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Standard Potentials of the Calcium Amalgam Electrode at Various Temperatures, with Related Thermodynamic Functions

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Standard potentials of the calcium amalgam electrode were determined over the temperature range 25° to 70° C and the standard thermodynamic functions at 25° C for the calcium amalgam were derived. Mean molal activity coefficients for aqueous $CaCl_2$ solutions were obtained over the same temperature range.

From a recent recalculation (*2*), it is apparent that a wide scatter exists among the few data available on the standard potential of the calcium amalgam electrode (*6, 7, 26, 27*).

The aim of the present work is to check these values of standard potential through a new determination which extends over a wide range of temperatures and includes such basic thermodynamic functions as the activity coefficients for aqueous $CaCl_2$ solutions up to 10^{-1} molal. For this purpose, the e.m.f. of cell 1

$$-\mathrm{Pt}/\mathrm{Ca}_x\mathrm{Hg}/\mathrm{CaCl}_2,\ m/\mathrm{AgCl}/\mathrm{Ag}/\mathrm{Pt}+ \qquad (1)$$

was measured over the temperature range 25° to 70° C, at different $CaCl_2$ molalities (6×10^{-3} to 10^{-1}). The mole fractions, X, of calcium in the amalgam were lower than 4×10^{-3}.

EXPERIMENTAL

The silver–silver chloride electrode used in cell 1 was of the electrolytic type (*15*). Its base was a smooth platinum wire, 1 mm in diameter, sealed into a soft-glass stem with ground cone joint, leaving a 30-mm length of the wire exposed for use as the electrode (Figure 1). This platinum wire, after cleaning in concentrated nitric acid, was repeatedly washed with triply distilled water, then silver-plated in a $KAg(CN)_2$ bath (10 grams per liter) prepared as recommended in the literature (*15*), under a current density of 0.5 ma per cm^2 for 4 hours. After soaking in NH_4OH and long washing in water, the silver-plated wire was chloridized in 0.1N HCl under a current density of 0.5 ma per cm^2 for half an hour, subsequently washed for a long time in triply distilled water, and eventually dried at 50° C in vacuo. Six such electrodes were intercompared at 25° C; their bias potential was 0.01 mv.

The glass apparatus illustrated in Figure 1 was used in the preparation and operation of the calcium amalgam electrode, which was of the "flowing amalgam" type (*9, 22*). This technique was chosen to get a continuous renewal of the amalgam surface because of its instability in contact with the aqueous $CaCl_2$ solutions. The calcium amalgam was prepared in compartment A by electrolyzing a 0.5M $Ca(ClO_4)_2$ solution under a current density of 5 A per dm^2. All the apparatus in Figure 1 was previously degassed by a prolonged hydrogen flow. From compartment A the amalgam was introduced into B and subsequently into C, where it was stirred and stored under hydrogen flow. Then, by manipulating the two-way stopcock, R, the amalgam was pushed from C into D by hydrogen pressure. Two capillary tubes, 150 mm long and 0.5 mm in diameter, provided with appropriate stopcocks, allowed the amalgam to flow from D into F in contact with the $CaCl_2$ solution at a flow rate of approximately 1 cm^3 every 30 seconds (*22*). In compartment E the amalgam was diluted with appropriate amounts of previously purified mercury. Stopcock S allowed quick removal of the amalgam from the $CaCl_2$ solution to prevent changes in ionic strength of the $CaCl_2$ solution due to the reaction

$$\mathrm{Ca(Hg)} + 2\ \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} + \mathrm{H_2} + \mathrm{Hg} \qquad (2)$$

The calcium content of the amalgam was determined just before and just after any series of e.m.f. measurements, by decomposing the amalgam with excess hydrochloric acid according to

$$\mathrm{Ca(Hg)} + 2\ \mathrm{HCl} \rightarrow \mathrm{CaCl_2} + \mathrm{Hg} + \mathrm{H_2} \qquad (3)$$

and titrating the excess HCl with standard NaOH solution by the potentiometric titration method (*17, 19*). The difference between the two determinations was less than 1% in each case.

The potentiometric measurements of the e.m.f. of cell 1 were carried out using a Type 602 Keithley electrometer, with input impedance greater than 10^{14} ohms and the lowest voltage range of 1 mv in 100 divisions, as a null detector. The standard cell reference system was a certified Eppley Model 121 standard voltage reference consisting of four

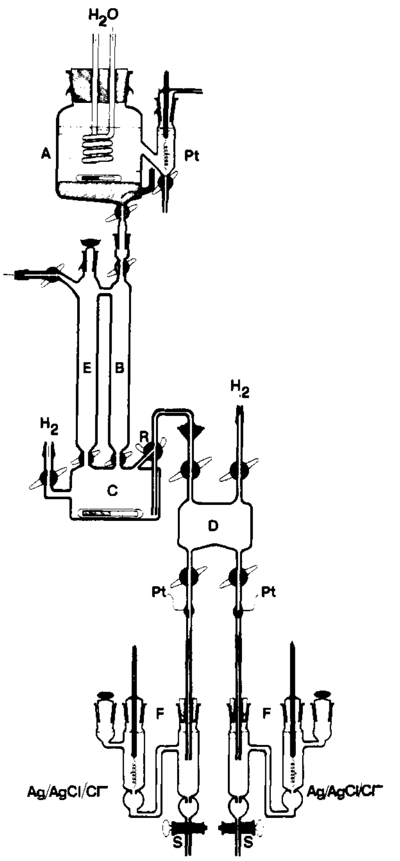

Figure 1. Diagrammatic representation of cell 1 with details of apparatus for preparation and storage of calcium amalgam

Eppley saturated cells kept under permanent thermostatic temperature control in a compact standard-type Eppley air thermostat.

The $CaCl_2$ solutions were degassed before each experiment by a 20-minute hydrogen flow into Friedrichs bottles. For each solution a large stock was previously prepared, sufficient for all experiments. Their concentrations were measured by determining the Cl^- ion potentiometrically (*18*) and the Ca^{2-} ion by the EDTA titration method (*20*). The deviation between the two determinations was less than 0.5%, and the average values are quoted in the tables.

The temperature of the cell was regulated to ±0.02° C by means of an air thermostat. This double-walled air-jacket metallic thermostat was designed and constructed especially for electrochemical measurements and is helpful in overcoming the difficulties caused by the use of water-filled or oil-filled thermostats. Such difficulties arise from possible contamination, leakage currents, and parasitic capacities. The present thermostat is based on the following specifications.

It is heated electrically by resistors stretched in the air, so as to avoid thermal inertia normally arising when heating elements wound on massive ceramic formers are used; it is cooled by water circulating through helical copper tubes. Heating and cooling can be regulated independently.

Air, after passing over the heating elements and the refrigerating coils, enters the ventilator and is mixed in such a way that the formation of air threads at different temperatures is avoided.

The ventilator drives air into a diffusor, from which air goes out through a number of little holes and then uniformly spreads over the electrochemical cell inside the thermostat.

The on-off switching of the heating elements is actuated by a fast-response transistorized Type RM 3 Reltrasis electronic regulator having a platinum-wire resistance thermometer as a sensitive element.

With these precautions, the temperature of air circulating into the thermostat follows a nearly sinusoidal law, where the amplitude of ΔT is less than 0.1° C and the period is 10 to 20 seconds. The temperature of solutions contained in a glass vessel which is closed and placed in this thermostat is very near the average temperature of air, and its variation limits are ±0.02° C, checked by means of a Beckman apparatus in a range from 15° to 50° C. The uniformity of temperature between different zones of the thermostat is also within ±0.02° C. The temperature of equilibration for the solutions contained in the glass vessels placed in the thermostat is generally reached after about 1 hour.

RESULTS AND DISCUSSION

The e.m.f. of cell 1 is given by

$$E = E^\circ_{\mathrm{Ag/AgCl/Cl^-}} - E^\circ_{\mathrm{Ca(Hg)}} + (k/2) \log (X_{\mathrm{Ca}} \gamma_{\mathrm{Ca}}) - (3k/2) \log (m\ (4)^{1/3} \gamma_{\pm})_{\mathrm{CaCl_2}} \quad (4)$$

where $k = (RT/F) \ln 10$, γ_{Ca} is the activity coefficient of calcium at a mole fraction X_{Ca} in the amalgam, $\gamma_{\pm}$ denotes the mean molal activity coefficient of $CaCl_2$ corresponding to molalities m at which e.m.f.'s E are measured, $E^\circ_{\mathrm{Ag/AgCl/Cl^-}}$ is the standard potential of the silver-silver chloride electrode [known from the literature (*1*)], and $E^\circ_{\mathrm{Ca(Hg)}}$ is the unknown standard potential of the calcium amalgam electrode. For calcium in the amalgam the solute standard state was chosen so that γ_{Ca} approaches unity in extremely dilute amalgams (Henry's law)—i.e., $\gamma_{\mathrm{Ca}} = a_{\mathrm{Ca}}/X_{\mathrm{Ca}} \rightarrow 1$ when $X_{\mathrm{Ca}} \rightarrow 0$ (*3, 4, 5, 16*). As X_{Ca} was lower than 4×10^{-3} γ_{Ca} was assumed to be unity (*2*), because of lack of data.

The measured E's are collected in Table I. The reproducibility of e.m.f. measurements of cell 1 depends on the $CaCl_2$ molalities. Within the molality range in Table I the e.m.f.'s were constant to within ±0.1 mv. At molalities lower than 5×10^{-3} the reproducibility was scanty [this behavior pattern of alkali and alkaline earth amalgam cells at low molalities of the supporting electrolyte had been reported (*12*)], probably because of changes of ionic strength in the $CaCl_2$ solutions caused by Reaction 2. Then the e.m.f. measurements at $m < 5 \times 10^{-3}$ were discarded. Evidence was produced that the calcium amalgam electrode behaves reversibly (*2*).

$E^\circ_{\mathrm{Ca(Hg)}}$ can be determined starting from Equation 4 by an extrapolation procedure, provided that an appropriate expression for log $\gamma_{\pm}$ is inserted into Equation 4. Hückel's (*13*) expression

Table I. E.M.F.'s of Cell 1, in Volts, at Various Temperatures and $CaCl_2$ Molalities

	Temperature, ° C			
	25	40	55	70
	X_{Ca} in Amalgam (×1000)			
$m_{\mathrm{CaCl_2}}$	3.21	1.73	1.17	3.45
0.005828	2.3361	. . .	2.3269	. . .
0.009197	2.3202	2.3165	2.3079	2.3278
0.01472	2.3050	. . .	2.2938	2.3093
0.01932	2.2969	2.2906	. . .	2.2998
0.02436	2.2886	. . .	. . .	. . .
0.02915	. . .	2.2770	2.2680	2.2858
0.03403	2.2770	. . .	2.2622	. . .
0.03883	2.2725	. . .	2.2581	. . .
0.04830	2.2656	2.2601	2.2503	2.2669
0.05848	2.2593	. . .	2.2447	2.2597
0.07236	2.2529	2.2470	. . .	2.2524
0.09680	2.2435	2.2357	2.2266	2.2420

$$\text{Log}\ \gamma_{\pm} = -\frac{A|z_+z_-|I^{1/2}}{1 + aBI^{1/2}} - \log\ (1 + 0.001\nu mW) + bI \qquad (5)$$

was used, where A and B are Debye-Hückel constants, I is the ionic strength of solutions, m is the molality of electrolyte, a is the distance of closest approach of ions [the selected value for $CaCl_2$ is a = 4.575 A (*11*)], b is a constant characteristic of each electrolyte to be studied, z_+ and z_- are the valencies of cation and anion, respectively, ν is the total number of ions originated by the ionization of one molecule of electrolyte, and W is the molecular weight of the solvent.

Guggenheim's (*8*) expression

$$\text{Log}\ \gamma_{\pm} = -\frac{A|z_+z_-|I^{1/2}}{1 + I^{1/2}} + b'I \qquad (6)$$

was also tested. In Equation 6 b' is again a constant obviously peculiar to the electrolyte to be studied, and the other symbols retain the same meaning as in Equation 5.

Combining Equation 5 (or 6) with Equation 4 and rearranging, recalling the assumption that $\gamma_{Ca} = 1$, one gets

$$E + (3k/2)\log\ (4^{1/3}m) - \frac{3kAI^{1/2}}{1 + aBI^{1/2}} - (3k/2)\log\ (1 + 0.003mW) - E^{\circ}_{Ag/AgCl/Cl} - (k/2)\log X_{Ca} = -E^{\circ}_{Ca(Hg)} - (3k/2)bI = \phi \qquad (7)$$

$$E + (3k/2)\log\ (4^{1/3}m) - \frac{3kAI^{1/2}}{1 + I^{1/2}} - E^{\circ}_{Ag/AgCl/Cl} - (k/2)\log X_{Ca} = -E^{\circ}_{Ca(Hg)} - (3k/2)b'I = \phi \qquad (8)$$

respectively, where functions ϕ and ϕ' are defined completely in terms of measurable or known quantities. Equations 7 and 8 require that plotting ϕ, or ϕ', against ionic strength I should produce a straight line whose intercept at I = 0 is $-E^{\circ}_{Ca(Hg)}$ and whose slope gives b, or b', respectively. The ϕ and ϕ' straight lines converge satisfactorily. As Figure 2 shows, the two intercepts differ by only 0.6 mv at 25° C and 0.9 mv at 70° C. These small differences are due to the fact that Guggenheim's expression actually implies that aB = 1, a simplification equivalent to putting a = 3.04 A for all aqueous electrolytes (*23*) at 25° C, as shown by comparing Equation 5 with 6.

Table II. Mean Molal Activity Coefficients of Aqueous $CaCl_2$ Solutions at Various Molalities and Temperatures

m_{CaCl_2}	Temperature, ° C 25	25	40	55	70
0.0001	0.961	0.961 (*10*)	0.960	0.959	0.958
0.0002	0.946	. . .	0.945	0.943	0.941
0.0003	0.935	. . .	0.933	0.931	0.929
0.0005	0.918	. . .	0.916	0.913	0.911
0.0007	0.904	. . .	0.902	0.899	0.896
0.001	0.888	0.888 (*10*)	0.885	0.882	0.879
0.002	0.850	0.850 (*10*)	0.846	0.842	0.837
0.003	0.824	. . .	0.819	0.814	0.809
0.005	0.786	0.784 (*10*)	0.780	0.774	0.768
0.007	0.758	0.755 (*10*)	0.752	0.745	0.738
0.01	0.727	0.724 (*10*)	0.720	0.712	0.704
0.02	0.663	. . .	0.654	0.642	0.633
0.03	0.624	. . .	0.613	0.600	0.590
0.05	0.576	. . .	0.563	0.546	0.535
0.07	0.547	. . .	0.532	0.515	0.500
0.1	0.518	0.518 (*24*)	0.501	0.477	0.463

The values of activity coefficients, and of standard potentials $E^{\circ}_{Ca(Hg)}$, quoted in Tables II and III, are, of course, those obtained through the elaboration based on Hückel's expression. The $\gamma_{\pm}$ values in Table II were obtained at round molalities of $CaCl_2$ by means of Equation 5, where the b value is obtained from the least-squares slope of the ϕ *vs.* I straight line at the appropriate temperature. Some available $\gamma_{\pm}$ data for aqueous $CaCl_2$ at 25° C based on diffusion measurements (*10*), a completely independent method, are inserted in Table II, third column, for comparison. The agreement is excellent, and so is it with other independent data (*24, 25*). Using Guggenheim's expression 6 with insertion of the experimental b' value would lead to $\gamma_{\pm}$ values in good agreement with those obtained starting from Hückel's expression. A discrepancy of less than 2.5%

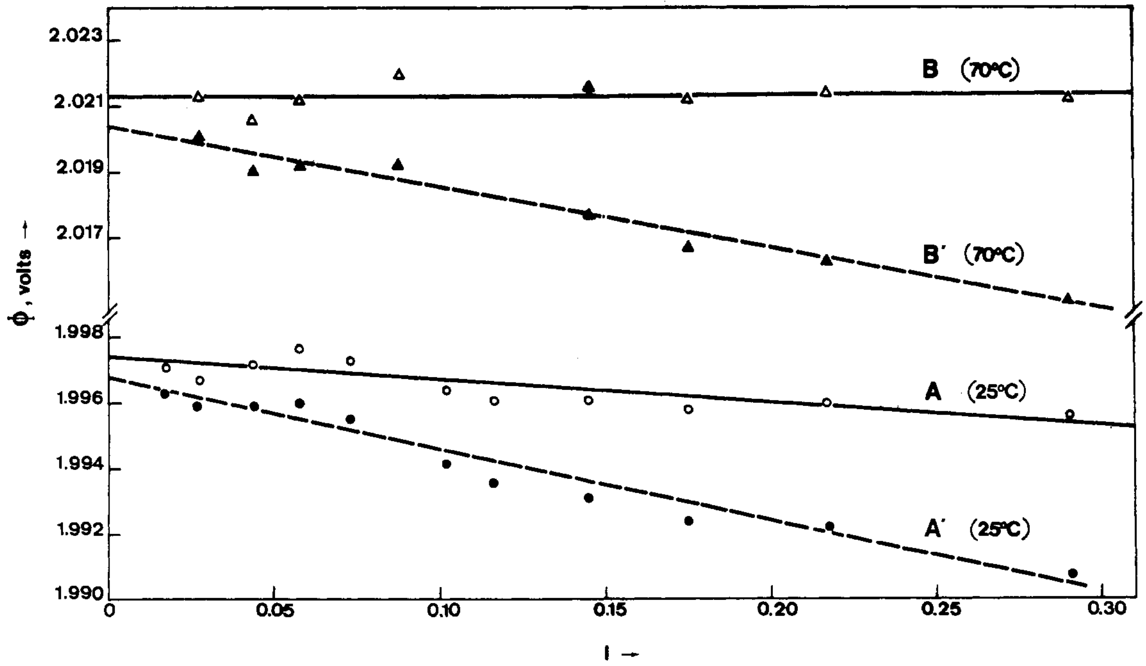

Figure 2. Extrapolation of functions ϕ (*A* and *B*) and ϕ' (*A'* and *B'*) at I = 0, at 25° and 70° C, to determine standard potentials $E^{\circ}_{Ca(Hg)}$ of calcium amalgam electrode

See Equations 7 and 8

Table III. $E^\circ_{Ca(Hg)}$ Values

Temp., ° C	$E^\circ_{Ca(Hg)}$, Volts
25	−1.9974 (±0.0004)
40	−2.0065 (±0.0006)
55	−2.0111 (±0.0007)
70	−2.0213 (±0.0006)

may be observed when approaching the upper limit of $CaCl_2$ molalities used here (0.1*m*). One can infer, therefore, that in the case of such uni-bivalent electrolytes as $CaCl_2$ Guggenheim's expression can still be used, as a practical simplification, with good success up to ≅0.1 mole per kg.

The $E^\circ_{Ca(Hg)}$ values obtained over the temperature range of experiment are collected in Table III, and can be represented by least-squares Equation 9,

$$E^\circ_{Ca(Hg)} = -1.97129 + (2.75163 \times 10^{-4})\, T - (1.22225 \times 10^{-6})\, T^2 \quad (9)$$

where T is the absolute temperature, with a mean deviation of fit of 1 mv, which is of the same order as the experimental uncertainty. The present $E^\circ_{Ca(Hg)}$ value at 25° C substantiates the value $E^\circ_{Ca(Hg)} = -1.996 \pm 0.001$ volts as recalculated by Butler (*2*) from Drucker and Luft's (*6*) results.

Once the $E^\circ_{Ca(Hg)}$ and $dE^\circ_{Ca(Hg)}/dT$ values are known, the latter taken from the first derivative of Equation 9, the standard thermodynamic functions G°, H°, and S° for the calcium amalgam can be determined. Referring to the amalgam electrode reaction,

$$Ca^{2+} + 2\,e \rightarrow Ca(Hg) \quad (10)$$

for which $\Delta G^\circ = -2FE^\circ_{Ca(Hg)}$, $\Delta S^\circ = 2FdE^\circ_{Ca(Hg)}/dT$, $\Delta H^\circ = -2E^\circ_{Ca(Hg)}F + 2FTdE^\circ_{Ca(Hg)}/dT$, one gets at 25° C $G^\circ_{Ca(Hg)} = -40.06$ kcal mole^{-1}, $H^\circ_{Ca(Hg)} = -43.88$ kcal mole^{-1}, $S^\circ_{Ca(Hg)} = -2.9$ cal deg^{-1} mole^{-1}. The data for the aqueous Ca^{2+} ion, required by Equation 10, were taken from the standard literature (*21*).

As the $S^\circ_{Ca^{2+}}$ value at 25° C in the literature (*21*) is referred to the convention $S^\circ_{H^+} = 0$ at all temperatures, a correction of 2 × 15.605 cal deg^{-1} mole^{-1} has been applied to make the value of $S^\circ_{Ca^{2+}}$ consistent with the convention $E^\circ_{H^+/H_2} = 0$ at all temperatures, which in turn implies that $S^\circ_{H^+} = \frac{1}{2}\, S^\circ_{H_2} = 15.605$ cal deg^{-1} mole^{-1} at 25° C (*14*).

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Effect of Organic and Inorganic Salts on Relative Volatility of Nonaqueous Systems

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The components of some liquid binary solutions may be either impossible or difficult to separate by normal distillation owing to the existence of an azeotrope or a very small relative volatility. Often the desired separation can be achieved by the technique of extractive distillation in which a third component, the extractive agent, is added to the solution. The extractive agent enhances the relative volatility of the close boiling compounds or it destroys the azeotrope.

The majority of work in the field of extractive distillation has dealt with the addition of an organic liquid component as the extractive agent. However, extractive distillation can also be carried out by utilizing soluble salts as the separating agent in aqueous solution (*1, 3*). If the dissolved salt can selectively form a liquid phase association complex with one of the two components present, the volatility of this component will be reduced. The net effect will be to enhance the volatility of the second component, said to be "salted out" with respect to the first. Also, the salting out effect depends on the radius and charge of the ions; it increases with increasing charge and decreasing radius of the ion (*2*).

Although the effect of salts on the relative volatility of the components of aqueous solutions has been studied rather extensively, essentially no work has been done in the area of nonaqueous solutions, probably owing to the

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