[Contribution from the Department of Chemistry, Columbia University]

The Temperature Coefficients of the Electromotive Force of the Cell Cd (metal), $CdSO_4$, Cd (satd. amalgam)

By W. George Parks[1] and Victor K. La Mer[2]

In the previous paper[3] in this series we obtained an estimate of the partial molal heat capacity of cadmium sulfate by studying the temperature coefficients of a galvanic cell in which the cell process

$$\text{Cd (s, satd. with Hg)} + PbSO_4\text{ (s)} = CdSO_4\text{ (M)} + \text{Pb (s, satd. with Hg)} \quad (1)$$

occurs, by employing the heat capacity of the solid metals in the absence of data on the heat capacity of these metals when saturated with mercury. In an attempt to estimate this correction we have studied the temperature coefficients of the cell

$$\text{Cd (s, satd. with Hg)}, CdSO_4\text{ (0.5 M)}, \text{Cd (metal)} \quad (2)$$

corresponding to the process

$$\text{Cd (s)} = \text{Cd (s, satd. with Hg)} \quad (3)$$

Although amalgam electrodes are highly reproducible it is well known that the electromotive force of solid metals depends upon the history of their preparation. Three methods for preparing the metal electrodes were employed: (1) sticks of cadmium specially purified for use in standard cells were machined to a thickness of approximately 3.5 mm. (2) The same material was melted and molded in small Pyrex tubes. (3) Crystals of cadmium were prepared by electrolysis of a purified cadmium sulfate solution. The crystals were then washed, dried, melted and molded as in method 2. All three types of electrodes were then annealed in test-tubes in an oil-bath at 180° for eight hours to reduce strains within the metal. The temperature was lowered slowly over a period of two days. Immediately before use the electrodes were scraped clean of oxide film and then the rigorous nitrogen technique described previously was adhered to in preparing the cells for measurement. Figure 1 shows a top view of the cell vessel. Three amalgam half-cells (A) are connected to a central chamber (B) which contained six metallic electrodes. This electrode vessel was the same as that employed recently in measuring the e. m. f. of thallium amalgam, TlCl, AgCl, Ag cells.[4] The 11% cadmium amalgam was identical with the preparation used in reference 3. The results are given in Table I.

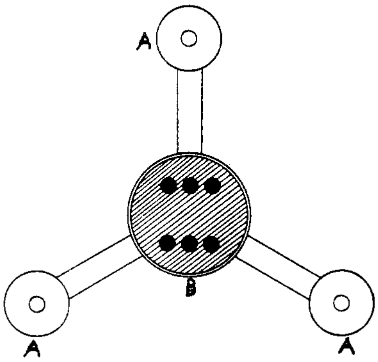

Fig. 1.—Electrode vessel, top view.

Table I

The Electromotive Force of the Cell Cd (s, Sat. with Hg), $CdSO_4$ (0.5 M), Cd (Metal) Corresponding to the Spontaneous Process Cd (s) = Cd (s, Sat. with Hg)

Nature of metal electrode	0°	10°	20°	30°
Electrolytic	0.05536	0.05357	0.05164	0.04964
	.05550	.05360	.05150	.04943
Melted and molded	.05527	.05368	.05148	.04950
	.05534	.05362	.05139	.04946
Turned on lathe	.05546	.05359	.05142	.04950
	.05537	.05349	.05148	.04945
Average	.05538	.05359	05148	.04950
Average error of mean	± .00003	± .00002	± .00002	± .00002

The values of the electromotive force became constant to less than ±0.02 mv. in one to two days. In spite of the care taken in annealing, individual differences between metallic electrodes still exist but the average values appear to be fairly reliable.

The data for the cell (2) can be represented by the formula

$$10^5E_{(t)} = 5538 - 14.8t - 0.385t^2 + 0.0075t^3 \quad (4)$$

Horsch[5] reports $E_{298.1} = 0.0534$, which is not in good agreement with the earlier results of Hulett (0.0505) or of Getman[6] (0.05047). The latter value, however, is in excellent agreement

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[3] La Mer and W. G. Parks, This Journal, **55**, 4343 (1933).

[4] Cowperthwaite, La Mer and Barksdale, *ibid.*, **56**, in press (1934).

[5] Horsch, *ibid.*, **41**, 1787 (1919); Lewis and Randall, "Thermodynamics," p. 419.

[6] Hulett, *Trans. Electrochem. Soc.*, **7**, 333 (1905); Getman, This Journal, **39**, 1806 (1917).

with our result of 0.05045 interpolated when $t = 25°$ in equation 4.

In Table II will be found the thermodynamic transfer quantities which can be calculated from these data by the equations valid for a bi-valent salt, namely

$$-\Delta F = 46148\ E_{(t)};\quad -\Delta H = 46148\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right];$$
$$\Delta S = 46148\left(\frac{\partial E}{\partial T}\right);\quad \Delta C_P = 46148\ T\left(\frac{\partial^2 E}{\partial T^2}\right)$$

TABLE II

THERMODYNAMIC TRANSFER QUANTITIES IN CALORIES PER MOLE OF CADMIUM FOR THE PROCESS Cd (s) = Cd (s, SAT. WITH Hg) CONSISTENT WITH THE ELECTROMOTIVE FORCE DATA AT 0, 10, 20 AND 30°

T	$\Delta\bar{F}$	$\Delta\bar{S}$	$T\Delta\bar{S}$	$\Delta\bar{H}$	$\Delta\bar{C}_P$
273.1	−2556				
283.1	−2473	9.345	2646	−5119	−42
288.1	−2426	9.824	2830	−5256	−13
293.1	−2376	9.783	2867	−5243	+18
298.1	−2328	9.225	2750	−5079	+49
303.1	−2284				

From the average error of the mean we estimate that $\Delta\bar{F}$ is correct to 0.05% or 1 calorie; $\Delta\bar{S}$ to 3% and $\Delta\bar{H}$ to 1.5% or 75 calories. The values for $\Delta\bar{C}_P$ are consistent with the experimental data for each temperature but no great weight should be attached to the individual values, though the trend from a negative to a positive value is undoubtedly significant. Teeter[7] by combining the measurements of Bijl,[8] F. Smith[9] and Hulett and De Lury[10] on Weston and dilute amalgam cells calculates a value of $E = 0.04990$; an average $\Delta E/\Delta T = -0.02335$ volt per degree or $\Delta H = -5515$ calories for 25°, which is in fairly good agreement with our result (−5243) for the heat of transfer of one mole of Cd (s) to a saturated amalgam, when one considers the uncertainties of combining the results of different investigators as well as using difference coefficients instead of derivatives.

By combining equation (4) with the values for the cell process (1) at unit activity of cadmium sulfate given in the preceding paper,[11] we obtain for the process

$$\text{Cd (s)} + \text{PbSO}_4\text{ (s)} = \text{CdSO}_4\ (a = 1) + \text{Pb (s, satd. with Hg)} \tag{5}$$

$$10^5\ E° = 7194 - 45.85t - 1.855t^2 + 0.021t^3 \tag{6}$$

Also $\Delta F_{298.1} = 2833$ calories, $\Delta S_{298.1} = -45{,}935$ e. u., $\Delta H_{298.1} = 16{,}578$ calories, $\Delta Cp_{298.1} \cong -77$ calories per degree.

Gerke[12] measured the cell corresponding to the process

$$\text{Pb(s)} = \text{Pb (s, satd. with Hg)} \tag{7}$$

and found $E^\circ_{298.1} = 0.00586$; $10^5\Delta E/\Delta T = 1.6$; whence $\Delta F_{298.1} = -270$ cal., $\Delta S_{298.1} = 0.74$ e. u., and $\Delta H_{298.1} = 42.4$ cal. By subtracting these results from (6) we get

$$\text{Cd (s)} + \text{PbSO}_4\text{ (s)} = \text{CdSO}_4\ (a = 1) + \text{Pb (s)} \tag{8}$$

$\Delta F_{298.1} = 3153$ cal., $\Delta S_{298.1} = -45.20$ e. u., $\Delta H_{298.1} = 16{,}536$ cal.

In Table III we compute the heats of formation per mole of amalgam in joules at 25° as developed by Teeter. While the agreement with the results of Teeter as calculated from his heats of solution and our own from e. m. f. data is not good, nevertheless our data are in better agreement than the values Teeter calculated from the Bijl–Smith e. m. f. data.

TABLE III

HEAT OF FORMATION PER MOLE OF AMALGAM IN JOULES AT 25°

N_2	Teeter (thermal)	La Mer and Parks, W. G. (e. m. f.)	Bijl-Smith (e. m. f.)
0.200	−3220	−3911	−4302
.209	−3450	−4091	−4497
.216	−3600	−4232	−4647

Summary

Electromotive force measurements on the cell Cd (metal), $CdSO_4$, Cd (2-phase amalgam) are reported at 10° intervals from 0 to 30°. From these data the free energy, entropy and heat content changes for the process Cd (metal) = Cd (s, satd. with Hg) are computed.

These data are combined with the data available in the literature to calculate the same thermodynamic quantities for the process Cd (s) + $PbSO_4$ (s) = $CdSO_4$ (a = 1) + Pb (s) and for comparison with the calorimetric heats of formation of cadmium amalgams.

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(7) Teeter, THIS JOURNAL, **53**, 3927 (1931), Table V, p. 3933. This paper contains a comprehensive treatment of the various kinds of thermodynamic data on Tl and Cd amalgams.

(8) Bijl, *Z. physik. Chem.*, **41**, 641 (1902).

(9) F. Smith, *Phil. Mag.*, [6] **19**, 250 (1910).

(10) Hulett and De Lury, THIS JOURNAL, **30**, 1805 (1908).

(11) Ref. 3, Table I, values for $E°$.

(12) Gerke, THIS JOURNAL, **44**, 1684 (1922).