

scaled from Table V of Webb, Neu and Pitzer,<sup>9</sup> at the respective temperatures of 180.68 and 230°K.

TABLE V

COMPARISON OF THIRD LAW ENTROPIES WITH THOSE COMPUTED STATISTICALLY BY WEBB, NEU AND PITZER

Temp., °K.	Third law	Statistical
180.68	49.46	49.91
230.00	51.93	52.51

The statistical calculations<sup>9</sup> were made on the basis of a bridge structure for B<sub>2</sub>H<sub>6</sub> and on the assignment of a 369 wave number frequency as the lowest fundamental.

The discrepancies, which amount to approximately a half entropy unit in each instance, are outside the limits of accuracy of either the calorimetric data or the statistical computations but

(9) A. N. Webb, J. T. Neu and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1007 (1949).

may arise from one of the following causes: (1) an undetected and not apparent source of random entropy in the solid lattice; (2) an incorrect selection of structure for the molecule (not likely) in the statistical calculations; or (3) an incorrect assignment of fundamental frequencies—more particularly in the low frequency assignment.<sup>10</sup> We do not see a means of distinguishing between these at the present time.

(10) Only the 369 cm.<sup>-1</sup> assignment makes any significant vibrational contribution at these temperatures. Preliminary statistical calculations carried out some time ago in this Laboratory,<sup>11</sup> based on a low fundamental assignment of 412 wave numbers (a frequency assigned as an overtone by Bell and Longuet-Higgins<sup>12</sup>) gave somewhat better agreement with the Third Law entropies. Discrepancies were: 0.24 e.u. at 180.68° and 0.06 e.u. at 230°K.

(11) C. W. Beckett, J. T. Clarke and H. L. Johnston, Technical Report to the Office of Naval Research (1948).

(12) R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A183**, 357 (1945).

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## Polarographic Current-Time Relation during Individual Drop Life

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An improved technique of measuring the current-time curve during an individual drop life is described. Current-time curves at various mercury pressures and correspondingly various drop times have provided evidence that a major cause of divergence of the observed curves from those predicted by either the original or modified Ilkovic equation is the variation of the rate of mercury flow during the drop life. The back pressure due to the interfacial tension is much larger at the beginning than at the end of the drop life and correspondingly the instantaneous area (and hence current) is smaller at the beginning of the drop life than it would be if the mercury flow rate were constant. This effect becomes more pronounced the smaller the total applied pressure. When the difference between the total applied pressure and the back pressure is very small, the current-time curve shows a measurable pause at zero current immediately after the drop falls. Apparently after a drop falls the mercury thread retracts into the capillary lumen and the pause at zero current corresponds to the time required for it to re-emerge. At very small net driving pressures the curves also show a distinct inflection as soon as the new drop begins to form. This inflection probably reflects the non-spherical and varying geometry of the very young mercury surface. At short drop times the current-time curve goes through a flat maximum, because the stirring produced by the rapid dropping movement disturbs the diffusion layer and enhances the current. With an electrode whose characteristics correspond to those normally employed, and a drop time in the neighborhood of 3.0 to 3.5 sec., the observed current-time curve does approximate quite closely during the last three-fourths of the drop life to that predicted from the modified Ilkovic equation.

The original Ilkovic equation<sup>1,2</sup> for the instantaneous diffusion current during the life of an individual mercury drop is

$$i_t = 709 nD^{1/2}Cm^2/t^{1/2} \text{ (microamp.)} \quad (1)$$

If the rate of flow of mercury,  $m$ , is constant, this predicts that the current-time curve should be a sixth-order parabola,  $i_t = kt^{1/6}$ .

Steghart<sup>3</sup> and McKenzie<sup>4</sup> were the first to report that oscilloscopically observed current-time curves deviated considerably from the above relation; in particular the current during the very early life of the drop was much too small. This was confirmed by Taylor, Smith and Cooter<sup>5</sup> in the case of cadmium ion in 0.1  $M$  potassium chloride. From attempts to fit their data to an equation of the form

$i_t = kt^y$ , Taylor, Smith and Cooter concluded that no single value of  $y$  applied over the entire drop life; from 0.1, 0.5, 1 and 2 sec. to the end of the drop life (ca. 3.5 sec.) the observed values of  $y$  were *seriatim* 0.31, 0.249, 0.227 and 0.186, instead of the 0.167 predicted by eq. 1. Kambara, Suzuki and Tachi<sup>6</sup> also reported that the value of  $y$  during the later life of the drop is between  $1/4$  and  $1/5$ , but they do not provide sufficient experimental information to permit one to judge the precision of their measurements. From a very well executed study, using cupric ion in dilute sulfuric acid, MacDonald and Wetmore<sup>7</sup> also concluded that the current-time curve does not follow a simple parabola but that the average value of  $y$  is close to 0.21.

On the other hand Airey and Smales<sup>8</sup> reported that the relation  $i_t = kt^{1/6}$  was obeyed to  $\pm 2.5\%$  from 0.75 sec. to the end of the life of a 3.9 sec.

(1) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934); *J. chim. phys.*, **35**, 129 (1938).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 34 *et seq.*

(3) F. L. Steghart, *Chemistry and Industry*, 157 (1948).

(4) H. A. McKenzie, *This Journal*, **70**, 3147 (1948).

(5) J. K. Taylor, R. E. Smith and I. L. Cooter, *J. Research Natl. Bur. Standards*, **42**, 387 (1949).

(6) T. Kambara, M. Suzuki and I. Tachi, *Bull. Chem. Soc. Japan*, **23**, 220 (1950).

(7) J. J. MacDonald and F. E. W. Wetmore, *Trans. Faraday Soc.*, **47**, 533 (1951).

(8) L. Airey and A. A. Smales, *Analyst*, **75**, 287 (1950).

drop, but they agree with the other investigators that the current is abnormally small when the drop is very young.

Divergence of observed current-time curves from a simple parabola is expected from the modified equation for the instantaneous current

$$i_t = 709nD^{1/2}Cm^{2/3}t^{1/6} + 31,560nDCm^{1/3}t^{1/3} \quad (2)$$

which was proposed independently by Lingane and Loveridge<sup>9</sup> and Strehlow and von Stackelberg<sup>10</sup> (the latter authors use 13,760 rather than 31,560 for the constant in the second term). Kambara, Suzuki and Tachi<sup>6</sup> later derived an equation identical with eq. 2, including the same constants. The second term in eq. 2 takes account of the curvature of the electrode which is neglected in the original Ilkovic equation.

If  $m$  were constant during the drop life it follows from eq. 2 that the current-time curve would have the form  $i_t = \alpha t^{1/6} + \beta t^{1/3}$ , and a plot of the ratio  $i_t/t^{1/6}$  against  $t^{1/6}$  should produce a straight line with an intercept  $\alpha$  and a slope  $\beta$ . However,  $m$  is not constant, but increases continuously as the drop grows, because the back pressure exerted by the interfacial tension is inversely proportional to the drop radius. Consequently, instead of being true constants  $\alpha$  and  $\beta$  both increase during the drop life. It is to be expected that a plot of  $i_t/t^{1/6}$  versus  $t^{1/6}$  would be a curve rising rapidly during the very early life of the drop and then approaching a straight line of slope  $\beta$  toward the end of the drop life. Meites and Meites<sup>11</sup> plotted the data of Taylor, Smith and Cooter in this way and the resulting curve conforms qualitatively to the expected shape. Meites and Meites expressed the opinion that these particular data do not conform any better to eq. 2 than to the original Ilkovic equation. However, the current-time curves obtained in the present study with capillaries of widely different characteristics at different pressures and drop times, definitely conform more closely to eq. 2 than to eq. 1 when the variability of  $m$  is taken into account.

### Experimental Technique

The current-time curves were measured oscillographically using the circuit shown in Fig. 1. The current was measured in terms of the  $iR$  drop across the precision resistor  $R$  in series with the d.e. cell. A Dumont 304-H cathode ray oscilloscope was used. The self-contained vertical d.c. amplifier in this instrument has sufficient sensitivity (30 mv./inch) so that currents of the order of 20 microamp. can be measured accurately without an intermediate amplifier when  $R$  is 2000 ohms or greater. This instrument also has a self-contained very slow horizontal sweep circuit; by connecting external capacitors (16 to 20 microfarads) to the horizontal input terminals the required slow sweep time of the order of 6 to 8 sec. is obtained very simply, and a control on the panel permits the sweep time to be decreased at will to any desired smaller value. By using the slowest sweep time one or more complete current-time curves can be presented on the screen of the oscilloscope, and by using more rapid sweeps details during the very early life of the drop can be observed.

At the slowest sweep times (6 to 8 sec.) the sweep is not strictly linear with time and special means are necessary to precisely define the time axis. This was accomplished by connecting a motor driven Micro switch (Type JV-5.

(9) J. J. Lingane and B. A. Loveridge, *THIS JOURNAL*, **72**, 438 (1950).

(10) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

(11) L. Meites and T. Meites, *THIS JOURNAL*, **72**, 4843 (1950).

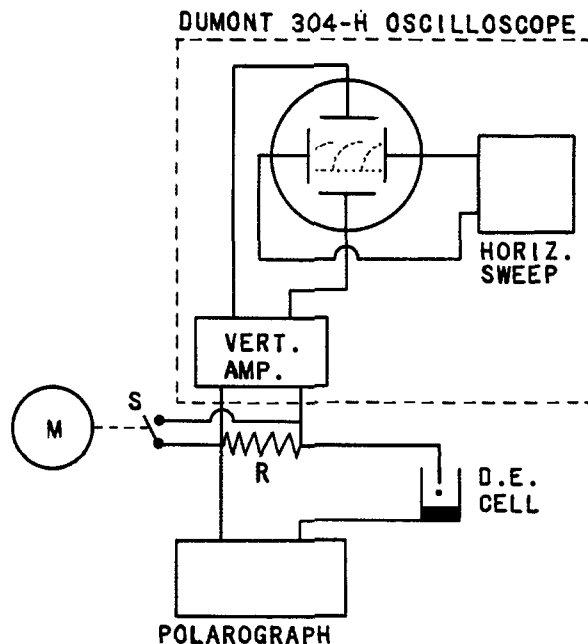


Fig. 1.—Schematic circuit: the components within the dashed block are self contained in the Dumont 304-H oscilloscope.

Micro Switch Division, First Industrial Corp., Freeport, Ill.) across the measuring resistance  $R$  to short out this resistance briefly at precisely spaced time intervals. The switch  $S$  was actuated by a cam (circle with one side partly flattened) driven by a synchronous motor  $M$  at exactly 180 r.p.m. to provide time marks at exact one-third second intervals. The cam was figured so that the switch remained closed for 0.05 sec., during which period the oscilloscope trace was returned to zero. In addition to providing precise time marks, this technique has the important virtue of establishing the zero line at frequent intervals during the drop life and it thus eliminates error due to amplifier zero drift. The simultaneous appearance of the current-time curve and the line of zero marks is also a convenience because only one exposure is needed when the traces are recorded photographically.

The traces were photographed on 35 mm. film using a Dumont type 296 oscillograph still camera (f 2.8 lens stopped down to f 8 and operated on "bulb"), and enlargement prints were made with a high quality enlarger (DeJure, f 4.5 lens stopped down to f 16). The over-all enlargement factor was such that 1 cm. on the oscilloscope face corresponded to 1.87 cm. on the final paper print.

To avoid possible non-linearity near the edges of the oscilloscope face, the horizontal and vertical positioning controls were adjusted so that the traces occupied only the center two inch square on the 5-inch diameter face. The over-all linearity of the vertical amplifier and the photographic process was verified with known currents.

Measurements were made from the final prints. Because of the dimensional variability of processed photo film and paper a standardized processing technique must be used when precise absolute current measurements are desired. The maximal current deflection on the final prints was 50 to 90 mm. and the precision of measurement was at least  $\pm 0.5$  mm.

Even though shielded leads were used there was a small 60 cycle pickup by the amplifier. This was small enough not to be troublesome and it should not cause any error provided measurements are made from the middle of the trace lines.

An ordinary polarograph was used to supply the constant voltage applied to the cell circuit, but a simple voltage-dividing rheostat (low resistance) powered by a dry cell would have served as well. Even though the total applied voltage is kept constant the actual potential of the dropping electrode decreases as the drop grows because of the  $iR$  loss across the measuring resistor. In most of the measurements the maximum current was approximately 20 micro

amperes, so that this variation amounted to 40 mv. when the measuring resistance was 2000 ohms. This causes no appreciable perturbation of the current-time curve provided the total applied voltage is large enough so that the potential of the dropping electrode remains in a range corresponding to the diffusion current plateau. In the following measurements with an ammoniacal cadmium solution the total applied voltage was 1.20 v., *i.e.*, 0.4 v. beyond the half-wave potential of the tetramminocadmium ion *vs.* S.C.E. Identical current-time curves resulted when the measuring resistance was varied from 2000 to 10,000 ohms, corresponding to a variation of the  $iR$  loss from 40 to 200 mv., or a variation of the potential of the dropping electrode from -1.20 to -1.00 v. *vs.* S.C.E. Because of this potential variation this circuit would not be suitable for measuring current-time curves on the rising part of a wave, or at a maximum. Such measurements would require a linear preamplifier of sufficient gain so that the measuring resistance could be decreased to a value small enough to render negligible the  $iR$  loss across it.

Two conventional dropping electrodes constructed from 5 mm. o.d. Corning "marine barometer" tubing were used. The capillary of No. 1 was 6.4 cm. long and its internal diameter was 0.062 mm. The rate of mercury flow (average during drop life) was 1.83 mg. sec.<sup>-1</sup> at  $h = 50.2$  cm., and by varying  $h$  between 78 and 20 cm. drop times from 2 to 9 sec. could be obtained. The capillary of No. 2 was 27.3 cm. long and its internal diameter was 0.056 mm. The rate of mercury flow at  $h = 100$  cm. was 0.793 mg. sec.<sup>-1</sup> The drop time of this capillary at  $h = 100$  cm. was 8.0 sec. and at  $h = 141$  cm. it was 5.6 sec. The characteristics of capillary No. 1 are those normally used. Capillary 2 was designed so that long drop times could be obtained at a relatively very large value of  $h$  to minimize the variation of  $m$  due to the changing back pressure during the growth of the drop.

An H-cell with saturated calomel anode was used for most of the measurements. Measurements were made at ambient room temperature (23 to 25°).

A solution of 3 millimolar cadmium in 0.2 *M* ammonia, 1 *M* ammonium chloride, 0.001% gelatin and 0.1 *M* sodium sulfite, was chosen as a test solution because the diffusion current plateau is excellently developed over a potential range of about 1 v. The ammoniacal supporting electrolyte also permits the use of sulfite ion to remove oxygen, which results in a very small residual current. The polarograph was set at 1.20 v., *i.e.*, 0.4 v. beyond the half-wave potential *vs.* S.C.E. of the tetramminocadmium ion.

To compare the present measuring technique with that of Taylor, Smith and Cooter, some measurements were also made with 3 millimolar cadmium ion in 0.1 *M* potassium chloride containing 0.01% gelatin. Nitrogen was used in these cases to remove dissolved air from the test solution. A silver wire helix wrapped on the d.e. served as anode and the polarograph was set at 0.90 v. (-0.86 v. *vs.* S.C.E.), as in the measurements of Taylor, Smith and Cooter.

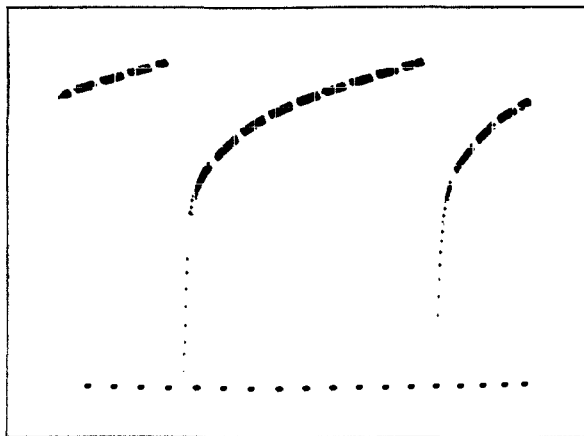


Fig. 2.—Current-time curves with 6 sec. sweep. Ammoniacal solution containing 3 *mM* cadmium. Drop time 3.2 sec. Time marks are at exact one-third second intervals.

## Results and Discussion

Figure 2 is a typical photograph obtained with a slow enough sweep (6 sec.) so that the current-time curve during the late life of one drop (leftmost trace), during the complete life of the succeeding drop (center trace) and the beginning of the next are observed. Figure 3 obtained with a faster sweep (*ca.* 1 sec.) shows in more detail the growth of current during the first half-second of the drop life.

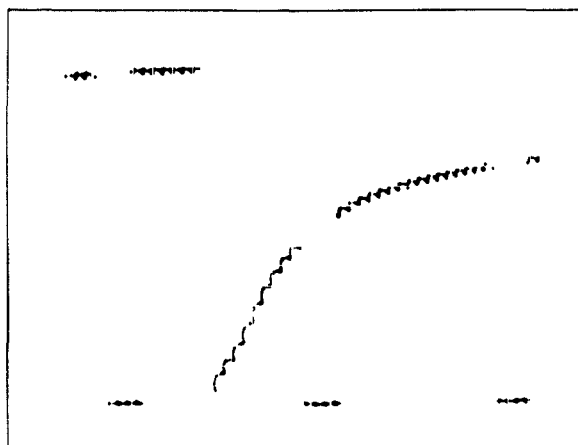


Fig. 3.—Current-time curve during initial stage of drop life. Ammoniacal 3 *mM* cadmium solution. Drop time 3.2 sec. The "wavy" trace is caused by a small pickup of 60 cycle a.c. Time marks define exact one-third second intervals.

Figure 4 is a residual current-time trace obtained with the ammoniacal supporting electrolyte alone and with all other conditions the same as those in Figs. 2 and 3. Immediately after the fall of a drop (between the third and fourth time marks) the current increases abruptly but then rapidly decays. This is characteristic of a charging or "condenser" current,<sup>12</sup> whose magnitude is proportional to the rate of change of electrode area which is maximal at the beginning of drop formation. With 3 millimolar cadmium ion the correction for this charging current was less than 2% after the first 0.05 sec. of a 3 sec. drop.

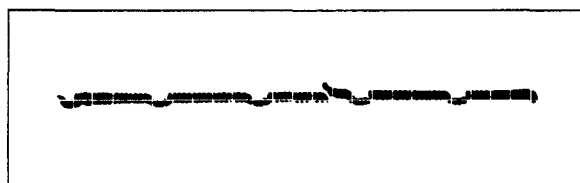


Fig. 4.—Residual current-time trace of ammoniacal supporting electrolyte alone. Drop time 3.2 sec. Time marks at one-third sec. intervals.

Typical data obtained with the two different capillaries at various drop times are shown in Fig. 5 as plots of the quotient  $i_d/t^{1/2}$  versus  $t^{1/2}$ . All of the curves, except 3, were obtained with the ammoniacal supporting electrolyte. Curve 3 obtained with 0.1 *M* potassium chloride as supporting electrolyte corresponds to the conditions employed by

Taylor, Smith and Cooter.<sup>5</sup> Curves 4 and 6 (solid points) were obtained with capillary no. 2 and all others with capillary no. 1. The drop times may be read from the abscissa scale.

If  $m$  were constant during the drop life the original Ilkovic equation predicts that these plots should be horizontal straight lines, whereas from eq. 2 with  $m$  constant

$$i_c/t^{1/2} = \alpha + \beta t^{1/2} \quad (3)$$

and the plots should be straight lines with a small positive slope. The two dashed lines are theoretical lines for curve 2 according to eq. 2, assuming  $m$  constant at its average value and using different values of the diffusion coefficient.

The value of  $D$  for the upper theoretical line was computed from the known diffusion current constant of the tetramminocadmium ion<sup>13</sup> ( $I = 3.68$ ) and the approximate relation  $D = (I/2 \times 607)^2 = 0.92 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>. The lower theoretical line results from using the diffusion coefficient of cadmium ion at infinite dilution ( $0.72 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>). Because neither of these  $D$  values is fully correct and the true value is not known, there is no justification in concluding that the experimental curve 2 agrees better with one line than the other. However, it is evident that during the last three fourths of the drop life the experimental points follow eq. 2 within the range of uncertainty of the  $D$  values.

The shapes of curves 2 to 6 in Fig. 5 conform qualitatively to what one would expect from eq. 2 when the non-constancy of  $m$  is recognized. With both the ammoniacal supporting electrolyte (curve 2) at a drop time of 3.2 sec., and 0.1  $M$  potassium chloride (curve 3) at a drop time of 3.7 sec., the plots do approximate closely to straight lines during the last 75% of the drop life and the slopes agree with the theoretical slope within experimental error. At longer drop times with this capillary (curve 5) the theoretical slope is approached only during about the last third of the drop life.

The relatively rapid increase in current during the infancy of the drop shown by curve 1 (drop time 2.2 sec.) clearly reflects stirring of solution near the drop surface when the drop time is relatively small and consequent disturbance of the diffusion layer. This stirring effect has also been observed by MacDonald and Wetmore.<sup>7</sup> The flat maximum results from the gradual cessation of stirring, and the establishment of diffusion control, as the drop grows. Current enhancement by stirring at small drop times is a familiar phenomenon in measurements by the ordinary technique of the average current,<sup>9,10,14-17</sup> and curve 1 demonstrates that stirring is operative at a considerably longer drop time than had been supposed from measurements of the average current.

An idea of the extent to which the variability of

(13) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 589 (1943).

(14) J. J. Lingane and B. A. Loveridge, *THIS JOURNAL*, **66**, 1425 (1944); **68**, 395 (1946).

(15) F. Brickley and J. K. Taylor, *J. Research Natl. Bur. Standards*, **54**, 97 (1945).

(16) L. Meites and T. Meites, *THIS JOURNAL*, **72**, 3686 (1950); **73**, 395 (1951).

(17) T. A. Krynokova and B. N. Kabanov, *J. Gen. Chem. U.S.S.R.*, **15**, 294 (1945).

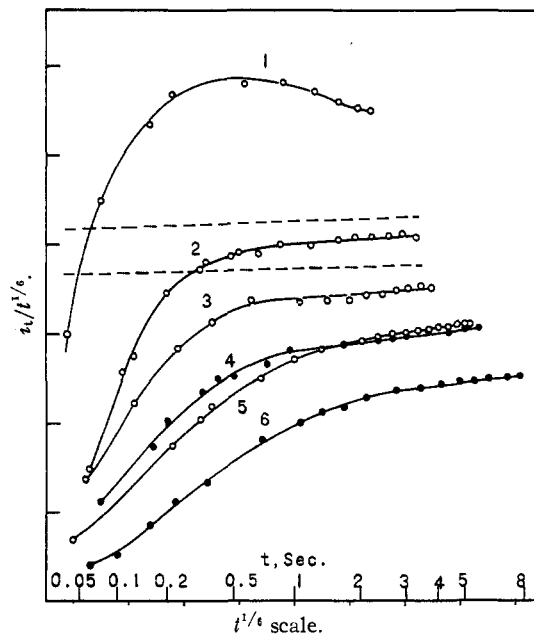


Fig. 5.—Current-time functions at various drop times. Curves 4 and 6 were obtained with capillary No. 2, and all others with capillary no. 1. Curve 3 was obtained with 0.1  $M$  potassium chloride as supporting electrolyte and all others with the ammoniacal supporting electrolyte (see text). In all cases the cadmium concentration was 3  $mM$ . Drop times were 1, 2.2; 2, 3.2; 3, 3.7; 4, 5.6; 5, 5.2; 6, 8.0 sec. The dashed lines are the theoretical lines according to eq. 2 for curve 2 only using two different values of  $D$  (see text).

$m$  is responsible for the abnormally small early current is obtained from the following considerations. The rate of mercury flow is expressible by<sup>18</sup>

$$m = k(h - h_{\text{back}}) \quad (4)$$

where  $h$  is the total pressure in cm. of mercury applied to the dropping electrode and  $h_{\text{back}}$  is the back pressure created by the interfacial tension at the mercury solution interface. The constant  $k$  is a known<sup>18</sup> function of the radius and length of the capillary lumen. The back pressure is given by  $h_{\text{back}} = 2\sigma/r$ , where  $\sigma$  is the interfacial tension, and  $r$  is the radius (cm.) of the capillary lumen when there is no pendant drop and the radius of the drop itself after it has formed. Assuming that  $\sigma = 400$  dyne cm.<sup>-1</sup>, the back pressure in cm. of mercury is  $h_{\text{back}} = 0.060/r$ .

For electrode no. 1 used to obtain curves 1, 2, 3 and 5 the maximal drop radius was 0.047 cm., from which the minimal back pressure just before each drop fell is calculated to be 1.3 cm. Since the radius of the capillary lumen was 0.0031 cm., the back pressure immediately after each drop fell increased abruptly to 19.5 cm. and then diminished as the drop grew. The values of  $h$  required to produce drop times of 2.2, 3.2, 5.2 and 9.2 sec. were, respectively, 79, 50, 33 and 19.9 cm. Dropping ceased at 19.5 cm. Consequently at  $h = 33$  cm. (curve 5 in Fig. 5) the net driving pressure  $h - h_{\text{back}}$  decreased from 32 cm. to 14 cm. immediately after a drop fell and correspondingly  $m$  decreased by a factor of 2.3. Consequently, for curve 5 the

(18) Reference 2, p. 80.

value of  $\alpha$  in eq. 3 is about 40% smaller at the beginning than at the end of the drop and  $\beta$  is about 25% smaller. For curve 4, which was obtained with a drop time (5.6 sec.) nearly the same as curve 5, but with capillary no. 2 at a much larger value of  $h$  (141 cm.), the variations of  $\alpha$  and  $\beta$  are much less because the back pressure (*ca.* 22 cm.) is a much smaller fraction of the total pressure. This is the reason that curve 4 rises more rapidly and approaches linearity sooner in the drop life than curve 5.

The variability of  $m$  has a more profound influence on the current-time relation than merely altering the parameters of eq. 2. Equation 2 is based on the assumption that  $m$  is constant and it is to be expected that a derivation that took account of the variability of  $m$  would result in a relation whose form would differ significantly from eq. 2 during the early life of the drop. Therefore one cannot expect to obtain quantitative reconciliation with the experimental curves simply by inserting instantaneous values of  $m$  into eq. 2.

Superimposed on the variability of  $m$  is the nonsphericity of the very young drop. Immediately following the fall of each drop the electrode surface consists of the mercury in or at the tip of the lumen and it approximates a plane electrode of area equal to the area of the lumen. The surface then bulges out to finally produce a globule. During the time of this transition, which evidently will be greater the smaller the value of  $h - h_{\text{back}}$ , the current grows according to a different function than it would if the electrode were spherical.

The result of these effects is believed to be manifested in Fig. 6, which shows the current-time curve early in the life of a very slowly forming drop (drop time 9.12 sec. at  $h = 19.9$  cm.). The time sequence of the traces is indicated by the numbers on the right side of the figure, and the timing marks are one-third second intervals. In this case the net pressure  $h - h_{\text{back}}$  decreased from approximately 18 cm. to only 0.4 cm. immediately after the fall of the drop. The striking feature is that immediately

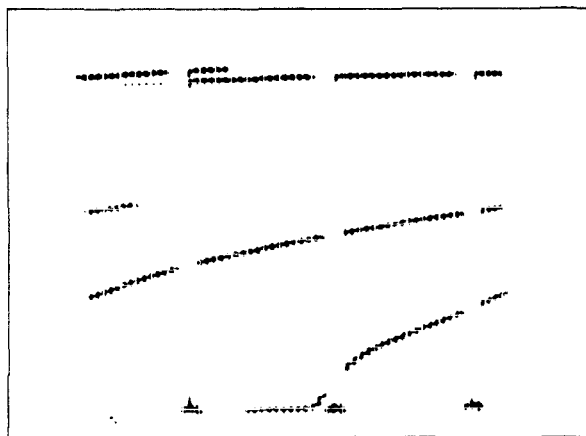


Fig. 6.—Current-time curve during initial life of very slowly forming drop. Drop time 9.2 sec. Ammoniacal solution of 3 mM cadmium. The time sequence of the traces is indicated by the ordinal numbers on the right-hand ordinate, and the timing marks are exact one-third sec. intervals. Trace 2 is the end of the life of one drop and trace 3 the beginning of the next.

after the drop fell the current decreased virtually to zero, and remained at zero for 0.13 sec. before it began to increase (trace 3).

That the initial pause at zero current results from a virtually zero rate of increase of area, rather than any effect of depleted solution or shielding of the mercury surface by the capillary tip, is confirmed by the charging current-time curve of the ammoniacal supporting electrolyte alone shown in Fig. 7. The drop time (9.2 sec.) and other conditions were the same as in Fig. 6, except that the measuring resistor was increased from 4000 to 10,000 ohms. The charging current, which is directly proportional to the rate of increase of the electrode area, decreases to zero immediately after the drop falls, and it displays the same 0.13 sec. pause at zero as the diffusion current. Evidently the electrode area remains constant during this period. The original photograph of Fig. 7 also shows a sudden very brief current increase at the instant preceding the abrupt decrease to zero as the drop falls. This reflects the momentary increase in area as the drop suddenly stretches in the act of disengagement.

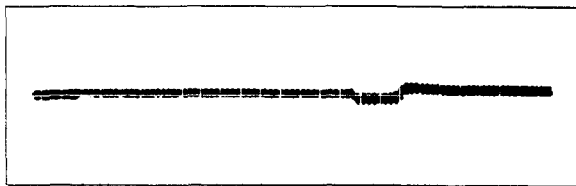


Fig. 7.—Charging current-time curve of ammoniacal supporting electrolyte at drop time of 9.2 sec. The pause at zero current after the drop fell corresponds to 0.13 sec.

It is quite possible, as suggested among others by Müller,<sup>19</sup> that the mercury thread may retract into the capillary after each drop falls. If this does occur, then the pause at zero current shown in Figs. 6 and 7 could correspond to the time required for the constant area surface to return to the tip of the capillary. For this particular capillary at a value of  $h - h_{\text{back}}$  equal to 0.4 cm. the 0.13 sec. pause corresponds to a retraction of about 6 mm., which is quite plausible.

Immediately following the pause at zero, the current at first increases relatively rapidly for about 0.1 sec. but then levels off and finally continues to increase in a normal manner (see trace 3 in Fig. 6). This inflection probably results from the varying geometry of the very young surface. As the surface begins to bulge out it is not spherical, and the rate of increase of area (and hence current) is greater than it would be for a sphere. Apparently at this small value of  $h - h_{\text{back}}$  about 0.2 sec. is required for the drop to become spherical.

In confirmation of this interpretation, curves obtained with capillary no. 2 at a drop time as long as that in Fig. 6, but with a much greater net driving pressure  $h - h_{\text{back}}$ , did not show the pause at zero current and the inflection was scarcely perceptible. From these observations it is clear that  $h - h_{\text{back}}$  is a much more critical factor than the drop time in determining the degree of agreement of observed current-time curves with eq. 2.

(19) O. H. Müller, "The Polarographic Method of Analysis," Chemical Education Publishing Co., Easton, Pa., 1951, p. 41.

Another factor which tends to cause the early current to be smaller than predicted by eq. 2 is the fact that the area of the actual drop is smaller than that of a complete sphere by the area of the capillary lumen. However, this effect is relatively small. The area of the lumen of capillary no. 1 is  $3.0 \times 10^{-5}$  cm.<sup>2</sup>. At a drop time of 3.2 sec., if one assumes that the drop is spherical after the first 0.03 sec. and that  $m$  is equal to its average value, the area of the drop at 0.03 sec. is computed to be  $1.2 \times 10^{-3}$  cm.<sup>2</sup>, or forty times the lumen area. Actually because  $m$  is smaller than the average value, the drop area probably is somewhat smaller than this. Even so it does not seem that the area of the lumen can amount to more than about 5% of the drop area even as early as 0.03 sec. and it rapidly becomes an even smaller fraction as the drop grows, until at the end of the drop life at 3.2 sec. it amounts to only 0.1%.

Laitinen and Kolthoff<sup>20</sup> demonstrated that the

(20) H. A. Laitinen and I. M. Kolthoff, *THIS JOURNAL*, **61**, 3347 (1939).

current observed with a *solid* spherical electrode is larger than corresponds to diffusion control because when the diffusion layer becomes thick the density gradients within it produce convective stirring which disturbs the diffusion gradient. With the dropping electrode, at a normal drop time of about 3 sec., this effect is greatly minimized because the diffusion layer does not have time to grow very thick. However, it is to be expected that at very long drop times it will become significant and cause the slope of the  $i_c/t^{1/2}$  versus  $t^{1/2}$  curve to be larger than predicted by eq. 2 during the late life of the drop. This is probably the reason why the final slopes of curves 4 and 6 in Fig. 5 tend to be somewhat greater than those of curves 2 and 3. This same effect very probably is also the cause of Smith's<sup>21</sup> observation that current-time curves at extremely long drop times (several minutes) correspond approximately to a second order parabola  $i_c = kt^{1/2}$ .

(21) G. S. Smith, *Nature*, **163**, 290 (1949).

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## Studies in Low Concentration Chemistry. III. The Radiocolloidal Properties of Yttrium-90

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Yttrium-90, the daughter of strontium-90 has been removed in the carrier-free form from its parent by utilization of the radiocolloidal properties of yttrium in low concentration solutions. Using solutions of yttrium-90, the effects of coagulation time, pH, the presence of various electrolytes and the presence of non-aqueous solvents upon the ease of removal of yttrium-90 from its solutions by filtration have been investigated. Also the ability of the radiocolloids to reform after an initial removal, as well as the efficiencies of various grades of filter paper in removal of the activity, has been studied. The results are in agreement with previous observations on this and other elements.

### Introduction

This paper constitutes the third<sup>1</sup> in a series of articles dealing with the radiocolloidal properties of low concentration radionuclides in solution.

Kurbatov<sup>2</sup> and Kurbatov<sup>2</sup> used yttrium-86 in solution as a means of investigating the radiocolloidal properties of this element. Employing filtration as a separation method, they determined the effects of pH, ammonium chloride concentration and yttrium concentration on the percentage yttrium that could be filtered from the solution. As the pH of an approximately  $10^{-11}$  g./l. solution of yttrium was increased, the percentage filterable increased. Experiments with higher concentrations of yttrium indicated a similar behavior. At a pH of 7.0, the percentage yttrium filtered from a solution in the concentration range  $3 \times 10^{-2}$  to  $10^{-5}$  g./l. coincides with the percentage yttrium removed from very low concentration solutions. As the concentration of ammonium chloride is increased in both 0.159 mg./l. and  $10^{-11}$  g./l. yttrium solutions, the percentage yttrium filtered decreases.

This investigation is a continuation of work on

yttrium to determine other factors which influence the formation and properties of the radiocolloidal aggregates.

### Experimental

**Materials.**—All inactive chemicals employed were of analytical reagent grade. Only triply distilled water which was preserved in carbon dioxide-free air was used.

**Measurement of Radioactivity.**—All radioactivities were measured with a Nuclear Model 163 Scaler connected to a Nuclear Neher-Pickering quenching unit and a Nuclear D-34 mica end-window Geiger tube. This tube was mounted in a Tracerlab SC-9 manual sample changer. All radioactivities were counted for times long enough to give a maximum standard deviation of 1%.

**Separation of Yttrium-90.**—Two millicuries of an equilibrium mixture of strontium-yttrium-90 as the chlorides in acid solution was obtained from the Oak Ridge National Laboratory. The yttrium-90 is the short-lived daughter (half-life 61 hr.)<sup>3</sup> of strontium-90, a  $\beta$ -emitter with a half-life of 19.9 yr. The yttrium-90 is a  $\beta$ -emitter of 2.18 mev. energy decaying to stable zirconium-90. Since no yttrium was added in the separation process, the yttrium-90 was assumed to be present in carrier-free form.

To the approximately 0.5 ml. of radioactive solution obtained from Oak Ridge, there were added 25 ml. of water and 5 ml. of concentrated hydrochloric acid. Five ml. of this resulting solution was taken, adjusted to a pH of 13.0 with concentrated carbon dioxide-free sodium hydroxide solution and filtered slowly through a very fine glass frit.

(1) G. K. Schweitzer and W. M. Jackson, *THIS JOURNAL*, **74**, 4178 (1952); G. K. Schweitzer and J. W. Nehls, *ibid.*, **74**, 6186 (1953).

(2) J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942).

(3) W. Meyerhoff, *Phys. Rev.*, **74**, 621 (1948); R. I. Powers and A. P. Voigt, *ibid.*, **79**, 175 (1950).