

smaller than one would have to assume in order to explain the abnormal vapor pressures on the basis of perturbation of the liquid in the capillaries by the glass.

The abnormal lowering of the vapor pressure may perhaps be explained on the basis of a wall effect on the vapor. Under the conditions of the present experiments, the mean free path of the water vapor is of the same order of magnitude as the capillary radii. Due to this a fraction of the molecules escaping from the liquid surface collide directly with the walls, from which they evaporate in all directions after a time-delay. This time-delay may be considered as equivalent to a decrease in the rate of change of momentum or pressure.

The present investigation is being extended to non-aqueous systems in order to eliminate beyond

doubt the solubility factor and to study the role of polarity of the solvent, and also to other temperatures to study the factor of the ratio of mean-free-path to capillary radius.

Summary

1. The validity of the Kelvin equation is discussed in light of available experimental studies.

2. An apparatus for measuring the vapor pressure of liquids in microscopic capillaries is described.

3. The lowering of vapor pressure of water in cone-shaped capillaries of 3 to 10 microns in radius is found to be greater from 7 to 80 times than the values calculated from the Kelvin equation.

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RECEIVED DECEMBER 10, 1949

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. I. The Effects of Gelatin on the Diffusion Current Constants of Cadmium and Bismuth

BY LOUIS MEITES AND THELMA MEITES

The most careful test yet made of the $i_d = km^2/t^{1/2}$ prediction of the Ilkovič equation¹⁻⁴ was that initiated by Lingane and Loveridge^{5,6} and continued by Loveridge.⁷ Plotting the diffusion current constant⁸ against the drop time, they obtained for lead in slightly acidic M potassium chloride and zinc in M ammonia- M ammonium chloride, both in the presence of 0.01% gelatin, a curve which was essentially flat at drop times above 6 seconds, fell about 5% to a minimum at about 1.6 seconds, and then rose very sharply and apparently without limit as the drop time was still further decreased.

Almost simultaneously there appeared a paper by Buckley and Taylor⁹ which cast doubt not only on the conclusions of Lingane and Loveridge on the dependence of the diffusion current on the capillary characteristics, but also on the conclusion reached by many observers that, under otherwise identical conditions, the diffusion current is directly proportional to the concentration of the reducible species. With respect to the first point, they found that, in general, solutions containing

as much as 0.01% gelatin gave "constant values of I over the entire drop-time range of 1 to 6 seconds," while such constancy was only rarely encountered in the absence of gelatin. With respect to the second, they mention a large "decrease of I with extreme dilution of reducible ion."

Although Buckley and Taylor state that their experimental error is of the order of 2-3%, while Loveridge claims an accuracy ten times as great, their conclusions cannot be reconciled on this ground alone. Hence, in view of the importance of the dispute to the theory and practice of quantitative polarographic analysis, we have repeated some of Buckley and Taylor's measurements in a search for the cause of the discrepancy.

Experimental

The stock bismuth(III) solution was prepared from pure bismuth metal. Cadmium(II) solutions were prepared from the reagent grade chloride and standardized by electrodeposition. Other chemicals were ordinary reagent grade.

Diffusion currents were measured with the manual polarograph diagrammed in Fig. 1. A few of the residual current measurements were made with the resistance-potentiometer circuit, but most of the measurements were made with the Type HS galvanometer. All measurements were made in duplicate at from three to six potentials: the mean and extreme differences in any such pair were 0.11 and 0.38%, respectively. Galvanometer calibrations were made in duplicate or triplicate every half-hour or so during use at the Ayrton-type shunt setting being employed.

Drop times were secured by timing sets of 5 to 50 drops each, depending on the drop time, with an electric stop-clock; these data were gathered concurrently with the diffusion current measurements. The mean difference between pairs of t values was 0.12%. The rate of flow of mercury through the capillary was determined for each

(1) D. Ilkovič, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934).

(2) D. Ilkovič, *J. chim. phys.*, **35**, 129 (1938).

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

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 30-39, 60-62.

(5) J. J. Lingane and B. A. Loveridge, *THIS JOURNAL*, **66**, 1425 (1944).

(6) J. J. Lingane and B. A. Loveridge, *ibid.*, **68**, 395 (1946).

(7) B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.

(8) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(9) F. Buckley and J. K. Taylor, *J. Res. National Bur. Standards*, **34**, 87 (1945).

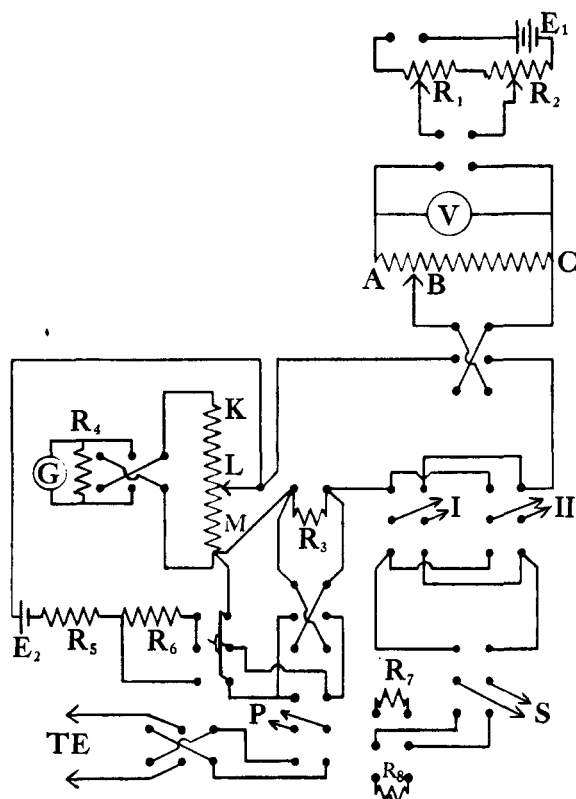


Fig. 1.—Manual polarograph: E_1 , E_2 : heavy-duty lead storage batteries; V : calibrated voltmeter, 1000 ohms/volt; ABC : 25-ohm, 10-turn Helipot, 0.1% linearity; KLM : 1000-ohm, 10-turn Helipot, 0.1% linearity; G : Leeds and Northrup Type HS galvanometer, sensitivity 0.01 microamp./mm., period 8 sec. (damped); I , II , cells; P , to potentiometer; R_1 : linear taper potentiometer, 1000 ohms; R_2 : linear taper potentiometer, 10 ohms; R_3 : General Radio Company Type 500-M, 10,000 ohms \pm 0.1%; R_4 : Nichrome coil, 0.31 ohm; R_5 : carbon, 0.5 megohm; R_6 : General Radio Company Type 500-M, 10,000 ohms \pm 0.1% (calibrated); R_7 : General Radio Company Type 500-L, 5000 ohms \pm 0.1%; R_8 : General Radio Company Type 500-K, 2000 ohms \pm 0.1%; S , to Sargent; TE , to titration electrodes.

driving head used by a slight modification of the apparatus described by Lingane and Kolthoff.¹⁰ There is such a preponderance of data showing that m is only extremely slightly affected by small variations in solution composition that the values of m in the presence of gelatin were taken as being equal to those measured in the absence of gelatin: this was not done for capillary II for cadmium because of a fancied small change in the position of the stand tube relative to the meter stick on which it was mounted between the two sets of measurements. The very few measurements of m made in duplicate indicated that the mean precision of these values was slightly better than 0.1%. All of these component errors are close to those reported by Loveridge.⁷

All measurements were made in a water thermostat operating at $25.00 \pm 0.05^\circ$. Volumetric equipment was calibrated by common methods.

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

Solutions of "Bacto" gelatin (Difco Laboratories, Inc., Detroit, Mich.) were freshly prepared as needed, and temperatures above 60° were avoided during their preparation to minimize denaturation by heat.

Air was removed from the solutions by tank hydrogen from which the oxygen had been removed by a train of vanadium(II) sulfate solutions¹¹ in Corning No. 31770 gas washing bottles. Measurements were begun only after thirty minutes of bubbling had produced no detectable effect on the measured current.

Data and Discussion

Cadmium(II).—The variation with the capillary characteristics of the diffusion current constant of cadmium(II) in an 0.1 F potassium chloride–0.1 F hydrochloric acid supporting electrolyte is shown in Table I and Fig. 2. The diffusion current constant, measured at -1.0 v. (*vs.* S.C.E.) is 5.2 at a drop time of 0.5 second and thence falls off rapidly to a very flat minimum of 3.48 at $t = 5$ sec., from which it again rises slowly to 3.56 at $t = 11.0$ sec. The slight difference between the values at these higher drop times and the corresponding figures given by Buckley and Taylor is probably due to the hydrochloric acid added in the present work to prevent the decomposition noted by Smith, Taylor and Smith.¹² However, at a drop time of 1.3 sec., their lowest value, Buckley and Taylor find a diffusion current constant (0.2 mM cadmium) of about 6.2, whereas our Fig. 2 shows 3.75. This is a recurring discrepancy between their work and ours, and it is so large as to demand an explanation.

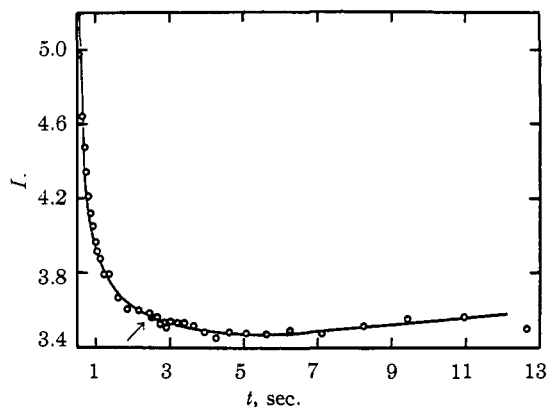


Fig. 2.—Diffusion current constant of cadmium(II) in 0.1 F potassium chloride and 0.1 F hydrochloric acid as a function of drop time. The solid circle (arrow) represents the superposition of the value from Table III and that from capillary I-95.

The diffusion currents reported by Buckley and Taylor were secured by extrapolating the "segment preceding the wave . . . to compensate for rise in residual current" and taking the wave height as "the vertical distance at the half-wave potential" between this extrapolated line and, sometimes, an extrapolation, but in some cases

(11) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(12) E. R. Smith, J. K. Taylor and R. E. Smith, *J. Res. National Bur. Standards*, **37**, 151 (1946).

TABLE I

THE DIFFUSION CURRENT CONSTANT OF CADMIUM IN 0.1 *F* POTASSIUM CHLORIDE-0.1 *F* HYDROCHLORIC ACID
Measurements were made at $E_{d.e.} = -1.00$ v. vs. S.C.E. The cadmium concn. was 5.728 millimolar.

Capillary and mercury "head," cm.	m , mg./sec.	t , sec.	$m^2/t^{1/2}$	i_d , microamp.	I
II-95	7.335	0.506	3.371	100.21	5.190
II-90	7.004	.518	3.280	93.38	4.970
II-85	6.663	.623	3.272	86.92	4.638
II-80	6.331	.673	3.203	82.11	4.475
II-75	6.059	.741	3.162	78.65	4.342
II-70	5.708	.783	3.066	73.96	4.211
II-65	5.393	.852	2.995	70.65	4.118
II-60	5.080	.908	2.908	67.45	4.049
II-55	4.715	.981	2.804	63.60	3.960
II-50	4.354	1.029	2.679	60.06	3.914
II-45	4.013	1.111	2.570	57.05	3.875
II-40	3.706	1.223	2.476	53.80	3.793
II-35	3.347	1.339	2.349	51.05	3.794
II-30	3.008	1.596	2.253	47.26	3.662
II-25	2.676	1.862	2.1375	44.13	3.604
II-20	2.324	2.155	1.994	41.11	3.599
II-16	2.038	2.450	1.866	38.34	3.587
I-95	2.814	2.490	2.320	47.36	3.564
I-90	2.703	2.640	2.281	46.55	3.563
I-85	2.569	2.725	2.216	45.37	3.574
I-80	2.433	2.86	2.154	43.58	3.532
II-12	1.768	2.90	1.746	35.08	3.508
I-75	2.305	3.03	2.099	42.56	3.540
I-70	2.162	3.21	2.030	41.09	3.534
I-65	2.018	3.41	1.959	39.63	3.532
I-60	1.908	3.66	1.911	38.43	3.511
I-55	1.776	3.92	1.842	36.76	3.484
I-50	1.647	4.25	1.774	35.10	3.454
I-45	1.512	4.62	1.699	33.90	3.483
I-40	1.381	5.06	1.6245	32.36	3.478
I-35	1.245	5.58	1.5415	30.68	3.475
I-30	1.109	6.23	1.453	29.08	3.494
I-25	.9797	7.085	1.3665	27.21	3.476
I-20	.8150	8.22	1.239	24.94	3.514
I-16	.7378	9.42	1.187	24.19	3.558
I-12	.6253	10.96	1.090	22.24	3.562
I-9	.5538	12.64	1.029	20.65	3.503

the highest point, of the following plateau. It seems to be characteristic of the polarograms secured at low values of t that the plateau has a slope less than, and frequently even opposite in sign to, the slope of the "residual current" line. This difference gradually lessens as the drop time is increased. Therefore either of these procedures would produce systematically high results at low drop times. If this type of wave form is actually attributable to maximum formation,¹³ as seems entirely probable, then these methods of measurement are likely to confuse deviations from the Ilkovič proportionality of i_d and $m^2/t^{1/2}$ with other factors related to maximum suppression.

We have found the same effect of drop time on

(13) Ref. 9, p. 111.

the wave form as was reported by Buckley and Taylor. This is illustrated by Fig. 3, which shows the variation with t of the ratio of the "diffusion" current constants measured at -0.8 v. and at -1.0 v. (To avoid superposition of points we have arbitrarily omitted every other point in each series of data at drop times greater than 2 seconds.) Clearly the addition of 0.01% gelatin decreases from 1.7 to 0.9 sec. the drop time above which extrapolation of the plateau at potentials more negative than -0.8 v. should give correct values of the diffusion current. With waves showing this type of maximum, however, Buckley and Taylor measured the highest possible value of the "wave height," thereby including the greatest possible contribution from any maximum which

TABLE II

THE DIFFUSION CURRENT CONSTANT OF CADMIUM IN 0.1 *F* POTASSIUM CHLORIDE-0.1 *F* HYDROCHLORIC ACID WITH 0.01% GELATIN

Measurements were made at $E_{d.e.} = -1.00$ v. vs. S.C.E. The cadmium concn. was 5.593 millimolar.

Capillary and mercury "head," cm.	m , mg./sec.	t , sec.	$m^2/t^{1/2}$	i_d , microamp.	I
II-95	7.335	0.550	3.417	84.78	4.432
II-90	7.004	.600	3.360	80.37	4.273
II-85	6.663	.624	3.272	71.87	3.924
II-80	6.331	.674	3.203	69.01	3.849
II-75	6.059	.732	3.154	65.52	3.711
II-70	5.708	.749	3.044	62.36	3.660
II-65	5.393	.800	2.963	58.87	3.549
II-60	5.080	1.055	2.982	58.10	3.480
II-55	4.715	1.126	2.868	55.61	3.464
II-45	4.013	1.232	2.615	50.16	3.427
II-40	3.706	1.352	2.524	48.98	3.467
II-35	3.347	1.470	2.386	46.70	3.496
II-30	3.008	1.682	2.272	44.50	3.499
II-25	2.676	1.850	2.1355	41.88	3.503
II-20	2.324	2.302	2.016	39.93	3.538
II-16	2.038	2.450	1.866	37.21	3.562
I-95	2.838	2.520	2.339	46.89	3.581
I-90	2.700	2.640	2.278	45.83	3.594
I-85	2.558	2.785	2.218	44.92	3.618
II-12	1.768	2.877	1.743	35.21	3.609
I-80	2.442	2.98	2.176	43.61	3.580
I-75	2.311	3.08	2.108	42.17	3.574
I-70	2.169	3.26	2.041	41.06	3.594
I-65	2.049	3.48	1.986	40.31	3.626
I-60	1.913	3.66	1.914	38.85	3.626
I-55	1.773	3.88	1.837	37.29	3.626
I-50	1.642	4.18	1.767	35.89	3.628
I-45	1.512	4.51	1.694	34.38	3.625
I-40	1.379	5.155	1.628	32.98	3.619
I-35	1.252	5.43	1.540	31.10	3.608
I-30	1.112	6.03	1.449	29.20	3.600
I-25	0.9643	6.98	1.343	26.99	3.590
I-20	.8025	7.90	1.2185	24.45	3.584
I-16	.7411	9.47	1.191	23.85	3.577
I-12	.6310	10.50	1.089	21.615	3.546
I-9	.5523	12.01	1.019	19.51	3.420

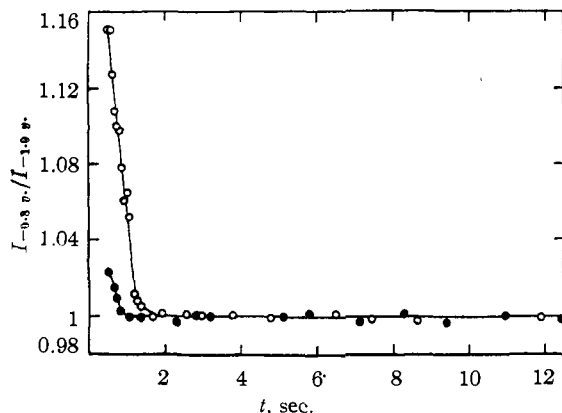


Fig. 3.—Ratio of diffusion current constants at -0.8 v. and -1.0 v. vs. S. C. E. for cadmium(II) in $0.1 F$ potassium chloride and $0.1 F$ hydrochloric acid, (a) \circ without gelatin, (b) \bullet with 0.01% gelatin.

was not "sharp," and greatly exaggerating the effect shown in Fig. 3. Buckley and Taylor themselves recognized the possibility that "some systematic error (might be) introduced by the method of measurement of the wave heights."¹⁴

The addition of 0.01% gelatin not only changes this "critical" drop time,¹⁵ but also radically alters the shape of the plot of I vs. t (Table II and Fig. 4). This curve is very similar to those found by Loveridge⁷ for the lead and tetrammino-zinc ions in the presence of 0.01% gelatin, although the minimum here occurs at 1.2 sec. instead of at 1.6 sec. as in these other curves. Buckley and Taylor report that, under these conditions, I is independent of t between 1 and 6 sec., but our values range between 3.46 and 3.63 . Furthermore, this variation is over twice as great as that observed in the absence of gelatin at drop times between 2 and 12 sec., so that, in this case, better agreement with the Ilkovič equation is secured in the absence of gelatin than in its presence.

It is also of interest to note that the addition of gelatin decreases the diffusion current constant at very low (less than 2.5 sec.) and at very high (greater than 10 sec.) drop times, but increases it between these limits, the greatest increase being nearly 4% at 5.5 sec.

Many investigators have claimed that the diffusion current constants of various ions increase with decreasing concentration.^{16,17} Maas, indeed, held that this was true for cadmium in a potassium chloride supporting electrolyte, but this was contradicted by Lingane and Kolthoff,¹⁰ who later stated that "it is significant that these authors all used empirical graphical methods for measuring the

(14) Ref. 9, p. 101, note 3.

(15) This is not the "critical drop-time" of Buckley and Taylor, who use the term to denote the drop time above which, according to their measurements, I is independent of t .

(16) Ref. 4, p. 60.

(17) NOTE ADDED IN PROOF: The most recent such assertion is that by Champa and Wallach (*Anal. Chem.*, **22**, 727-729 (1950)), which is subject to the same objections as those raised here to the conclusion of Buckley and Taylor.

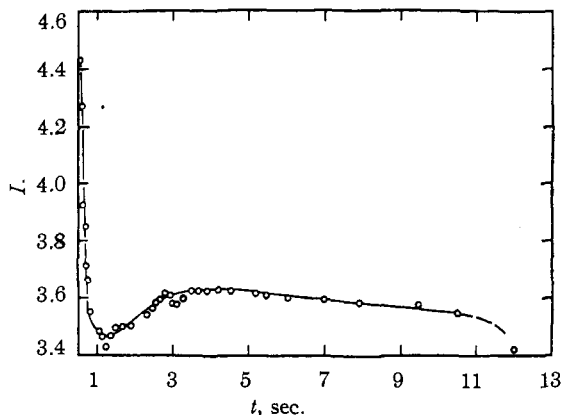


Fig. 4.—Diffusion current constant of cadmium(II) in $0.1 F$ potassium chloride, $0.1 F$ hydrochloric acid, and 0.01% gelatin, as a function of the drop time.

diffusion currents."¹⁵ It therefore seemed possible that the contradictory conclusion of Buckley and Taylor was a result of their methods of measurement. We have attempted to resolve the contradiction by securing the data presented in Table III. Over a 630-fold concentration range the diffusion current constant is independent of concentration to $\pm 0.17\%$ or better. The mean value of Table III has been plotted on Fig. 2 for comparison.

Bismuth(III).—The deviation from constancy of the diffusion current constant of bismuth in $1 F$ nitric acid without gelatin was stated by Buckley and Taylor to be much greater than with any of the other ions they studied: in fact, they reported that it decreased continuously between $t = 1$ and 6 sec. This is the same type of behavior that Loveridge found for hydroquinone in an $0.2 F$ phosphate buffer of $pH 7$, and his data led him to propose an empirical equation of the form $I = a - b \log t$. In order to determine whether a similar equation could be applied to bismuth, we have studied this system with the results given in Table IV and Fig. 5.

TABLE III

THE DIFFUSION CURRENT-CONCENTRATION RELATIONSHIP FOR CADMIUM IN $0.1 F$ POTASSIUM CHLORIDE- $0.1 F$ HYDROCHLORIC ACID

$t = 2.47_0$ sec., $m = 3.299$ mg./sec., $m^2/t^{3/2} = 2.576_5$ $\mu\text{g.}^2/\text{sec.}^{-1/2}$, $E_{d.c.} = -1.00$ v. vs. S. C. E.

Cd ⁺⁺ , millimolar	i_d , microamp.	i_d/C , microamp./millimole/liter
0.01935	0.178	9.20
.05538	0.507	9.15
.1245	1.146	9.20
.1847	1.700	9.20
.2392	2.202	9.21
1.614	14.79	9.16
4.221	38.87	9.21
6.667	61.25	9.19
12.19	112.0	9.19

Mean 9.19 ± 0.015

$i_d/Cm^{2/3}t^{1/6} = 3.567 \pm 0.006$

TABLE IV

THE DIFFUSION CURRENT CONSTANT OF BISMUTH IN 1.0 *F* NITRIC ACID

Measurements were made at -0.5 v. vs. S.C.E. with solutions containing 0.2465 millimolar bismuth(III).

Capillary and mercury "head," cm.	m , mg./sec.	t , sec.	$m^2/t^{1/2}$	i_d , microamp.	I
II-95	7.453	0.510	3.411	15.63	18.59
II-70	5.778	0.716	3.046	12.91	17.19
II-55	4.770	1.168	2.908	10.76	15.01
II-35	3.382	1.445	2.396	7.297	12.35
II-30	3.071	1.624	2.290	6.105	10.81
II-25	2.699	1.867	2.151	4.896	9.23
II-20	2.341	2.155	2.003	3.977	8.05
II-16	1.992	2.465	1.840	3.040	6.70
I-85	2.629	2.785	2.259	3.181	5.71
I-70	2.243	3.27	2.087	2.586	5.027
I-55	1.809	4.035	1.872	2.208	4.785
I-45	1.579	4.685	1.754	1.987	4.596
I-35	1.286	5.69	1.579	1.795	4.612
I-30	1.148	6.33	1.491	1.681	4.574
I-25	1.0435	7.13	1.427	1.619	4.603
I-20	0.9131	8.19	1.3355	1.479	4.493
I-16	.8062	9.26	1.256	1.372	4.431
I-13	.7241	10.26	1.189	1.270	4.333
I-10	.6508	11.55	1.128	1.210	4.352

We agree with Buckley and Taylor that bismuth shows greater deviations from a constant I than any other ion yet studied. Thus, the ratio of the diffusion current constant at 0.5 sec. to that at 6 sec. is 4.05 with bismuth, compared to only 1.49 for cadmium and about 1.25 for lead (with 0.01% gelatin). Nevertheless, there is a region of constancy, for at drop times between 4.5 and 7.5 sec. $I = 4.594 \pm 0.012$. At still longer drop

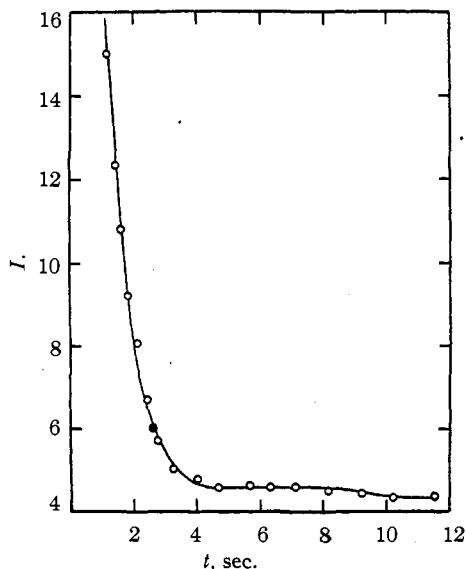


Fig. 5.—Diffusion current constant of bismuth(III) in 1.0 *F* nitric acid as a function of the drop time. The solid circle represents the value from Table V.

times the diffusion current constant again falls slightly, but much more slowly than before, finally reaching 4.35 at 11.5 sec. Including all the values at drop times greater than 3 sec., I is 4.58 ± 0.15 , a mean deviation scarcely greater than the combined errors of Buckley and Taylor's measurements. It may be stated here that these data could not be reproduced to better than 30% by an equation of the form given above.

Although at $t = 3.2$ sec. we find the diffusion current constant at -0.2 v. to be only 0.16% higher than that at -0.5 v., the effect of the maximum evidently persisting to much higher drop times, for the values of Buckley and Taylor are nearly 15% above ours even with 6-sec. drops.

Here as with cadmium, Buckley and Taylor report that the diffusion current constant increases with decreasing concentration. Our data (Table V) again indicate that the diffusion current, measured at a potential sufficiently negative to eliminate interference by maxima, is accurately proportional to the concentration of the reducible

TABLE V

THE DIFFUSION CURRENT-CONCENTRATION RELATIONSHIP FOR BISMUTH IN 1.0 *F* NITRIC ACID

$t = 2.65$ seconds, $m = 2.495$ mg./sec., $m^2/t^{1/2} = 2.164$ mg.²/s. sec.^{-1/2}. $E_{d.e.} = -0.50$ v. vs. S.C.E.

$C_{B(III)}$, millimolar	i_d , microamp.	i_d/C , microamp./millimole/liter
0.0248	0.325	13.10
.0496	0.644	12.98
.0989	1.290	13.04
.1483	1.919	12.94
.2454	3.188	12.99
.342	4.45	13.01
.533	6.93	13.00
.995	12.98	13.05
2.060	26.70	12.96

Mean 13.01 \pm 0.03g

$i_d/Cm^2/t^{1/2} = 6.01 \pm 0.02$

material over a wide concentration range. It appears plain that these recurring claims of deviations from proportionality between diffusion current and concentration were correctly explained by Kolthoff and Lingane.¹⁵ Buckley and Taylor appear to have proved conclusively that graphical methods of determining the diffusion current are inapplicable unless the slopes of the "residual current line" and the following plateau are identical. In other cases the quantity thus measured will be a complex function involving the effects of concentration and drop time on both the diffusion current and the superimposed maximum. These cases can only be treated by the construction of empirical curves which, it must be emphasized, cannot be interpreted in terms of the true diffusion current.

The data for bismuth in the same supporting electrolyte in the presence of 0.01% gelatin are given in Table VI and Fig. 6. While it has the same general form as the corresponding Fig. 4 for

cadmium, it shows a series of maxima and minima, representing an extreme variation of nearly 7% between 1.5 and 10 sec., for which no adequate explanation seems presently available.

TABLE VI

THE DIFFUSION CURRENT CONSTANT OF BISMUTH IN 1.0 *F* NITRIC ACID CONTAINING 0.01% GELATIN

Measurements were made at -0.5 v. vs. S.C.E. The concentration of bismuth(III) was 0.2405_5 millimolar.

Capillary and mercury "head," cm.	m	$m^2/3t^{1/2}$	t_d microamp.	i_d microamp.	i_d microamp.
II-95	7.453	0.643	3.545	5.160	6.051
II-70	5.778	0.843	3.130	3.768	5.004
II-55	4.770	1.014	2.8405	3.226	4.721
II-35	3.382	1.413	2.3875	2.625	4.571
II-30	3.071	1.527	2.267	2.487	4.561
II-25	2.699	1.707	2.1195	2.306	4.523
II-20	2.341	1.950	1.971	2.125	4.482
II-16	1.992	2.240	1.811	1.943	4.460
I-95	2.915	2.527	2.3815	2.549	4.450
I-85	2.629	2.79	2.260	2.425	4.461
I-70	2.243	3.23	2.083	2.261	4.512
I-55	1.809	3.917	1.864	2.064	4.603
I-45	1.579	4.505	1.755	1.971	4.669
I-40	1.412	4.965	1.661	1.8785	4.701
I-35	1.286	5.41	1.5665	1.790	4.750
I-30	1.148	6.04	1.479	1.6925	4.757
I-25	1.0435	6.84	1.417	1.599	4.691
I-20	0.9131	7.81	1.326	1.475	4.624
I-16	.8062	8.78	1.244	1.385	4.628
I-13	.7241	9.72	1.178	1.314	4.637
I-10	.6508	10.93	1.119	1.2495	4.642
I-9	.6278	11.38	1.055	1.206	4.752
I-8	.5335	11.86	0.9932	1.177	4.926

Theoretical

These four series of data nearly double our fund of precise information on the relationship between the diffusion current constant and the characteristics of the capillary. Thus far it seems to have been generally felt that such data as these, accumulated without regard for the presence or absence of gelatin, could be used to gain an insight into the theory of the diffusion current by subjecting them to a variety of empirical treatments.⁷

However, it now seems probable that the appearance of a pronounced minimum in the diffusion current-drop time curve is caused by the addition of gelatin (lead, zinc, cadmium, bismuth), and it is possible that the curves for hydroquinone, cadmium and bismuth in the absence of gelatin differ essentially only in the scale of the t -axis. It would appear that there are actually two phenomena to be considered: the effect of t on the

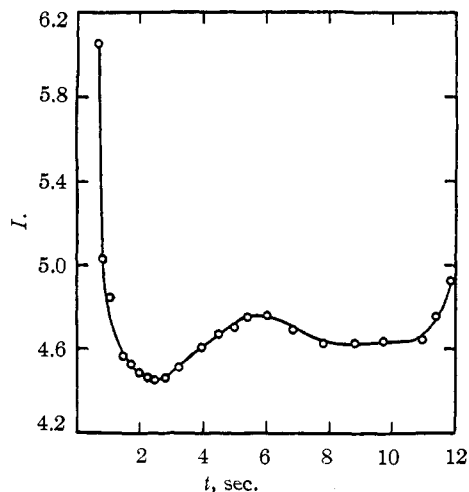


Fig. 6.—Diffusion current constant of bismuth(III) in 1.0 *F* nitric acid and 0.01% gelatin as a function of the drop time.

diffusion current constant, and the modification of this relationship by the addition of a maximum suppressor. There are too few data yet available to allow analysis of these effects, but even now we may regard it as established that no one equation expressing the diffusion current in terms of m and t alone can reproduce the curves found both in the presence and absence of gelatin.

Summary

Data are presented on the variation of the diffusion current constant with the capillary characteristics in solutions of bismuth(III) in 1 *F* nitric acid and of cadmium(II) in 0.1 *F* potassium chloride-0.1 *F* hydrochloric acid, with and without 0.01% gelatin. The anomalous results obtained with these systems by earlier writers are attributed to the failure of their graphical methods for the estimation of the height of a wave showing an un-sharp maximum.

The data now available indicate that there are two basic forms of the dependency of I on t . In one of these, there is a pronounced minimum caused by the addition of gelatin; the other, found in the absence of gelatin, may show either a very flat minimum (cadmium), a substantial independence of I and t above a certain, fairly low, drop time (iodate), or a nearly continuous decrease with increasing drop time (hydroquinone, bismuth). It does not appear possible to find an equation for the diffusion current in terms of m and t which will be valid both in the presence and in the absence of gelatin.

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RECEIVED DECEMBER 21, 1949