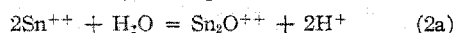


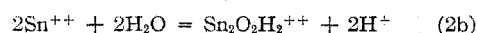
In the range of concentration up to an ionic strength of 0.2 the sodium ion and perchlorate ion activity coefficients are no doubt equal to within two or three per cent. Therefore the activity coefficients of hydrogen ion were computed and used in conjunction with the hydrogen ion activities in solutions of this investigation up to an ionic strength of 0.2 in the calculation of the concentrations of total hydrogen ion. With the aid of these latter values corrected concentrations of  $\text{SnOH}^+$  and stannous ion were calculated. Using these figures new equilibrium quotients were calculated according to equation 1 and their logarithms plotted against  $\mu^{1/2}$  as in Fig. 1, Curve II. The extrapolation to zero ionic strength was accomplished by the method of Randall and Vietti,<sup>5</sup> and the value of the equilibrium constant,  $K_1^0$ , is estimated to be 0.02.

According to Prytz<sup>1</sup> the hydrolysis of stannous ion is represented by the equation



(5) (a) Randall and Vietti, *THIS JOURNAL*, **50**, 1526 (1928); (b) Randall, *J. Chem. Ed.*, **8**, 1062 (1931); (c) see also Bray and Hershey, *THIS JOURNAL*, **56**, 1889 (1934).

or



The analytical data of Table I were used to calculate the composition of each stannous perchlorate solution and the equilibrium quotients based on equation 2. The logarithms of these equilibrium quotients when plotted against  $\mu^{1/2}$  give a U-shaped curve which does not permit extrapolation to zero ionic strength according to the limiting law of Debye and Hückel. Since Randall and Vietti have shown that in such a plot the curve will resemble one of the family of logarithm of activity coefficient *vs.*  $\mu^{1/2}$  for single electrolytes, it is obvious that equation 1, and not equation 2, represents the hydrolysis of stannous ion.

### Summary

Solutions of stannous perchlorate containing free perchloric acid have been analyzed. The variation of the equilibrium quotient,  $K_1$ , with ionic strength proves that the hydrolysis follows the equation  $\text{Sn}^{++} + \text{H}_2\text{O} = \text{SnOH}^+ + \text{H}^+$ . The value of the equilibrium constant,  $K_1^0$ , at 25° is 0.02.

SAN FRANCISCO, CALIF. RECEIVED SEPTEMBER 25, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

## A Study of Diffusion Processes by Electrolysis with Microelectrodes<sup>1</sup>

BY H. A. LAITINEN AND I. M. KOLTHOFF

### Introduction

The diffusion of an electro oxidizable or reducible substance in solution can be studied by measuring the current obtained using suitable electrodes in an electrolysis cell if the supply of electro reducible or oxidizable material is determined only by the rate of diffusion of the material to one of the electrodes, and if well-defined boundary conditions of concentration can be maintained at the electrode surface. The latter condition is fulfilled if the concentration of diffusing material is maintained at a value of practically zero at the electrode surface by maintaining a potential at the electrode such that the diffusing material is immediately oxidized or reduced upon reaching the electrode surface.

The theory of the diffusion process in the vicinity of an electrode depends upon the geometric

characteristics of the electrode and surrounding solution. Two extreme geometric cases are represented by a flat electrode, to which diffusion can occur from only one direction (linear diffusion), and a spherical electrode, to which diffusion can occur from all directions (spherically symmetrical diffusion). The equations for the current as a function of time, for linear and spherically symmetrical diffusion, are given below, as well as experimental results on the determination of current-time curves with microelectrodes of various types to determine the conditions under which theoretical diffusion conditions in electrolysis can be fulfilled.

The theoretical relation between current and time for linear diffusion has been derived by Cottrell<sup>2</sup> and MacGillavry and Rideal<sup>3</sup> and is

$$i = -A \sqrt{\frac{D}{\pi t}} nFC \quad (1)$$

(1) This paper is based on a thesis to be submitted by H. A. Laitinen to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1940.

(2) F. G. Cottrell, *Z. physik. Chem.*, **42**, 385 (1902).

(3) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

where  $A$  is the area of the electrode,  $D$  and  $C$  are the diffusion coefficient and concentration of the diffusing material in the bulk of the solution, respectively,  $n$  is the number of electrons involved in the electrode reaction, and  $F$  is the faraday.

It is seen that in a given case,  $i\sqrt{t}$  is a constant, and that the value of this constant can be calculated if the concentration  $C$ , and the diffusion coefficient of the electroactive substance, and the area of the electrode are known.

The corresponding theoretical current-time equation for spherical diffusion is<sup>2</sup>

$$i = -4\pi RnFDC - A\sqrt{\frac{D}{\pi t}}nFC \quad (2)$$

where  $R$  is the radius of the spherical electrode. By comparing equations (1) and (2) it is apparent that for spherical and linear diffusion to electrodes of equal area, the theoretical currents at any time differ by a constant amount, namely, the steady state current with spherical diffusion given by the first term of equation (2).

### Experimental

Platinum microelectrodes of various shapes as shown in Fig. 1 were constructed. The various flat electrodes, types A, C, D, F and G, were of very nearly equal area. Electrodes A, C and D permit only linear diffusion in horizontal, upward and downward directions, respectively, while electrodes B, E, F and G approach spherical diffusion to varying degrees of approximation. The linear diffusion electrodes were specially constructed to be as uniform as possible in cross-section by finely grinding the ends of two pieces of glass tubing and cementing a platinum plate between the two pieces of tubing with de Khotinsky cement using a larger piece of glass tubing as a mold. The details of construction are shown in Fig. 1, H. Electrode E most closely approached spherical diffusion, and consisted of a spherical ball of platinum of approximately the same area as the flat electrodes, on the end of a fine platinum wire coated with sealing wax, so that only the spherical surface acted as an electrode. Electrode B consisted of a platinum wire about 4 mm. in length and 0.5 mm. in diameter.

In general, the experiments were run by applying a constant potential to the microelectrode, this potential corresponding to a point near the middle of the diffusion current region of the electrolysis process as determined from a current-voltage curve obtained with the platinum wire microelectrode (type B, Fig. 1). At such a potential, the diffusing material undergoes an immediate electrode reaction upon reaching the electrode, so that its concentration is maintained at a value practically equal to zero at the electrode surface. A large silver-silver chloride electrode in 0.1  $N$  potassium chloride was used as the second electrode. The electrolysis cell was of the type previously described,<sup>4</sup> employing a sintered glass diaphragm to sepa-

rate the two electrodes. Hereafter, all potentials of the platinum micro-electrodes are referred to the 0.1  $N$  silver-silver chloride electrode.

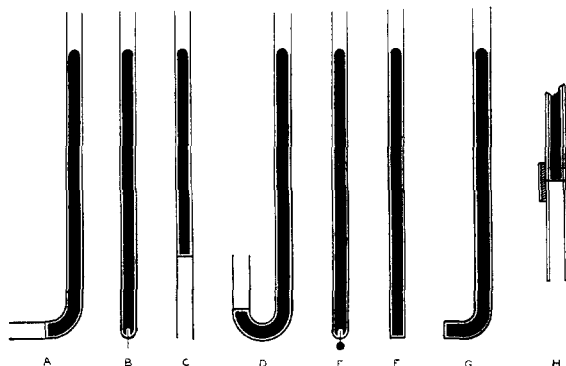


Fig. 1.—Various shapes of platinum electrodes.

The current was measured at various time intervals after beginning electrolysis by noting the deflection of a calibrated wall-type galvanometer in series with the electrolysis cell, and provided with a suitable shunt arrangement to change the galvanometer sensitivity during each run. The electrical circuit was the same as that described by Lingane and Kolthoff<sup>5</sup> except that the standard 10,000-ohm resistance used to calibrate the galvanometer was not left in series with the galvanometer and cell during the experiments, in order that the changing  $iR$  drop across this resistance during the experiments would not change the applied e. m. f. across the terminals of the cell. The small change in  $iR$  across the galvanometer itself, resulting in a slight shift of the potential of the micro electrode during an experiment, did not affect the current measurement since the same current was obtained over a range of potentials corresponding to the diffusion current region of the electrolysis process.

In the case of electroreductions, dissolved air was removed by bubbling nitrogen through the solution for about thirty minutes. In the case of electro-oxidations, it was found to be unnecessary to remove the dissolved oxygen because no reduction of oxygen occurred at the positive potential used.

The residual current in the absence of electroactive material was determined separately for each value of the time and was subtracted from the measured current. The current thus corrected was used in the calculation of  $i\sqrt{t}$ .

All measurements were made with the electrolysis cell in a water thermostat regulated to  $\pm 0.02^\circ$ , with the stirrer mounted on wall brackets so that mechanical vibrations were eliminated.

**The Oxidation of Ferrocyanide Ions.**—A solution  $1.00 \times 10^{-3} M$  in potassium ferrocyanide and 0.1  $N$  in potassium chloride was electrolyzed at  $25^\circ$ , applying a constant potential of +0.700 volt, and measuring the current at various times after beginning electrolysis. The current-time curves obtained with electrodes A, B, C, E, F and G (Fig. 1) are shown plotted in Fig. 2, together

(4) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(5) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939).

with the theoretical curves for linear and spherical diffusion calculated from equations (1) and (2). The areas of the various flat electrodes were all equal to 0.0707 sq. cm. The diffusion coefficient  $D$  was calculated using the equation given by Lingane and Kolthoff,<sup>5</sup> and found to be equal to  $0.74 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>. Introducing the values of  $D$  and  $C$  in equations (1) and (2) yields the theoretical equations

$$i\sqrt{t} = 10.4 \text{ (linear diffusion)} \quad (3)$$

$$i = 0.674 + 10.4t^{-1/2} \text{ (spherical diffusion)} \quad (4)$$

where the current is expressed in microamperes and the time in seconds.

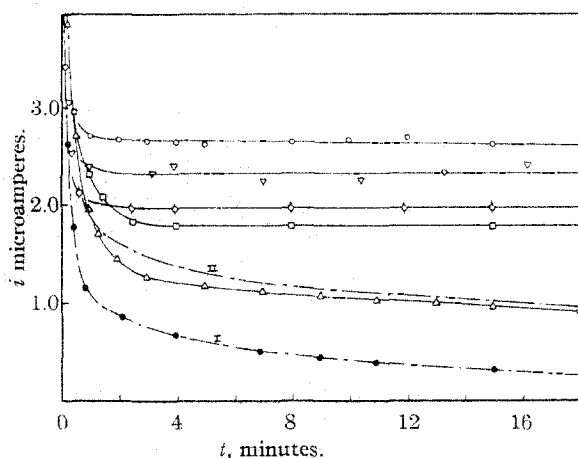


Fig. 2.—Current-time curves for electrolysis of 0.001  $M$   $K_4Fe(CN)_6$  in 0.1  $N$   $KCl$  with various shapes of platinum microelectrodes: ●, electrode C; △, electrode A; □, electrode F; ○, electrode B; ▽, electrode E; ○, electrode G. Dashed curves: theoretical curves for (I) linear diffusion, (II) spherically symmetrical diffusion.

From Fig. 2 it is evident that the theoretical results are obtained in this case only when the diffusion is linear and in an upward direction. With downward linear diffusion (electrode D) abnormally large currents were obtained which did not give a smooth current-time curve and were therefore not included in Fig. 2. After six to seven minutes, the current was about twice as large as calculated from equation (4), and after this length of time the current fluctuated irregularly, even increasing periodically.

Curve I, Fig. 2, which yielded results in close agreement with theory, was repeated several times using larger concentrations of potassium ferrocyanide so that better accuracy in current readings could be obtained. A typical set of data is given in Table I for the oxidation of  $4.88 \times 10^{-3}$   $M$  potassium ferrocyanide in 0.1  $N$  potas-

TABLE I  
VARIATION OF CURRENT WITH TIME IN THE ELECTROLYSIS OF 0.00488  $M$  POTASSIUM FERROCYANIDE IN 0.1  $N$  POTASSIUM CHLORIDE

Solution saturated with air;  $E_P = +0.700$  volt vs. 0.1  $N$   $AgCl$ ; temp., 25°; area of electrode, 0.1016 sq. cm.

$t$ , sec.	$i$ , $\mu$ amp.	$i$ (corr.), $\mu$ amp.	$i\sqrt{t}$ , $\mu$ amp. sec. <sup>1/2</sup>	$t$ , sec.	$i$ , $\mu$ amp.	$i$ (corr.), $\mu$ amp.	$i\sqrt{t}$ , $\mu$ amp. sec. <sup>1/2</sup>
110	6.90	6.85	71.8	540	3.125	3.107	72.2
120	6.62	6.57	71.9	600	2.975	2.958	72.4
150	5.92	5.88	71.7	630	2.895	2.878	72.7
180	5.41	5.37	72.1	660	2.830	2.814	72.3
210	5.02	4.99	72.3	720	2.715	2.099	72.4
240	4.70	4.67	72.3	780	2.605	2.590	72.3
270	4.40	4.37	71.8	840	2.515	2.500	72.5
300	4.19	4.16	72.1	900	2.433	2.419	72.6
330	4.00	3.98	72.3	960	2.355	2.342	72.6
360	3.82	3.80	72.1	1020	2.285	2.272	72.6
390	3.685	3.663	72.3	1080	2.215	2.203	72.4
420	3.540	3.519	72.1	1140	2.160	2.148	72.5
480	3.325	3.306	72.4	1200	2.102	2.091	72.4

sium chloride. The electrode area in this case was 0.1016 sq. cm., and the theoretical equation was  $i\sqrt{t} = 73.4$  microamp. sec.<sup>1/2</sup>. The average value of  $i\sqrt{t}$  from the 26 points in Table I is 72.3 microamp. sec.<sup>1/2</sup>, in excellent agreement with the theoretical value. Duplicate experiments gave results deviating only  $\pm 0.5$  to  $\pm 1.0\%$  in the value of  $i\sqrt{t}$ .

The reason for the deviating results obtained if the diffusion did not proceed in an upward direction becomes apparent when the relative densities of 0.001  $M$  potassium ferrocyanide (the diffusing material) and 0.001  $M$  potassium ferricyanide (the oxidation product near the electrode surface) are considered. Although the difference in density is only of the order of one unit in the fifth decimal place, 0.001  $M$  potassium ferricyanide is less dense than 0.001  $M$  potassium ferrocyanide.<sup>6</sup> Unless the direction of diffusion is such that the less dense solution (either the diffusing material or the electrode reaction product) lies above the denser solution, convection currents due to density gradients cause a greater supply of diffusing material to reach the electrode than by diffusion alone, and consequently the measured current is abnormally large.

A simple experimental check of this explanation was made as follows: a solution of 0.001  $M$  potassium ferrocyanide in 0.1  $M$  potassium chloride and 1% in cane sugar was prepared, thus a solution of the same electrolyte concentrations as the original ferrocyanide solution but somewhat more dense due to the presence of the sugar. A thin layer (1 or 2 mm.) of this solution was carefully placed near the platinum surface of elec-

(6) A. Heydweiller, *Z. anorg. allgem. Chem.*, **116**, 42 (1921).

trode D under the original solution by means of a capillary pipet and allowed to diffuse upward for about an hour, so that a sufficient downward density gradient should exist near the electrode surface to overcome any small density gradient in the opposite direction due to the electrode reaction. A current-time curve was then run and found to be identical with the curve obtained previously using electrode C (upward diffusion). This experiment gave conclusive proof that density gradients in the downward direction are necessary to stabilize concentration gradients and lead to theoretical diffusion conditions.

It is therefore to be expected that the theoretical current-time curve for spherical diffusion could never be obtained in aqueous solution, since, in general, spherically symmetrical concentration gradients result in spherically symmetrical density gradients, and convection currents around the electrode inevitably result. From Fig. 2 it is apparent that with various shapes of platinum electrodes approaching spherically symmetrical diffusion conditions, the current tends to approach a "steady state" value, *i. e.*, becomes practically constant after a few minutes. The steady state current, however, is a function not only of the electrode area, but also of the shape of the electrode, and in the case of the flat electrodes depends also on the position of the electrode with regard to the solution. Thus with two flat plates of platinum sealed on the ends of pieces of glass tubing (electrodes G and G'), but arranged vertically and horizontally, respectively, a smaller steady state current was obtained with the surface of the electrode horizontal than with a vertical surface, because the horizontal surface acted to stabilize to a certain extent the concentration gradient of ferrocyanide ions.

In general, the steady state current was found to be least subject to irregular periodic fluctuations in the case of the platinum wire electrode (type B) than in any other case investigated including flat surfaces in various orientations and a spherical platinum surface. Apparently the most uniform and reproducible state of convection is obtained with the platinum wire electrode. Since the current reaches a steady value after two to four minutes and remains very nearly constant for relatively long intervals of time, this electrode has been used by us for determining current-voltage curves similar to those obtained with the dropping mercury electrode.

**The Diffusion of Ferrocyanide Ions in Gelatin and Agar Gels.**—In order to check the theoretical current-time equation for spherically symmetrical diffusion, experiments were performed by allowing the diffusion process to occur in a stiff gel surrounding the electrode, instead of in less viscous aqueous media in which disturbing convection currents occurred.

The absence of convection currents due to density gradients in the vicinity of the electrode was shown by electrolyzing 0.0200 *M* potassium ferrocyanide in 0.5 *N* potassium chloride in a 3% agar gel and in a 4% gelatin gel using electrodes C and D, in which linear diffusion occurred in upward and downward directions, respectively. Identical current-time curves were obtained with the two electrodes, in contrast to the results obtained in aqueous medium.

From the values of  $i\sqrt{t}$  thus obtained, which remained constant to  $\pm 0.5\%$  for a period of twenty minutes, the diffusion coefficient of the ferrocyanide ion was calculated to be  $0.65 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup> for the 3% agar gel and  $0.61 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup> for the 4% gelatin gel, as compared with the value  $0.74 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup> for an aqueous solution at infinite dilution.

The theoretical current-time curve for spherical diffusion to electrode E for the electrolysis of 0.0200 *M* potassium ferrocyanide in 0.5 *N* potassium chloride in a 3% agar gel becomes

$$i = 15.45 + 322 t^{-1/2} \text{ microamperes} \quad (5)$$

when  $t$  is expressed in seconds.

Equation (5) and the experimental curve obtained with electrode E in the 3% agar gel are shown plotted in Fig. 3.

It is evident from Fig. 3 that the theoretical and experimental curves are almost identical in shape from a period of five minutes to 110 minutes, although the experimental points in general lie about 5 to 7% below the corresponding theoretical points. The gelatin gel showed a similar behavior, both curves being lower than for the agar gel because of the lower diffusion coefficient in the gelatin gel.

The low observed current and the increasing percentage deviation with time may be explained by the fact that a truly spherical diffusion field does not exist, due to the presence of the coated platinum wire and glass tube above the spherical electrode. The theoretical diffusion layer extends a distance of several millimeters from the electrode surface after a time of two hours, so that a hindering effect becomes quite possible.

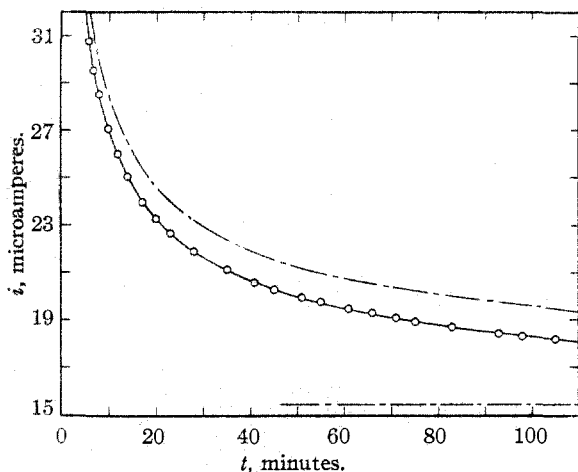


Fig. 3.—Current-time curves for electrolysis of 0.0200  $M$   $K_4Fe(CN)_6$  in 0.5  $N$   $KCl$  in 3% agar gel. Spherical platinum electrode,  $R = 0.0950$  cm. Full curve, experimental; dashed curve, theoretical; lower dashed line, theoretical steady state current.

**The Reduction of Ferricyanide Ions.**—An air-free solution of  $5.01 \times 10^{-3} M$  potassium ferricyanide in 0.1  $N$  potassium chloride was electrolyzed at  $25^\circ$  using electrodes C and D by applying a constant potential of  $-0.50$  volt and determining the current-time curves.

A constant value of  $i\sqrt{t}$  was obtained with electrode D (downward diffusion). The experimental value of  $i\sqrt{t}$  is compared with the calculated value in Table II.

With electrode C (upward diffusion) abnormally large currents were obtained and irregular fluctuations occurred after about eight minutes of electrolysis.

It is evident that exactly the opposite results (with respect to direction of diffusion) were obtained with the reduction of ferricyanide ions as compared with the oxidation of ferrocyanide ions. Since the electrode reaction is opposite in the two cases, opposite changes in density near the electrode occur, and the results obtained are exactly those predicted on the basis of the direction of the density gradients.

TABLE II

ELECTROLYSIS OF  $K_4Fe(CN)_6$ ,  $K_3Fe(CN)_6$  AND  $AgNO_3$  IN EXCESS OF INDIFFERENT ELECTROLYTE

Area of electrode 0.1016  $cm.^2$ , temp. =  $25^\circ$ .

Ion	Concn. mmol./liter	$D^0$ $cm.^2$ $sec.^{-1}$ $\times 10^{-5}$	$i\sqrt{t}$ microamp. $sec.^{1/2}$		Diff., %
			Calcd.	Obsd.	
$Fe(CN)_6^{--}$	4.88	0.74	73.4	72.3	-1.5
$Fe(CN)_6^m$	5.01	.89	82.8	80.4	-2.9
$Ag^+$	5.00	1.69	113.7	115.4	+1.5

**The Deposition of Silver Ions.**—Current-time curves were obtained using electrode C in an air-free solution of  $5.00 \times 10^{-3} M$  silver nitrate in 0.1  $N$  potassium nitrate at  $25^\circ$ , with an applied potential of  $-0.10$  volt on the microelectrode. The average value of  $i\sqrt{t}$  obtained in several such experiments is compared with the calculated value in Table II.

**The Temperature Coefficient of the Quantity  $i\sqrt{t}$ .**—For a given linear diffusion electrode and solution, equation (1) may be written in terms of ionic equivalent conductance and temperature<sup>4</sup> to give

$$i\sqrt{t} = k(\lambda^0 T)^{1/2} \quad (6)$$

where  $T$  is the absolute temperature. Differentiating equation (6) with respect to the temperature, we have

$$\frac{d(i\sqrt{t})}{dT} = \frac{k}{2} (\lambda^0 T)^{-1/2} \left( \lambda^0 + T \frac{d\lambda^0}{dT} \right) \quad (7)$$

Equation (7) may be expressed in terms of the fractional changes of  $i\sqrt{t}$  and  $\lambda^0$  per degree by dividing by the value of  $i\sqrt{t}$  at the temperature  $T$ , as given by equation (6). The temperature coefficient of  $i\sqrt{t}$  becomes

$$\frac{1}{i\sqrt{t}} \frac{d(i\sqrt{t})}{dT} = \frac{1}{2} \left( \frac{1}{T} + \frac{1}{\lambda^0} \frac{d\lambda^0}{dT} \right) \quad (8)$$

The values of  $i\sqrt{t}$  have been measured for temperatures of  $25$  to  $35^\circ$  for the ferrocyanide, ferricyanide and silver ions. The measured values of the temperature coefficient and the values calculated from equation (8) are given in Table III.

TABLE III

TEMPERATURE COEFFICIENT OF THE QUANTITY  $i\sqrt{t}$  IN LINEAR DIFFUSION

Ion	$\frac{1}{\lambda^0} \frac{d\lambda^0}{dT}$ deg. <sup>-1</sup>	$\frac{1}{i\sqrt{t}} \frac{d(i\sqrt{t})}{dT}$ deg. <sup>-1</sup>	
		Calcd.	Obsd.
$Fe(CN)_6^{--}$	0.0195	0.0114	0.0101
$Fe(CN)_6^m$	.0185	.0109	.0118
$Ag^+$	.0200	.0116	.0116

The calculated and measured values are average temperature coefficients over the temperature range  $25$  to  $35^\circ$ , expressed in terms of the fraction of the  $30^\circ$  value of  $i\sqrt{t}$  and  $\lambda^0$ . For the silver and ferrocyanide ions, the conductance data of Johnston<sup>7</sup> and Swift<sup>8</sup> were used; for the ferricyanide ion the value of  $\lambda^0$  of Hartley and Donaldson<sup>9</sup> was used, and the temperature coefficient

(7) J. Johnston, *THIS JOURNAL*, **31**, 1010 (1909).

(8) E. Swift, Jr., *ibid.*, **60**, 728 (1938).

(9) G. S. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, **33** 457 (1937).

of  $\lambda$  was calculated from the data of Watkins and Jones<sup>10</sup> on the equivalent conductance of potassium ferricyanide at various temperatures, and the values given by Johnston<sup>7</sup> for the equivalent ionic conductance of the potassium ion at various temperatures.

### Discussion

Cottrell<sup>2</sup> has shown in a linear diffusion experiment on zinc sulfate that the quantity  $i\sqrt{t}$  remained constant to  $\pm 5\%$  for a period of over two days, but made no theoretical calculation of the value of the constant obtained.

It is evident from the data given in Table I that in our experiments the extreme limits of fluctuation in  $i\sqrt{t}$  were only  $\pm 0.5\%$  from the average value, in 26 readings over a period of twenty minutes. In other experiments a constancy was obtained over a period of several hours, but in general a slight drift toward higher values with very long periods of time was observed, due to unavoidable vibrations.

The data given in Table II show that the observed values for the quantity  $i\sqrt{t}$  show a deviation from those calculated from the equivalent ionic conductances at infinite dilution of  $-1.5$ ,  $-2.9$  and  $+1.5\%$  for the ferrocyanide, ferricyanide, and silver ions, respectively. These data

(10) C. Watkins and H. C. Jones, *THIS JOURNAL*, **37**, 2626 (1915).

are in essential agreement with those of Lingane and Kolthoff<sup>6</sup> on diffusion currents with the dropping mercury electrode.

The observed values of the temperature coefficient of  $i\sqrt{t}$  are in good agreement with the calculated values over the same temperature range, as is evident from the data given in Table III. The agreement is probably within the experimental error, since the measurements were made only over a temperature range of ten degrees.

### Summary

1. Current-time curves with various shapes of electrodes and diffusion fields in the electro-oxidation of ferrocyanide ions were determined, and the condition under which theoretical diffusion conditions can be obtained are discussed. Theoretical conditions were not obtained with spherically symmetrical diffusion in aqueous solution, but were approached in 3% agar and in 4% gelatin gels.

2. With linear diffusion in such a direction as to produce a density gradient in the downward direction, the quantity of  $i\sqrt{t}$  was found to be constant to  $\pm 0.5\%$  over a period of twenty minutes.

3. The temperature coefficient of the quantity  $i\sqrt{t}$  was found to be in agreement with the calculated value.

MINNEAPOLIS, MINN.

RECEIVED AUGUST 22, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

## The Specific Heat of Some Ethylene Halides<sup>1</sup>

BY WILFORD E. RAILING<sup>2</sup>

The problem whether there is free or restricted rotation about the carbon-carbon bond in ethane and its derivatives has led to considerable research upon the 1,2-disubstituted ethanes. Of these, the chloro and bromo derivatives have received the greatest attention. Time-temperature heating curves made by White and Morgan<sup>3</sup> revealed a transition or hump in the specific heat curve in 1,2-dibromoethane at  $-23^\circ$ . Since the dielectric constant is only minutely affected by the transition, it is likely that the change of state does not affect the polarity of the molecule. Since these

(1) Part of a dissertation presented to the Faculty of Philosophy of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Master of Arts.

(2) Present address: E. I. du Pont de Nemours and Co., Box 389, Wilmington, Del.

(3) White and Morgan, *J. Chem. Phys.*, **6**, 655 (1937).

transitions are most effectively studied by means of heat capacity measurements, the heat capacities of 1,2-dibromoethane (ethylene bromide), 1,2-dichloroethane (ethylene chloride), and 1,2-bromochloroethane (ethylene chlorobromide) have been determined in the range  $90$ – $320^\circ\text{K}$ .

### Apparatus and Procedure

The calorimeter employed was the same calibrated conduction calorimeter and the procedure was the same as employed by Stull.<sup>4</sup>

### Materials

**Benzene.**—J. T. Baker c. p. thiophene-free material was distilled through a five-foot (1.5 m.) column packed with glass helices similar to those described by Young and Jasaitis.<sup>5</sup> The middle fraction was then fractionally

(4) Stull, *THIS JOURNAL*, **59**, 2729 (1937).

(5) Young and Jasaitis, *ibid.*, **58**, 377 (1936).