\text{V}$	$x$	$E_1/\text{V}$	$x$	$E_1/\text{V}$	$x$	$E_1/\text{V}$	$x$	$E_1/\text{V}$
	0.00095	0.64485	0.00094	0.64245	0.00103	0.64165	0.00099	0.63951	0.00100	0.63745
	0.00458	0.66440	0.00456	0.66243	0.00472	0.66119	0.00444	0.65914	0.00461	0.65773
	0.01480	0.67903	0.01539	0.67782	0.01572	0.67675	0.01526	0.67537	0.01540	0.67384
	0.02421	0.68522	0.02466	0.68395	0.02652	0.68356	0.02615	0.68250	0.02631	0.68105
	0.04170	0.69212	0.04176	0.69065	0.02682	0.68371	0.02655	0.68270	0.02879	0.68227
	0.04360	0.69269	0.04507	0.69164	0.04317	0.68997	0.04157	0.68869	0.04190	0.68737
	0.06275	0.69737	0.06500	0.69658	0.04383	0.69017	0.04175	0.68875	0.04215	0.68745
	0.06500	0.69782	0.06551	0.69654	0.06325	0.69505	0.05858	0.69332	0.05855	0.69196
	0.07975	0.70049	0.08062	0.69929	0.06500	0.69541	0.06500	0.69473	0.06500	0.69340
					0.08415	0.69890	0.08217	0.69795	0.08203	0.69665

Harned and Fitzgerald's data,<sup>(16)</sup> and are reported at the bottom of table 2. Combining equation (2) with (3) and rearranging one can define the extrapolation function:

$$E_{\text{AgCl}}^{\circ} - E_1 + (k/2) \log_{10} \{x/(4m^3 \gamma_{\pm}^3)\} = E_{\text{Cd+Hg}}^{\circ} - (k/2) Qx = \Phi. \quad (9)$$

As required by equation (9), at any given temperature, plotting  $\Phi$  against  $x$  produces a straight line whose intercept at  $x = 0$  gives  $E_{\text{Cd+Hg}}^{\circ}$  whereas the slope gives the parameter  $Q$  for equation (3), thus *a posteriori* confirming the regular-solution behaviour for the dilute cadmium amalgams. The sought values of  $E_{\text{Cd+Hg}}^{\circ}$ , together with those of the standard e.m.f.  $E_1^{\circ} = E_{\text{AgCl}}^{\circ} - E_{\text{Cd+Hg}}^{\circ}$  of cell (1) and those of the parameter  $Q$ , are collected in table 2 with the corresponding standard errors. It is seen at once that, within the temperature range explored here,  $E_{\text{Cd+Hg}}^{\circ}$  has a (very small) negative temperature coefficient and  $Q$  has a (very small) positive temperature coefficient: both are, in practice, invariant. For interpolation purposes  $E_{\text{Cd+Hg}}^{\circ}$  and  $Q$  are best represented by the linear relations:

$$E_{\text{Cd+Hg}}^{\circ}/\text{V} = -0.3736907 - 2.099557 \times 10^{-5}(T/\text{K}), \quad (10)$$

$$Q = 0.039362 + 8.3999 \times 10^{-4}(T/\text{K}), \quad (11)$$

the standard deviations of fit being 0.19 mV and 0.004 respectively.  $E_1^{\circ}$  also shows a precise linear dependence on temperature, but with a conspicuous non-zero negative

TABLE 2. Standard potential  $E_{\text{Cd}+\text{Hg}}^{\circ}$  of the cadmium amalgam electrode, standard e.m.f.  $E_1^{\circ}$  of the cell (1),  $Q$  parameter of equation (3), and standard potential  $E_{\text{Cd}}^{\circ}$  of the cadmium electrode, at temperatures  $T$  from 288.15 to 308.15 K. Also reported are the values of the activity coefficients  $\gamma_{\pm}$  of aqueous  $\text{CdCl}_2$  at  $m = 0.1 \text{ mol kg}^{-1}$  used for the analysis

$T/\text{K}$	288.15	293.15	298.15	303.15	308.15
$E_{\text{Cd}+\text{Hg}}^{\circ}/\text{V}$ <sup>a</sup>	-0.37992	-0.37964	-0.37978	-0.38027	-0.38013
	$\pm 0.00002$	$\pm 0.00003$	$\pm 0.00002$	$\pm 0.00002$	$\pm 0.00002$
$E_1^{\circ}/\text{V}$ <sup>a</sup>	-0.37974	-0.37985	-0.37995	-0.38006	-0.38016
	$\pm 0.00001$	$\pm 0.00002$	$\pm 0.00001$	$\pm 0.00001$	$\pm 0.00001$
$Q$ <sup>a</sup>	$0.60849$	$0.60521$	$0.60212$	$0.59931$	$0.59578$
	$\pm 0.00001$	$\pm 0.00002$	$\pm 0.00001$	$\pm 0.00001$	$\pm 0.00001$
$Q$ <sup>b</sup>	$0.60845$	$0.60532$	$0.60218$	$0.59905$	$0.59592$
$E_{\text{Cd}}^{\circ}/\text{V}$ <sup>c</sup>	$0.286 \pm 0.005$	$0.279 \pm 0.024$	$0.290 \pm 0.006$	$0.295 \pm 0.002$	$0.299 \pm 0.011$
$\gamma_{\pm}$ <sup>d</sup>	0.281	0.286	0.290	0.294	0.298
$E_{\text{Cd}}^{\circ}/\text{V}$ <sup>c</sup>	-0.40121	-0.40171	-0.40212	-0.40242	-0.40262
$\gamma_{\pm}$ <sup>d</sup>	0.2334	0.2311	0.2283	0.2251	0.2215

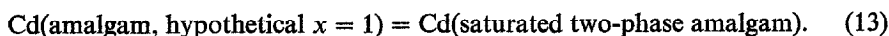
<sup>a</sup> Observed values. <sup>b</sup> Smoothed values. <sup>c</sup> Recalculated from data in references 10, 11, and 12;

<sup>d</sup> Interpolated from data in reference 16.

temperature coefficient:

$$E_1^{\circ}/\text{V} = 0.7889303 - 6.263515 \times 10^{-4}(T/\text{K}), \quad (12)$$

the standard deviation of the fit being 0.16 mV. At 298.15 K,  $E_{\text{Cd}+\text{Hg}}^{\circ} = -(0.37978 \pm 0.00002) \text{ V}$ . No datum is available in literature for comparison, and the reader should be aware that a comparison of the present  $E_{\text{Cd}+\text{Hg}}^{\circ}$  value with the values,  $-0.3515 \text{ V}$ ,<sup>(17)</sup> or  $-0.352 \text{ V}$ ,<sup>(18)</sup> reported in the literature under the  $E^{\circ}$  heading, is wholly meaningless because the latter values do not concern a truly *standard* amalgam electrode potential—which, as repeatedly described,<sup>(1-5,8)</sup> implies an extrapolation to  $x = 0$ —but simply the reference potential offered by a saturated two-phase amalgam electrode dipping into an aqueous solution at unit  $\text{Cd}^{2+}$  activity at 298.15 K. The difference between  $-0.37978 \text{ V}$  and  $-0.3515 \text{ V}$  is thus a measure of the standard e.m.f. for the process of cadmium transfer:



The same remarks hold obviously also for the corresponding temperature coefficients.<sup>(17)</sup>

Over the same temperature range of the present measurements, the standard potential  $E_{\text{Cd}}^{\circ}$  of the cadmium electrode has been determined from equation (8) where for the standard e.m.f.  $E_7^{\circ}$  of cell (7) the accurate recent retermination by Hetzer, Robinson, and Bates<sup>(12)</sup> has been exploited. Parks and La Mer's data for  $E_3^{\circ}$  are available at 10 K intervals just up to 303.15 K,<sup>(10)</sup> and can be reproduced by the least-squares equation:

$$E_3^{\circ}/\text{V} = 0.0708559 + 7.04117 \times 10^{-5}(T/\text{K}) - 4.64883 \times 10^{-7}(T/\text{K})^2, \quad (14)$$

with a standard deviation of fit of 0.06 mV; the missing  $E_3^{\circ}$  datum at 308.15 K can safely be extrapolated with no loss of accuracy from equation (14). The parallel  $E_6^{\circ}$  and  $E_7^{\circ}$  values can be reproduced by the equations:

$$E_6^{\circ}/\text{V} = 0.0763490 + 2.53259 \times 10^{-3}(T/\text{K}) - 4.59843 \times 10^{-6}(T/\text{K})^2, \quad (15)$$

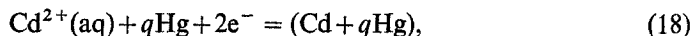
$$E_7^{\circ}/\text{V} = -0.0519312 + 1.31194 \times 10^{-3}(T/\text{K}) - 3.01650 \times 10^{-6}(T/\text{K})^2, \quad (16)$$

with standard deviations of fit of 0.02 and 0.05 mV. For the present determination of standard potentials and the derived standard thermodynamic functions smoothed  $E^\circ$  values, resulting from equations (10), (12), (14), (15), and (16), have always been used. The  $E_{\text{Cd}}^\circ$ 's thus obtained are reported in table 2. Addition of equations (14), (15), and (16) according to (8) leads to the expression for  $E_{\text{Cd}}^\circ$ :

$$E_{\text{Cd}}^\circ/\text{V} = -0.1991361 - 1.29106 \times 10^{-3}(T/\text{K}) + 2.04681 \times 10^{-6}(T/\text{K})^2, \quad (17)$$

The  $E_{\text{Cd}}^\circ$  value at 298.15 K turns out as  $-0.40212$  V, and the earlier selected  $E_{\text{Cd}}^\circ$  data in literature<sup>(11,16-21)</sup> group into less than a  $\pm 2$  mV span around the above value. From equation (17) the temperature coefficient of the standard potential of the cadmium electrode at 298.15 K is found to be close to zero:  $dE_{\text{Cd}}^\circ/dT = -0.070547$  mV K<sup>-1</sup> (the parallel  $dE_{\text{Cd+Hg}}^\circ/dT$  for the cadmium amalgam electrode is 0.020996 mV K<sup>-1</sup>), and the corresponding literature values range from  $-0.053$  to  $-0.093$  mV K<sup>-1</sup>.<sup>(17)</sup>

Now, taking the required  $E^\circ$  and  $dE^\circ/dT$  values from equations (10), (12), and (17), and the corresponding first derivatives, the standard thermodynamic functions  $\Delta G^\circ$ ,  $\Delta S^\circ$ , and  $\Delta H^\circ$  have been determined at 298.15 K for the cadmium amalgam electrode reaction:



the overall reaction of cell (1):



the cadmium electrode reaction:



and the cadmium amalgamation reaction (4). The values of the above thermodynamic functions for the said sequence of reactions are to be found in the table 3, together with the corresponding standard errors. It is seen that  $\Delta G^\circ$ ,  $\Delta S^\circ$ , and  $\Delta H^\circ$  for the amalgamation reaction (4) are very low as are the corresponding quantities for the zinc amalgamation reaction.<sup>(22)</sup> The standard thermodynamic functions for reactions

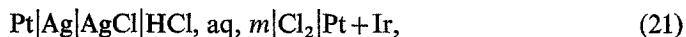
TABLE 3. Standard thermodynamic functions at 298.15 K, with standard errors, for different reactions, or species, related to the cadmium amalgams;  $q = (1-x)/x$ , where  $x$  denotes the mole fraction of Cd in the amalgam

Reaction, or species	$\frac{\Delta G^\circ}{\text{J mol}^{-1}}$	$\frac{\Delta H^\circ}{\text{J mol}^{-1}}$	$\frac{\Delta S^\circ}{\text{J K}^{-1} \text{ mol}^{-1}}$ <sup>a</sup>
$\text{Cd}^{2+}(\text{aq}) + q\text{Hg} + 2e^- = (\text{Cd} + q\text{Hg})$	$73320 \pm 38$	$72111 \pm 38$	$-4.0518 \pm 0.0021$
$(\text{Cd} + q\text{Hg}) + 2\text{AgCl} = \text{CdCl}_2(\text{aq}) + 2\text{Ag} + q\text{Hg}$	$-116206 \pm 29$	$-152243 \pm 29$	$-120.867 \pm 0.029$
$\text{Cd}^{2+}(\text{aq}) + 2e^- = \text{Cd}$ <sup>a</sup>	$77596 \pm 17$	$73538 \pm 17$	$-13.615 \pm 0.025$
$\text{Cd} + q\text{Hg} = (\text{Cd} + q\text{Hg})$	$-4276 \pm 42$	$-1427 \pm 42$	$9.565 \pm 0.025$
$(\text{Cd} + q\text{Hg})$	$-4276 \pm 42$	$-1427 \pm 42$	$61.34 \pm 0.08$
$\text{CdCl}_2(\text{aq})$	$-339691 \pm 50$	$-407287 \pm 50$	$47.99 \pm 0.17$
$\text{Cd}^{2+}(\text{aq})$	$-77580 \pm 50$	$-73580 \pm 50$	$-65.40 \pm 0.17$
$\text{AgCl}$ <sup>b</sup>	$-109605 \pm 4$	$-126810 \pm 4$	$96.44 \pm 0.08$
$\text{Cl}^-(\text{aq})$ <sup>c</sup>	$-131056 \pm 3$	$-166853 \pm 4$	$56.702 \pm 0.013$

<sup>a</sup> Recalculated from references 10, 11, and 12. <sup>b</sup> Recalculated from references 24 and 27.

<sup>c</sup> Recalculated from references 24 to 27. <sup>d</sup> Referred to  $S^\circ(\text{H}^+, \text{aq}) = 0$  at 298.15 K; but see text.

(18), (19), (20), and (4) being known, it has been possible to determine the standard molar  $G^\circ$ ,  $H^\circ$ , and  $S^\circ$  for the species:  $(\text{Cd} + q\text{Hg})$ ,  $\text{CdCl}_2(\text{aq})$ , and  $\text{Cd}^{2+}(\text{aq})$ , also quoted in the table 3. For the latter calculation, the required values of  $S^\circ$  for Cd and Ag have been taken from the N.B.S. tabulation,<sup>(23)</sup> whereas those concerning AgCl and  $\text{Cl}^-(\text{aq})$ , for reasons of consistency, have been taken from the critical re-determinations of the standard e.m.f. of the cell:



over a wide range of temperatures by Faita, Longhi, and Mussini,<sup>(24)</sup> and the standard potential of the chlorine electrode by Mussini and his colleagues.<sup>(24-27)</sup> The latter quantities are quoted at the bottom of the table 3. It is seen that the N.B.S. Value<sup>(28)</sup> for  $G^\circ$  of  $\text{Cd}^{2+}(\text{aq})$  is identical to that in table 3, and there is also a good agreement for  $G^\circ$  of  $\text{CdCl}_2(\text{aq})$ ; however the N.B.S. values for both  $S^\circ$  of  $\text{Cd}^{2+}(\text{aq})$  and  $S^\circ$  of  $\text{CdCl}_2(\text{aq})$  differ by as much as  $8 \text{ J K}^{-1} \text{ mol}^{-1}$  from the corresponding values re-determined in the present work; this obviously results in discrepancies of about  $2400 \text{ J mol}^{-1}$  in the respective  $H^\circ$  values. It must be pointed out, to facilitate the comparison with the data in Latimer's<sup>(19)</sup> and N.B.S.<sup>(7)</sup> tables, that the standard entropies of ions in table 3 are still quoted relative to the convention:<sup>(29)</sup>

$$S^\circ(\text{H}^+, \text{aq}) = 0 \text{ at } 298.15 \text{ K}, \quad (22)$$

which is however inconsistent with the universally accepted convention:

$$E^\circ(\text{H}^+, \text{aq} + \text{e}^- = \frac{1}{2}\text{H}_2) = 0, \quad (23)$$

at all temperatures: in fact, the latter implies that,<sup>(30-32)</sup> at 298.15 K:

$$S^\circ(\text{H}^+, \text{aq}) = \frac{1}{2}S^\circ(\text{H}_2) = 65.287 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (24)$$

Therefore, for consistency with (23) any standard ionic entropy so far quoted relative to (22) should be corrected by addition to the quantity  $65.287z_i$ , where  $z_i$  is the signed charge number of the ion. Thus the standard entropies of  $\text{Cd}^{2+}$  and  $\text{Cl}^-$  in table 3 should correctly read as  $S^\circ(\text{Cd}^{2+}, \text{aq}) = (65.02 \pm 0.17) \text{ J K}^{-1} \text{ mol}^{-1}$  and  $S^\circ(\text{Cl}^-, \text{aq}) = -(8.586 \pm 0.013) \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

## REFERENCES

- 1(a). Mussini, T., Maina, A.; Pagella, A. *J. Chem. Thermodynamics* **1971**, *3*, 281.
- 1(b). Mussini, T.; Longhi, P.; Riva, G. *J. Chem. Thermodynamics* **1972**, *4*, 591.
- 1(c). Longhi, P.; Mussini, T.; Osimani, C. *J. Chem. Thermodynamics* **1974**, *6*, 227.
- 1(d). Giordano, G. M.; Longhi, P.; Mussini, T.; Rondinini, S. *J. Chem. Thermodynamics* **1977**, *9*, 997.
2. Longhi, P.; Rondinini, S.; Ardizzone, S.; Mussini, T. *Ann. Chim. Rome* **1377**, *67*, 177.
3. Ardizzone, S.; Longhi, P.; Mussini, T.; Rondinini, S. *Ann. Chim. Rome* **1975**, *65*, 753.
4. Longhi, P.; Mussini, T.; Vaghi, E. *Chim. Ind. Milan* **1975**, *57*, 169.
- 5(a). Longhi, P.; Mussini, T.; Vaghi, E. *J. Chem. Thermodynamics* **1975**, *7*, 767.
- 5(b). Ardizzone, S.; Longhi, P.; Mussini, T.; Rondinini, S. *J. Chem. Thermodynamics* **1976**, *8*, 557.
6. Bates, R. G.; Bower, V. E. *J. Res. Natl. Bur. Stand.* **1954**, *53*, 282.
7. Wagman, D. D.; Evans, V. H.; Parker, V. B.; Halow, J.; Bailey, S. M.; Schumm, R. M. *National Bureau of Standards, Technical Note* 270-3, Washington, D.C. **1968**, p. 4.
8. Galli, R.; Longhi, P.; Mussini, T.; Tropeano, F. A. *Electrochim. Acta* **1974**, *19*, 551.
9. Lewis, G. N.; Randall, M. *Thermodynamics*, 2nd Edition. Revised by K. S. Pitzer and L. Brewer. McGraw-Hill: New York. **1961**, pp. 246, 247, 258, 259.
10. Parks, W. G.; La Mer, V. K. *J. Am. Chem. Soc.* **1934**, *56*, 90.
11. Bates, R. G. *J. Am. Chem. Soc.* **1939**, *61*, 308.

12. Hetzer, H. B.; Robinson, R. A.; Bates, R. G. *J. Phys. Chem.* **1962**, 66, 1423.
13. Mussini, T.; Longhi, P. *Ric. Sci. (II-A)* **1965**, 35, 1352.
14. Ives, D. J. G.; Janz, G. J. *Reference Electrodes*. Academic Press: New York. **1961**, pp. 204, 207.
15. Mussini, T.; Pagella, A. *J. Chem. Eng. Data*. **1971**, 16, 49.
16. Harned, H. S.; Fitzgerald, M. E. *J. Am. Chem. Soc.* **1936**, 58, 2624.
17. De Bethune, A. J.; Swendeman-Loud, N. A. *Standard Aqueous Electrode Potentials and Temperature Coefficients at 25 °C*. C. A. Hampel: Skokie, Illinois. **1964**, p. 9.
18. Charlot, G. *Selected Constants: Oxidation-Reduction Potentials of Inorganic Substances in Aqueous Solutions*. Butterworths: London. **1971**, p. 13.
19. Latimer, W. M. *Oxidation Potentials*, 2nd Edition. Prentice-Hall: Englewood Cliffs, New Jersey. **1952**, p. 172.
20. Burnett, J. L.; Zirin, M. H. *J. Inorg. Nucl. Chem.* **1966**, 28, 902.
21. Treumann, W. B.; Ferris, L. M. *J. Am. Chem. Soc.* **1936**, 58, 2624.
22. Longhi, P.; Mussini, T.; Rondinini, S.; Vaghi, E. *Ann. Chim. (Rome)* **1976**, 66, 645.
23. Reference 7, pp. 248, 263.
24. Faita, G.; Longhi, P.; Mussini, T. *J. Electrochem. Soc.* **1967**, 114, 340.
25. Cerquetti, A.; Longhi, P.; Mussini, T. *J. Chem. Eng. Data*. **1968**, 13, 458.
26. Cerquetti, A.; Longhi, P.; Mussini, T.; Natta, G. *J. Electroanal. Chem.* **1969**, 20, 411.
27. Mussini, T.; Faita, G. *Encyclopedia of Electrochemistry of the Elements*, Vol. 1. Bard, A. J.; Editor. Marcel Dekker: New York. **1973**, p. 4, 8.
28. Reference 7, pp. 248, 249.
29. Reference 7, p. 3.
30. Reference 14, pp. 14, 26, 72.
31. Bianchi, G.; Mussini, T. *Elettrochimica*. Tamburini-Masson: Milan. **1976**. pp. 237, 241, 243, 245.
32. Reference 7, p. 12.