POLAROGRAPHIC STUDIES WITH DROPPING AMALGAM ELECTRODES

A THESIS

by

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INTRODUCTION

The polarographic method of chemical analysis was introduced by Professor J. Heyrovsky in a series of papers published between 1922 and 1926. The method is based on interpretation of the current-potential curves obtained when electro-reducible or electro-oxidizable substances are reduced or oxidized at a dropping mercury electrode. The complete electrolytic cell usually consists of a dropping mercury electrode, an electrolyte and a quiet pool of mercury in the bottom of the cell which acts as the other electrode.

During any process of electrolysis, reduction occurs at one of the electrodes (cathode) and oxidation at the other (anode). The amount of electro-reduction at the cathode is always exactly equivalent to the amount of electro-oxidation at the anode. The magnitude of the current is a measure of the net rate of the electrode reactions. The curve obtained by plotting the external voltage applied against the resulting current is known as the current-voltage curve. If the one electrode has a constant potential this curve actually corresponds to a plot of the potential

of the other electrode against the current obtained and is called the current-potential curve. Since polarographic analysis depends entirely on certain unique characteristics of these current-potential curves a brief review of the principles involved is given here.

The current is carried through the solution by the ions present and the chemical reactions take place when the current passes from the solution to the electrodes. At the cathode electrons are given up by the electrode and accepted by substances in solution, while at the anode the reverse process takes place. The substances that are involved in these reactions may be either positively charged ions at the cathode and negatively charged ions at the anode or uncharged molecules at either or both electrodes. Only electro-reduction and electro-oxidation of charged ions will be dealt with. If the solution consists of only one cationic and one anionic species there is no doubt as to the ions involved in the reactions at the electrodes. However, when there are a variety of ions present, the question as to which ions take part in electrolysis is not so easily answered.

An electrolytic cell which consists of a flat mercury electrode in combination with an electrode

of constant potential will be considered first. The reaction which takes place at such a mercury electrode may be either reduction or oxidation depending on the direction of the electric current. If the reaction is the reduction of metal ions to the corresponding metal, the metal may be either soluble or insoluble in the mercury. Only the latter case, that is, the reduction of positive ions to metals soluble in mercury need be considered here. Such a reaction is illustrated by the equation

$$Hg + M^{n+} + ne = M_{(Hg)}$$

where Hg represents mercury in the amalgam which is formed at the mercury surface immediately the reaction starts, M^{n+} the metal ions in solution, n the valence of the ions or the number of electrons per ion involved in the reaction, e the charge on an electron, and $M_{(Hg)}$ the metal in the amalgam. Such reactions are reversible and the free energy change from left to right may be written

$$-\Delta G = RT \ln K - RT \ln \frac{a_m}{a_{Hg}\, a_{m+}} \qquad (1)$$

where ΔG is the change in free energy, K the equilibrium constant of the reaction, a_m the activity of the metal in the mercury, a_{Hg} the activity of the mercury, a_{m+} the activity of the metal ions in the solution, R the gas constant and T the absolute

temperature. Since

$$-\Delta G = nFE \qquad (2)$$

where F is the faraday, E the potential of the electrode and the other terms have the same meaning as before,

$$nFE = RT \ln K - RT \ln \frac{a_m}{a_{Hg}\, a_{m+}} \qquad (3)$$

or

$$E = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln \frac{a_m}{a_{Hg}\, a_{m+}} \qquad (4)$$

which can be written

$$E = E_o - \frac{RT}{nF} \ln \frac{a_m}{a_{Hg}\, a_{m+}} \qquad (5)$$

where E_o is the standard potential of the electrode, that is, the e.m.f. of the cell "Reference electrode versus the electrode M^{n+}, $M_{(Hg)}$" where

$$\frac{a_m}{a_{Hg}\, a_{m+}} = 1$$

Since the amalgam formed at the electrode is very dilute a_{Hg} will be practically constant so that (5) may be written[1]

$$E = E' - \frac{RT}{nF} \ln \frac{a_m}{a_{m+}} \qquad (6)$$

where

$$E' = \frac{RT}{nF} \ln K + \frac{RT}{nF} \ln a_{Hg} \qquad (7)$$

In terms of concentrations (6) is written

$$E = E' - \frac{RT}{nF} \ln \frac{f_a\, C_m}{f_s\, C} \qquad (8)$$

where f_s and f_a are the activity coefficients of the

ions in solution and the metal in the amalgam, respectively, and C and C_m are the respective concentrations in moles per liter.

From the derivation of (8), it is apparent that the potential, versus any given electrode, at which a given cation will be reduced is a characteristic of that particular cation. This indicates how it is possible to predict which ionic species is involved in an electrode reaction when the electrolytic solution contains a variety of ions.

The next point to be considered is the magnitude of the current obtained with any given concentration of the cation in the solution. It is obvious that C and C_m in (8) refer to the concentrations at the surface of the electrode. As E is increased, that is, made more negative in the cathodic process, if all other factors are kept constant, the ratio of C_m to C must also increase. A clearer picture of what actually takes place when E is varied can be obtained by considering the resulting current. In so doing it will become clear how the current-potential curve can be used to calculate the concentration of a given ionic species in solution.

The case considered here is that in which there is no slow process hindering the discharge of the ions at the electrode, that is, the value of E

at which the process occurs is expressed exactly by (8). As electrolysis proceeds the cations at the electrode surface are used up and must be replaced by ions from the body of the solution. At the theoretical steady state of constant potential and constant current the rate of the reaction must equal the rate at which the ions are supplied to the surface of the electrode. The ions can be brought up to the electrode by two distinct processes, migration and diffusion. In the presence of an excess of an indifferent electrolyte the current is carried almost entirely by these extraneous ions so that the ions under consideration are brought up to the electrode surface almost entirely by diffusion alone.

According to Fick's Law[2] the rate of diffusion of ions across the concentration gradient between the body of the solution and the surface of the electrode is given by the expression

$$\frac{dN}{dt} = \frac{AD}{\delta} (C - C_e) \qquad (9)$$

where A is the Area of the electrode, δ the thickness of the diffusion layer, C and C_e are the concentrations of the ions in the body of the solution and at the surface of the electrode respectively, $\frac{dN}{dt}$ is the rate of diffusion in moles per second and D the diffusion coefficient in centimeters squared per second. There

is some confusion in the literature as to whether or not C and C_e should be replaced by the corresponding activities. Glasstone[3] states "Although Fick's Law was originally stated in terms of concentrations, it is quite certain that diffusion is determined by the difference of free energy between two points in a solution; it is consequently the difference in activities rather than that of concentrations which is employed." On the other hand, Kolthoff and Lingane[1] follow Heyrovsky and Ilkovic[4] and assume that the rate of diffusion is directly proportional to the differences in concentrations. However, Heyrovsky[4,5] usually writes (6) with activities replaced by concentrations whereas Kolthoff and Lingane[1] use activities as was done above. The practice followed by Kolthoff and Lingane, of using activities in (6) and concentrations when dealing with diffusion rates, will be followed in this thesis.

At equilibrium the rate of discharge of the ions is equal to the rate of diffusion up to the electrode. The rate of discharge of ions per unit area is equal to I/nF, where I is the current per unit area, F is the faraday and n has its usual meaning. Substitution of I/nF for dN/dt into (9) gives

$$\frac{I}{nF} = \frac{D}{\delta}(C - C_e) \qquad (10)$$

where A = 1 and is omitted from the equation

or $$i = \frac{A\ D\ n\ F}{\delta}\ (C - C_e) \qquad (11)$$

where i is the current obtained at an electrode of area A.

Since A, D, n, F and δ are all constants for any given system, (11) can be written

$$i = k_s\ (C - C_e) \qquad (12)$$

where

$$k_s = \frac{A\ D\ n\ F}{\delta} \qquad (14)$$

It is obvious that the maximum current is obtained when C_e becomes essentially zero, that is,

$$I_d = k_s\ C \qquad (15)$$

where I_d is the limiting current. The maximum or limiting current is proportional to the concentration of the ions in solution.

Equation 12 may now be written

$$i = I_d - k_s\ C_e \qquad (16)$$

or

$$C_e = \frac{I_d - i}{k_s} \qquad (17)$$

Substitution of the expression for C_e in (17) into (8) in place of C gives

$$E = E' - \frac{RT}{nF} \ln \frac{f_a\ C_m}{f_s\ \frac{(I_d - i)}{k_s}} \qquad (18)$$

The concentration of the metal in the amalgam at the surface of the drop will be proportional to the rate

at which the metal is produced by the electrode reaction, that is, it is proportional to the current. Therefore

$$C_m = ki$$

or

$$C_m = \frac{i}{k_a}$$

where k_a is simply a proportionality constant. Equation 18 now becomes

$$E = E' + \frac{RT}{nF} \ln \frac{f_s\ k_a}{f_a\ k_s} - \frac{RT}{nF} \ln \frac{i}{I_d - i} \qquad (19)$$

Now when the current is one-half the limiting current, that is, when i is equal to $I_d/2$ the last term in (19) becomes zero and

$$E_{\frac{1}{2}} = E' + \frac{RT}{nF} \ln \frac{f_s\ k_a}{f_a\ k_s} \qquad (20)$$

where $E_{\frac{1}{2}}$ is the potential when the current is one half the limiting current. All the terms on the right hand side of (20) are constants except f_s and f_a. Since the concentration of the amalgam is always small, f_a is very nearly unity. The activity coefficient of an ion in solution is affected by the concentration of other ions present. Consequently, f_s is probably less than unity, owing to the relatively high concentration of the indifferent electrolyte, but should be nearly constant over the small variations in concentration of the ions under consider-

ation in polarographic analysis. Therefore, $E_{\frac{1}{2}}$, called the half-wave potential, is essentially a constant for any ionic species in a given electrolytic solution.

Substitution of the value of E' in (8) into (20) gives

$$E_{\frac{1}{2}} = Eo + \frac{RT}{nF} \ln A_{Hg} + \frac{RT}{nF} \ln \frac{f_s \, k_a}{f_a \, k_s} \qquad (21)$$

which shows that the half-wave potential differs from the standard potential of the electrode reaction by the values represented by the last two terms in (21).

The treatment so far illustrates the fundamental theory upon which polarographic analysis is based. It is necessary now to consider the polarographic cell, which differs from the above in that one of the electrodes is not a flat pool of mercury but consists of mercury flowing dropwise from a fine capillary. The other electrode is essentially a constant potential electrode; it may, in fact, be an external half cell such as a calomel electrode, or, as is often the case, it may be simply a quiet pool of mercury in the bottom of the cell. If the supporting electrolyte in the cell is a chloride the quiet pool of mercury is actually a calomel electrode, since sufficient mercurous chloride is formed by interaction of mercury with chloride ions, hydrogen

ions and dissolved oxygen to saturate the solution with calomel before the oxygen is removed[1]. The reaction at the quiet pool of mercury (calomel electrode) when ions are reduced at the dropping electrode is represented by the equation

$$2\ Cl^- + 2\ Hg = Hg_2\ Cl_2$$

Since the area of the quiet pool of mercury is large compared with that of the dropping electrode the current density at the former is extremely small. Consequently, a current that causes complete concentration polarization at the small mercury drops will leave the other electrode virtually unpolarized.

At the dropping electrode the reduction of metal ions to atoms is fundamentally the same as the cathodic process at a quiet mercury electrode. An important difference, however, is in the relation between the concentration of the ions being reduced and the limiting current obtained. Although (19) and (20) apply as well to the polarographic cell as to the quiet mercury electrode, k_s and probably k_a take on new values. It will be recalled that in the development of (15) the element of the time was omitted. This was done for the sake of simplicity and the treatment was sufficient to illustrate the real meaning of k_s and I_d. However, the relation is mainly

of theoretical interest because it holds only for the hypothetical steady state period which strictly speaking is of infinitesimally short duration. In polarographic analysis it is necessary to include the time factor. Ilkovic[6] was the first to solve the problem of diffusion to a dropping electrode and obtain an equation for the resultant limiting current. The differential equation for diffusion is[1]

$$\frac{\partial C}{\partial t} = \frac{Dr^4}{\rho^3}\left\{\rho\frac{\partial^2 C}{\partial \rho^2}+\frac{2(\rho^3-r_o)}{\rho^3+r_o}\cdot\frac{\partial C}{\partial \rho}\right\} \qquad (22)$$

where r_o is the radius of the drop, r the radial distance from a point in the solution to the center of the drop, D the diffusion coefficient of the diffusing substance, C the concentration, t the time and

$$\rho^3 = r^3 - r_o^3 \qquad (23)$$

For the region very close to the surface of the drop, (22) becomes somewhat simpler and the solution of it leads eventually to the following equation

$$I_d = 0.732\ n\ F\ D^{\frac{1}{2}}\ C\ m^{2/3}\ t^{1/6} \qquad (24)$$

In this equation I_d is the limiting current in amperes, 0.732 a combination of numerical constants, F the faraday in coulombs, D the diffusion coefficient of the ions in centimeters squared per second, C the concentration in moles per liter, m the number of grams of mercury flowing per second and t the time

per drop in seconds. When the current is expressed in microamperes, the concentration in millimoles per liter and 96,500 substituted for the faraday the equation becomes

$$I_d = 706\ n\ D^{\frac{1}{2}}\ C\ m^{2/3} t^{1/6} \qquad (25)$$

Equation 25 represents the maximum current but the galvanometer usually used in polarographic work is not sensitive enough to follow the growth of the current exactly. Consequently the average of the oscillations of the galvanometer is read and the above equation is changed to

$$I_d = 605\ n\ D^{\frac{1}{2}}\ C\ m^{2/3} t^{1/6} \qquad (26)$$

where I_d is the average current and is defined as the hypothetical constant current which, flowing over a period of time equal to the dropping time, would produce the same quantity of electricity as the quantity associated with each drop[1].

Equation 26 may now be written

$$I_d = k_1\ C$$

where

$$k_1 = 605\ n\ D^{\frac{1}{2}}\ m^{2/3} t^{1/6} \qquad (27)$$

It is now apparent that k_s, which represented A D n F/6 in (19) and (20) for the hypothetical steady state with a quiet mercury electrode, is equal to $605\ n\ D^{\frac{1}{2}}\ m^{2/3} t^{1/6}$ for the dropping electrode.

For the purpose of reference (19) and (20) are re-written as (28) and (29), respectively, which refer specifically to the dropping mercury electrode.

$$E = E' + \frac{RT}{nF} \ln \frac{f_s \, k_a}{f_a \, k_s} - \frac{RT}{nF} \ln \frac{i}{I_d - i} \qquad (28)$$

$$E_{\frac{1}{2}} = E' + \frac{RT}{nF} \ln \frac{f_s \, k_a}{f_a \, k_s} \qquad (29)$$

where

$$k_s = 605 \; n \; D^{\frac{1}{2}} \; m^{2/3} t^{1/6}$$

$$I_d = 605 \; n \; D^{\frac{1}{2}} \; m^{2/3} t^{1/6} \; C$$

$$i = 605 \; n \; D^{\frac{1}{2}} \; m^{2/3} t^{1/6} \; (C - C_e)$$

and the other terms have the same meaning as before.

The discussion so far has dealt with a dropping electrode of pure mercury. In 1939, Lingane[7] discovered that, when a cadmium amalgam was used as the dropping electrode dropping into a solution which contained $CdCl_2$, the current-potential curve was continuous but consisted of a part which was below zero current, that is, a negative current portion, and part which was positive in the ordinary polarographic sense. He concluded that the negative current was due to the electrode reaction

$$M_{(Hg)} = M^{n+} + ne + Hg$$

Heyrovsky and Kalousek[8] studied the effect on the half-wave potentials when dilute amalgams

were used in place of pure mercury as the dropping electrodes, with the ions corresponding to the metals in the solution. They found that the half-wave potential, described as the potential required to obtain a current half way from the bottom to the top of the wave, remained constant regardless of the concentration of either the amalgam or of the ions in solution.

As pointed out by Heyrovsky and Kalousek, these results are consistant with the theory that the current-potential curve is expressed by (28). In this case, however, there is a negative as well as a positive i and I_d which changes the equation to

$$E = E' + \frac{RT}{nF} \ln \frac{f_s\ k_a}{f_a\ k_s} - \frac{RT}{nF} \ln \frac{i - I_{d-}}{I_{d+} - i} \qquad (30)$$

where I_{d+} refers to the limiting current resulting from the reduction of ions in solution and I_{d-} to that from the oxidation of the metal in the amalgam.

The half-wave potential occurs when

$$i = \frac{I_{d+} + I_{d-}}{2}$$

Substitution of this value for i into (30) gives

$$E = E' + \frac{RT}{nF} \ln \frac{f_s\ k_a}{f_a\ k_s} \qquad (31)$$

which shows that $E_{\frac{1}{2}}$, the half-wave potential, is independant of concentrations except insofar as f_s and f_a are affected.

Lingane[7], and Heyrovsky and Kalousek[8], believed from their results that the negative limiting current obtained with a dropping amalgam electrode is proportional to the concentration in the amalgam of the metal being oxidized; they assumed too that this negative limiting current is expressed by the equation

$$I_{d-} = 605\ n\ C\ D_a^{\frac{1}{2}}\ m^{2/3} t^{1/6} \qquad (32)$$

Where the right hand side of the equation is exactly the same as that in (26) except that now C and D_a refer to the metal in the amalgam instead of the ions in solution. This means that k_a has the same meaning with respect to the amalgam as k_s has with respect to the solution. Consequently the ratio k_a/k_s is equal simply to $(D_a/D_s)^{\frac{1}{2}}$. Kolthoff and Lingane[1] present further indirect experimental evidence in support of this theory in their treatment of the thermodynamic significance of the half-wave potential.

It is evident, if the limiting current for the anodic reaction at an amalgam dropping electrode is expressed exactly by (32), that it should be possible to determine the amount of a metal in mercury by using the amalgam as the dropping electrode in a polarographic cell. Furthermore, such a method of analysis should have the same degree of accuracy as the usual polarographic method. The possibility

of analyzing alloys by dissolving them in mercury and using the amalgams so formed as dropping electrodes at once presents itself.

There is, however, no experimental evidence reported in the literature to show that the limiting current, obtained from the oxidation reaction at a dropping amalgam electrode, is proportional to the concentration of the metal so oxidized. The authors mentioned above used amalgams in which the concentration of the metals was only approximately known. In fact, Heyrovsky and Kalousek[8] stated that they were unable to make a careful study of the effect of concentration because of the instability of the amalgams. Stackelburg and Freyhold[9] used dropping amalgam electrodes to study the reversibility of certain electrode reactions but reported only an approximate concentration.

The work reported in this thesis was undertaken with the following objectives in view: (a) to determine whether or not the magnitude of the negative limiting current is proportional to the concentration of the metal in the amalgam; (b) to obtain direct experimental evidence necessary to test (32); (c) to investigate the possibility that the anodic process at the electrode, that is, the diffusion of

the ions so formed away from the amalgam drops, affects the magnitude of the negative limiting current obtained; and (d) to study the effect of the presence of other metals in the amalgam on the limiting current from a given metal.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

(a) Electrical Circuits. The electrical circuits used are shown schematically in Figure 1. The battery slide wire circuit consisted of a six volt storage battery, B; a variable resistor, R_1; a slide wire (Leeds and Northrup student type potentiometer), S; and a switch, K_1, for making and breaking the circuit. In the cell circuit, M is a unipivot millivoltmeter; K_2 is a switch for introducing the millivoltmeter into the circuit; R_2, R_3 and R_4 are standard resistance boxes; G is a galvanometer and C is the polarographic cell.

With the variable resistance R_1, in the battery circuit, the voltage across the potentiometer could be adjusted as desired up to the full capacity of the battery. R_2 and R_3 together provided an Ayrton shunt by means of which the fraction of the cell circuit passing through the galvanometer could be varied as required. The galvanometer, an ordinary moving coil box type, with a straight scale, was over damped with R_4 to give a period of about 20 seconds.

(b) Calibration of Electrical Equipment. With the cell replaced by a 30,000 ohms standard resistance, R_1 was adjusted so that the millivoltmeter read 37.5 millivolts when 1/32 of the total voltage across the

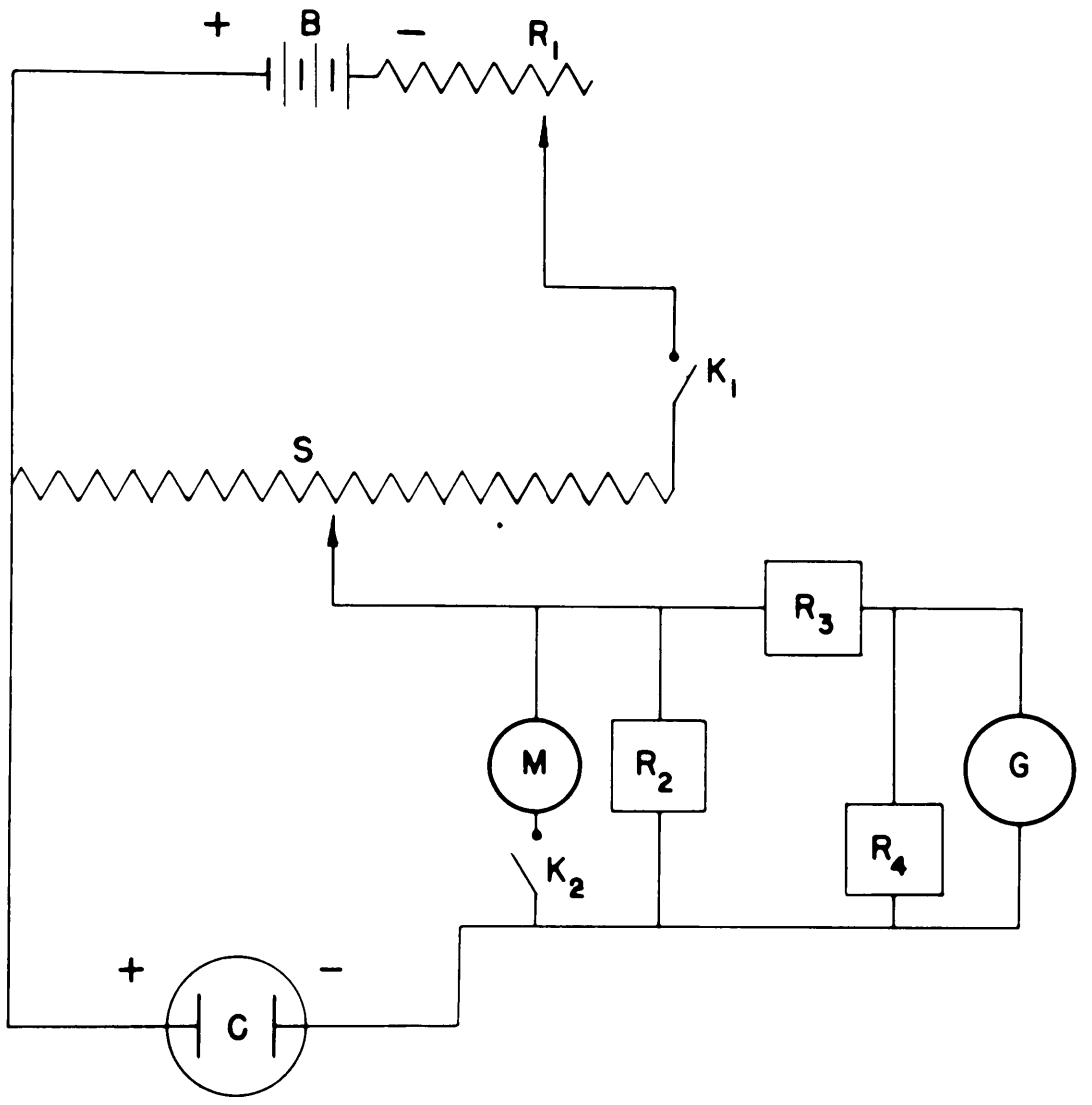


Figure 1. Electric circuits.

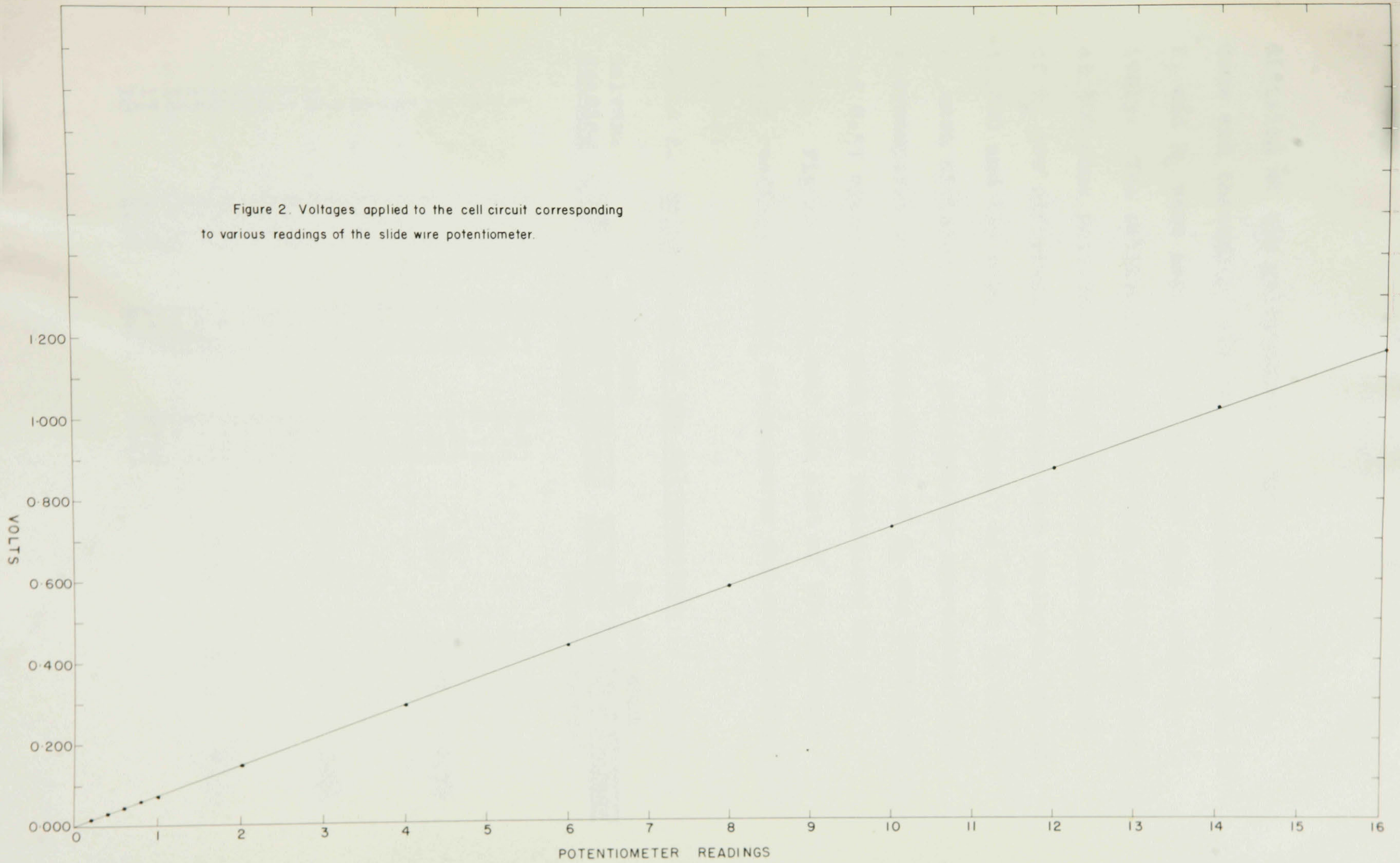
student type potentiometer was allowed to pass through the cell circuit. With R_1 at this setting the millivoltmeter was replaced with a type K potentiometer. The potential across the student type potentiometer was 1.169 volts and the relation between the potential and the reading on the student type potentiometer was found to be linear as shown in Table 1 and Figure 2. This potentiometer reading multiplied by 1/16 equals the fraction of the total voltage applied to the cell circuit.

TABLE 1. Voltage Applied to the Cell Circuit for Various Settings of the Potentiometer.

Potentiometer Reading	Voltage
0.20	0.015
0.40	0.029
0.60	0.044
0.80	0.059
1.00	0.073
2.00	0.146
4.00	0.293
6.00	0.439
8.00	0.586
10.00	0.731
12.00	0.877
14.00	1.023
16.00	1.169

The current represented by the galvanometer deflections was determined by replacing the cell with a standard resistance box. The current in microamperes was calculated by ohms law from the potential across the standard resistance for each

Figure 2. Voltages applied to the cell circuit corresponding to various readings of the slide wire potentiometer.



division of the galvanometer. While this was being done and throughout all the later experimental work R_3 and R_4 were kept at 1000 and 200 ohms, respectively. The calibration was done with R_2 at 1000 and at 300 ohms resistance. For each of these settings of R_2 two different resistances were employed, one of 10,000 and the other 30,000 ohms. As shown in Table 2, each division of the galvanometer represented 0.25 microamperes when the resistance of R_2 was 1000 ohms and 0.57 microamperes when the resistance was 300 ohms. Figure 3 shows that the plot of the galvanometer readings against microamperes was essentially linear.

TABLE 2. Calibration of the Galvanometer.

Galvan. Reading	R_2 1000 ohms			R_2 300 ohms		
	10,000*	30,000*	Average	10,000*	30,000*	Average
	(microamperes)			(microamperes)		
1	0.23	0.27	0.25			
2	0.46	0.54	0.50			
3	0.71	0.80	0.76			
4	0.97	1.04	1.01			
5	1.16	1.30	1.23	2.67	2.89	2.78
6	1.42	1.52	1.47			
7	1.70	1.76	1.73			
8	1.98	1.99	1.99			
9	2.19	2.23	2.21			
10	2.44	2.50	2.47	5.37	5.50	5.44
11	2.70	2.73	2.72			
12	2.95	3.00	2.98			
13	3.19	3.24	3.22			
14	3.44	3.50	3.47			
15	3.68	3.78	3.73	8.16	8.39	8.28
16	3.92	4.01	3.97			
17	4.16	4.21	4.19			
18	4.40	4.41	4.41			

19	4.68	4.78	4.73			
20	4.88	5.02	4.95	10.98	11.32	11.15
21	5.14	5.26	5.20			
22	5.39	5.52	5.46			
23	5.64	5.79	5.72			
24	5.88	6.05	5.92			
25	6.13	6.31	6.22	13.92	14.20	14.06
26	6.38	6.58	6.48			
27	6.63	6.82	6.73			
28	6.88	7.09	6.99			
29	7.12	7.33	7.23			
30	7.33	7.59	7.46	16.75	17.45	17.10
31	7.58	7.83	7.71			
32	7.84	8.09	7.97			
33	8.09	8.36	8.23			
34	8.33	8.59	8.46			
35	8.61	8.90	8.76	19.56	19.73	19.65
36	8.90	9.17	9.04			
37	9.13	9.43	9.28			
38	9.38	9.68	9.53			
39	9.63	9.94	9.79			
40	9.87	10.19	10.03	22.44	22.85	22.65
45	11.22	11.46	11.34	25.73	25.80	25.77
Average per division			0.25			0.57

* Refer to the resistance across which the potential was measured.

(c) Polarographic Cell and Attachments. Figure 4 is a diagram of the cell and attachments.

A is a 125 ml. Erlenmeyer flask. A hole was blown in the bottom of the flask and a glass tube, about one and one-half centimeters long and of such a diameter that the fine capillary would just fit into it, was sealed on. The fine capillary, diameter 0.05 millimeter, was placed in the tube so that the upper end protruded just above the bottom of the flask, and was held in place by a rubber band around the end of

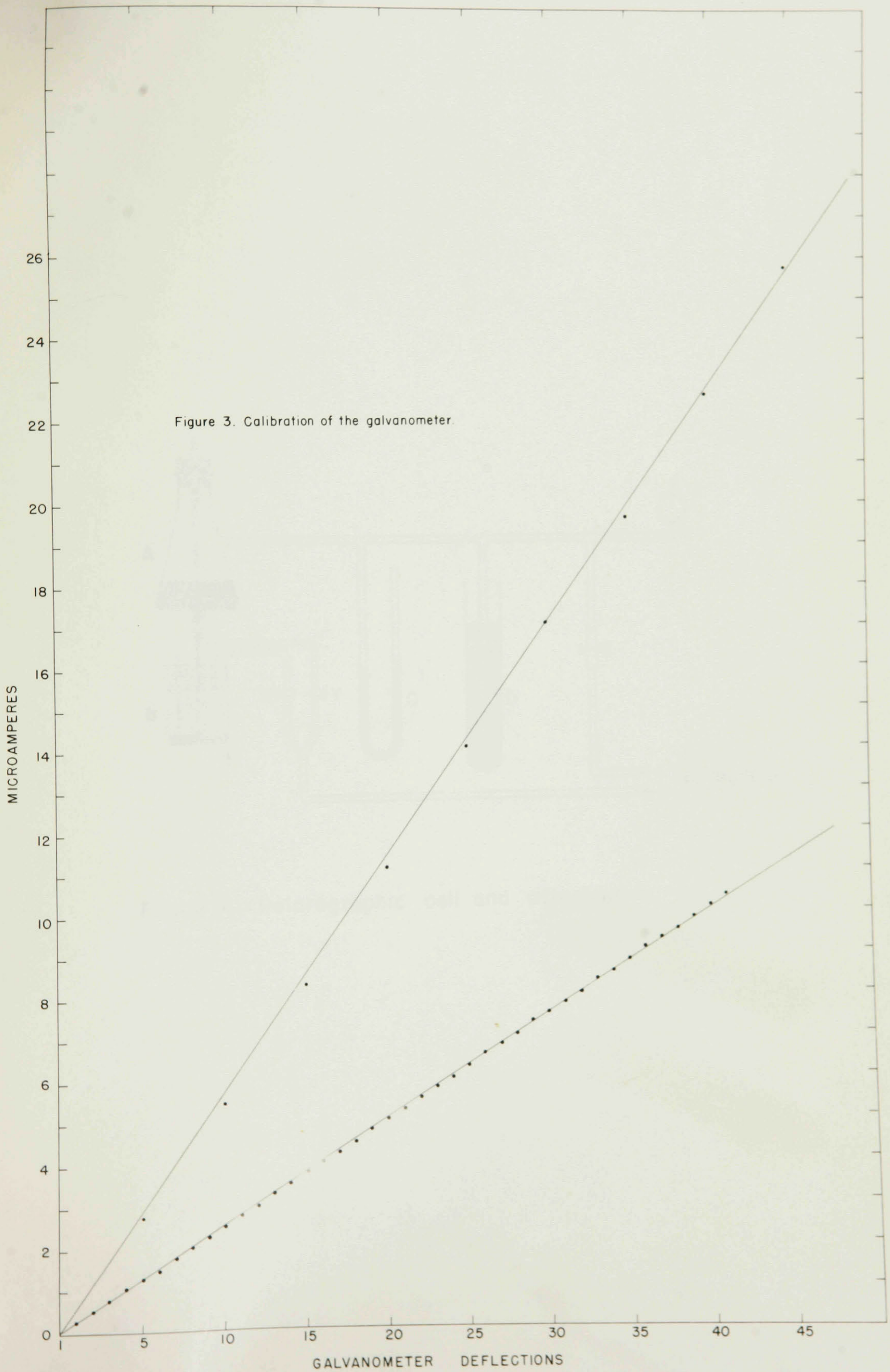


Figure 3. Calibration of the galvanometer.

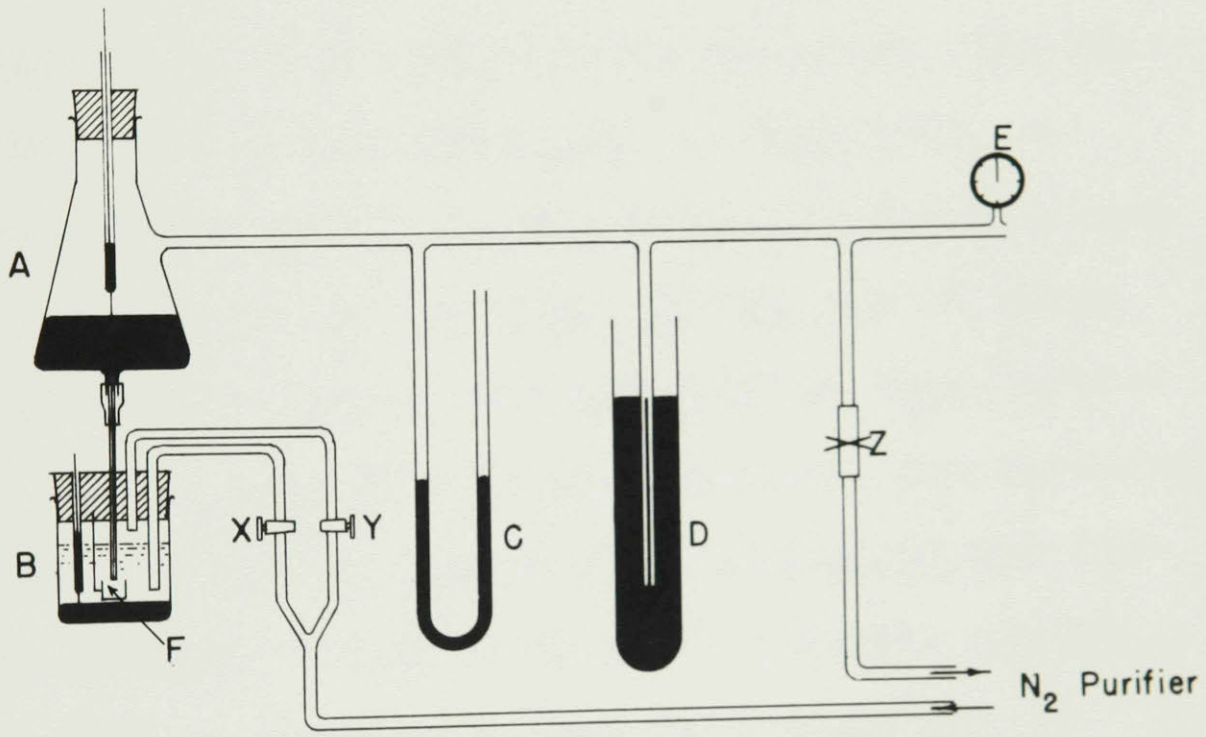


Figure 4. Polarographic cell and attachments.

the tube and the capillary. Another tube was sealed to the side of the flask to permit introduction of nitrogen. A glass tube fitted with a sealed-in tungsten electrode and filled with mercury passed through the stopper to allow for electrical contact with the contents of the flask.

A manometer and a blow-off, C and D, respectively, were sealed into the nitrogen line running from the reducing valve, E, to the flask, A. The blow-off was simply a tube immersed into a column of mercury so that the pressure in the system could not be increased beyond that required to force nitrogen out of the tube through the mercury. The reducing valve was attached to a tank of nitrogen and was fitted with a needle valve so that the pressure in the system could be adjusted to any desired height of mercury in the manometer.

The container, B, for the electrolyte and the quiet pool of mercury, was a 50 c.c. beaker. There were four holes in the stopper that fitted into the beaker. The fine capillary from the flask, A, passed through one of the holes into the solution and a small cup, F, supported by a glass rod which fitted into a second hole in the stopper, was held just under the end of the fine capillary. All the mercury that passed through the capillary was caught in this

cup. Two tubes carried nitrogen through the stopper into the beaker, one ending just above the level of the solution and the other in the solution just above the pool of mercury. Passage of nitrogen through these tubes was controlled by the stopcocks, x and y, after it had passed through an apparatus for removing the last traces of oxygen from it. This latter apparatus is described by Uhrig, et al[10]. A side arm from the main nitrogen line supplied the nitrogen to the purifier and the rate of flow through this side arm was controlled by a screw type pinchcock, Z, on a piece of rubber tubing introduced into the gas line.

(d) General Procedure. Before each experiment, flask A, with all attachments removed, was soaked in a hot acid bath, rinsed with distilled water and dried in an oven. The fine capillary was blown out with nitrogen and then cleaned by sucking concentrated nitric acid through it for $\frac{1}{2}$ hour and following this with distilled water. It was then dried by blowing nitrogen through it again.

The apparatus was completely assembled. A layer of mercury was placed in the bottom of the beaker B, and about 30 c.c. of the electrolytic solution added. With the bottom end of the fine capillary just above the solution, the air in the flask

A was replaced with nitrogen by blowing nitrogen into it, with the stopper loosened, for about 20 minutes. The stopper was then placed tightly into position and the pressure of nitrogen was adjusted to about 20 cm. of mercury for about 20 minutes. The stopper was then removed without stopping the flow of nitrogen and 500 grams of mercury was introduced into the flask. The stopper was replaced and flask A was lowered so that the bottom of the fine capillary was immersed in the solution. Nitrogen was bubbled through the solution for thirty minutes and during this interval the pressure on the mercury in flask A was kept constant so that the dropping rate, determined periodically, indicated whether or not the capillary was allowing a free flow of the mercury. Without stopping the flow of nitrogen a weighed amount of the metal required was added to the mercury (4 to 8 milligrams). The stopper was replaced and the flask shaken gently for a few minutes to give the mercury a swirling motion. Homogeneous distribution of the metal in the mercury was easily obtained by shaking for a few seconds 2 or 3 times at short intervals. The cell was now ready to be used with a dropping amalgam electrode.

The concentration of the amalgam was easily calculated since the mercury that passed through the capillary prior to the addition of the

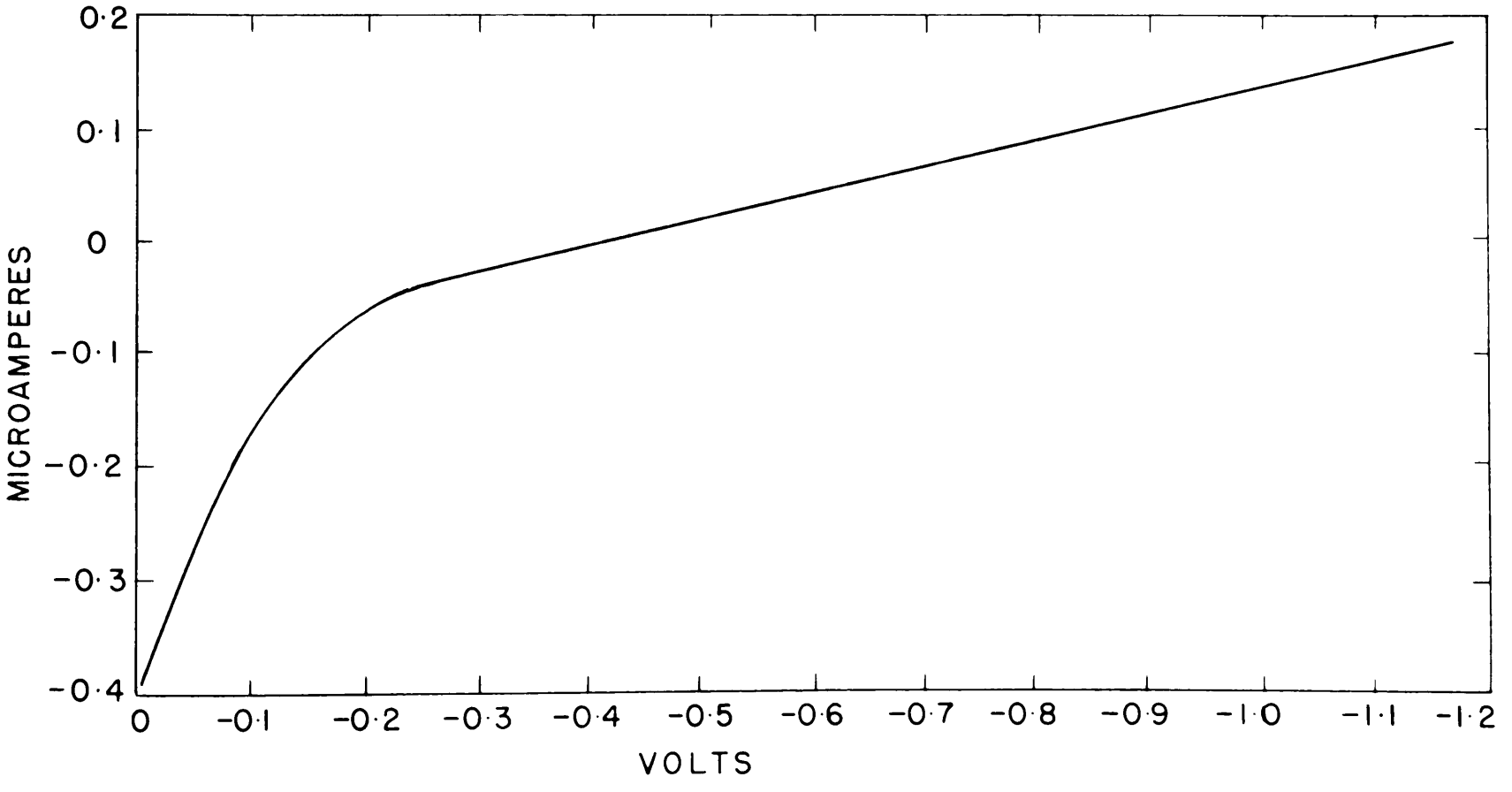
metal was caught in the cup and weighed.

Amalgams of lead, cadmium and zinc were used in the experiments. Lead and cadmium were always freshly cut just before being added to the mercury while the zinc, which was reagent grade, was cleaned by washing with dilute HCl, then with water and was finally dried between filter papers. Lead and cadmium disappeared in a matter of seconds but zinc required from 10 to 20 minutes to disappear completely from the surface of the mercury. It was found that lead and cadmium amalgams at concentrations up to 15 parts per million by weight could be prepared in this way and they appeared to be stable for at least 24 hours. The zinc amalgams always had a peculiar surface; they looked as if there was a thin layer of a foreign material on the surface.

The cell solution was always 0.1 N to KCl, 0.002 N to HCl and it contained sufficient methyl violet to give the solution a faint colour; for the sake of convenience the solution of this composition will be refered to as the basic cell solution. Modifications of the basic cell solution for any particular experiment will be indicated when the results are presented. The dropping rate, unless otherwise indicated, was 15 drops per minute. The drops were

never allowed to fall into the quiet pool of mercury but were caught in the small cup mentioned above. The mass of amalgam or mercury flowing per second was determined by weighing the amount collected in this cup during a measured length of time. The cell was maintained at 25° C. in a constant temperature water bath during all the experiments.

Experiments were made to determine the current-potential curve for pure mercury dropping electrodes with the basic cell solution and the average of the curves obtained is shown below:



The so-called residual current represented in this curve was considered like a reagents blank, that is, the current obtained for any voltage applied was corrected by algebraically subtracting from it the currented represented in this curve for the same voltage.

EXPERIMENTAL RESULTS

With a view to attaining maximum clarity of presentation, the detailed experimental results are contained in an appendix, only the curves constructed from these data and summaries being given in the body of the thesis.

The results are presented in the following order: (1) To show the effect of the concentration of a metal in an amalgam on the negative limiting current obtained; (2) To test Equation 32; (3) To show whether the rate of diffusion of the metal ions formed away from the drop affects the negative limiting current; and (4) To show the effect of the presence of other metals in the amalgam on the negative limiting current obtained from a given metal.

(a) Relation between the Negative Limiting Current and the Concentration of Lead in an Amalgam. Current-potential curves were obtained for dropping amalgam electrodes of the following lead concentrations; 0.05, 0.19, 0.42, 0.73 and 0.89 millimoles per liter of amalgam, the three weaker ones being prepared by diluting more concentrated ones. Sufficient lead acetate was added to the basic cell solution to make the concentration of this salt 0.50 millimolar. These curves are shown in Figure 5. The negative and positive

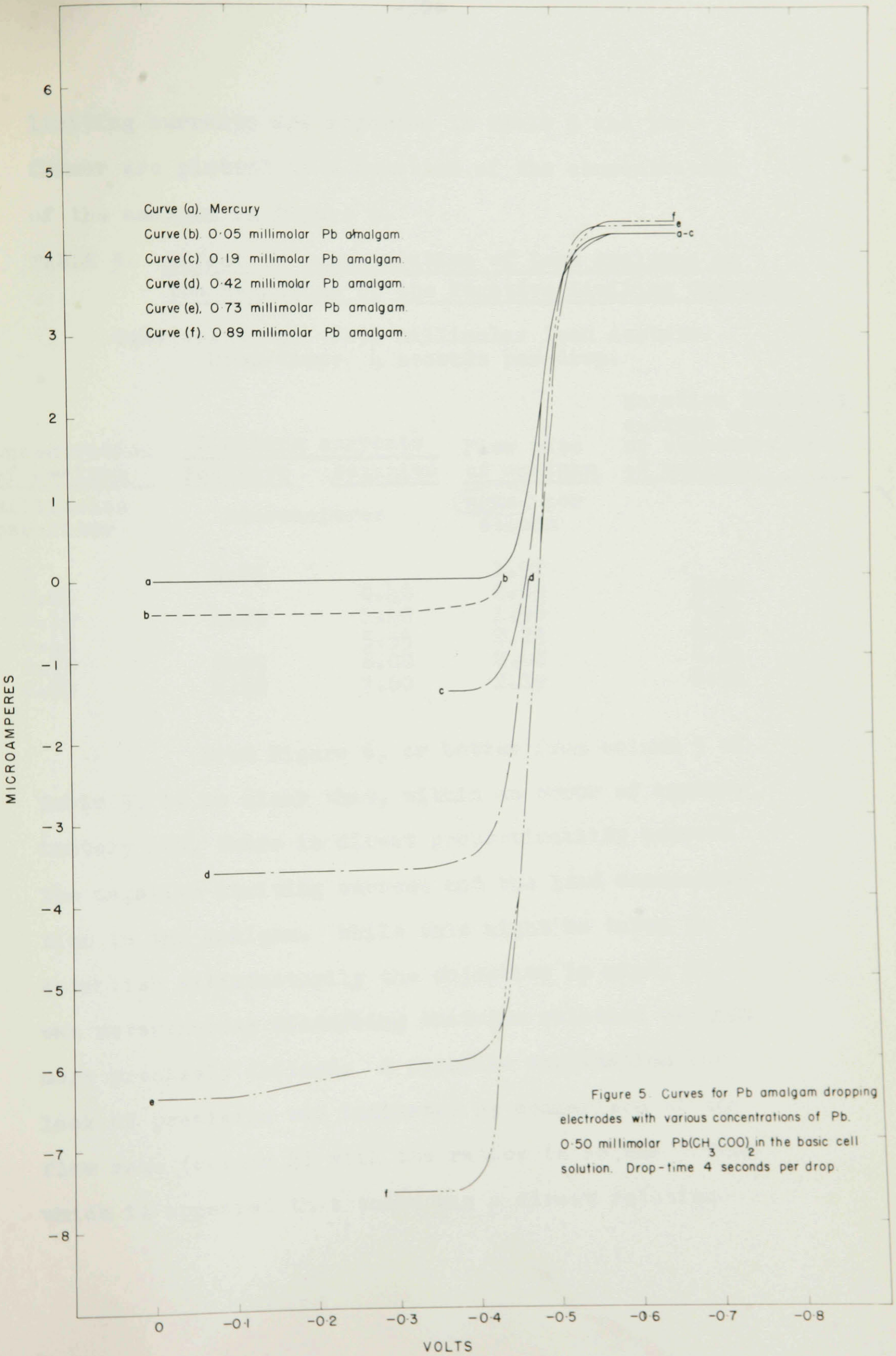


Figure 5. Curves for Pb amalgam dropping electrodes with various concentrations of Pb. 0·50 millimolar $Pb(CH_3COO)_2$ in the basic cell solution. Drop-time 4 seconds per drop.

limiting currents are reported in Table 3 and the former are plotted as a function of the concentration of the amalgam in Figure 6.

TABLE 3. Effect of Concentration of Lead Amalgams on the Magnitude of the Negative Limiting Current.

Cell solution: 0.50 millimolar lead acetate.
Drop-time: 4 seconds per drop.

Concentration of amalgam	Limiting currents		Flow rate of amalgam	Negative limiting current divided by concentration of amalgam
	Positive	Negative		
millimoles per liter	microamperes		(mgms. per second	
0	4.25		1.97	
0.05		0.40	2.09	8.00
0.19	4.25	1.40	1.96	7.37
0.42		3.55	2.22	8.70
0.73	4.35	6.00	2.08	8.22
0.89	4.40	7.60	2.19	8.54

From Figure 6, or better from column 5 of Table 3, it is clear that, within an error of approximately 10%, there is direct proportionality between the negative limiting current and the lead concentration in the amalgam. While this might be taken to establish satisfactorily the objective in mind, it was nevertheless disturbing that the relation was not more precisely defined. A possible explanation for lack of precision was indicated by comparison of the flow rate (column 4) with the ratios in column 5 from which it appeared that there was a direct relation

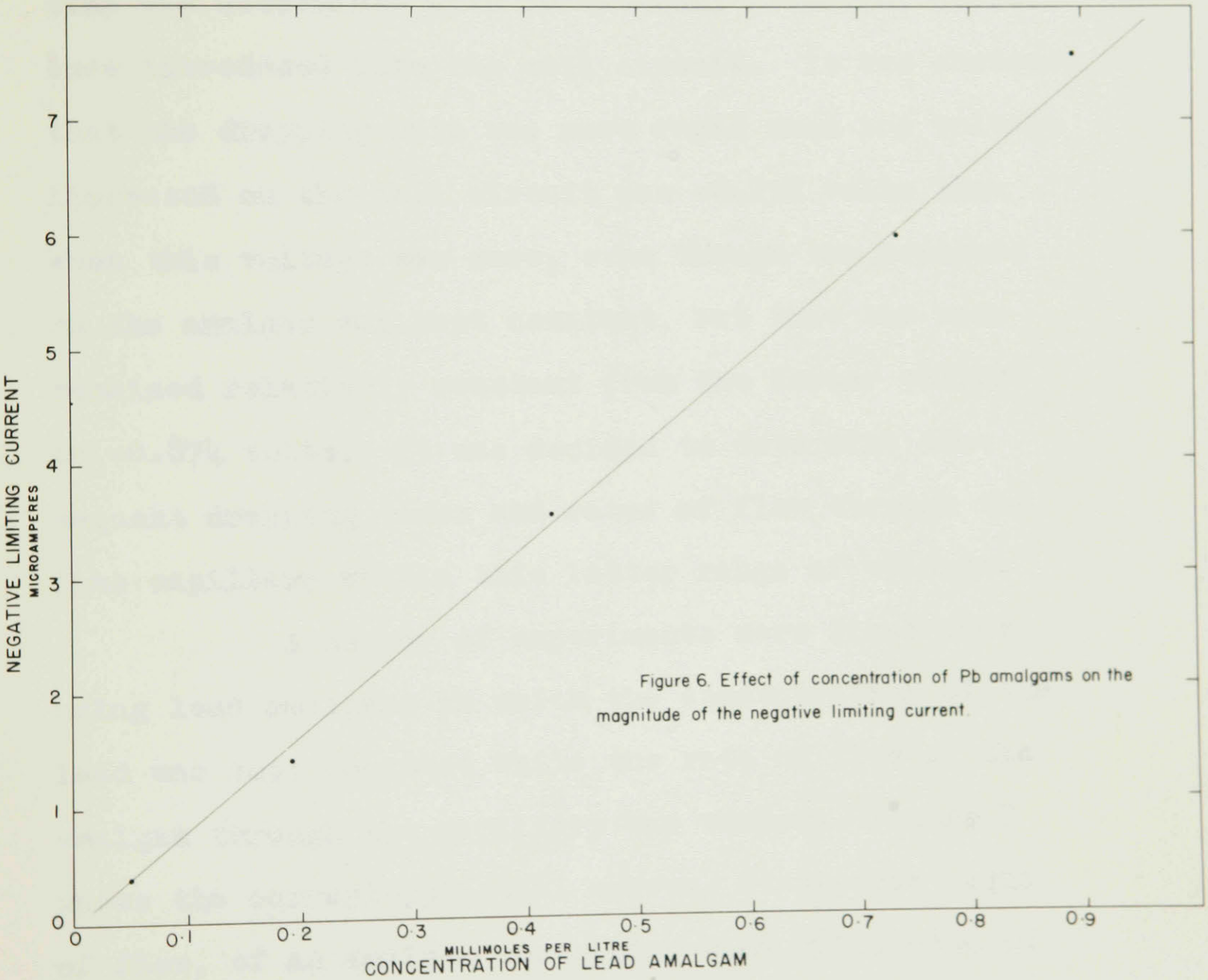


Figure 6. Effect of concentration of Pb amalgams on the magnitude of the negative limiting current.

between rate and the magnitude of the negative limiting current. A study was, therefore, made of the effect of flow rate on limiting currents.

(b) Effect of Flow Rate on Limiting Currents. In obtaining the above current-potential curves the drop-time was determined with no external potential difference introduced into the cell circuit. It was observed that the dropping rate was more rapid when the voltage impressed on the cell circuit was -0.292 volts than when this voltage was zero, even though the pressure on the amalgam was kept constant, but that the rate remained relatively constant from the former voltage to -0.874 volts. It was decided to determine subsequent dropping times and rates of flow through the fine capillary within this latter range of voltage.

A number of experiments were first made using lead amalgams in which the concentration of the lead was kept constant while the rate of flow of the amalgam through the capillary was varied. Figure 7 shows the current-potential curves, at various rates of flow, of an amalgam containing 0.69 millimoles of lead per liter dropping into a solution which was 0.50 millimolar to lead acetate. The same capillary was used throughout but the pressure of nitrogen on the amalgam was adjusted to cause the amalgam to flow

Curve (a) 2 seconds per drop. Flowrate not determined.
Curve (b) 3 seconds per drop. 2·49 mgm. per second.
Curve (c) 4 seconds per drop. 1·93 mgm. per second.
Curve (d) 5 seconds per drop. 1·59 mgm. per second.
Curve (e) 6 seconds per drop. 1·29 mgm. per second.

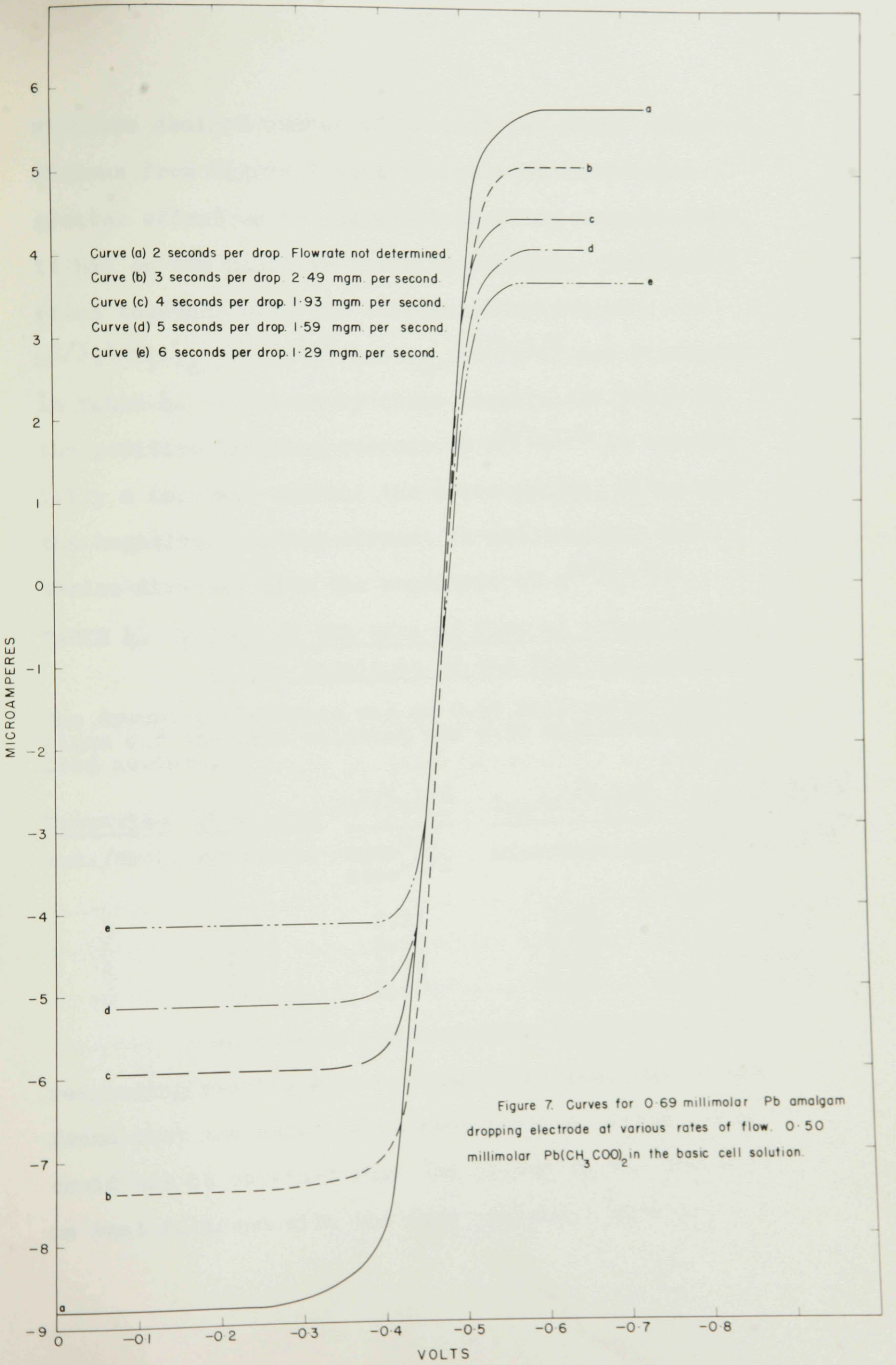


Figure 7. Curves for 0·69 millimolar Pb amalgam dropping electrode at various rates of flow. 0·50 millimolar $Pb(CH_3COO)_2$ in the basic cell solution.

with the desired number of seconds per drop. It is obvious from Figure 7 that the rate of flow had a greater effect on the negative limiting current than it had on the positive limiting current. The flow rates together with the calculated values of $m^{2/3}t^{1/6}$, $I_{d+}/m^{2/3}t^{1/6}$ and $I_{d-}/m^{2/3}t^{1/6}$ are presented in Table 4. As shown by these results the ratio of the positive limiting current to $m^{2/3}t^{1/6}$ is essentially a constant whereas the corresponding ratio for the negative limiting current is not constant but varies directly with the magnitude of $m^{2/3}t^{1/6}$.

TABLE 4. Effect of the Rate of Flow of a Lead Amalgam on the Magnitude of the Limiting Currents.

The dropping electrode was an 0.69 millimolar lead amalgam and the cell solution was 0.50 millimolar to lead acetate.

Drop-time	Flow rate	$m^{2/3}t^{1/6}$	$I_{d+}/m^{2/3}t^{1/6}$	$I_{d-}/m^{2/3}t^{1/6}$
sec./drop	mgms/sec.	$mgms^{2/3}\ secs^{-1/2}$	microamps.$mgms^{-2/3}.secs^{1/2}$	
3	2.49	2.21	2.31	3.33
4	1.93	1.95	2.28	3.05
5	1.59	1.78	2.30	2.89
6	1.29	1.60	2.31	2.59

An attempt was next made to obtain corresponding results with a cadmium amalgam, but it was found that the negative current portion of the curve could not be obtained when the procedure was the same as that followed with the lead amalgam. When the

external potential difference applied to the cell circuit was less negative than that required for zero current, the negative deflection of the galvanometer, for any setting of the potentiometer, was not steady but always drifted back towards zero after reaching a maximum. As indicated previously, when the reaction at the dropping electrode is one of reduction that at the quiet pool of mercury is

$$2\ Hg + 2\ Cl^- = Hg_2Cl_2$$

When oxidation takes place at the dropping electrode the reaction at the other electrode must be the reverse of the above, that is,

$$Hg_2Cl_2 = 2\ Hg + 2\ Cl^-$$

From this it is apparent that while the negative part of the curve is being produced mercurous chloride is being used up. If the concentration of the calomel falls below its saturation value at the surface of the mercury, the potential of that electrode would not be constant. It was thought possible that this was the cause of the difficulty encountered with the cadmium amalgam. Mercurous chloride was added to the surface of the pool of mercury and after this was done the galvanometer deflections, whether positive or negative, were always steady for any setting of the potentiometer.

The curves obtained with a dropping amalgam electrode which contained 1.20 millimoles of cadmium per liter, dropping into a cell solution made one millimolar to $CdCl_2$ and with Hg_2Cl_2 added to the surface of the pool of mercury, are presented in Figure 8. Table 5 shows the calculated values of $m^{2/3}t^{1/6}$, $I_{d+}/m^{2/3}t^{1/6}$ and $I_{d-}/m^{2/3}t^{1/6}$. It is evident from these results that, with cadmium as with lead, the positive limiting current is proportional to the magnitude of $m^{2/3}t^{1/6}$ within a reasonably small error whereas for the negative limiting current there is a positive correlation between the two sets of values $m^{2/3}t^{1/6}$ and $I_{d-}/m^{2/3}t^{1/6}$.

TABLE 5. Effect of the Rate of Flow of a Cadmium Amalgam on the Magnitude of the Limiting Currents.

The dropping electrode was a 1.20 millimolar cadmium amalgam and the cell solution was 1.00 millimolar to $CdCl_2$.

Drop-time	Flow rate	$m^{2/3}t^{1/6}$	$I_{d+}/m^{2/3}t^{1/6}$	$I_{d-}/m^{2/3}t^{1/6}$
sec./drop	mgms/sec.	$mgms^{2/3}\ secs^{-1/2}$	microamps.$mgms^{-2/3}.secs^{1/2}$	
3	2.62	2.28	3.71	7.57
4	2.14	2.09	3.57	6.00
5	1.67	1.84	3.66	5.82
6	1.40	1.69	3.73	5.75

Similar experiments were made to determine the effect of flow rate on the negative limiting current with a zinc amalgam. A 2.08 millimolar zinc

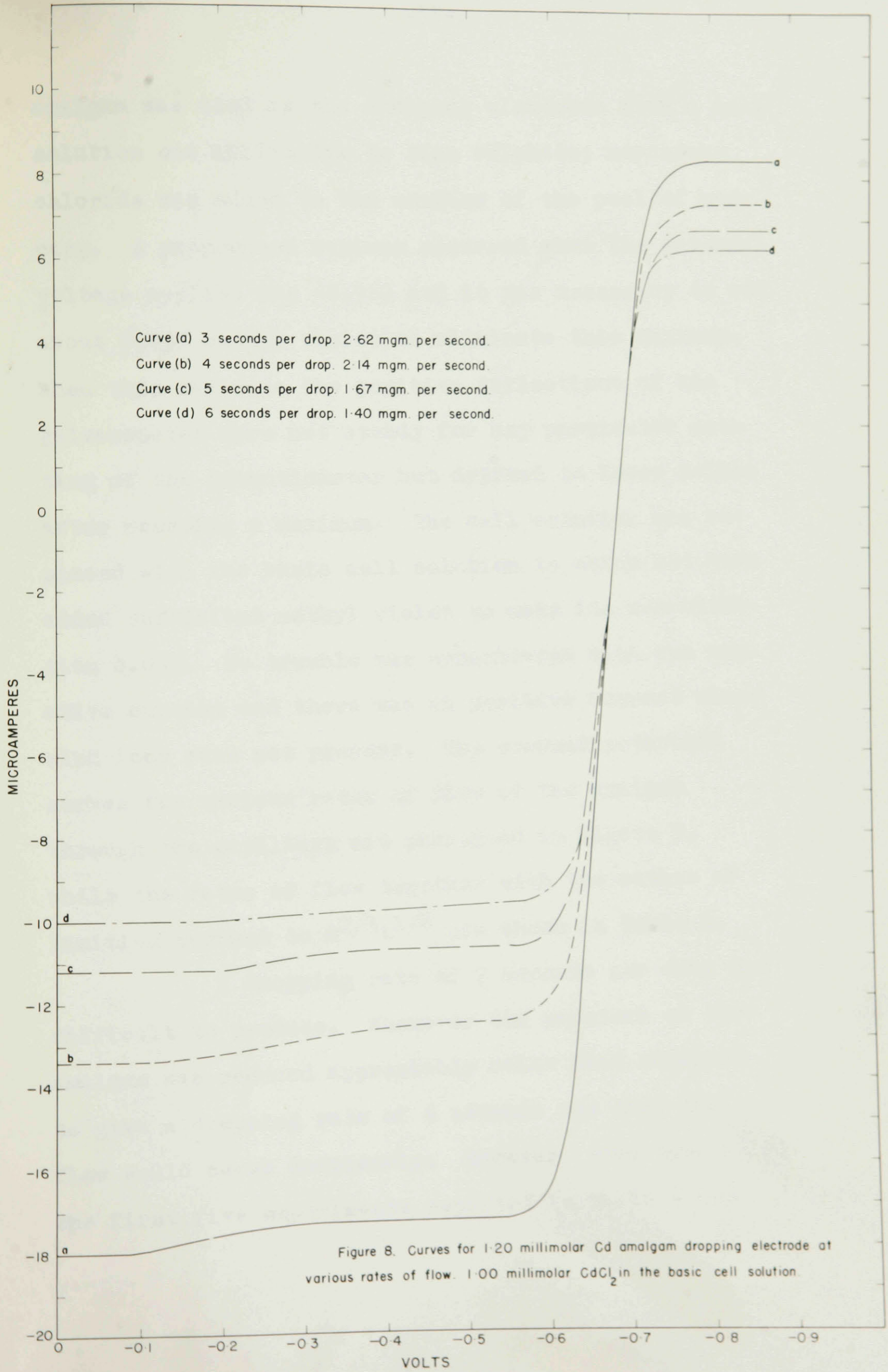


Figure 8. Curves for 1·20 millimolar Cd amalgam dropping electrode at various rates of flow. 1·00 millimolar $CdCl_2$ in the basic cell solution.

amalgam was used as the dropping electrode with a cell solution one millimolar to zinc sulphate; mercurous chloride was added to the surface of the pool of mercury. A pronounced maximum occurred when the external voltage applied was -0.969 and it was necessary to add about 0.05% methyl violet to eliminate this maximum. When this was done the positive deflections of the galvanometer were not steady for any particular setting of the potentiometer but drifted to lower values after reaching a maximum. The cell solution was replaced with the basic cell solution to which had been added sufficient methyl violet to make its concentration 0.05%. No trouble was encountered with the negative current and there was no positive current since zinc ions were not present. The current-potential curves for various rates of flow of the amalgam through the capillary are presented in Figure 9, while the rates of flow together with the ratios of limiting current to $m^{2/3}t^{1/6}$ are shown in Table 6.

A dropping rate of 7 seconds per drop was difficult to produce. Whenever the pressure on the amalgam was reduced appreciably below that required to give a dropping rate of 6 seconds per drop the flow would cease completely. However, some time after the first five experiments reported in Table 6 had

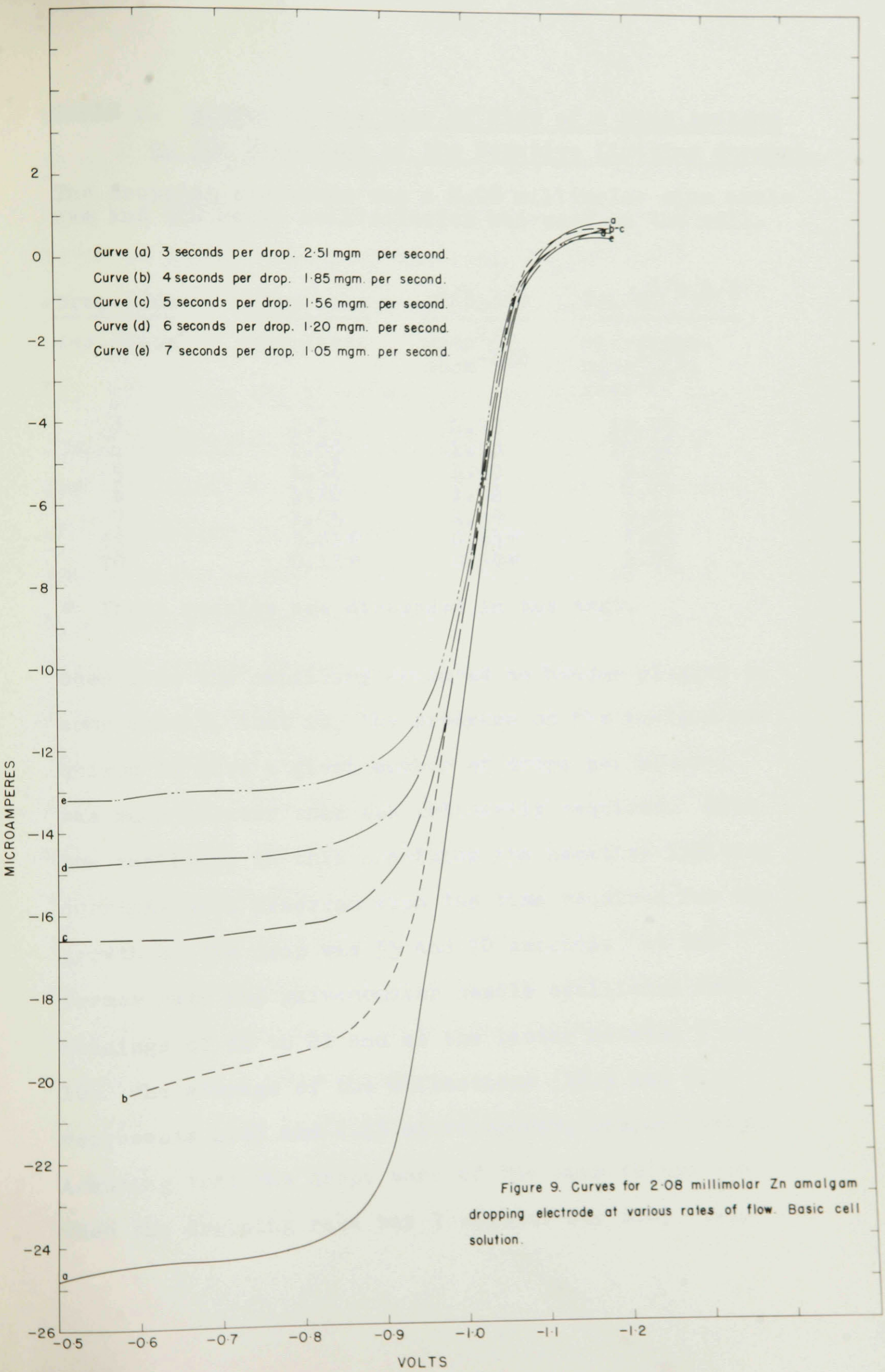


Figure 9. Curves for 2·08 millimolar Zn amalgam dropping electrode at various rates of flow. Basic cell solution.

TABLE 6. Effect of the Rate of Flow of a Zinc Amalgam on the Magnitude of the Negative Limiting Current.

The dropping electrode was a 2.08 millimolar zinc amalgam and the basic cell solution was used in the cell.

Drop-time	Flow rate	$m^{2/3}t^{1/6}$	$I_{d-}/m^{2/3}t^{1/6}$
sec./drop	mgms/sec.	$mgms^{2/3}$ $secs^{-1/2}$	microamps. $mgms^{-2/3}$. $secs^{1/2}$
3	2.51	2.22	10.95
4	1.85	1.90	10.32
5	1.56	1.69	9.88
6	1.20	1.52	9.67
7	1.05	1.43	9.09
35	0.21*	0.64*	7.25
70	0.11*	0.50*	4.57

* These results are discussed in the text.

been made the capillary appeared to become plugged to some extent, that is, the pressure on the amalgam required to give a given number of drops per minute, was much greater than was ordinarily required. With the capillary in this condition the negative limiting currents were observed when the time required for the growth of the drop was 35 and 70 seconds. At the former rate the galvanometer needle oscillated from readings of 16 to 21 and at the latter between 7 and 10. The average of the deflections (18.5 and 8.5) represents 4.63 and 2.13 microamperes, respectively. Assuming that the drops were of the same volume as when the dropping rate was 7 seconds per drop, the

ratio of limiting current to $m^{2/3}t^{1/6}$ was calculated to be 7.25 when the dropping rate was 35 seconds per drop and 4.57 when it was 70 seconds. Apparently the trend to lower values, of the ratio $I_{d-}/m^{2/3}t^{1/6}$ shown in Table 6, was consistent down to extremely slow rates of flow.

(c) Effect on the Negative Limiting Current of the Ion Concentration in the Solution. It was thought possible that the marked effect of the rate of flow of the amalgam on the negative limiting current obtained might be due to the rate at which the metal ions formed diffused away from the amalgam drops. However, Figure 10 shows that the concentration of lead ions in solution had little, if any, effect on the magnitude of the negative limiting current from a lead amalgam. The amalgam was the same (0.82 millimolar) for all the curves but the concentration of the ions in solution was different in each case. Although the positive limiting currents was varied from about 22 microamperes to zero in the four experiments the negative limiting current was constant to within a fraction of a microampere.

(d) Application to Analysis of Simple Mixed Amalgams. It has been shown above that there is a relation between the negative limiting current and the flow rate.

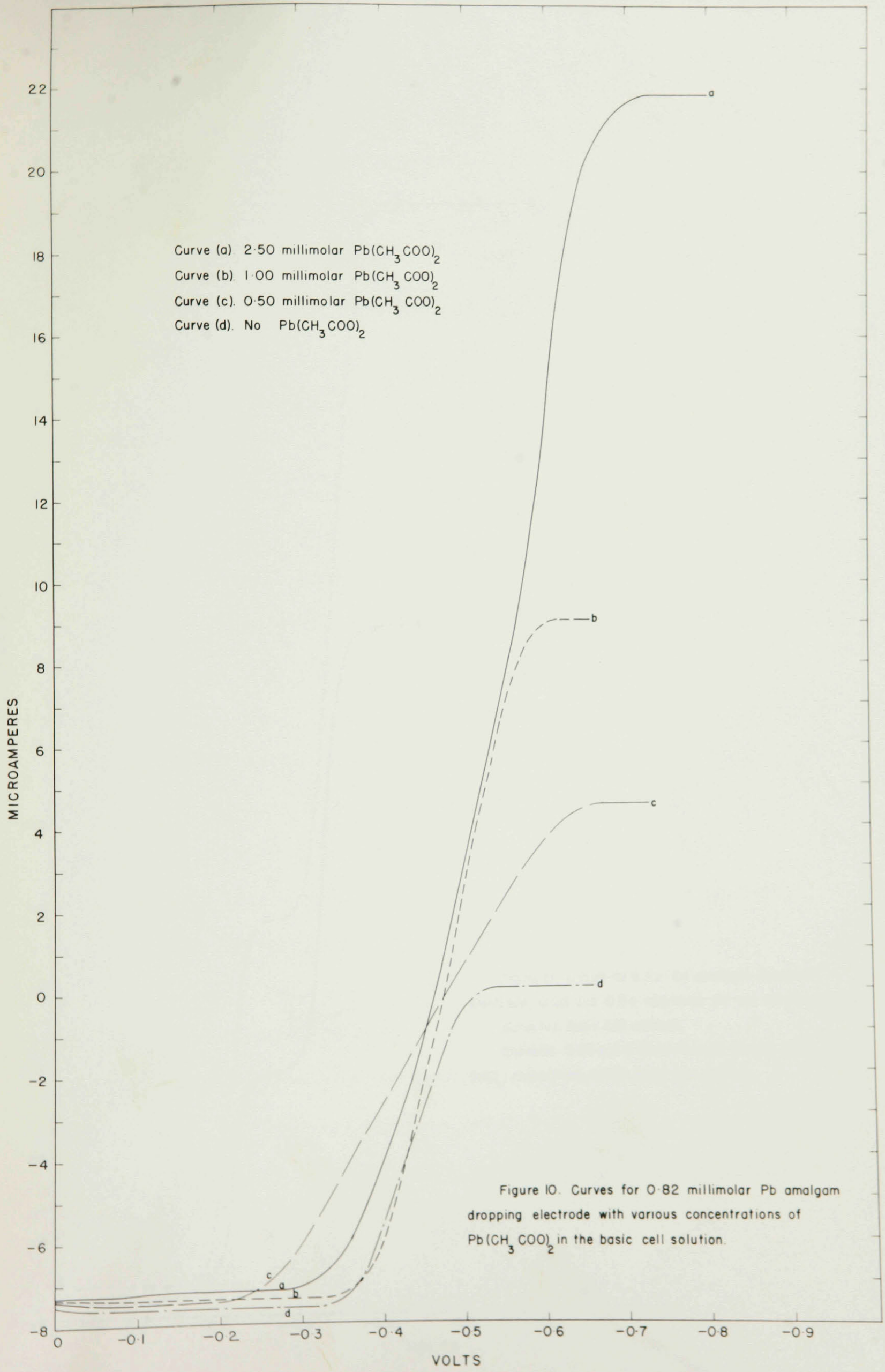


Figure 10. Curves for 0·82 millimolar Pb amalgam dropping electrode with various concentrations of $Pb(CH_3COO)_2$ in the basic cell solution.

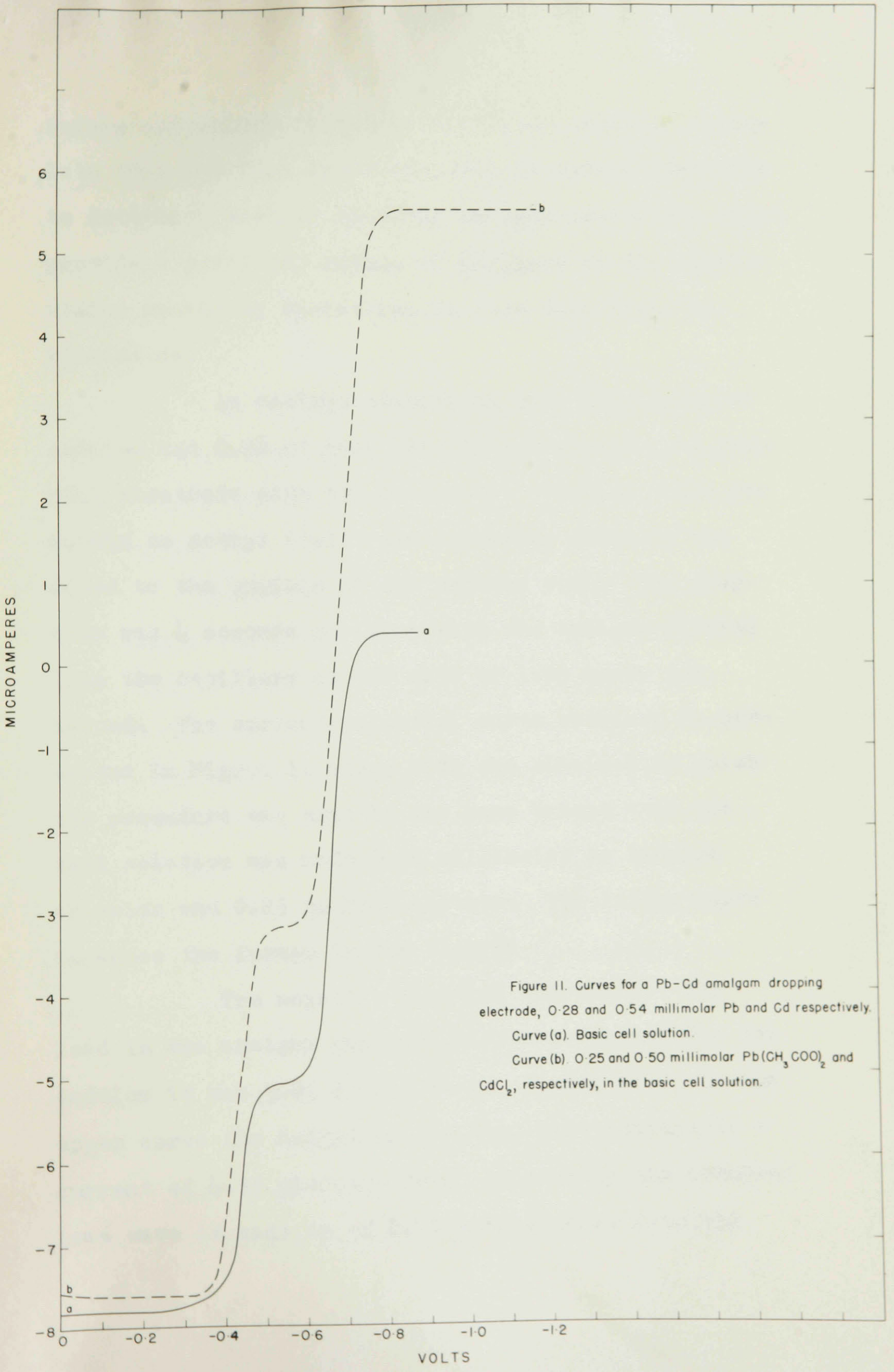


Figure 11. Curves for a Pb–Cd amalgam dropping electrode, 0·28 and 0·54 millimolar Pb and Cd respectively.

Curve (a). Basic cell solution.

Curve (b). 0·25 and 0·50 millimolar $Pb(CH_3COO)_2$ and $CdCl_2$, respectively, in the basic cell solution.

Before attempting to obtain sufficient data to formulate this relation quantitatively it seemed advisable to determine whether dropping amalgam electrodes might provide a practical method of analysis if the difficulties caused by variations in flow rate could be eliminated.

An amalgam containing 0.54 millimoles of cadmium and 0.28 of lead per liter was used as a dropping electrode with the basic cell solution which was 0.005% to methyl violet and mercurous chloride was added to the surface of the mercury pool. The drop-rate was 4 seconds per drop with the amalgam flowing from the capillary at the rate of 1.93 mgms. per second. The current-potential curve obtained is presented in Figure 11 along with one obtained in which the procedure was exactly the same except that the cell solution was made 0.50 millimolar to cadmium chloride and 0.25 to lead acetate. The latter curve is above the former in the Figure.

The negative limiting current for the lead in the amalgam was 2.70 microamperes and for the cadmium it was 5.05 (lower curve, Figure 11). In the upper curve the height of the lead wave represents a current of 4.55 microamperes. Apparently the complete lead wave is made up of 2.70 microamperes from the

lead in the amalgam and 1.85 from the lead ions in solution even though the net current was negative for the cell during the production of the wave. The cadmium wave in the latter curve represents a current of 8.65 microamperes, 5.05 from the cadmium in the amalgam and 3.65 from the corresponding ions in solution. The part of the cadmium wave above zero current represents about 5.55 microamperes which is about equal to the sum of the currents from the two kinds of ions in solution.

Sufficient zinc metal was added to the lead-cadmium amalgam, used to produce the curves in Figure 11, to make it 1.12 millimolar to this metal. The procedure with this amalgam was exactly the same as that followed with the lead-cadmium amalgam except that in the second experiment the salts added to the basic cell solution were lead acetate, cadmium chloride and zinc sulphate and their concentrations were 0.17 millimolar for the lead ions and 0.33 for the latter two.

The two current potential curves showing the results of this last experiment are shown in Figure 12. The lower curve shows that the limiting currents due to the lead, cadmium and zinc were 2.6, 5.2 and 12.4 microamperes, respectively. When the

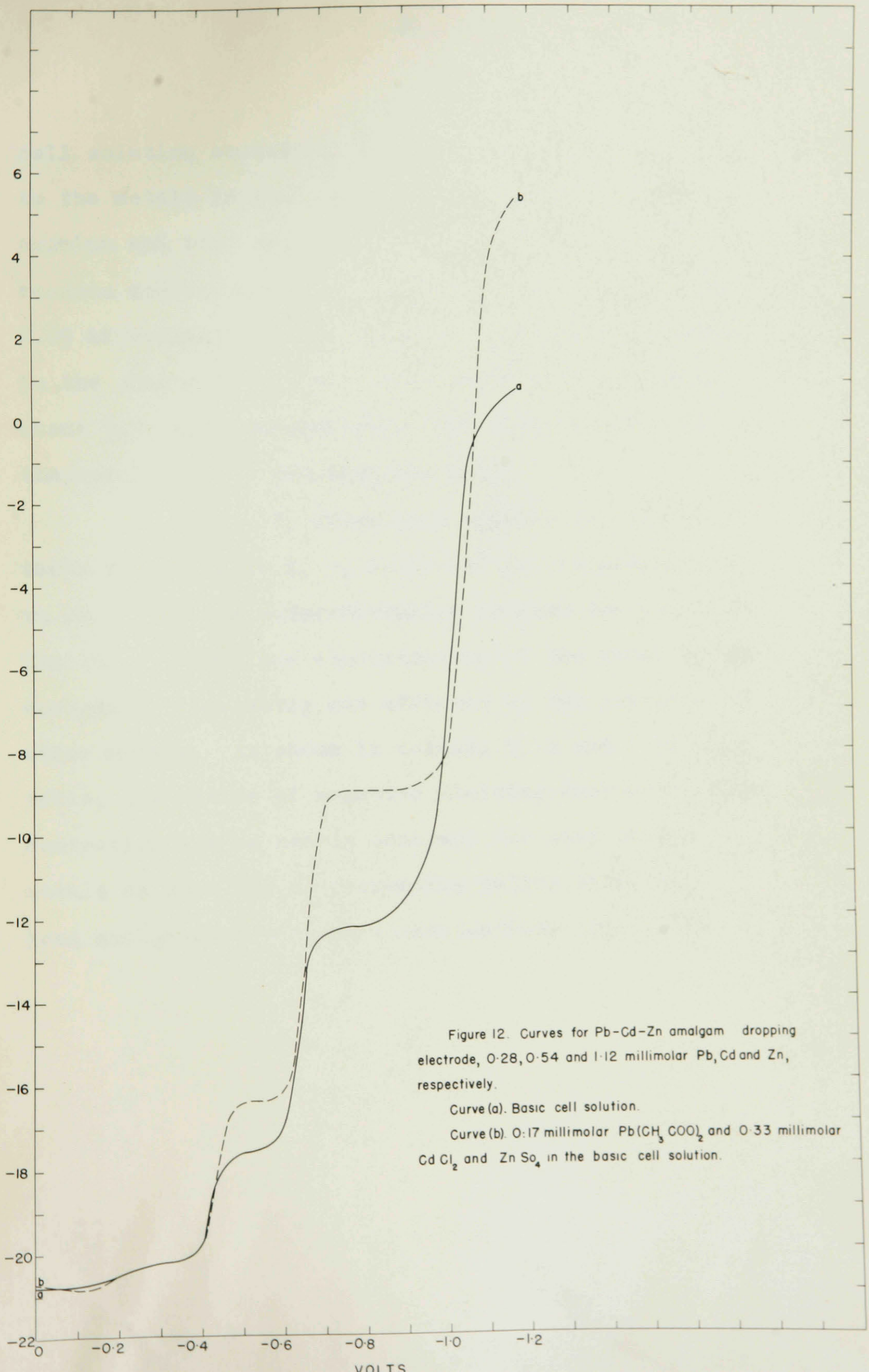


Figure 12. Curves for Pb-Cd-Zn amalgam dropping electrode, 0·28, 0·54 and 1·12 millimolar Pb, Cd and Zn, respectively.

Curve (a). Basic cell solution.

Curve (b). 0·17 millimolar $Pb(CH_3COO)_2$ and 0·33 millimolar $CdCl_2$ and $ZnSo_4$ in the basic cell solution.

cell solution contained the three ions corresponding to the metals in the amalgam (upper curve) the lead, cadmium and zinc waves were increased in height by amounts corresponding to approximately 1.20, 2.20 and 2.05 microamperes, respectively. The positive current in the zinc wave in the latter curve was apparently about 5.55 microamperes while the total current due to the metal ions in solution was 5.45.

Table 7, which is a summary of results taken from Figures 4, 5, 6, 11 and 12, is presented to show that the proportionality between the negative limiting current and concentration of the metal in the amalgam is apparently not affected by the presence of other metals. As shown in columns 5, 6 and 7 of this table, the ratios of negative limiting current to concentration are as nearly constant for each of the metals as were the corresponding ratios with pure lead amalgams at various concentrations (Table 3).

TABLE 7. Effect of Other Metals in an Amalgam on the Negative Limiting Current for a Given Metal.

Amalgam used as the dropping electrode	Concentration			Negative limiting current divided by concentration		
	Lead	Cadmium	Zinc	Lead	Cadmium	Zinc
	millimoles per liter			microamps.liters.millimoles^{-1}		
Lead	0.69			8.62		
Cadmium		1.20			10.46	
Zinc			2.08			9.42
Lead-cadmium	0.28	0.54		9.29	9.35	
Lead-cadmium-zinc	0.28	0.54	1.12	9.64	9.72	10.98

DISCUSSION

A general outline of the object of the work was presented in the Introduction. Before discussing the results in the light of these main objectives, two important facts revealed during the experimental work will be dealt with. Both are concerned with the make up of the electrolytic cell.

The first deals with the potential of the quiet mercury pool. In ordinary polarographic analysis the reaction at this electrode is usually one of oxidation, that is, mercurous chloride is plated out on the surface of the mercury when the solution contains a chloride salt. Providing the solution at this surface is saturated with calomel in the beginning, the potential of the electrode will remain constant while electrolysis takes place; this has been demonstrated experimentally by Tomes[11] who found that the potential of the mercury pool was changed by only about 2 or 3 millivolts. When an amalgam is used as the dropping electrode, the reaction at this electrode, which is of primary concern here, is the oxidation of the metals in the amalgam to the corresponding ions, that is, the direction of the current is the reverse of that mentioned above. In this case mercurous chloride is used up at the pool of mercury and, unless

there is a sufficient excess of the precipitated salt present to supply that required for the reaction, the potential of this electrode will change as electrolysis proceeds. When this happens the potential of the dropping electrode, corresponding to a given external potential applied, changes with time and it is impossible to obtain the results necessary to construct a current-potential curve for the electrode reaction. In fact, the same situation arises in ordinary polarographic analysis when the reaction at the dropping mercury electrode consists of the oxidation of substances in solution. Muller[12] encountered this difficulty while working with organic compounds and circumvented his troubles by using an external constant potential electrode in place of the pool of mercury. He makes the following statement, however: "The potential of the large pool of mercury, when used as the cathode, is poorly poised unless a layer of calomel has been previously deposited on its surface." It is not clear whether Muller means that the calomel should be placed on the mercury mechanically or deposited electrolytically; the final result is the same in either case.

The results with cadmium, zinc and mixed amalgam dropping electrode show that mercurous chloride may be added to the quiet pool of mercury to

maintain an excess of the salt during the oxidation of these metals (Figures 8, 9, 11 and 12). It is difficult to explain why it was not necessary to add the calomel with lead amalgams (Figures 5, 7 and 10) unless it was because of the magnitude of the negative currents involved. The maximum negative current from a lead amalgam was about 9 microamperes (curve a, Figure 7) whereas with cadmium, where it was first found necessary to add the calomel, the corresponding current was 12.55 (curve b, Figure 8). It should be noted, however, that the curves are not uniform in shape in Figure 10 and this may be due to a poorly poised potential at the quiet pool of mercury. Another factor which was not controlled was the time which elapsed between the make up of the cell and the beginning of an experiment; the longer this period of time the more calomel would be formed. Since the currents involved are very small, only a trace of the salt is required providing it is evenly distributed over the surface of the mercury. If only a small spot of calomel existed on the surface, concentration polarization might come into play at this electrode.

The second fact revealed by the present study pertaining to the make up of the electrolytic cell deals with the composition of the cell solution.

Figures 11 and 12 illustrate clearly that the current, represented in a wave of a current-potential curve for a given metal, may consist of that due to the reduction of the corresponding ions in solution as well as to the oxidation of the metal in the amalgam. In each Figure the wave for an individual metal was of greater magnitude in the upper curves, where the corresponding ions were present, than it was in the lower ones where potassium and hydrogen were the only cations present. The increment in every case was roughly equal to the current expected from the ions in solution. Consequently, if it is desired to determine the magnitude of the current representative of a given concentration of a metal in an amalgam, the solution should be free from all ions except those that would not be reduced in the range of electrode potentials used. Incidentally, these results also show why the mercury used for the dropping electrode in ordinary polarographic analysis should be free from contamination by metals.

With regard to the main objectives, it has been shown with some degree of precision that the negative limiting current resulting from the oxidation of a metal in an amalgam dropping electrode is proportional to the concentration of the metal. This is illustrated in Figure 6 as far as lead amalgams are

concerned, where the plot of negative limiting current against concentration of lead shows a straight line relation. Although no special experiments were made to show that the same proportionality holds with cadmium and zinc amalgams, the results in Table 7 show that it does. This relation between concentration of the metal in the amalgam and the negative limiting current is not affected by the presence of other metals in the amalgam.

Although the above results show in general a direct proportionality between the concentration of the metal in the amalgam and the magnitude of the limiting current resulting from its oxidation, it must be admitted that an error of roughly 10% was involved in arriving at this conclusion. This error is thought to be caused by day to day variations in the rate of flow of the amalgam through the fine capillary even though the same capillary was used throughout. For instance, the results in Table 3 show that, when the rate of flow was 1.96 milligrams per second, the ratio of negative limiting current to concentration of lead in the amalgam was 7.73, whereas it was 8.70 when the amalgam flowed at the rate of 2.22 milligrams per second. The necessity of learning, if possible, the relation existing between the negative limiting current and the rate of flow of the amalgam was

apparent as soon as the results in Table 3 were obtained.

As pointed out previously, Kolthoff and Lingane[1] and Heyrovsky and Kalousek[8] assumed that the relation between the negative limiting current and the concentration of the metal in the amalgam is expressed by the equation

$$I_{d-} = 605\ n\ C\ D_a^{\frac{1}{2}}\ m^{2/3} t^{1/6} \qquad (32)$$

which means that the limiting current is proportional to $m^{2/3}t^{1/6}$ if the concentration is kept constant. However, the results in Tables 4, 5 and 6 show that this proportionality does not hold for amalgams of lead, cadmium and zinc. In fact, the ratio $I_{d-}/m^{2/3}t^{1/6}$ varies directly with the magnitude of $m^{2/3}t^{1/6}$ in each case. The above authors based their conclusion on the fact that the half-wave potential for a given metal is relatively constant even though such factors as drop-time, rate of flow and concentration (metal in the amalgam or metal ions in solution) are varied. From the remarks to follow it will become clear that constancy of half-wave potential is, however, a poor criterion to use in support of the theory that equation 32 is correct.

Although the results in Tables 4, 5 and 6 show that the half-wave potential would not remain constant with varying rates of flow of the amalgam,

they do not give any indication as to the extent of the change to be expected. With the lead amalgam (Table 4) the increase in $I_{d-}/m^{2/3}t^{1/6}$ from 2.54 to 3.33, corresponding to an increase of from 1.60 to 2.21 in the value of $m^{2/3}t^{1/6}$, would cause a calculated increase of only about 3.2 millivolts in the half-wave potential. The change would be about the same with the cadmium amalgam (Table 5). With zinc, no results for the positive current are available (Table 6) but if it can be assumed that (26) is correct for a drop-time of 70 seconds, the change would be only about 10 millivolts, even though the drop-time was varied from 3 to 70 seconds. The calculations were made by substituting the experimental values for k_s and k_a for the greatest and least values of $m^{2/3}t^{1/6}$ in each case into (31). For example,

$$E_{\frac{1}{2}} = E' + \frac{RT}{nF} \ln \frac{f_s\ k_a}{f_a\ k_s} \qquad (31)$$

Substitution of the values calculated from the results in Table 4, where $E^1_{\frac{1}{2}}$ and $E^2_{\frac{1}{2}}$ refer to the results corresponding to the greatest and least values of $m^{2/3}t^{1/6}$, respectively, gives

$$E^1_{\frac{1}{2}} = E' + \frac{RT}{nF} \ln \frac{f_s}{f_a} + \frac{RT}{nF} \ln \frac{10.65}{10.20} \quad \text{volts}$$

$$E^2_{\frac{1}{2}} = E' + \frac{RT}{nF} \ln \frac{f_s}{f_a} + \frac{RT}{nF} \ln \frac{6.00}{7.40} \quad \text{volts}$$

$$E^1_{\frac{1}{2}} - E^2_{\frac{1}{2}} = \frac{RT}{nF} \ln \frac{10.65 \times 7.40}{10.20 \times 6.00} \quad \text{volts}$$

$$= 0.029 \log 1.21 \quad \text{volts}$$

$$= 0.0032 \quad \text{volts}$$

It is obvious, therefore, that no serious error is involved in assuming (32) to be correct as far as half-wave potentials are concerned but this is not true when dealing with the relation existing between limiting currents and concentrations of amalgams with various rates of flow of the amalgam through the fine capillary.

It is surprising that (32) does not apply for the oxidation of the metal atoms as well as does the corresponding equation for reduction of the ions in the solution (26). The derivation of (26), given by Kolthoff and Lingane in their book "Polarography"[1] (pages 32 to 36), can be used with slight variation, but apparently with the same reasoning, to arrive at the corresponding equation for the limiting current from the oxidation of the metals in

the amalgams (equation 32). That the former equation applies with cadmium ions insofar as the interrelation between $m^{2/3}t^{1/6}$, concentration and limiting current are concerned, has been shown experimentally by Maas[13]. It is gratifying to find that the average of the values for $I_{d+}/m^{2/3}t^{1/6}$ reported in Table 5 is within one percent of that reported by Maas.

In search of an explanation of this discrepancy between theory and experimental results it was considered possible that the limiting currents from a dropping amalgam electrode might be affected by the anodic process on the solution side of the mercury-solution interface. If the rate of diffusion of the metal ions formed, away from the surface of the electrode, were not fast enough to keep the concentration of the metal chloride below its saturation value, precipitation on the electrode of the salt so formed might take place. This would cause a reduction in the effective surface area of the electrode and in the extreme case could cause a limiting current in itself. Such a possibility would be less probable with cadmium and zinc amalgams, where the chlorides are quite soluble, than with lead, since lead chloride is relatively insoluble. However, when the concentration of the lead ions in the solution was varied from

2.5 millimolar to zero concentration with an amalgam which contained 0.82 millimoles of lead per liter the variation in the magnitude of the negative limiting currents was very small (Figure 10). The fact that this limiting current became slightly greater as the concentration in solution was decreased may have some significance but the only safe conclusion to draw is that this experiment failed to prove that the negative limiting current caused by an amalgam dropping electrode was affected by the anodic process at the electrode.

Another possible explanation for the discrepancy noted in the last paragraph is that the metal atoms are brought from the interior of the drops to the surface by some other agency in addition to diffusion. The agency in mind is that of mechanical mix- which is always tacitly ignored in theoretical interpretations of the process that takes place in the drop, not only with amalgam dropping electrodes but also with pure mercury. However, an investigation of this possibility was beyond the scope of this thesis.

The work is being continued in an effort to find the relation existing between the magnitude of the negative limiting current and the rate of flow of the amalgam from the fine capillary, when all

other factors are kept constant, and to explain why this relation does not agree with theory. The former problem must be solved before a method of analysis, based on the negative limiting current from a dropping amalgam electrode, can be used with a high degree of accuracy. If both of the problems can be solved, it may be possible to develop a simple and accurate method for determining the rate of diffusion of metals in mercury.

SUMMARY

A study has been made of dropping amalgam electrodes in a polarographic cell. The following conclusions are indicated:

1. The magnitude of the limiting current, obtained from the reaction that takes place when the metal in the dropping amalgam electrode is oxidized to the corresponding ions, is proportional to the concentration of the metal in the amalgam.
2. The equation relating the magnitude of the negative limiting current to the rate of flow of the amalgam from the fine capillary is not known. It has been established, however, that it cannot be assumed to be the same as that which exists in ordinary polarographic analysis.
3. The cell solution should be free from the ions corresponding to the metals in the amalgam if it is desired to determine the height of the wave in the current-potential curve corresponding to a given concentration of the metal in the amalgam.
4. The magnitude of the limiting current from one metal in the amalgam is not affected by the presence of other metals.

5. Mercurous chloride may be added to the surface of the quiet pool of mercury to maintain a constant potential at this electrode during the time it is acting as a cathode. If this is not done, an external constant potential electrode should be used.

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APPENDIX

Data from which the Current-Potential Curves in the Text were Constructed.

The corrected averages were obtained by subtracting the residual current from the currents actually obtained. These corrected averages, which were rounded off to the nearest 0.05 microampere, were used in plotting the curves. The volts shown in the tables are all negative. The cell solutions were always made up in the basic cell solution.

TABLE I

For Curve (a) Figure 5

Dropping Electrode: Pure Hg.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 1.88 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.657	4.31	4.25	4.28	4.25
0.584	4.31	4.25	4.28	4.25
0.569	4.25	4.25	4.25	4.20
0.554	4.19	4.19	4.19	4.15
0.539	4.13	4.13	4.13	4.10
0.525	3.94	3.94	3.94	3.90
0.511	3.63	3.63	3.63	3.60
0.496	2.94	2.94	2.94	2.95
0.482	2.00	2.00	2.00	2.00
0.467	1.13	1.06	1.10	1.10
0.453	0.44	0.44	0.44	0.55
0.438	0.13	0.13	0.13	0.15
0.401	0	0	0	0
0.365	0		0	0
0.292	0		0	0
0.219	0		0	0
0.146	-0.06	-0.06	-0.06	0
0.073	-0.13		-0.13	+0.05
0	-0.44		-0.44	-0.05

Positive limiting current: 4.25 microamperes.

TABLE II

For Curve (b) Figure 5

Dropping Electrode: 0.05 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 2.08 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.438	0	0	0	0
0.423	-0.25	-0.25	-0.25	-0.25
0.409	-0.25	-0.28	-0.27	-0.25
0.394	-0.31	-0.31	-0.31	-0.30
0.380	-0.31	-0.31	-0.31	-0.30
0.365	-0.31	-0.35	-0.33	-0.30
0.350	-0.31	-0.35	-0.33	-0.30
0.336	-0.38	-0.38	-0.38	-0.35
0.321	-0.38	-0.38	-0.38	-0.35
0.306	-0.38	-0.38	-0.38	-0.35
0.292	-0.44	-0.38	-0.41	-0.40
0.219	-0.50	-0.38	-0.44	-0.40
0.146	-0.50	-0.44	-0.47	-0.40
0.073	-0.50	-0.50	-0.50	-0.30
0	-0.75	-0.75	-0.75	-0.35

Positive limiting current: Not determined.

Negative limiting current: -0.40 microamperes.

TABLE III

For Curve (c) Figure 5

Dropping Electrode: 0.19 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 1.96 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.657	4.25	4.38	4.32	4.25
0.584	4.25	4.31	4.28	4.25
0.566	4.19	4.31	4.25	4.20
0.540	4.13	4.19	4.16	4.15
0.526	4.00	4.00	4.00	4.00
0.511	3.50	3.63	3.57	3.55
0.504	3.13	3.38	3.26	3.25
0.489	2.25	2.75	2.50	2.50
0.482	1.25	1.44	1.40	1.40
0.475	0.56	0.75	0.66	0.65
0.467	0	0	0	0
0.460	-0.25	-0.25	-0.25	-0.25
0.453	-0.56	-0.56	-0.56	-0.55
0.438	-1.00	-1.00	-1.00	-1.00
0.423	1.25	1.25	1.25	-1.25
0.409	-1.38	-1.38	-1.38	-1.35
0.394	-1.44	-1.44	-1.44	-1.40
0.380	1.44	1.44	1.44	-1.40
0.365	1.44	1.44	1.44	-1.40

Positive limiting current: 4.25 microamperes.

Negative limiting current: -1.40 microamperes.

TABLE IV

For Curve (d) Figure 5

Dropping Electrode: 0.42 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 2.22 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.470	0	0	0	0
0.467	-0.31		-0.31	-0.30
0.453	-1.75	-1.63	-1.69	-1.70
0.438	-2.69	-2.50	-2.60	-2.60
0.423	-3.13	-3.06	-3.10	-3.10
0.409	-3.38	-3.38	-3.38	-3.35
0.394	-3.44	-3.50	-3.47	-3.45
0.379	-3.50	-3.56	-3.53	-3.50
0.365	-3.56	-3.56	-3.56	-3.55
0.292	-3.56	-3.56	-3.56	-3.55
0.219		-3.63	-3.63	-3.60
0.146		-3.69	-3.69	-3.60
0.073		-3.75	-3.75	-3.55
0		-3.94	-3.94	-3.55

Positive limiting current: Not determined.

Negative limiting current: -3.55 microamperes.

TABLE V

For Curve (e) Figure 5

Dropping Electrode: 0.73 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 2.08 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.657	+4.38		4.38	4.35
0.584	+4.37		4.38	4.35
0.555	+4.38		4.38	4.35
0.548	+4.38		4.38	4.35
0.540	+4.31		4.31	4.30
0.533	+4.13		4.13	4.10
0.526	+4.06		4.06	4.05
0.518	+3.81		3.81	3.80
0.511	+3.38		3.38	3.35
0.504	+2.88		2.88	2.85
0.496	+2.13		2.13	2.10
0.489	+1.19		1.19	1.20
0.482	+0.25		0.25	0.25
0.480	+0		0	0
0.467	-1.63	-1.75	-1.69	-1.70
0.453	-3.81	-3.75	-3.78	-3.80
0.438	-5.06	-5.06	-5.06	-5.10
0.423	-5.63	-5.63	-5.63	-5.65
0.409	-5.94	-5.88	-5.91	-5.90
0.394	-6.00	-5.94	-5.97	-5.95
0.380		-6.00	-6.00	-6.00
0.365	-6.00	-6.00	-6.00	-6.00
0.292	-6.00	-6.06	-6.03	-6.00
0.219		-6.31	-6.31	-6.25
0.146		-6.44	-6.44	-6.35
0.073		-6.56	-6.56	-6.35
0		-6.81	-6.81	-6.40

Positive limiting current: 4.35 microamperes.

Negative limiting current: -6.00 microamperes.

TABLE VI

For Curve (f) Figure 5

Dropping Electrode: 0.89 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 2.19 mgms. per second.

Volts	Microamperes			
	1	2	Av.	Corrected Av.
0.657	4.44	4.44	4.44	4.40
0.584	4.44	4.44	4.44	4.40
0.569	4.44	4.44	4.44	4.40
0.555	4.44	4.38	4.41	4.40
0.540	4.19	4.19	4.19	4.15
0.526	4.00	3.88	3.94	3.90
0.511	3.31	3.19	3.25	3.25
0.496	2.00	1.81	1.91	1.90
0.489	1.06	0.81	0.94	0.95
0.482	0	0	0	0
0.475	-1.00	-0.75	-0.88	-0.90
0.467	-2.19	-1.94	-2.07	-2.10
0.453	-4.19	-3.88	-4.04	-4.05
0.438	-5.63	-5.38	-5.51	-5.50
0.423	-6.63	-6.38	-6.51	-6.50
0.409	-7.19	-7.31	-7.25	-7.25
0.394	-7.38	-7.63	-7.52	-7.50
0.380	7.50	7.63	-7.57	-7.55
0.365	7.56	7.63	-7.60	-7.60
0.292	7.63	7.69	-7.66	-7.65

Positive limiting current: 4.40 microamperes.

Negative limiting current: -7.60 microamperes.

TABLE VII

For Curve (a) Figure 7

Dropping Electrode: 0.69 millimolar Pb amalgam

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 2 seconds per drop.

Flow Rate: Not determined.

Volts	Microamperes	
	i	Corrected
0.730	5.88	5.80
0.657	5.88	5.80
0.584	5.81	5.80
0.569	5.75	5.70
0.555	5.69	5.65
0.540	5.44	5.40
0.526	5.13	5.10
0.511	4.19	4.20
0.496	2.69	2.70
0.467	0	0
0.453	-2.75	-2.75
0.438	-4.88	-4.90
0.423	-6.38	-6.40
0.409	-7.38	-7.40
0.394	-8.00	-8.00
0.380	-8.31	-8.30
0.365	-8.44	-8.40
0.292	-8.69	-8.65
0.146	-8.88	-8.80
0.073	-9.00	-8.80
0	-9.25	-8.85

Positive limiting current: 5.80 microamperes.

Negative limiting current: -8.80 microamperes.

TABLE VIII

For Curve (b) Figure 7

Dropping Electrode: 0.69 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 3 seconds per drop.

Flow Rate: 2.49 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.657	5.13			5.10
0.584	5.13			5.10
0.569	5.13			5.10
0.555	5.00			4.95
0.540	4.88			4.85
0.526	4.50			4.50
0.511	3.69			3.70
0.496	2.25			2.25
0.479	0			0
0.467	-2.00	-2.00	-2.00	-2.00
0.453	-4.06	-4.06	-4.06	-4.05
0.438	-5.56	-5.68	-5.62	-5.60
0.423	-6.38	-6.38	-6.38	-6.40
0.409	-6.98	-7.00	-6.94	-6.95
0.394	-7.06	-7.19	-7.13	-7.10
0.380	-7.13	-7.13	-7.13	-7.10
0.365	-7.13	-7.38	-7.26	-7.25
0.292	-7.19	-7.44	-7.32	-7.30
0.219	-7.31	-7.50	-7.41	-7.35
0.146	-7.50	-7.63	-7.57	-7.45
0.073	-7.69	-7.81	-7.75	-7.35

Positive limiting current: 5.10 microamperes.

Negative limiting current: -7.35 microamperes.

TABLE IX

For Curve (c) Figure 7

Dropping Electrode: 0.69 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 1.93 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.657	4.50			4.45
0.584	4.50			4.45
0.569	4.50			4.45
0.555	4.44			4.40
0.540	4.38			4.35
0.526	4.13			4.10
0.511	3.56			3.55
0.496	2.63			2.65
0.482	0.75			0.75
0.475	0			0
0.467	-1.38	-1.25	-1.32	-1.30
0.453	-3.13	-3.00	-3.07	-3.05
0.438	-4.38	-4.25	-4.32	-4.30
0.423	-5.19	-5.19	-5.19	-5.20
0.409	-5.63	-5.63	-5.63	-5.60
0.394	-5.81	-5.81	-5.81	-5.80
0.380	-5.88	-5.88	-5.88	-5.85
0.365	-5.94	-5.94	-5.94	-5.90
0.292	-5.94	-6.00	-5.97	-5.95
0.219	-6.00	-6.00	-6.00	-5.95
0.146				
0.073	-6.13	-6.13	-6.13	-5.95

Positive limiting current: 4.45 microamperes.

Negative limiting current: -5.95 microamperes.

TABLE X

For Curve (d) Figure 7

Dropping Electrode: 0.69 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 5 seconds per drop.

Flow Rate: 1.59 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.657	4.13	4.13	4.13	4.10
0.584	4.13	4.13	4.13	4.10
0.569	4.06	4.13	4.10	4.05
0.555	3.94	4.06	4.00	3.95
0.540	3.81	3.94	3.88	3.85
0.526	3.69	3.69	3.69	3.65
0.511	3.13	3.13	3.13	3.10
0.496	2.00	1.94	1.97	1.95
0.482	0	0	0	0
0.467	-1.31			-1.30
0.453	-2.88			-2.90
0.438	-4.00			-4.00
0.423	-4.63			-4.65
0.409	-4.88			-4.85
0.394	-5.13	-5.13	-5.13	-5.10
0.380	-5.13	-5.13	-5.13	
0.365	-5.13	-5.13	-5.13	-5.10
0.292	-5.19	-5.13	-5.16	-5.15
0.219	-5.19	-5.19	-5.19	-5.15
0.146	-5.25	-5.25	-5.25	-5.15
0.073	-5.31	-5.31	-5.31	-5.10

Positive limiting current: 4.10 microamperes.

Negative limiting current: -5.15 microamperes.

TABLE XI

For Curve (e) Figure 7

Dropping Electrode: 0.69 millimolar Pb amalgam.

Solution: 0.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 6 seconds per drop.

Flow Rate: 1.29 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.730	3.75	3.81	3.78	3.70
0.657	3.75	3.75	3.75	3.70
0.584	3.69	3.75	3.72	3.65
0.569	3.69	3.69	3.69	3.65
0.555	3.63	3.69	3.66	3.65
0.540	3.50	3.56	3.53	3.50
0.526	3.25	3.38	3.32	3.30
0.511	2.63	2.75	2.69	2.70
0.496	1.63	1.75	1.69	1.70
0.482	0	0	0	0
0.467	-1.31	-1.38	-1.35	-1.35
0.453	-2.63	-2.63	-2.63	-2.65
0.438	-3.38	-3.38	-3.38	-3.40
0.423	-3.88	-3.88	-3.88	-3.90
0.409	-4.13	-4.13	-4.13	-4.10
0.394	-4.13	-4.13	-4.13	-4.10
0.380	-4.19	-4.19	-4.19	-4.15
0.365	-4.19	-4.19	-4.19	-4.15
0.292	-4.19	-4.19	-4.19	-4.15
0.219	-4.19	-4.25	-4.22	-4.15
0.146	-4.31	-4.38	-4.35	-4.25
0.073	-4.44	-4.44	-4.44	-4.25

Positive limiting current: 3.70 microamperes.

Negative limiting current: -4.15 microamperes.

TABLE XII

For Curve (a) Figure 8

Dropping Electrode: 1.20 millimolar Cd amalgam.

Solution: 1.00 millimolar $CdCl_2$.

Drop-time: 3 seconds per drop.

Flow Rate: 2.62 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.876	8.55			8.45
0.803	8.55			8.45
0.774	8.41			8.35
0.759	8.27			8.20
0.745	8.12			8.05
0.730	7.55			7.50
0.715	6.13			6.05
0.701	3.71			3.65
0.686	0			-0.05
0.671	-3.85	-3.56	-3.71	-3.75
0.657	-7.84	-6.84	-7.34	-7.40
0.642	-11.26	-10.83	-11.05	-11.10
0.628	-13.82	-13.68	-13.75	-13.80
0.613	-15.39	-15.96	-15.68	-15.70
0.599	-16.10	-17.39	-16.75	-16.80
0.584	-16.53	-17.96	-17.25	-17.30
0.555	-16.53	-17.96	-17.25	-17.30
0.526	-16.53	-17.96	-17.25	-17.25
0.511	-16.53	-17.96	-17.25	-17.25
0.438	-16.53	-17.96	-17.25	-17.25
0.365	-16.53	-17.96	-17.25	-17.25
0.292	-16.67	-17.96	-17.32	-17.30
0.219	-16.96	-18.24	-17.60	-17.55
0.146	-17.24	-18.38	-17.81	-17.70
0.073	-17.67	-19.10	-18.39	-18.20
0	-17.81	-19.10	-18.46	-18.05

Positive limiting current: 8.45 microamperes.

Negative limiting current: -17.25 microamperes.

TABLE XIII

For Curve (b) Figure 8

Dropping Electrode: 1.20 millimolar Cd amalgam.

Solution: 1.00 millimolar $CdCl_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 2.14 mgms. per second.

Volts	Microamperes			
	1	2	Av.	Corrected Av.
0.867	7.55			7.45
0.803	7.55			7.45
0.774	7.41			7.35
0.759	7.27			7.20
0.745	7.13			7.05
0.730	6.70			6.65
0.715	5.56			5.50
0.701	3.42			3.35
0.686	0			-0.05
0.671	-2.85	-2.85	-2.85	-2.90
0.657	-6.27	-6.13	-6.20	-6.25
0.642	-9.12	-8.84	-8.98	-9.05
0.628	-10.97	-10.40	-10.69	-10.75
0.613	-11.83	-11.26	-11.55	-11.60
0.599	-12.54	-11.69	-12.12	-12.15
0.584	-12.54	-11.97	-12.26	-12.30
0.555	-12.83	-12.11	-12.47	-12.50
0.526	-12.83	-12.26	-12.55	-12.55
0.511	-12.83	-12.26	-12.55	-12.55
0.438	-13.11	-12.26	-12.69	-12.70
0.365	-13.11	-12.26	-12.69	-12.65
0.292	-13.40	-12.54	-12.97	-12.95
0.219	-13.54	-12.97	-13.26	-13.20
0.146	-13.68	-13.11	-13.40	-13.30
0.076	-13.97	-13.11	-13.54	-13.35
0	-14.11	-13.40	-13.76	-13.35

Positive limiting current: 7.45 microamperes.

Negative limiting current: -12.55 microamperes.

TABLE XIV

For Curve (c) Figure 8

Dropping Electrode: 1.20 millimolar Cd amalgam.

Solution: 1.00 millimolar $CdCl_2$.

Drop-time: 5 seconds per drop.

Flow Rate: 1.67 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.876	6.84			6.75
0.803	6.84			6.75
0.774	6.84			6.75
0.759	6.70			6.65
0.745	6.56			6.50
0.730	5.99			5.90
0.715	4.99			4.90
0.701	3.28			3.20
0.686	0			-0.05
0.671	-2.85	-2.71	-2.78	-2.85
0.657	-5.99	-5.56	-5.78	-5.85
0.642	-8.27	-7.70	-7.99	-8.05
0.628	-9.69	-8.84	-9.27	-9.30
0.613	-10.55	-9.41	-9.98	-10.00
0.599	-10.69	-10.12	-10.42	-10.45
0.584	-10.83	-10.26	-10.55	-10.60
0.555	-10.97	-10.26	-10.62	-10.65
0.526	-11.16	-10.26	-10.71	-10.75
0.511	-11.16	-10.26	-10.71	-10.70
0.438	-11.16	-10.26	-10.71	-10.70
0.365	-11.40	-10.26	-10.83	-10.80
0.292	-11.40	-10.40	-10.90	-10.90
0.219	-11.67	-10.69	-11.18	-11.15
0.146	-11.67	-10.97	-11.32	-11.20
0.073	-11.83	-10.97	-11.40	-11.20
0	-11.97	-11.40	-11.69	-11.30

Positive limiting current: 6.75 microamperes.

Negative limiting current: -10.70 microamperes.

TABLE XV

For Curve (d) Figure 8

Dropping Electrode: 1.20 millimolar Cd amalgam.

Solution: 1.00 millimolar $CdCl_2$.

Drop-time: 6 seconds per drop.

Flow Rate: 1.40 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.876	6.41			6.30
0.803	6.41			6.30
0.774	6.41			6.35
0.759	6.27			6.20
0.745	6.27			6.20
0.730	6.13			6.05
0.715	4.85			4.80
0.701	3.28			3.20
0.686	0			-0.05
0.671	-2.56	-2.28	-2.42	-2.50
0.657	-5.56	-5.56	-5.56	-5.60
0.642	-7.55	-7.41	-7.48	-7.55
0.628	-8.69	-8.27	-8.48	-8.55
0.613	-9.12	-8.84	-8.98	-9.00
0.599	-9.69	-9.12	-9.41	-9.45
0.584	-9.69	-9.40	-9.55	-9.60
0.555	-9.83	-9.40	-9.62	-9.65
0.526	-9.98	-9.40	-9.69	-9.70
0.511	-9.98	-9.40	-9.69	-9.70
0.438	-9.98	-9.55	-9.77	-9.75
0.365	-9.98	-9.55	-9.77	-9.75
0.292	-9.98	-9.69	-9.84	-9.80
0.219	-10.26	-9.69	-9.98	-9.95
0.146	-10.40	-9.83	-10.12	-10.00
0.073	-10.55	-9.83	-10.19	-10.00
0	-10.83	-10.26	-10.55	-10.15

Positive limiting current: 6.30 microamperes.

Negative limiting current: -9.70 microamperes.

TABLE XVI

For Curve (a) Figure 9

Dropping Electrode: 2.08 millimolar Zn amalgam.

Solution: Basic cell solution.

Drop-time: 3 seconds per drop.

Flow Rate: 2.51 mgms. per second.

Volts	Microamperes	
	i	Corrected
1.186	1.14	0.95
1.095	0.29	0.10
1.080	-0.43	-0.60
1.066	-1.57	-1.70
1.051	-3.28	-3.40
1.037	-5.27	-5.40
1.022	-7.55	-7.70
1.007	-9.69	-9.85
0.993	-11.69	-11.85
0.978	-13.68	-13.80
0.964	-15.68	-15.80
0.949	-17.67	-17.80
0.934	-19.95	-20.05
0.920	-20.52	-20.65
0.905	-21.66	-21.75
0.891	-22.52	-22.65
0.876	-23.09	-23.20
0.840	-23.66	-23.75
0.803	-23.94	-24.05
0.730	-24.23	-24.30
0.657	-24.37	-24.40
0.584	-24.51	-24.55
0.511	-24.80	-24.80

Negative limiting current: -24.30 microamperes.

TABLE XVII

For Curve (b) Figure 9

Dropping Electrode: 2.08 millimolar Zn amalgam.

Solution: Basic cell solution.

Drop-time: 4 seconds per drop.

Flow Rate: 1.85 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
1.186	0.86	1.14	1.00	0.80
1.095	0.14	0.57	0.36	0.20
1.080	-0.43		-0.43	-0.60
1.066	-1.28	-0.57	-0.93	-1.10
1.051	-2.71		-2.71	-2.85
1.037	-4.56	-3.14	-3.85	-4.00
1.022	-6.74	-4.98	-5.86	-6.00
1.007	-8.55	-6.84	-7.70	-7.85
0.993	-9.98	-8.55	-9.27	-9.40
0.978	-11.97	-10.69	-11.33	-11.45
0.964	-13.11	-12.83	-12.97	-13.10
0.949	-14.68	-14.54	-14.61	-14.75
0.934	-15.82	-16.25	-16.04	-16.20
0.920	-16.53	-17.39	-16.96	-17.05
0.905	-17.10	-17.96	-17.53	-17.65
0.891	-17.39	-18.53	-17.96	-18.05
0.876	-17.67	-19.10	-18.39	-18.50
0.840	-18.24	-19.67	-18.96	-19.05
0.803	-18.53	-20.52	-19.53	-19.60
0.730	-18.67	-20.38	-19.53	-19.60
0.657	-19.67	-20.52	-20.10	-20.15
0.584	-19.67	-21.10	-20.39	-20.45

Negative limiting current: -19.60 microamperes.

TABLE XVIII

For Curve (c) Figure 9

Dropping Electrode: 2.08 millimolar Zn amalgam.

Solution: Basic cell solution.

Drop-time: 5 seconds per drop.

Flow Rate: 1.56 mgms. per second.

	Microamperes	
Volts	i	Corrected
1.186	1.00	0.80
1.095	0	-0.15
1.080	-0.43	-0.60
1.066	-1.14	-1.30
1.051	-2.42	-2.55
1.037	-3.99	-4.15
1.022	-6.13	-6.25
1.007	-7.98	-8.15
0.993	-9.26	-9.40
0.978	-10.83	-10.95
0.964	-12.26	-12.40
0.949	-13.11	-13.25
0.934	-14.00	-14.10
0.920	-14.54	-14.65
0.905	-14.96	-15.05
0.891	-15.53	-15.65
0.876	-15.53	-15.65
0.840	-15.82	-15.90
0.803	-16.14	-16.25
0.730	-16.37	-16.45
0.657	-16.53	-16.60
0.584	-16.53	-16.60
0.511	-16.67	-16.70

Negative limiting current: -16.60 microamperes.

TABLE XIX

For Curve (d) Figure 9

Dropping Electrode: 2.08 millimolar Zn amalgam.

Solution: Basic cell solution.

Drop-time: 6 seconds per drop.

Flow Rate: 1.20 mgms. per second.

	Microamperes	
Volts	i	Corrected
1.186	0.86	0.70
1.095	0	0
1.080	-0.43	-0.30
1.066	-1.14	-1.30
1.051	-2.08	-2.20
1.037	-3.85	-4.00
1.022	-5.56	-5.70
1.007	-6.98	-7.10
0.993	-8.69	-8.75
0.978	-9.98	-10.10
0.964	-11.11	-11.25
0.949	-12.11	-12.25
0.934	-12.79	-12.90
0.920	-13.53	-13.65
0.905	-13.53	-13.65
0.891	-13.68	-13.80
0.876	-14.00	-14.10
0.840	-14.25	-14.35
0.803	-14.25	-14.35
0.730	-14.54	-14.60
0.657	-14.54	-14.60
0.584	-14.82	-14.85
0.511	-14.82	-14.85

Negative limiting current: -14.60 microamperes.

TABLE XX

For Curve (e) Figure 9

Dropping Electrode: 2.08 millimolar Zn amalgam.

Solution: Basic cell solution.

Drop-time: 7 seconds per drop.

Flow Rate: 1.05 mgms. per second.

	Microamperes	
Volts	i	Corrected
1.186	0.71	0.55
1.095	0	0.15
1.080	-0.29	-0.45
1.066	-1.14	-1.30
1.051	-2.14	-2.30
1.037	-3.56	-3.70
1.022	-5.13	-5.25
1.007	-6.74	-6.90
0.993	-7.98	-8.10
0.978	-8.97	-9.10
0.964	-10.12	-10.25
0.949	-10.83	-10.95
0.934	-11.40	-11.50
0.920	-11.69	-11.80
0.905	-11.97	-12.10
0.891	-11.97	-12.10
0.876	-12.26	-12.35
0.840	-12.54	-12.60
0.803	-12.83	-12.90
0.730	-12.97	-13.00
0.657	-12.97	-13.00
0.584	-13.11	-13.15
0.511	-13.11	-13.15

Negative limiting current: -13.00 microamperes.

TABLE XXI

For Curve (a) Figure 10

Dropping Electrode: 0.82 millimolar Pb amalgam.

Solution: 2.50 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 2.23 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.803	21.95			21.85
0.730	21.95			21.90
0.715	21.95			21.90
0.701	21.66			21.60
0.686	21.38			21.30
0.672	21.09			21.05
0.657	21.09			21.05
0.642	19.69			19.65
0.628	17.96			17.90
0.613	15.96			15.90
0.599	13.97			13.95
0.584	11.83			11.80
0.569	9.55			9.50
0.555	8.41			8.35
0.540	6.84			6.80
0.526	5.56			5.55
0.511	4.13			4.10
0.496	2.85			2.85
0.482	1.71			1.70
0.467	0.43			0.45
0.460	0			0
0.453	-0.69	-0.63	-0.66	-0.65
0.438	-1.63	-1.50	-1.57	-1.55
0.423	-2.69	-2.63	-2.66	-2.65
0.409	-3.50	-3.50	-3.50	-3.50
0.394	-4.38	-4.38	-4.38	-4.35
0.380	-5.13	-4.94	-5.05	-5.05
0.365	-5.75	-5.69	-5.72	-5.70
0.350	-6.25	-6.25	-6.25	-6.25
0.336	-6.63	-6.69	-6.66	-6.65
0.321	-6.89	-7.00	-6.95	-6.90
0.307	-7.00	-7.13	-7.07	-7.05
0.292	-7.00	-7.25	-7.13	-7.10

TABLE XXI (continued)

Volts	Microamperes			
	1	2	Av.	Corrected Av.
0.277	-7.06	-7.31	-7.19	-7.15
0.263	-7.06	-7.31	-7.19	-7.15
0.248	-7.13	-7.38	-7.26	-7.20
0.234	-7.13	-7.38	-7.26	-7.20
0.219	-7.13	-7.38	-7.26	-7.20
0.146	-7.25	-7.44	-7.35	-7.25
0.073	-7.38	-7.63	-7.51	-7.30
0	-7.50	-7.75	-7.63	-7.25

Positive limiting current: 21.85 microamperes.

Negative limiting current: -7.20 microamperes.

TABLE XXII

For Curve (b) Figure 10

Dropping Electrode: 0.82 millimolar Pb amalgam.

Solution: 1.00 millimolar $Pb(CH_3COO)_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 2.23 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.657	9.13	9.13	9.13	9.10
0.642	9.13	9.13	9.13	9.10
0.628	9.13	9.13	9.13	9.10
0.613	9.13	9.13	9.13	9.10
0.599	9.00	9.00	9.00	8.95
0.584	8.81	8.75	8.78	8.75
0.569	8.25	8.25	8.25	8.20
0.555	7.50	7.44	7.47	7.45
0.540	6.38	6.25	6.31	6.30
0.526	5.06	5.00	5.03	5.00
0.511	3.69	3.63	3.66	3.65
0.496	2.25	2.25	2.25	2.25
0.482	0.75	0.75	0.75	0.75
0.475	0	0	0	0
0.453	-1.94	-1.88	-1.91	-1.90
0.438	-3.13	-3.06	-3.10	-3.10
0.423	-4.38	-4.31	-4.35	-4.35
0.409	-5.38	-5.31	-5.35	-5.35
0.394	-6.19	-6.35	-6.27	-6.25
0.380	-6.88	-6.75	-6.82	-6.80
0.365	-7.13	-7.13	-7.13	-7.10
0.350	-7.31	-7.25	-7.28	-7.25
0.336	-7.31	-7.31	-7.31	-7.30
0.321	-7.38	-7.31	-7.35	-7.35
0.306	-7.38	-7.38	-7.38	-7.35
0.292	-7.38	-7.38	-7.38	-7.35
0.256	-7.44	-7.38	-7.41	-7.35
0.219	-7.50	-7.38	-7.44	-7.40
0.146	-7.50	-7.44	-7.47	-7.35
0.073	-7.63	-7.50	-7.57	-7.35
0	-7.69	-7.63	-7.66	-7.25

Positive limiting current: 9.10 microamperes.

Negative limiting current: -7.35 microamperes.

TABLE XXIII (continued)

Volts	Microamperes			
	1	2	Av.	Corrected Av.
0.248	-7.25	-7.13	-7.19	-7.15
0.234	-7.38	-7.31	-7.35	-7.30
0.219	-7.44	-7.44	-7.44	-7.40
0.204	-7.50	-7.50	-7.50	-7.45
0.190	-7.50	-7.50	-7.50	-7.45
0.161	-7.50	-7.50	-7.50	-7.45
0.146	-7.56	-7.50	-7.53	-7.45
0.073	-7.69	-7.69	-7.69	-7.50
0	-7.75	-7.75	-7.75	-7.35

Positive limiting current: 4.55 microamperes.

Negative limiting current: -7.45 microamperes.

TABLE XXIV

For Curve (d) Figure 10

Dropping Electrode: 0.82 millimolar Pb amalgam.

Solution: Basic cell solution.

Drop-time: 4 seconds per drop.

Flow Rate: 2.23 mgms. per second.

	Microamperes	
Volts	I	Corrected
0.657	0.13	0.10
0.584	0.13	0.10
0.511	0	0
0.496	-0.31	-0.30
0.482	-0.94	-0.95
0.467	-1.75	-1.75
0.453	-2.56	-2.55
0.438	-3.38	-3.40
0.423	-4.19	-4.20
0.409	-5.00	-5.00
0.394	-5.88	-5.90
0.380	-6.56	-6.55
0.365	-7.13	-7.10
0.350	-7.38	-7.35
0.336	-7.56	-7.55
0.321	-7.63	-7.60
0.307	-7.63	-7.60
0.292	-7.63	-7.60
0.219	-7.63	-7.60
0.146	-7.63	-7.55
0.073	-7.81	-7.60
0	-7.88	-7.50

Negative limiting current: -7.55 microamperes.

TABLE XXV

For Curve (a) Figure 11

Dropping Electrode: Amalgam 0.25 and 0.54 millimolar Pb and Cd, respectively.

Solution: Basic cell solution.

Drop-time: 4 seconds per drop.

Flow Rate: 1.93 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
0.876	0.44	0.50	0.47	0.35
0.803	0.44	0.50	0.47	0.40
0.730	0.25	0.38	0.32	0.25
0.715	0.08	0.19	0.14	0.05
0.701	-0.13	-0.13	-0.13	-0.20
0.686	-0.69	-0.69	-0.69	-0.75
0.672	-1.50	-1.50	-1.50	-1.55
0.657	-2.56	-2.56	-2.56	-2.60
0.642	-3.56	-3.56	-3.56	-3.60
0.628	-4.25	-4.25	-4.25	-4.30
0.613	-4.63	-4.56	-4.60	-4.65
0.599	-4.88	-4.88	-4.88	-4.90
0.584	-4.94	-4.94	-4.94	-4.95
0.569	-4.94	-5.00	-4.97	-5.00
0.555	-5.00	-5.00	-5.00	-5.05
0.540	-5.00	-5.00	-5.00	-5.05
0.526	-5.00	-5.06	-5.03	-5.05
0.511	-5.06	-5.06	-5.06	-5.10
0.496	-5.13	-5.13	-5.13	-5.15
0.482	-5.19	-5.19	-5.19	-5.20
0.467	-5.38	-5.38	-5.38	-5.40
0.453	-5.75	-5.81	-5.78	-5.80
0.438	-6.38	-6.38	-6.38	-6.40
0.423	-6.88	-6.88	-6.88	-6.90
0.409	-7.25	-7.38	-7.32	-7.30
0.394	-7.50	-7.56	-7.53	-7.50
0.380	-7.63	-7.63	-7.63	-7.60
0.365	-7.63	-7.63	-7.63	-7.60
0.292	-7.75	-7.75	-7.75	-7.70

TABLE XXV (continued)

Volts	Microamperes			
	1	2	Av.	Corrected Av.
0.219	-7.88	-7.88	-7.88	-7.85
0.146	-7.88	-7.88	-7.88	-7.80
0.073	-7.94	-7.94	-7.94	-7.75
0	-8.13	-8.13	-8.13	-7.75

Limiting current corresponding to lead wave:
2.70 microamperes.

Limiting current corresponding to cadmium wave:
5.05 microamperes.

TABLE XXVI

For Curve (b) Figure 11

Dropping Electrode: Amalgam 0.25 and 0.54 millimolar Pb and Cd, respectively.

Solution: 0.25 $Pb(CH_3COO)_2$ and 0.50 millimolar $CdCl_2$.

Drop-time: 4 seconds per drop.

Flow Rate: 1.93 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
1.168	5.75	5.69	5.72	5.55
1.095	5.69	5.69	5.69	5.55
1.022	5.69	5.69	5.69	5.55
0.949	5.69	5.69	5.69	5.55
0.876	5.69	5.69	5.69	5.60
0.861	5.69	5.69	5.69	5.60
0.847	5.69	5.69	5.69	5.60
0.832	5.63	5.69	5.66	5.55
0.817	5.63	5.63	5.63	5.55
0.803	5.63	5.63	5.63	5.55
0.788	5.56	5.50	5.53	5.45
0.774	5.44	5.38	5.41	5.35
0.759	5.19	5.19	5.19	5.10
0.745	4.88	4.88	4.88	4.80
0.730	4.13	4.13	4.13	4.05
0.715	3.38	3.44	3.41	3.35
0.701	2.44	2.44	2.44	2.40
0.686	1.31	1.44	1.38	1.30
0.672	0.25	0.31	0.28	0.20
0.667	0	0	0	-0.05
0.657	-0.75	-0.75	-0.75	-0.80
0.642	-1.50	-1.56	-1.53	-1.60
0.628	-2.19	-2.25	-2.22	-2.25
0.613	-2.56	-2.75	-2.66	-2.70
0.599	-2.94	-3.00	-2.97	-3.00
0.584	-3.00	-3.00	-3.00	-3.05
0.569	-3.06	-3.06	-3.06	-3.10
0.555	-3.06	-3.13	-3.10	-3.15
0.540	-3.06	-3.13	-3.10	-3.15
0.526	-3.13	-3.13	-3.13	-3.15
0.511	-3.19	-3.19	-3.19	-3.20
0.496	-3.25	-3.25	-3.25	-3.25

TABLE XXVI (continued)

Volts	Microamperes			
	1	2	Av.	Corrected Av.
0.482	-3.38	-3.38	-3.38	-3.40
0.467	-3.69	-3.69	-3.69	-3.70
0.453	-4.19	-4.19	-4.19	-4.20
0.438	-4.94	-4.94	-4.94	-4.95
0.423	-5.63	-5.63	-5.63	-5.60
0.409	-6.31	-6.31	-6.31	-6.30
0.394	-6.88	-6.88	-6.88	-6.85
0.380	-7.25	-7.25	-7.25	-7.25
0.365	-7.38	-7.38	-7.38	-7.35
0.350	-7.56	-7.56	-7.56	-7.55
0.336	-7.63	-7.63	-7.63	-7.60
0.292	-7.63	-7.63	-7.63	-7.60
0.219	-7.69	-7.69	-7.69	-7.65
0.146	-7.75	-7.75	-7.75	-7.65
0.073	-7.81	-7.81	-7.81	-7.60
0	-7.88	-7.88	-7.88	-7.50

Limiting current corresponding to lead wave:
4.55 microamperes.

Limiting current corresponding to cadmium wave:
8.65 microamperes.

TABLE XXVII

For Curve (a) Figure 12

Dropping Electrode: Amalgam 0.28, 0.54 and 1.12 millimolar Pb, Cd and Zn, respectively.

Solution: Basic cell solution.

Drop-time: 4 seconds per drop.

Flow Rate: 1.93 mgms. per second.

	Microamperes			
Volts	1	2	Av.	Corrected Av.
1.168	1.00	1.00	1.00	0.80
1.095	0.29	0.29	0.29	0.15
1.080	0	0	0	-0.15
1.066	-0.57	-0.71	-0.64	-0.80
1.051	-1.57	-1.85	-1.71	-1.85
1.037	-2.85	-3.14	-3.00	-3.15
1.022	-4.28	-4.70	-4.49	-4.65
1.007	-5.99	-6.27	-6.13	-6.30
0.993	-7.41	-7.84	-7.63	-7.75
0.978	-8.55	-8.98	-8.77	-8.90
0.964	-9.55	-9.83	-9.69	-9.85
0.949	-10.12	-10.40	-10.26	-10.40
0.934	-10.83	-11.12	-10.48	-10.60
0.920	-11.12	-11.40	-11.26	-11.35
0.905	-11.40	-11.54	-11.47	-11.60
0.891	-11.54	-11.69	-11.62	-11.70
0.876	-11.69	-11.83	-11.76	-11.85
0.803	-12.11	-12.11	-12.11	-12.20
0.730	-12.26	-12.26	-12.26	-12.30
0.686	-12.40	-12.40	-12.40	-12.45
0.672	-12.68	-12.68	-12.68	-12.75
0.657	-13.11	-13.11	-13.11	-13.15
0.642	-13.97	-14.25	-14.11	-14.15
0.628	-14.96	-15.53	-15.25	-15.30
0.613	-15.96	-16.39	-16.18	-16.20
0.599	-16.82	-16.96	-16.89	-16.95
0.584	-17.24	-17.39	-17.32	-17.35
0.569	-17.39	-17.39	-17.39	-17.40
0.555				

TABLE XXVII (continued)

Volts	Microamperes			
	1	2	Av.	Corrected Av.
0.540	-17.53	-17.53	-17.53	-17.55
0.526	-17.53	-17.53	-17.53	-17.55
0.511	-17.53	-17.53	-17.53	-17.55
0.496	-17.67	-17.67	-17.67	-17.70
0.482	-17.67	-17.67	-17.67	-17.70
0.467	-17.67	-17.67	-17.67	-17.70
0.453	-17.96	-17.96	-17.96	-17.95
0.438	-18.10	-18.24	-18.17	-18.15
0.423	-18.81	-18.81	-18.81	-18.80
0.409	-19.38	-19.38	-19.38	-19.35
0.394	-19.81	-19.67	-19.74	-19.75
0.380	-20.24	-19.95	-20.10	-20.10
0.365	-20.24	-20.10	-20.17	-20.15
0.292	-20.24	-20.24	-20.24	-20.20
0.219	-20.52	-20.52	-20.52	-20.45
0.146	-20.81	-20.81	-20.81	-20.70
0.073	-20.95	-20.95	-20.95	-20.75
0	-21.10	-21.23	-21.17	-20.75

Limiting current corresponding to lead wave:
2.60 microamperes.

Limiting current corresponding to cadmium wave:
5.25 microamperes.

Limiting current corresponding to zinc wave:
12.30 microamperes.

TABLE XXVIII

For Curve (b) Figure 12

Dropping Electrode: Amalgam 0.25, 0.54 and 1.12 millimolar Pb, Cd and Zn, respectively.

Solution: 0.17 millimolar $Pb(CH_3COO)_2$ and 0.33 millimolar $CdCl_2$ and $ZnSO_4$.

Drop-time: 4 seconds per drop.

Flow Rate: 1.93 mgms. per second.

Volts	Microamperes	
	i	Corrected
1.168	-5.56	5.40
1.153	5.42	5.25
1.139	5.13	5.00
1.124	4.85	4.70
1.110	4.28	4.10
1.095	3.14	3.10
1.080	1.14	1.00
1.066	-0.86	-1.00
1.051	-2.99	-3.15
1.037	-4.85	-5.00
1.022	-6.41	-6.55
1.007	-7.41	-7.55
0.993	-7.98	-8.10
0.978	-8.27	-8.40
0.964	-8.41	-8.55
0.949	-8.55	-8.65
0.876	-8.84	-8.95
0.803	-8.84	-8.95
0.788	-8.84	-8.95
0.759	-8.84	-8.90
0.730	-8.84	-8.90
0.715	-8.98	-9.05
0.701	-9.26	-9.30
0.686	-9.98	-10.05
0.672	-10.83	-10.90
0.657	-12.26	-12.30
0.642	-13.82	-13.90
0.628	-14.96	-15.00
0.613	-15.68	-15.70
0.599	-16.10	-16.15
0.584	-16.25	-16.30

TABLE XXVIII (continued)

Volts	Microamperes	
	1	Corrected
0.569	-16.25	-16.30
0.555	-16.25	-16.30
0.540	-16.39	-16.40
0.526	-16.39	-16.40
0.511	-16.39	-16.40
0.496	-16.39	-16.40
0.482	-16.39	-16.40
0.467	-16.82	-16.80
0.453	-17.39	-17.40
0.438	-18.10	-18.10
0.423	-19.10	-19.10
0.409	-19.52	-19.50
0.394	-19.81	-19.80
0.380	-20.10	-20.10
0.365	-20.24	-20.20
0.292	-20.24	-20.20
0.219	-20.52	-20.45
0.146	-20.95	-20.85
0.073	-20.95	-20.75
0	-20.95	-20.55

Limiting Current corresponding to lead wave:
3.80 microamperes.

Limiting current corresponding to cadmium wave:
7.45 microamperes.

Limiting current corresponding to zinc wave:
14.35 microamperes.