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Berkeley, California

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John L. Burnett and Moshè H. Zirin

July 1965

THE STANDARD EMF OF  $\text{Cd}_{(s)}/\text{Cd}^{++}$  AT  $25^{\circ}\text{C}^*$ John L. Burnett<sup>\*\*</sup> and Moshè H. Zirin<sup>†</sup>Lawrence Radiation Laboratory and  
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A number of attempts have been made to determine the standard potential of the  $\text{Cd}_{(s)}/\text{Cd}^{++}$  half-cell. Most of the attempts to 1936 were summarized and evaluated by Harned and Fitzgerald.<sup>(1)</sup> More recent results are those of Bates<sup>(2)</sup> and Treumann and Ferris.<sup>(3)</sup> The  $E^{\circ}$  values thus far determined range from 0.3960 to 0.4026 v.

Cadmium amalgam electrodes gave highly reproducible results; two phase cadmium amalgam electrodes ( $\geq 10\%$  Cd) were usually employed, and to convert the resulting EMF's to the solid cadmium electrode the value determined by Parks and La Mer<sup>(4)</sup> (0.05049 v) has been used. Parks and La Mer<sup>(4)</sup> also demonstrated that solid cadmium electrodes, with different history, gave different EMF values, but those same electrodes gave concordant results after annealing. Getman has shown<sup>(5)</sup> that  $E^{\circ}_{(s)} - E^{\circ}_{(p)} = 0.002$  v, where  $E^{\circ}_{(s)}$  and  $E^{\circ}_{(p)}$  stand for the potentials of single crystal and polycrystalline, cadmium, respectively. Usually a cadmium halide solution was used as the electrolyte and the reference electrode was a silver-silver chloride or calomel half-cell.

This work describes the measurements of the EMF of  $\text{Cd}_{(s)}/\text{Cd}^{++}$ , using a solid cadmium electrode, a commercial calomel half-cell and cadmium perchlorate in dilute perchloric acid—a combination apparently not reported hitherto.

## EXPERIMENTAL

Cadmium perchlorate solutions were prepared by dissolving Baker and Adamson Reagent Grade CdO in G. Frederick Smith, 70% double vacuum distilled  $\text{HClO}_4$  in stoichiometric amounts; the solution was filtered and the pH and  $\text{Cd}^{++}$  concentration were adjusted to the desired values by adding standardized  $\text{HClO}_4$  and conductivity water.

The cadmium electrodes were prepared by plating a 2-3 mils thick coat of cadmium over a copper base on platinum electrodes; the resulting plate was polycrystalline cadmium, of purity of 99.9% or better. The reference electrode was Beckman's Fiber Type, saturated calomel electrode No. 1170. A Leeds and Northrup Type K2 potentiometer was used to measure the EMF values. Two cadmium electrodes were immersed in the same electrolyte, and their potentials were checked alternately. Only those potential measurements that stayed constant to  $\pm 0.0001$  v for more than 30 minutes and gave the same value for both electrodes were accepted. The electrolyte was kept stirred by a flow of argon, which had been bubbled through acid of the same concentration as the electrolyte. Access to the atmosphere was prevented by a mercury pool. The positive pressure helped to exclude atmospheric gases from the reasonably well closed cell.

After each measurement at one  $\text{Cd}^{++}$  concentration an aliquot portion of the electrolyte was withdrawn and analyzed for  $\text{Cd}^{++}$  and  $\text{H}^+$ , and the electrolyte was replenished with an acid solution of the same concentration as the original one. Another measurement was taken and so on until the cadmium ion concentration was reduced to  $10^{-3}$  M. Two sets of measurements were made at pH 3 and 4 respectively.

## RESULTS AND DISCUSSION

The plots of  $E^{\circ}$  [ $E^{\circ} = E_{\text{meas}} + \frac{RT}{2F} \ln(\text{Cd}^{++}) + E_{\text{ref}}$ ] vs  $\sqrt{\mu}$  ( $\mu$  = ionic strength) are given in Fig. 1 for the two sets of measurements. Although the contribution of  $\text{H}^+$  to  $\mu$  was negligible compared with that of  $\text{Cd}^{++}$ , there is a noticeable effect of the pH on the  $E_{\text{meas}}$  values. This effect is greater than can be ascribed to the  $\text{Cd}^{++}$  hydrolysis, accepting published value of this hydrolysis constant.<sup>(6)</sup> Extrapolation of our curves to zero ionic strength yields  $E^{\circ}$  for the cell, which in this case is found to be  $0.6475 \pm 0.0001$ . Correcting for the EMF values of single-crystal/polycrystalline cadmium electrode ( $=0.002 \text{ v}^{(5)}$ ) and of the calomel half-cell ( $= -0.246 \text{ v}^{(7)}$ ), we find the  $E^{\circ}$  of  $\text{Cd}_{(s)}/\text{Cd}^{++}$  to be  $0.4035 \text{ v}$ .

The variation in previously reported values for the potential may be ascribed to a variety of sources: uncertainties in EMF values of the reference half-cells, the methods of extrapolation<sup>(1)</sup>; the possible association between ion involved in the net cell reaction and systematic errors in the activity coefficients used.<sup>(3)</sup> On the other hand,  $\text{Cd}(\text{ClO}_4)_2$  has been found<sup>(8)</sup> to be completely dissociated at concentrations of less than 0.1 M and should give more dependable results upon extrapolation. Maintaining the pH of the electrolyte on the acidic side should prevent the possibility of formation of  $\text{Cd}(\text{OH})^+$  and  $\text{Cd}(\text{OH})_2$  species.

There is one uncertainty in the values used, which has already been mentioned by Harned and Fitzgerald,<sup>(1)</sup> and that is the nature of the single crystal cadmium electrode used by Getman<sup>(5)</sup>; the  $E^{\circ}$  of  $\gamma\text{-Cd}_{(s)}/\alpha\text{-Cd}_{(s)}$

is 0.0031 v,<sup>(1)</sup> and if Getman's  $E^{\circ}_{(s)} - E^{\circ}_{(p)} = 0.002$  v refers to  $\alpha$  - Cd single crystal, then for  $\gamma$  - Cd,  $E^{\circ}_{(s)} - E^{\circ}_{(p)} = 0.005$  v and the value determined here—as well as those others arrived at by using Getman's value—should be handled accordingly.

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#### REFERENCES

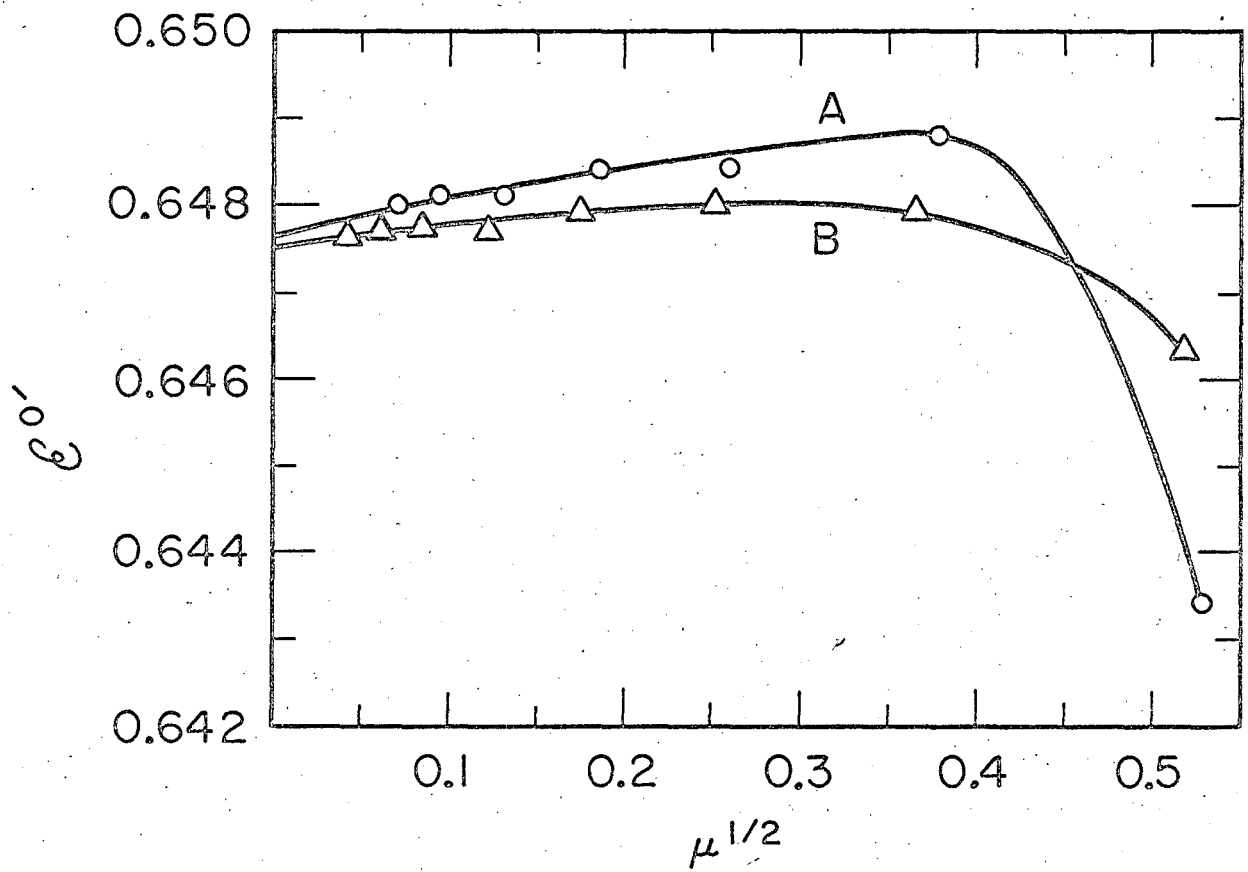
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- (1) H. S. Harned and M. E. Fitzgerald, J. Am. Chem. Soc. 58, 2624 (1936).
- (2) R. G. Bates, *ibid* 61, 308 (1939).
- (3) W. B. Treumann and L. M. Ferris, *ibid* 80, 5048 (1958).
- (4) W. G. Parks and V. K. La Mer, *ibid* 56, 90 (1934).
- (5) F. H. Getman, J. Phys. Chem. 35, 588 (1931).
- (6) Y. Marcus, Acta Chem. Scand. 11, 690 (1957).
- (7) W. J. Blaedel and V. W. Meloche, Elementary Quantitative Analysis, Theory and Practice, 1963 (2nd ed.), Harper and Row, Publishers, New York, p. 418.
- (8) P. K. Jena and B. Prasad, J. Indian Chem. Soc. 31, 480 (1954).





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FIGURE CAPTION

Fig. 1. Plot of  $E^{o'}$  [ $E^{o'} = E_{\text{meas}} + (RT/2F)\ln(\text{Cd}^{++}) + E_{\text{ref}}$ ] vs square root of ionic strength for cadmium perchlorate solution in perchloric acid media of  $\text{H}^+ = 0.001$  (curve A) and  $\text{H}^+ = 0.0001$  (curve B).

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