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### Summary

1. The reaction between silver ion and hydroquinone in slightly acid solution is strongly catalyzed by colloidal silver, gold, palladium and silver sulfide.

2. The rate of the reaction catalyzed by silver varies as the first power of the hydroquinone concentration and as the  $2/3$  power of the silver-ion concentration. The dependence of the rate upon

the hydroxyl-ion concentration indicates that both un-ionized hydroquinone and the univalent ion take part in the reaction in the pH range 5.15–6.27.

3. The rate of the catalyzed reaction varies proportionately with the surface of the catalyst, and inversely with the concentration of gum arabic present as stabilizer. The temperature coefficient at pH 5.74 is approximately 2.1.

4. The indicated mechanism involves primary adsorption of silver ions to the surface of the catalyst.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

## Saturated Standard Cells with Small Temperature Coefficients. III. Cadmium-Bismuth Amalgams of Constant Cadmium Activity

BY W. C. VOSBURGH AND HELEN C. PARKS

A modified Weston standard cell has been described<sup>1</sup> that has a temperature coefficient less than a third that of the Weston cell and seems to be as satisfactory otherwise as the Weston cell. One respect in which this cell is different from the Weston cell is in the use of a cadmium-bismuth amalgam instead of the cadmium amalgam. Vosburgh<sup>2</sup> made a brief preliminary study of cadmium-bismuth amalgams, and it is the purpose of this paper to report an investigation of the composition limits within which such amalgams have a constant cadmium activity.

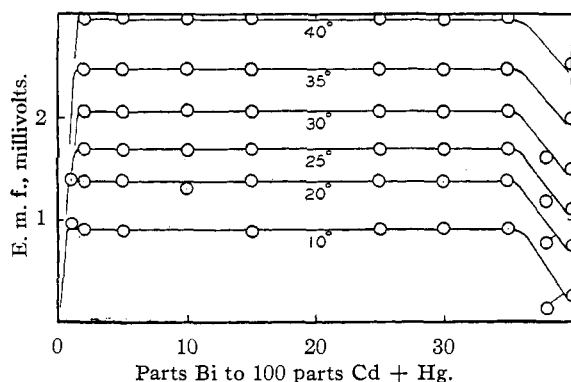


Fig. 1.—Electromotive force of the cell  $\text{Cd}(\text{Bi}, \text{Hg})/\text{Cd}^{++}/\text{Cd}(\text{Hg})$  when the proportion of bismuth in the ternary amalgam varies and the ratio of cadmium to mercury is fixed at 13:87 parts by weight.

(1) Paper II, Vosburgh, Guagenty and Clayton, *THIS JOURNAL*, **59**, 1256 (1937).

(2) Vosburgh, *ibid.*, **47**, 2531 (1925); see also ref. 1.

Amalgam concentration cells were made in which one amalgam was a two-phase cadmium amalgam containing about 10% cadmium and the other a cadmium-bismuth amalgam. The compositions by weight of the various ternary

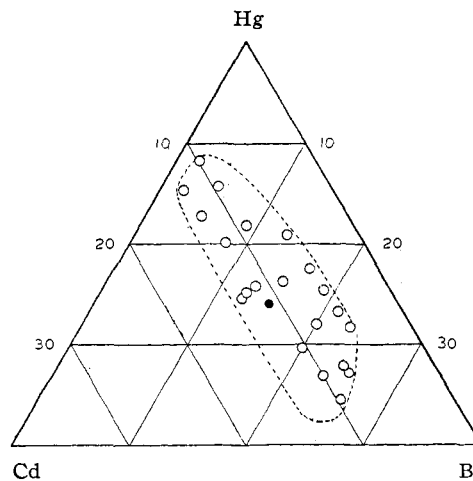


Fig. 2.—Cadmium-bismuth amalgams of constant cadmium activity at 25°. The dotted line is the approximate boundary of the region of constant cadmium activity. Circles represent experimental points; ●, represents the composition 11% Cd, 15% Bi and 74% Hg.

amalgams used are given in Table I. The electrolyte was saturated cadmium sulfate solution, with an excess of cadmium sulfate crystals at each electrode.

TABLE I  
THE CELL Cd(Bi, Hg)/Cd<sup>++</sup>/Cd(Hg) WITH VARYING COMPOSITION OF THE TERNARY AMALGAM

Bi to 100 parts Cd + Hg	Cd %	Bi %	Electromotive force, mv.					
			10°	20°	25°	30°	35°	40°
A. Ratio of Cd to Hg by weight, 7:93								
1	6.9	1.0	0.70	0.65	0.60	0.56	-0.78	-2.62
2	6.8	2.0	.91	1.11	1.06	.52	-1.27	-3.14
3	6.8	2.9	.91	1.38	1.45	.23	-1.58	-3.44
15	6.1	13.0	.90	1.38	1.69	-.22	-2.18	-4.23
20	5.8	16.7	..	1.35	1.67	-.23	-2.18	..
25	5.7	19.1	.85	1.36	1.69	-.19	-2.16	-4.21
27	5.5	21.3	.90	1.38	1.69	-.19	-2.16	-4.21
30	5.4	23.1	.61	1.27	1.68	-.15	-2.11	-4.15
35	5.2	25.9	.29	0.88	1.22	-.43	-2.37	-4.38
40	5.0	25.6	.42	.85	1.19	-.73	-2.72	-4.71
B. Ratio of Cd to Hg by weight, 10:90								
1	9.9	1.0	0.89	0.78	0.75	0.70	0.66	0.62
2	9.8	2.0	.90	1.35	1.70	2.03	2.44	1.75
5	9.5	4.8	.94	1.37	1.68	2.05	2.47	2.54
10	9.1	9.1	.90	1.37	1.69	2.06	2.48	2.60
15	8.7	13.0	.91	1.37	1.67	2.05	2.46	2.55
25	8.0	20.0	.86	1.36	1.68	2.04	2.46	2.62
29	7.8	22.4	.91	1.38	1.69	2.06	2.47	2.57
30	7.7	23.1	.88	1.38	1.69	2.06	2.47	2.56
31	7.6	23.7	.38	0.94	1.29	1.68	2.15	2.21
34	7.5	25.4	.26	.87	1.22	1.67	2.14	2.18
C. Ratio of Cd to Hg by weight, 13:87								
1	12.8	1.0	0.96	1.39	1.36	1.27	1.10	1.04
2	12.7	2.0	.91	1.38	1.69	2.06	2.47	2.96
5	12.4	4.8	.92	1.39	1.69	2.06	2.47	2.97
10	11.8	9.1	..	1.31	1.68	2.07	2.47	2.96
15	11.3	13.0	.91	1.38	1.69	2.06	2.47	2.96
25	10.4	20.0	.91	1.38	1.69	2.06	2.47	2.96
30	10.0	23.1	.92	1.38	1.69	2.06	2.47	2.96
35	9.6	25.9	.91	1.38	1.69	2.06	2.47	2.97
38	9.4	27.5	.12	0.76	1.18	1.61	1.45	-0.45
40	9.4	27.9	.24	.74	1.10	1.49	1.98	2.51
44	9.0	30.6	.35	.86	1.24	1.65	2.14	2.65
D. Ratio of Bi to Hg by weight, 14.3:85.7								
Cd to 100 parts Bi + Hg								
3	2.9	13.9	-2.62	-6.98	-9.12	-11.36	-13.61	-15.94
5	4.8	13.6	+0.88	-0.03	-2.03	-4.12	-6.19	-8.34
14	12.3	12.5	.94	+1.38	+1.69	+2.06	+2.47	+2.95
15	13.0	12.4	.90	1.38	1.69	2.06	2.47	2.96
18	15.3	12.1	6.97	4.35	3.02	1.90	2.16	2.66
25	20.0	11.4	12.13	9.53	8.20	6.86	5.40	4.03

For the preparation of the cadmium-bismuth amalgams, weighed quantities of mercury, cadmium and bismuth were placed in one leg of an H-shaped cell vessel, covered with sulfuric acid solution of about 0.01 M concentration and heated in a bath of hot water. The mixture was shaken frequently and a small current of electricity passed between the amalgam and an auxiliary platinum electrode, with the amalgam as cathode. The cadmium and bismuth used were of the best

commercial grade, and the mercury had been redistilled in a current of air.

Some of the cadmium amalgam used was prepared electrolytically, and some was prepared by the dissolving of cadmium in mercury at an elevated temperature.

The cells came to equilibrium soon after preparation and with few exceptions were constant in electromotive force at constant temperature during the period of observation of between two and

three months. The electromotive forces at six temperatures are given in Table I. Figure 1 shows the variation in electromotive force in one series of cells as the bismuth content of the ternary amalgam varied. The curves for the other series were similar. In Fig. 2 the compositions of the amalgams having the same cadmium activity at 25° are plotted. The dotted line is the approximate boundary of the region of constant cadmium activity.

The region of constant cadmium activity is sufficiently large to allow easy reproducibility of electromotive force in cells in which the ternary amalgam is used, and to prevent any probable

changes in composition from affecting the electromotive force. An amalgam of a composition in the neighborhood of 11% Cd, 15% Bi and 74% Hg, which is shown in Fig. 2 by a black dot, should be satisfactory for use in modified Weston cells. This composition is well within the constant-activity region from 10 to 40°.

### Summary

An investigation has been made of the composition limits for cadmium-bismuth amalgams within which the cadmium activity is independent of the composition between 10 and 40°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## Measurements of the Viscosity of Liquid Helium II

BY W. F. GIAUQUE, J. W. STOUT AND R. E. BARIEAU

In connection with the design of apparatus for adiabatic demagnetization investigations at low temperatures, we became interested in the viscosity of liquid helium near 1°K. Moreover, several investigators have recently reported experiments which show that liquid helium II is a substance of great interest. Wilhelm, Misener and Clark<sup>1</sup> have measured the relative viscosity of liquid helium from 4.2 to 2.2°K. They found that the viscosity increased normally with decreasing temperature until the region of the so-called "lambda point" was reached. At about 2.2° the viscosity decreased rapidly.

Burton<sup>2</sup> used the above measurements as a basis for the calculation of absolute values of the viscosity,  $\eta$ . At the boiling point he found  $\eta = 1.1 \times 10^{-4}$  poise. At 2.3°K. it increased to  $2.7 \times 10^{-4}$ . It then dropped to  $3.3 \times 10^{-5}$  poise at 2.2°K.

More recently Kapitza<sup>3</sup> and Allen and Misener<sup>4</sup> have reported that at lower temperatures the viscosity decreased to such a phenomenally low value that it could not be determined from their experiments. Allen and Misener used a fine capillary of thermometer tubing and Kapitza experimented with optically plane plates in contact with each other. In each case flow was produced by a small head of liquid helium. The

above workers concluded that even under the above conditions the flow was turbulent. Kapitza estimated that the viscosity below the "lambda point" was less than  $10^{-9}$  poise. Allen and Misener, whose experiments were made at the temperatures 1.07 and 2.17°K., estimated  $4 \times 10^{-9}$  poise as the upper limit of viscosity in this region. These conclusions are not in agreement with measurements of the present authors<sup>5</sup> to be described below. Kapitza considered the flow to be turbulent, with a Reynolds number of 750,000, in his experiment. Allen and Misener stated that the flow in their experiments was neither ordinary laminar nor turbulent and suggested the possibility of slip at the surface.

It has since become evident that the conclusions quoted above are not valid due to misinterpretation as to what actually occurred in the experiments.

Kürti, Rollin and Simon<sup>6</sup> have suggested that the seemingly very high thermal conductivity along a tube leading to a chamber in which liquid helium is being evaporated under reduced pressure is due to a film on the tube surface. We have enjoyed the opportunity of discussing this question with Dr. B. V. Rollin on several occasions. Some of our adiabatic demagnetization experiments have been hindered by effects of this

(1) Wilhelm, Misener and Clark, *Proc. Roy. Soc. (London)*, **A151**, 342 (1935).

(2) Burton, *Nature*, **135**, 265 (1935).

(3) Kapitza, *ibid.*, **141**, 74 (1938).

(4) Allen and Misener, *ibid.*, **141**, 75 (1938).

(5) Giauque, Stout and Barieau, *Phys. Rev.*, **54**, 147 (1938).

(6) (a) Kürti, Rollin and Simon, *Physica*, **3**, 266 (1936); (b) Rollin, *Actes 7th Cong. int. du Froid*, **1**, 187 (1936).