

missible only when an error that may amount to as much as 2 or 3% is tolerable.

Summary

The diffusion current constant $i_d/(Cm^{3/2}t^{1/2})$ of lead ion in 1 *N* potassium chloride was determined over a range of $m^{3/2}t^{1/2}$ values from about 1 to 6 mg.^{3/2} sec.^{-1/2}. The ratio $i_d/(Cm^{3/2}t^{1/2})$ decreased by about 3.0 per cent. per unit increases in $m^{3/2}t^{1/2}$ between 1 and about 3.2 mg.^{3/2} sec.^{-1/2}, but with larger values of $m^{3/2}t^{1/2}$ the ratio $i_d/(Cm^{3/2}t^{1/2})$ increased rapidly.

Diffusion currents measured from the potential drop across a standard resistance agreed within about 0.5%, on the average, with value obtained by direct measurement with calibrated galvanometers.

Identical results were obtained with hand drawn capillaries and with those made from commercial capillary tubing.

The observed value of the diffusion current (average of the galvanometer oscillations) was independent of the relative galvanometer period when the ratio of half-period to drop time was varied from 1 to 4.

An equation relating the residual current to capillary characteristics has been presented and shown to be in harmony with experimental residual current data.

Experimental data obtained with several different capillaries demonstrate that the rate of mercury flow from the dropping electrode, with all other conditions constant, is smaller in 1 *N* potassium chloride solution than in air; the difference is inversely proportional to the pressure on the dropping electrode, and, depending on the characteristics of the capillary, it varies from about 0.5 to 3.6%.

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 3, 1944

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Polarographic Behavior of Alkaline Earth Metals. I. Barium and Strontium

BY I. ZLOTOWSKI^{1a} AND I. M. KOLTHOFF

Few polarographic studies on alkaline earth metals have been made. Heyrovsky and Berezičky^{1b} found that both barium and strontium produce well-defined waves in 0.1 *N* lithium chloride with half-wave potentials of about -1.9 volts and -2.1 volts, respectively (*vs.* S. C. E. = saturated calomel electrode). They found that the diffusion currents were no longer proportional to the concentration of barium ions when the latter was less than 5×10^{-4} molar. The observed discrepancy probably is due² to the fact that the authors failed to correct the measured diffusion currents for the residual current of the supporting electrolyte. With properly corrected values we found a satisfactory proportionality at dilutions far beyond the above limit. Furthermore, because of its more positive half-wave potential, barium could be determined in the presence of large amounts of strontium. However, when dealing with mixtures of both cations containing a large excess of barium, the determination of strontium became inaccurate.

Experiments conducted by Kimura³ indicated that calcium produces a wave at about -2.2 v. (*vs.* S. C. E.) in the presence of tetraethylammonium salts as supporting electrolytes. However in view of the fact that the waves displayed very pronounced maxima, which could not be eliminated and which were suppressed with difficulty

by the usual maximum suppressors, they were not suitable for analytical purposes. No suitable procedure is available for the polarographic determination of calcium.

In the present study we have determined the polarographic behavior of barium and strontium separately and in mixtures. In a subsequent paper the polarography of calcium alone and in mixtures with barium and strontium will be presented.

Experimental

The current-voltage curves were measured with a manual apparatus described elsewhere.⁴ Although this method is not as convenient as the use of an automatic polarograph, it has the advantage of greater precision and accuracy, which is particularly important for determining the diffusion coefficients of alkaline earth metal ions in various media. The electrolytic cells used in this work and the method of measurement of the cell resistance were described in detail in a previous paper.⁵ The reported values of the cathode potential refer to the saturated calomel electrode and were properly corrected for iR drop. All electrolyses were carried out in a thermostat at 25°. Except for the measurements carried out in studying the effect of the mercury drop time upon the diffusion current, the initial free dropping time of the dropping mercury electrode in all of the experiments was 3 ± 0.2 sec.

Kahlbaum reagent tetraethylammonium iodide, purified by repeated recrystallizations from ethanol-water mixtures, was used as supporting electrolyte in this work. In order to get the true diffusion currents, the residual current of the supporting electrolyte solution determined in a blank experiment was subtracted from the measured values of all diffusion currents. For all solutions of the alkaline earth metal salts, Merck reagent chlorides were used. The ethanol for alcohol-water mixtures was redistilled azeotropically and kept in a vacuum.

(1a) Present address: Vassar College, Poughkeepsie, N. Y.

(1b) J. Heyrovsky and S. Berezičky, *Coll. Czechoslov. Chem. Commun.*, **1**, 19 (1929).

(2) Cf. I. Zlotowski and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 473 (1942).

(3) G. Kimura, *Coll. Czechoslov. Chem. Commun.*, **4**, 492 (1932).

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

(5) I. Zlotowski and I. M. Kolthoff, *ibid.*, **64**, 1297 (1942).

Experimental Results

Barium- and Strontium-ion Waves in Water and Alcohol-Water Mixtures.—The characteristics of the capillary used in these experiments were as follows: initial drop time in a disconnected electric circuit, $t_0 = 3.1$ sec.; at -2.20 ± 0.05 v. where the diffusion current of barium was measured, $t_{2.20} = 1.60$ sec.; the weight of mercury flowing from the capillary per second at the same cathode potential was $m_{2.20} = 2.045$ mg./sec. Hence the Ilkovič equation product $m^{2/3}t^{1/6}$ for the diffusion current evaluation equals $(2.045)^{2/3}(1.60)^{1/6} = 1.74$ mg.^{2/3} sec.^{-1/6} at -2.2 volts.

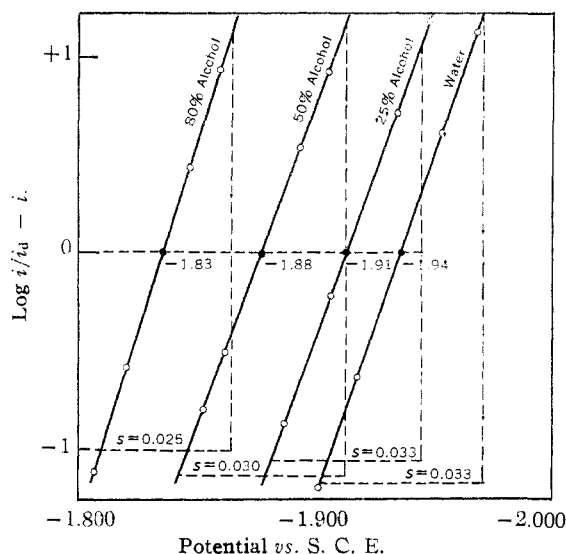


Fig. 1.—Log plots of Ba⁺⁺ waves in various C₂H₅OH-H₂O mixtures.

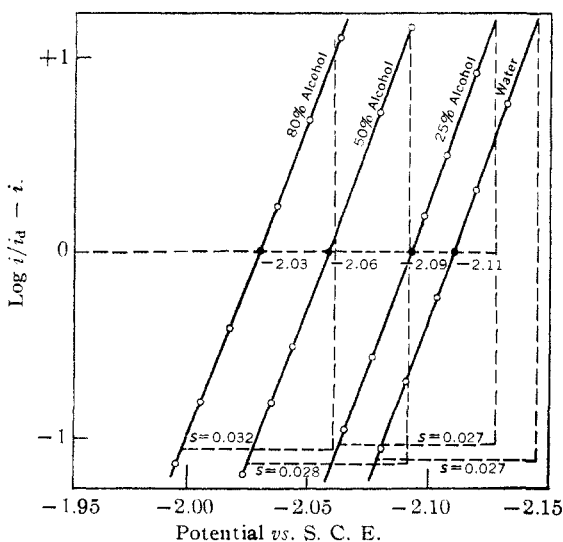


Fig. 2.—Log plots of Sr⁺⁺ waves in C₂H₅OH-H₂O mixtures.

The barium and strontium polarograms yield normal S-shaped current-voltage curves without maxima. Several of the polarograms obtained in

water or alcohol-water mixtures using tetraethylammonium iodide as supporting electrolyte were analyzed by plotting $\log i(i_d - i)$ vs. the corrected (for the iR drop) mercury cathode potential. The results of the analyses are given in Figs. 1 and 2. The plots yield straight lines with slopes varying from 0.033 in pure water to 0.025 in 80% ethanol solutions for barium, and from 0.029 to 0.027, respectively, for strontium ion solutions. The slopes are in reasonable agreement with that calculated from the Heyrovsky-Ilkovič equation (0.0296), corresponding to a reversible reduction of a di-valent ion at the dropping mercury electrode. With alkali metals the best agreement between the experimental value of the slope and that calculated from the Ilkovič wave equation was found in 50% alcohol medium.⁶ With barium and strontium the best agreement between experimental and theoretical slopes was found also in 50% ethanol.

Tables I and II show the dependence of the half-wave potentials of both barium and strontium ions upon the alcohol concentration. As expected, the half-wave potentials shift to more positive values with increasing alcohol concentrations. From the plotted experimental data (Fig. 3) it is seen that the half-wave potentials are practically a linear function of the alcohol concentration, following the respective equations

$$\begin{aligned}\pi_{1/2}(\text{Ba}) &= \pi_{1/2}(\text{H}_2\text{O}) + 0.0015 C \\ \pi_{1/2}(\text{Sr}) &= \pi_{1/2}(\text{H}_2\text{O}) + 0.0010 C\end{aligned}$$

where C is the ethanol concentration in volume per cent. The values for 100% ethanol were extrapolated. It is to be noted that the half-wave potentials were found to be practically constant within a fairly large concentration range (0.6 to 10 millimolar for Ba, and 0.4 to 7 millimolar for Sr) as well as for various capillary drop times (1.9 to 6.3 sec.). Both the barium and strontium half-wave potentials in water are in reasonable agreement with those reported by Heyrovsky and Berežický.

TABLE I
DEPENDENCE OF THE HALF-WAVE POTENTIAL OF BARIUM ON ALCOHOL CONCENTRATION

Medium	H ₂ O	25	50	80	90	100
Half-wave potential, v. vs. S. C. E.	-1.940	-1.915	-1.875	-1.835	-1.820	(~1.8) ^a

^a Extrapolated value.

TABLE II
DEPENDENCE OF THE HALF-WAVE POTENTIAL OF STRONTIUM UPON ALCOHOL CONCENTRATION

Medium	H ₂ O	25	50	80	90	100
Half-wave potential vs. S. C. E., v.	-2.110	-2.095	-2.060	-2.030	-2.020	(~2.010) ^a

^a Extrapolated value.

(6) Zlotowski and Kolthoff, THIS JOURNAL, 64, 1297 (1942).

TABLE III
PROPORTIONALITY BETWEEN DIFFUSION CURRENT AND BARIUM ION CONCENTRATION

$t_0 = 3.0 \text{ sec.}; \pi = -2.25 \text{ v.}$ H ₂ O			$t_0 = 2.9 \text{ sec.}; \pi = -2.15 \text{ v.}$						$t_0 = 2.8 \text{ sec.}; \pi = -2.15 \text{ v.}$ 80% C ₂ H ₅ OH		
$C_{Ba^{++}}$ $M \times 10^3$	i_d μa	i_d/c $\mu\text{a/m.}$ mole/liter	25% C ₂ H ₅ OH			50% C ₂ H ₅ OH			$C_{Ba^{++}}$ $M \times 10^3$	i_d μa	i_d/c $\mu\text{a/m.}$ mole/liter
			$C_{Ba^{++}}$ $M \times 10^3$	i_d μa	i_d/c $\mu\text{a/m.}$ mole/liter	$C_{Ba^{++}}$ $M \times 10^3$	i_d μa	i_d/c $\mu\text{a/m.}$ mole/liter			
0.335	2.06	6.16	0.265	1.48	5.59	0.355	1.78	5.01	0.355	1.56	4.66
0.74	4.65	6.28	0.76	4.35	5.72	0.63	3.21	5.10	0.575	2.59	4.51
1.13	7.17	6.35	1.56	8.89	5.69	1.37	6.94	5.05	1.00	4.55	4.55
2.74	17.22	6.28	2.45	14.12	5.77	2.07	10.52	5.09	1.83	8.27	4.51
4.5	28.53	6.32				2.54	12.91	5.09			
						4.08	20.86	5.11			

TABLE IV
PROPORTIONALITY BETWEEN DIFFUSION CURRENT AND STRONTIUM ION CONCENTRATION

H ₂ O			50% C ₂ H ₅ OH			80% C ₂ H ₅ OH		
$C_{Sr^{++}}$ $M \times 10^3$	i_d μa	i_d/c $\mu\text{a/m.}$ mole/liter	$C_{Sr^{++}}$ $M \times 10^3$	i_d μa	i_d/c $\mu\text{a/m.}$ mole/liter	$C_{Sr^{++}}$ $M \times 10^3$	i_d μa	i_d/c $\mu\text{a/m.}$ mole/liter
0.36	2.12	5.89	0.33	1.80	5.46	0.18	0.79	4.38
0.83	5.00	6.02	0.625	3.47	5.55	0.305	1.30	4.27
1.38	8.35	6.05	0.85	4.72	5.55	1.07	4.58	4.27
3.15	19.10	6.07	1.65	9.13	5.53	2.05	8.74	4.26
			3.55	19.60	5.52			

From the theoretical as well as analytical viewpoint it was of importance to test the proportionality between diffusion current and the ion concentration in various water-alcohol mixtures. Tables III and IV give a summarized survey of the results obtained in a series of measurements carried out with a practically constant initial drop time of three seconds. From the data it may be inferred that the linear relation holds within 1 to 2% for barium and strontium ion concentrations varying between 0.5 and 4.5 millimolar. In order to obtain this linear relationship it is necessary to keep the concentration of supporting electrolyte about 60 to 100 times as large as that of the alkaline earth ions. Moreover, the initial drop time should be equal to or greater than 2.5 seconds. The best proportionality is found in 50% ethanol medium. In mixtures which contain less than 50% ethanol, the measured diffusion current values become higher with increasing concentrations than those predicted by the analytically evaluated ion concentration ratio (positive deviation); while in mixtures which contain more than 50% ethanol, the reverse is found. In all cases the deviation from proportionality is small.

In Tables I and II, it is seen that the half-wave potentials of barium are about 200 millivolts more positive than those of strontium in the various media. Therefore, it may be expected that a small amount of barium in the presence of a large amount of strontium can be determined as well as both cations when they are present in practically the same concentrations, or even a small amount of strontium in the presence of an excess of barium ions. As a matter of fact the polarograms shown in Fig. 4 indicate that when dealing with a mixture containing about 20 times as much barium as strontium two distinct diffusion waves are still obtained. Moreover, from the data summarized

in Table V, it may be stated that the use of a dropping mercury cathode is admirably suitable for a simultaneous determination of strontium and barium within a relatively large range of concentration ratios of both ions, in both water and 50% ethanol media.

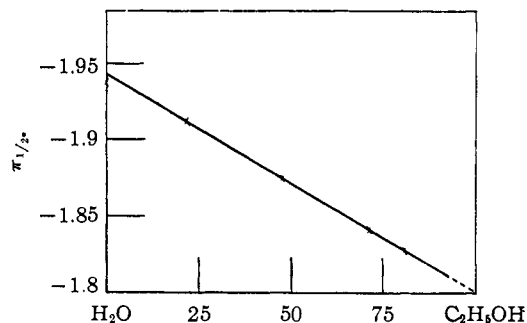


Fig. 3a.— $\pi_{1/2}$ of Ba^{++} as a function of alcohol concentration.

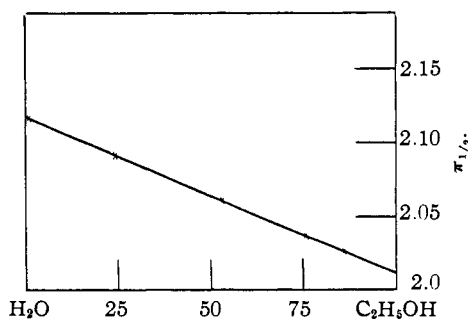


Fig. 3b.— $\pi_{1/2}$ of Sr^{++} as a function of alcohol concentration.

It is apparent that in order to find the true diffusion current of strontium in a mixture with barium it is necessary to subtract from the total

TABLE V
DIFFUSION CURRENTS IN MIXTURES OF BARIUM AND STRONTIUM

Reference to Fig. 4	Composition of solution	H ₂ O			50% C ₂ H ₅ OH		
		i_d' Calculated	i_d Measured	$\frac{i_d - i_d'}{i_d}$ %	i_d' Calculated	i_d Measured	$\frac{i_d - i_d'}{i_d}$ %
Pol. 1 (Fig. 4)	$C_{Ba^{++}} = 0.0035 M +$	21.77	21.16	-2.7	17.85	17.50	-2.0
	$C_{Sr^{++}} = 0.00018 M$	1.09	1.04	-4.6	0.92	0.96	+4.0
Pol. 2	$C_{Ba^{++}} = 0.00044 M +$	2.70	2.78	+2.9	2.22	2.25	+1.4
	$C_{Sr^{++}} = 0.0005 M$	3.02	2.96	-2.0	2.50	2.46	-1.6
Pol. 3	$C_{Ba^{++}} = 0.000335 M +$	2.08	2.17	+4.3	1.70	1.74	+2.4
	$C_{Sr^{++}} = 0.00335 M$	20.87	20.74	-0.7	17.25	17.03	-1.3

current measured at a cathode potential between -2.15 and -2.25 v. in water or between -2.0 and -2.10 in 50% ethanol, the residual current due to the supporting electrolyte and the diffusion current of barium at the potential at which the strontium current is measured. The cathode

upon the alcohol concentration in the solution. This is readily seen from the data in Table VI, where the diffusion current constants are summarized for various media, with tetraethylammonium iodide as supporting electrolyte. Fur-

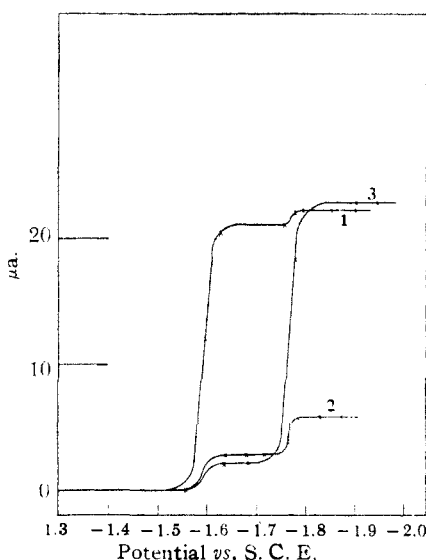


Fig. 4.—Simultaneous determination of Ba⁺⁺ and Sr⁺⁺ in water (see Table V), anode potential $\pi_a = -0.345$ v.

potential affects the diffusion current constant only in so far as it has an effect upon the product $m^2/t^{1/2}$. According to our previous results⁷ as well as those published by Kolthoff and Orlemann⁸ the relative change of the value of $m^2/t^{1/2}$ with cathode potential in the region between -2.0 and -2.2 volts is less than 1% per 0.1 volt. Therefore, for most practical purposes the correction can be neglected and the diffusion current of strontium is found from the equation

$$i_{d_{Sr^{++}}} = i_{d(\text{total})} - i_r - i_{d_{Ba^{++}}}$$

where both i_d and i_r are measured at the strontium wave voltage, while i_d (Ba) is measured at the constant region of the barium diffusion wave.

The diffusion current constants of both barium and strontium ions were found to be dependent

(7) I. Zlotowski and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 473 (1942).

(8) I. M. Kolthoff and E. F. Orlemann, *THIS JOURNAL*, **63**, 2085 (1941).

TABLE VI

THE DEPENDENCE OF THE DIFFUSION CURRENT [(C₂H₅)₄N⁺I⁻] UPON ALCOHOL CONCENTRATION

Ion Medium	H ₂ O	Ethyl Alcohol, %				100
		25	50	80	90	
Sr ⁺⁺	6.05	5.55	5.00	4.40	4.50	(4.70) ^a
Ba ⁺⁺	6.22	5.72	5.10	4.65	4.75	(4.90) ^a

^a Extrapolated value.

thermore, plotting of the numerical values reveals that the diffusion current constant and the diffusion coefficient of both barium and strontium attain a minimum value in about 80% ethanol.

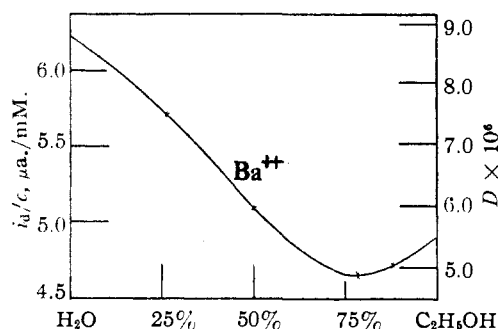


Fig. 5a.—Diffusion current constant and diffusion coefficient of barium as a function of alcohol concentration.

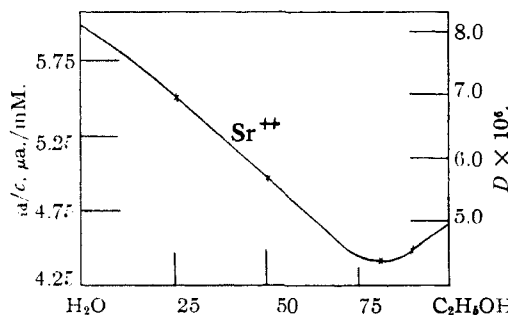


Fig. 5b.—Diffusion current constant and diffusion coefficient of strontium as a function of alcohol concentration.

It should be noted that each of the foregoing values represents an average obtained with several concentrations of solutions of barium and strontium electrolyzed under exactly the same conditions so far as the medium, the excess of supporting electrolyte, and the characteristics of the capillary are concerned. Since, according to the Ilkovič equation, the absolute values of the diffusion current constants are a function of the diffusion coefficient and the capillary characteristics expressed in terms of the $m^{3/2}t^{1/2}$ products, it is apparent that by keeping the latter constant the diffusion current constants depend exclusively on the diffusion coefficients of the ions in the particular media.

When the diffusion current constants K_i are expressed in microamperes per millimole per liter, the diffusion coefficients D in sq. cm./sec., and the product $m^{3/2}t^{1/2}$ in the units $\text{mg.}^{3/2}\text{sec.}^{-1/2}$, the Ilkovič equation reads as follows

$$K_i = 605nD^{1/2}m^{3/2}t^{1/2}$$

where n is the valency of the ion.

Using the conductivity data for barium and strontium chloride in water it is possible to test the validity of the Ilkovič equation in aqueous solutions. Fergusson and Vogel⁹ give for the mobility of barium and strontium ions in water at 18°, the value of $\lambda_{\text{Ba}}^0 = 55.04 \text{ cm.}^2/\text{ohm equiv.}$ and of $\lambda_{\text{Sr}}^0 = 51.66$. Accepting for both barium and strontium ions the same value of the temperature coefficient $a = 1/\lambda^0(d\lambda^0/dt) = 0.0238$ as reported by Kohlrausch,¹⁰ we find for the mobility of the ions at 25°

$$\begin{aligned}\lambda_{\text{Ba}}(25^\circ) &= 64.2 \text{ cm.}^2/\text{ohm equiv., and} \\ \lambda_{\text{Sr}}(25^\circ) &= 60.3 \text{ cm.}^2/\text{ohm equiv.}\end{aligned}$$

Using the above data it is possible to calculate the diffusion coefficients of barium and strontium ions by means of the Nernst formula.¹¹ The obtained values are $8.57 \times 10^{-6} \text{ cm.}^2/\text{sec.}$ for barium and $8.04 \times 10^{-6} \text{ cm.}^2/\text{sec.}$ for strontium. Hence the diffusion current constants calculated from the Ilkovič equation with the given values of $m^{3/2}t^{1/2}$ of our capillary are

$$K_{\text{Ba}}(\text{H}_2\text{O}, 25^\circ) = 605 \times 2 (8.57 \times 10^{-6})^{1/2} \times 1.74 = 6.17 \mu\text{a./mM. per liter}$$

$$K_{\text{Sr}} = 605 \times 2 (8.04 \times 10^{-6})^{1/2} \times 1.76 = 5.98 \mu\text{a./mM. per liter}$$

in excellent agreement with the experimentally determined values 6.22 and 6.05 $\mu\text{a./mM.}$ per liter, given in Table VI.

After having established the validity of the Ilkovič equation in pure water medium, it is

(9) A. Fergusson and I. Vogel, *Phil. Mag.*, **4**, 233 (1927).

(10) F. Kohlrausch, *Z. Elektrochem.*, **14**, 129 (1908).

(11) Previous paper gives a complete description of the procedure employed in these evaluations.

reasonable to assume that it holds with the same accuracy in case of ethanol-water mixtures. The polarographic method presents a simple method for the determination of the diffusion coefficient of barium and strontium ions in these media by introducing into the Ilkovič equation the experimentally determined diffusion current constants from Table VI. The following numerical values for the diffusion coefficients are obtained (Table VII, Fig. 5).

TABLE VII

DIFFUSION COEFFICIENT OF Sr^{++} AND Ba^{++} IN $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ MIXTURES (CALCULATED FROM THE DIFFUSION CURRENT VALUES)

Medium	H_2O	Ethyl Alcohol, %			
		25	50	80	90
$\text{Sr}^{++}, D \times 10^6 \text{ cm.}^2/\text{sec.}$	8.26	6.95	5.64	4.37	4.57 (4.95) ^a
$\text{Ba}^{++}, D \times 10^6 \text{ cm.}^2/\text{sec.}$	8.70	7.38	5.87	4.88	5.09 (5.42) ^a

^a Extrapolated value.

Acknowledgment is made to the Carnegie Corporation of New York for a grant which enabled us to carry out the present work.

Summary

1. In ethanol-water mixtures the half-wave potentials of barium and strontium are given by the equations

$$\begin{aligned}\pi_{1/2}(\text{Ba}) &= \pi_{1/2}(\text{H}_2\text{O}) + 0.0015 C (25^\circ) \\ \pi_{1/2}(\text{Sr}) &= \pi_{1/2}(\text{H}_2\text{O}) + 0.0010 C (25^\circ)\end{aligned}$$

in which C is the concentration of ethanol in volume per cent. The half-wave potential (*vs.* S.C.E.) of barium in water is -1.94 v. and of strontium -2.11 v. Barium and strontium in mixtures can be determined within a wide range of concentration ratios with the ordinary polarographic accuracy.

2. The diffusion coefficients of barium and strontium in aqueous medium as calculated from the diffusion current constants with the aid of the Ilkovič equation are $8.7 \times 10^{-6} \text{ cm.}^2/\text{sec.}$ and $8.3 \times 10^{-6} \text{ cm.}^2/\text{sec.}$ The corresponding values calculated from conductivity data are 8.6×10^{-6} and $8.04 \times 10^{-6} \text{ cm.}^2/\text{sec.}$ (25°).

3. The analysis of the barium and strontium waves is given by the Ilkovič equation.

4. In water-ethanol mixtures the diffusion current constants and the diffusion coefficients of barium and strontium decrease with increasing alcohol concentration. A minimum value of the diffusion coefficient is found in approximately 80% (by volume) ethanol. At this alcohol concentration the diffusion coefficient of barium is 5.1×10^{-6} and of strontium $4.6 \times 10^{-6} \text{ cm.}^2/\text{sec.}$ The corresponding values calculated by extrapolation to 100% ethanol are 5.4 and 5.0×10^{-6} , respectively.