

at high temperatures. The melting point of ZnF_2 is given from the literature as 872° .⁸ A check was obtained on a strip furnace run which indicated only that the m.p. was above 860° and below 885° . A high temperature X-ray diffraction study of the 80 mole % ZnF_2 mixture was undertaken in the hope that an accurate and direct estimate of the exsolution temperature might be obtained. The amount of $AgZnF_3$ in the sample as judged by the relative peak heights definitely appeared to decrease from room temperature to 325° and further to 450° . However, above this temperature the ZnF_2 is quite unstable in air and reacts to give ZnO , the pattern for which appears in a fresh sample in 15 minutes at 600° . Visual observation also established the existence of an unreacted solid phase

present when this mixture was held at 700° as described above. Accuracy in this second diagram is poor, being about $\pm 10^\circ$ and $\pm 1.5\%$ on composition.

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A Millicoulometer Method for the Determination of Polarographic n -Values

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It is possible to determine the value of n , the number of faradays per mole of electrode reaction, by using two polarographic cells in series and extending the electrolysis until a reasonable decrease in the concentration of the reducible or oxidizable compounds has occurred. The method was shown to give results within 2% for several inorganic and organic compounds.

There is much interest in knowing the number of electrons, n , involved per molecule during the reaction at the dropping mercury electrode. The use of the Ilkovic equation, $i_d = 607nD^{1/2}Cm^{2/3}t^{1/6}$, to determine n from the average diffusion current, i_d , and other quantities, requires a knowledge of the

diffusion coefficient of the substance undergoing electrochemical reaction. This obviously has its limitations. Another method based on a fundamental equation for the polarographic wave, $E_{d.e.} = E_{1/2} - 0.0591/n \log i/(i_d - i)$, is even more restricted because it applies only to electrochemically reversible reactions. Lingane² developed a method in which the current used during the reaction at a large stirred mercury cathode was integrated with a hydrogen-oxygen volume coulometer. Bogan³ and co-workers designed an electronic circuit incorporating a Weston integrating relay to be used in conjunction with a dropping electrode to measure the millicoulombs effecting a measurable change in concentration in a micro H-cell.⁴ Because such apparatus is not generally available, a method was devised which requires no elaborate equipment.

Apparatus.—When current is passed through two polarographic cells in series, an equivalent amount of electrochemical reaction will occur in each cell. The change in concentration in each cell can be determined from the decrease in wave height, and a comparison of these changes leads to a determination of the number of electrons used in a unit of reaction for an unknown substance in terms of a known in one of the cells. The potential across the two cells is held at a constant value but it must be selected with a knowledge of the polarographic behavior of the ions in cell A for which n is known and for the compound in cell B for which n is to be determined. If products are formed during prolonged electrolysis which give waves at a higher potential than the primary reaction, no difficulty will arise if a careful choice is made of the total voltage across the two cells.

In Fig. 1 are given idealized polarographic waves for compounds A and B, and the composite curve which is obtained when a potential is impressed across both cells in series. When a potential E_6 , which is the sum of E_1 and E_3 , is im-

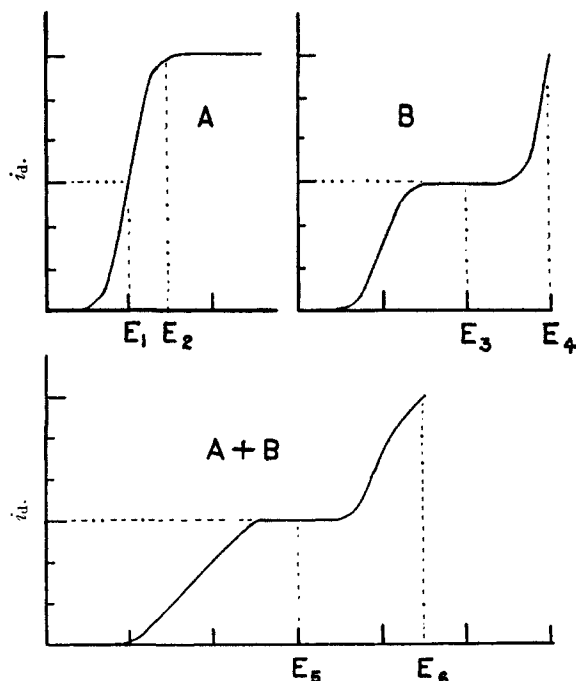


Fig. 1.—Idealized polarographic waves for materials A and B when the same current passes through both cells.

(1) Material abstracted from a thesis to be submitted by J. L. Kroon for the degree of Doctor of Philosophy.

(2) J. J. Lingane, *THIS JOURNAL*, **67**, 1916 (1945).

(3) S. Bogan, L. Meites, E. Peters and J. M. Sturtevant, *ibid.*, **73**, 1584 (1951).

(4) T. Meites and L. Meites, *Anal. Chem.*, **23**, 1893 (1952).

pressed across the cell, the current will be i_1 and reduction of both A and B only will occur. This optimum potential across the two cells can usually be varied within 0.3 v. of the selected value E_5 . If the potential E_6 , which is the sum of E_2 and E_4 , is selected with the corresponding current i_2 , there will be reduction of A and B and some reduction of the supporting electrolyte. In Fig. 2 is shown part of the polarographic curve obtained with cadmium chloride in one cell and p -nitrobenzoic acid in the other. For this pair 1.5 v. was selected as the potential across the cells for the determination of n . The fluctuations of the maximum of the diffusion current result because the drops do not fall in unison.

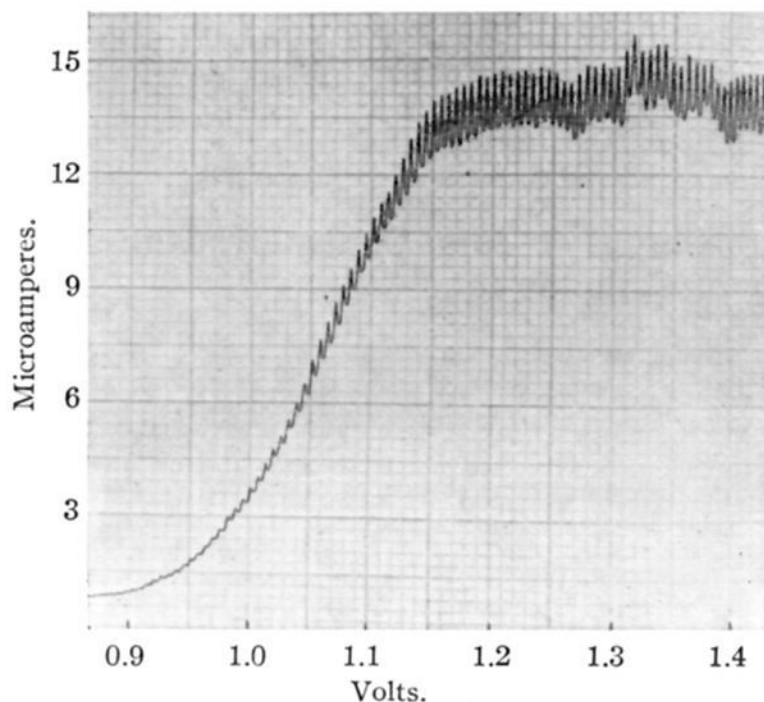


Fig. 2.—Polarographic wave obtained with 0.002 M CdCl_2 in one cell and 0.001 M p -nitrobenzoic acid in the other cell in appropriate supporting electrolytes.

For optimum precision it is best to select concentrations of A and B such that approximately the same percentage change will occur in each of the two cells.

Micro-cells were made from 4 and 10 mm. tubing of a design shown in Fig. 3. Oxygen-free nitrogen was passed over the solutions during the electrolysis. Oxygen was removed from the solutions in a separate small wash bottle which could also be weighed together with a medicine dropper. Weighed amounts of the solution were transferred to the cells after degassing. In order to keep the mercury pool in the cells at a constant level, the excess mercury from the dropping electrode accumulated in a leveling bulb of much larger diameter, attached to the cell by flexible tubing. The cells were designed so that 0.1 to 0.3 ml. of solution could be electrolyzed. The time of a run varied from 100 to 200 minutes.

Capillaries were made by drawing out thermometer tubing to a diameter of 1.5–2.0 mm. This was found to be more practical than grinding marine barometer tubing to a smaller diameter. A silver–silver chloride electrode was used as anode. It was made from silver wire, 0.05 inch in diameter, and flattened somewhat into a ribbon. This was wrapped helically around the end of the capillary and then anodized to silver chloride.

A Leeds and Northrup "Electrochemograph" was used for the measurements. The current for the electrolyses was obtained from storage batteries.

Results

According to the Ilkovic equation, the diffusion current is, besides other factors, dependent on the drop time to the one-sixth power. It was observed that the drop time changed during a run, hence the concentration is more accurately calculated to be proportional to $i_d t^{-1/6}$. The factor $m^{2/3}$ did not change appreciably during a determination. The amount of material which is reduced or oxidized

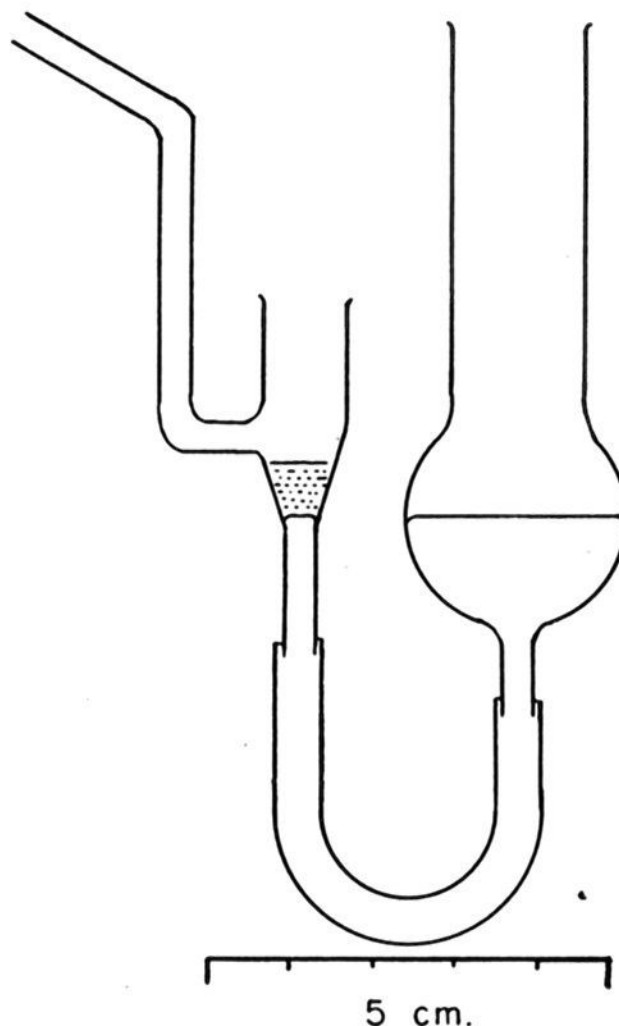


Fig. 3.—Millicoulometer cell.

is given by the equation

$$\Delta N = \left[1 - \frac{i_2}{i_1} \left(\frac{t_1}{t_2} \right)^{1/6} \right] N$$

where i_1 and i_2 are the diffusion currents at the start and end of a run, the drop times being t_1 and t_2 , and N is the number of moles of the compound in the cell at the beginning of the electrolysis.

TABLE I
REDUCTION OF VARIOUS COMPOUNDS

Cell no.	Solutions, mM	Ml. used	i_d , microamp. Initial	Final	Drop time, sec. Initial	Final	Moles red. $\times 10^7$
Potential, 1.8 v.; time, 202 min.; ratio, 1.014							
1A	2.05 CdCl_2^a	0.115	10.90	0.95	3.90	3.78	2.16
1B	2.05 CdCl_2^a	.136	10.02	2.40	3.37	3.52	2.13
Potential, 1.5 v.; time, 103 min.; ratio, 0.50							
2A	2.05 CdCl_2^a	0.136	10.40	5.49	3.78	3.98	1.33
2B	2.47 TlNO_3^b	.120	10.78	1.11	3.56	3.54	2.66
Potential, 1.6 v.; time, 100 min.; ratio, 0.988							
3A	1.99 CdCl_2^a	0.105	10.00	2.20	4.04	4.00	1.63
3B	2.60 f.a. ^c	.121	15.00	7.14	3.40	3.42	1.65
Potential, 1.5 v.; time, 125 min.; ratio, 1.98							
4A	1.99 CdCl_2^a	0.151	14.82	4.83	3.30	2.26	1.96
4B	1.10 p.a. ^d	.112	10.59	2.07	3.56	3.38	0.99

^a Cadmium chloride in 0.1 M potassium chloride. ^b Thallous nitrate in 0.1 M potassium chloride and trace of gelatin. ^c Fumaric acid in 0.12 M hydrochloric acid. ^d p -Nitrobenzoic acid in potassium hydrogen phthalate buffer (pH 2.65) plus 10% ethanol.

Some typical results are given in Table I. With 0.002 M cadmium chloride and 0.1 M potassium chloride in both cells, the values 0.94, 0.97, 1.014

and 1.02 were obtained for the ratio between the change in the cadmium ion concentration in each cell. Tests were also carried out using the cadmium ion solution in one cell and 0.0025 *M* thallos nitrate with 0.1 *M* potassium chloride in the other cell. Ratios obtained were 0.487, 0.500, 0.515 and 0.526. The reduction of several organic compounds was also studied. With the cadmium chloride solution in the one cell and 0.0026 *M* fumaric acid with 0.12 *M* hydrochloric acid in the second cell, ratios obtained were 0.97, 0.99, 1.01 and 1.04. The average value 1.00 gives $n = 2.00$ which is

reasonable for fumaric acid reduction on the basis to other experimental evidence. Another series of determinations were made with 0.0011 *M* *p*-nitrobenzoic acid in a potassium hydrogen phthalate buffer with a *pH* of 2.65 and containing about 10% ethanol to increase the solubility of the acid. In this case the ratios obtained gave values of n as follows: 3.92, 3.96, 4.16 and 4.22. The average value of 4.07 is within 2% of the literature value of 4 (necessarily an integer) for similar mono-nitroaromatics.

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Theory of Electrolysis at Constant Current with Partial or Total Control by Diffusion—Application to the Study of Complex Ions¹

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A mathematical analysis is made for the potential-time curves which are observed in electrolysis at constant current with mass transfer partially or totally controlled by semi-infinite linear diffusion. Three cases are considered: (1) reversible electrochemical process; (2) irreversible electrochemical process; (3) electrochemical process preceded by a first-order chemical reaction. The potential-time curves are characterized by a *transition time* whose value is derived for the above three cases. The transition time for given conditions of electrolysis is the same whether the electrode process is reversible or irreversible (cases 1 and 2). In the third case mentioned above, the transition time depends on the kinetics of the reaction preceding the electrochemical process. Conditions under which the theoretical treatment can be applied to the reduction of complex ions are stated. It is shown that for certain complexes (cadmium cyanide) dissociation must precede the electrochemical reaction, whereas other complexes (copper ethylenediamine) are reduced directly. The rate of recombination of Cd^{++} and CN^- ions is evaluated as being of the order of 4×10^9 (moles per l.)⁻¹ sec.⁻¹. Experimental methods are briefly discussed, and the potentialities of the method as a tool in electrochemical studies are evaluated.

Electrolysis at constant current density with mass transfer partially or totally controlled by diffusion has been studied for many years. Early investigations²⁻⁵ were concerned with the verification of Fick's laws of diffusion, but more recent work⁶⁻⁸ has been oriented toward the study of electrode processes and toward analytical applications. Recently, Gierst and Juliard⁸ developed a very ingenious method for the oscillographic recording of voltage-time curves. These authors made some very interesting observations on electrode processes, and their study brought to light some of the potentialities of electrolysis at constant current. The theoretical treatment of this type of electrolysis is rather limited at the present, and it is the purpose of this paper to give a mathematical analysis of the boundary value problems encountered in this method. Only cases involving semi-infinite linear diffusion in an unstirred solution will be discussed,

since cases of spherical or cylindrical diffusion can be treated as linear diffusion problems provided that the duration of electrolysis is sufficiently short (1 second)—a condition which is generally fulfilled in the present type of electrolysis. Convection effects will be neglected on account of the short duration of electrolysis. Furthermore, it will be assumed that the solution being electrolyzed contains a large excess of supporting electrolyte, and that migration effects can be neglected. The discussion is divided in three parts according to the nature of the electrode process involved; a fourth part deals with the application of the method to the study of complex ions.

Reversible Electrode Processes

Potential-Time Variations.—Consider the reduction of a substance Ox, and assume that the reduction product Red is soluble either in solution (or in mercury in the case of the deposition of an amalgam forming metal on a mercury electrode). The value of the concentration of substance Ox during electrolysis at constant current was calculated by Weber,² Sand,³ and Rosebrugh and Miller.⁹ Karaoglanoff⁵ derived the equation of the complete potential-time curve. His treatment need not be discussed here, but it is worth noticing that the curve representing the potential *versus* the square root of the electrolysis time is similar to a polarographic wave for the reversible process being considered here. If one assumes that the concentration of substance Red is equal to zero before elec-

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