Summary

1. Electromotive force measurements of the cell

$$\text{Zn–Hg (2-phase)/ZnI}_2\ (m)\text{/AgI–Ag}$$

have been made at 5° intervals from 5 to 40° and at molalities of zinc iodide from 0.005 to 0.8.

2. The standard potential of the cell has been evaluated, and from it the electromotive forces of the hypothetical cells

$$\text{Zn (s)/Zn}^{++}\ (a = 1),\ \text{H}^{+}\ (a = 1)\text{/H}_2,\ \text{and}$$
$$\text{Zn–Hg (2-phase)/Zn}^{++}(a = 1),\ \text{H}^{+}\ (a = 1)\text{/H}_2$$

have been computed from 5 to 40°.

3. Calculations of the stoichiometrical activity coefficient, relative partial molal heat content and relative partial molal specific heat of zinc iodide in aqueous solution have been made.

4. Zinc iodide has been shown to be a normal bi-univalent electrolyte in aqueous solutions more dilute than 0.8 molal. Whereas the abnormalities of incomplete dissociation and complex ion formation indicated by transference and conductivity studies of strong zinc iodide solutions cause profound changes in the behavior of the salt in the concentrated range, they are of inappreciable influence below 0.8 *m*.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

A Rapid Method for Traces of Metals by the Dropping Mercury Electrode[1]

BY RALPH H. MÜLLER AND JOHN F. PETRAS

Introduction

In developing and testing the cathode ray tube polarograph[2] the authors required some means for obtaining the conventional Heyrovsky current–potential curves. It is obvious that these can be obtained manually and indeed the earliest studies were made in this fashion. It was to relieve the tedium of this procedure that Heyrovsky developed the automatically recording polarograph. The polarograph has the further advantage of providing a permanent record. On the other hand, the "manual" curves may be obtained with relatively inexpensive and commonly available equipment. The marked symmetry of the curves at once suggests a simple and rapid increment method for determining the concentration of a given ion.[2a] The object of this paper is to demonstrate the validity of the increment method and to illustrate its applicability.

Apparatus

It is common knowledge that a potentiometer will deliver at its e. m. f. terminals the potential which is set on the dials. In our work a Leeds and Northrup student-type potentiometer was used to deliver the desired potentials. The working current of the potentiometer was balanced against a standard cell in the usual manner. The e. m. f. terminals were connected to the electrode vessel in series with a wall-type galvanometer L and N Type P, 103 megohm sensitivity, resistance 126 ohms, period 8.9 sec. The latter was used in conjunction with an Ayrton shunt carefully adjusted to provide the critical damping resistance. The suspension was turned so that readings could be taken over more than half the scale length. The entire assembly was calibrated for linearity of response and used over that range. The electrode was of the type commonly used in polarographic work,[3] and consisted of a small Erlenmeyer flask with a platinum wire inseal for making connection with the mercury anode, and a bubbler inseal for flushing the contents of the vessel with hydrogen. The capillaries for the dropping mercury cathode were hand drawn from 1-mm. capillary tubing. They were graded for suitable lumen by examination under a low power microscope fitted with a micrometer ocular. The vessel was also provided with a salt bridge communicating with a saturated calomel electrode. In this way the anode potential could be measured. A switching arrangement enabled the operator to check the anode potential with the potentiometer. The mercury dropping rate was controlled by the pressure unit previously described.[2] It was found to be far more convenient and flexible.

Solutions

The solutions used in this work were prepared from reagent quality chemicals without further purification. Eastman purified de-ashed gelatin was added to all solutions to give a final concentration of 0.2%. A wide choice of addition agents is feasible. In routine work,

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[1] Presented before the Microchemical Division of the American Chemical Society, Milwaukee, Wisconsin, Meeting, September, 1938.

[2] R. H. Müller, R. L. Garman, M. E. Droz and J. F. Petras, *Ind. Eng. Chem., Anal. Ed.*, **10**, 339 (1938).

[2a] After this paper was submitted for publication the authors learned of similar work by Petering and Daniels in which the increment technique has been applied to the micro-analysis of oxygen. Their application undoubtedly precedes this contribution, and we regard our work as a general confirmation of the validity of the increment principle. The senior author is indebted to Professor Daniels for helpful discussion and exchange of opinions at the Milwaukee meeting and subsequently at his laboratory in Madison.

[3] J. Heyrovsky, in W. Böttger, "Physikalische Methoden der chemischen Analyse," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935; Hohn, "Chemische Analysen mit dem Polarographen," Verlag von Julius Springer, Berlin, 1937.

common glue has been found satisfactory by some investigators. A fairly complete list of suitable supporting solutions is given in Hohn's monograph. The indifferent electrolyte which was used in each case is indicated in the appropriate place. Oxygen was removed from all solutions just before use by bubbling pure hydrogen through the vessel. The formation of persistent bubbles due to the gelatin content was very annoying, but it was eliminated completely by the addition of a trace of caprylic alcohol. We were agreeably surprised to note that neither the dropping rate nor values of the potentials were adversely affected.

Experimental Results

A typical current-voltage curve is shown in Fig. 1. In this case equal amounts of cadmium and zinc nitrates were used with 0.1 M potassium chloride as the indifferent electrolyte. At each applied potential the galvanometer deflections are pulsating due to the dropping of the mercury at the cathode. The recorded values represent the maximum "throw" or excursion of the galvanometer. These are highly reproducible and it was rarely necessary to observe more than two or three "throws." The "Halbwellen" potential, defined as that potential on the curve corresponding to one-half the distance between the horizontal plateaus, is indicated in Fig. 1, for each ion. From each potential the anode correction of 0.04 v. was subtracted, yielding Cd = −0.64 v., and Zn = −1.07 v.

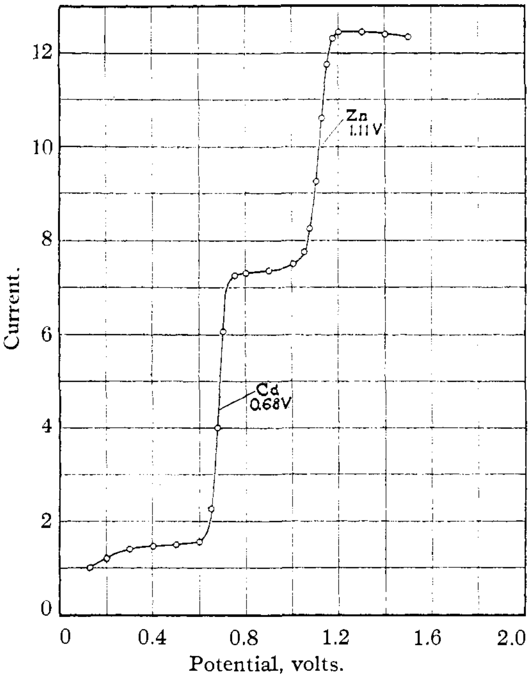

Fig. 1.—0.001 M Zn(NO$_3$)$_2$, 0.001 M Cd(NO$_3$)$_2$, 0.1 M KCl, 0.2% gelatin.

Figure 2 shows a family of curves obtained in this manner for cadmium at various concentrations. It is customary in polarographic work to draw the best straight line through each plateau and then estimate the difference in height (ΔI). Alternative schemes for estimating the correct wave height are discussed in the above monographs and in the paper by Borcherdt, Meloche and Adkins.[4] Due to the marked symmetry of the curves, it would seem that the current values obtained for two potentials more or less equidistant from the characteristic "Halbwellen" potential would yield a ΔI value which is equally reliable.

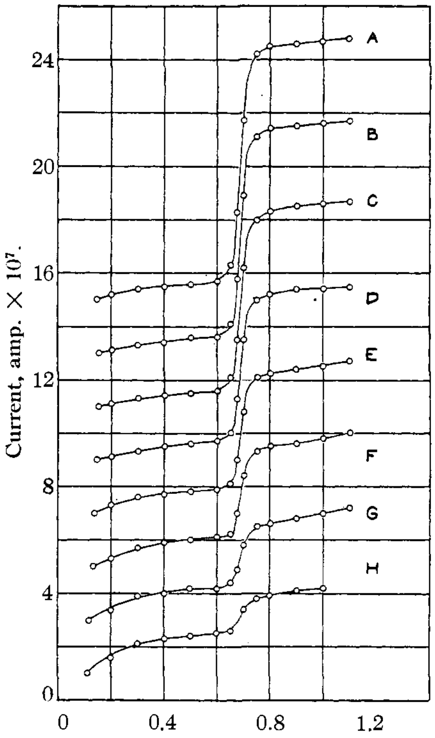

Fig. 2.—Concn. CdCl$_2$: A, 30 × 10^{-6} M; B, 27 × 10^{-6} M; C, 23 × 10^{-6} M; D, 19 × 10^{-6} M; E, 15 × 10^{-6} M; F, 11 × 10^{-6} M; G, 7.5 × 10^{-6} M; H, 4.0 × 10^{-6} M. All 0.1 M BaCl$_2$, 0.2% gelatin.

A cross plot of Fig. 2 is shown in Fig. 3. By inspection it was decided to select 0.6 and 0.8 v. For each concentration of cadmium the difference in current obtained at 0.8 and 0.6 v. was interpolated. These ΔI values were plotted against the

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(4) G. F. Borcherdt, V. W. Meloche and H. Adkins, THIS JOURNAL, 59 2171 (1937).

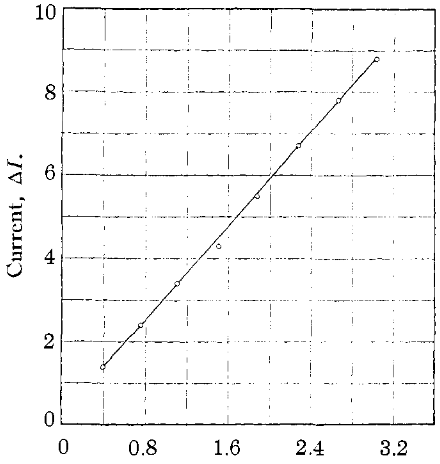

Fig. 3.—Cross plot of data in Fig. 2, illustrating linearity obtained by the increment method.

concentration of cadmium. With one exception the points lie closely on a straight line. This represents the worst condition for checking the relationship, in that considerable time elapsed in taking the whole family of curves. Succeeding runs with the simplified technique of merely measuring the respective currents for applied potentials of 0.6 and 0.8 v., amply confirmed this point.

A typical example is shown in Fig. 4. In this and all subsequent runs, a titration procedure was used to change the concentration. Specifically (Fig. 4), the electrolyte contained 0.1 M barium chloride as the indifferent electrolyte, 0.2% gelatin and to it were added from a microburet successive portions of 0.01 M cadmium chloride in 0.1 M barium chloride containing 0.2% gelatin. The final concentrations of cadmium ion were corrected for the small change in total volume.

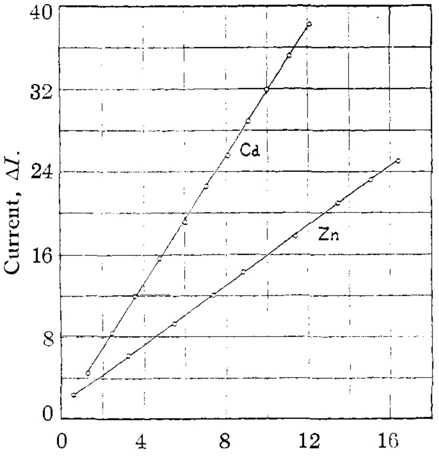

Fig. 4.—Upper curve: 0.01 M $CdCl_2$ in 0.1 M $BaCl_2$ + 0.2% gelatin titrated into 0.1 M $BaCl_2$ + 0.2% gelatin. Lower curve: 0.01 M $ZnCl_2$ in 1.0 M KOH + 0.2% gelatin titrated into 1.0 M KOH + 0.2% gelatin.

The method is quite satisfactory for traces of one ion in the presence of a large amount of other ions, provided the latter are reduced at higher potentials, and further that the interval between the respective potentials is great enough. In general the same limitations that apply to polarographic methods apply here, and certain cases can only be treated after preliminary separation or after conversion to suitable complex ions, etc.

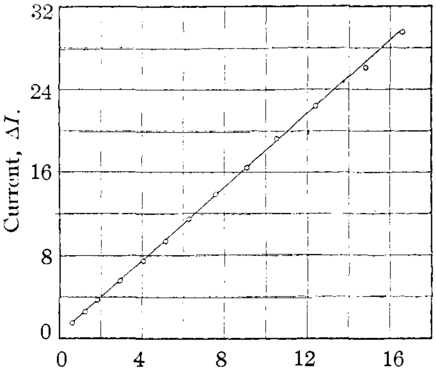

Fig. 5.—Traces of Cd in a large amount of zinc: 0.01 M $Cd(NO_3)_2$ in 0.1 M $ZnCl_2$ + 0.2% gelatin titrated into 0.1 M $ZnCl_2$ + 0.2% gelatin.

Figure 5 illustrates the results for small amounts of cadmium in the presence of a large but constant amount of zinc. It will be observed that the slopes for the ΔI-concn. curves for Cd^{++} ion in Fig. 4 and Fig. 5 are quite different. The actual slope depends upon the size of the mercury drop, the dropping rate, the concentration and nature of the indifferent electrolyte, and the galvanometer sensitivity. In a given run these factors are constant. To the extent that they might be reproduced in subsequent runs, the slopes would be correspondingly similar. For routine work this would seem to be a source of great trouble and inconvenience. This is a general limitation of all existing polarographic methods; they all assume that a preliminary calibration has been made under conditions closely approximating the intended analysis.

It is always possible, however, to include within the solution of the indifferent electrolyte a suitable "indicator" ion in known amount, preferably one which is not likely to be present in the "unknown." The indicator ion may then be used to evaluate the prevailing constants of the apparatus, thus furnishing a factor for the observed slopes.

Figure 6 shows results obtained for lead in strong alkaline solution. A complete curve for lead is shown merely to illustrate the choice of the two symmetric potentials which were selected for the analysis by the increment method. The adjoining curve shows the ΔI values as a function of lead concentration.

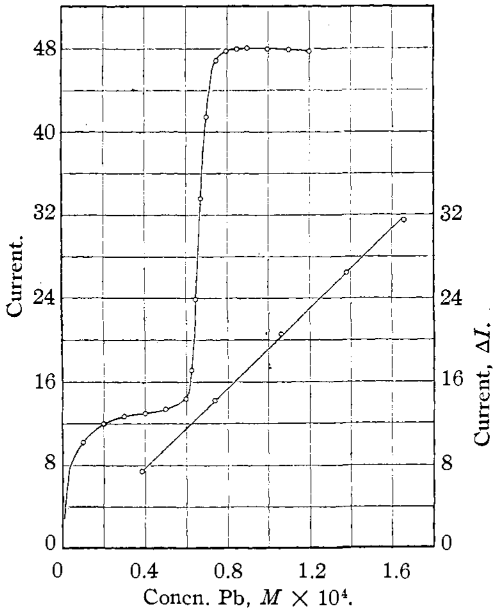

Fig. 6.—Upper curve: typical current–voltage curve for lead in alkaline solution. Lower curve: increment method, 0.01 M $Pb(NO_3)_2$ in 1.0 M KOH + 0.2% gelatin titrated into 1.0 M KOH + 0.2% gelatin.

Figure 4 is the incremental plot as a function of zinc concentration in alkaline solution and Fig. 7 shows the behavior of small amounts of lead in the presence of a large but constant amount of zinc, again in alkaline solution.

Discussion

The increment method which has been suggested for the evaluation of current–potential curves for the dropping mercury electrode has been shown to be reliable for three commonly occurring ions and mixtures of the same in neutral and alkaline solutions. In principle it is exactly similar to the practice of evaluating curves which have been recorded on a polarograph. It is extremely simple and rapid and merely assumes a reasonable degree of symmetry in the curve. Its applicability can be ascertained very quickly in any case. For cases in which the deposition potentials are too close, difficulties will be encountered to the same extent that they are in the conventional method. The use of gelatin or related substances, and the de-oxygenation by a stream of hydrogen are essential to success; the well-defined plateaus are largely dependent upon these factors.

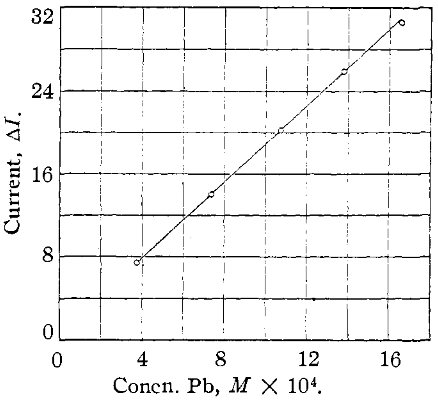

Fig. 7.—Traces of Pb in a large amount of zinc (alkaline solution): 0.01 M $Pb(NO_3)_2$ + 0.1 M $Zn(NO_3)_2$ in 1.0 M KOH + 0.2% gelatin titrated into 0.1 M $Zn(NO_3)_2$ in 1.0 M KOH + 0.2% gelatin.

For anyone slightly acquainted with electrical instruments, it will be apparent that a good potentiometer is not essential for this method. Any simple voltage divider with suitable means for adding and subtracting the required v.'s will suffice. In this general investigation we retained the more elegant arrangement because of its greater convenience and flexibility.

Summary

1. Current–potential curves may be obtained from the dropping mercury electrode with very simple equipment.
2. The marked symmetry of these curves suggests a simple increment method in which the change in current is noted for two applied potentials more or less equidistant from the characteristic "Halbwellen" potential. The current increments are a linear function of the concentration of the given ion.
3. The presence of other ions does not interfere with this relationship to any greater extent than it does with conventional polarographic methods.
4. The method has been illustrated with lead, zinc and cadmium ions, and pairs of these in neutral and alkaline solution.

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