direction. This hole was adjusted to a depth of about 0.5 cm. below the surface of the liquid. The lower 0.5 cm. of the stirrer was bent at an angle of 45 to 60°. The stirrer was run at such a rate (400 to 500 r. p. m.) that the excess solid in the tube was uniformly suspended in the liquid. Duplicate samples of the pure salts and the isothermally invariant mixtures were run. At temperatures above 0° one sample was started from a lower temperature while the other sample was heated well above the bath temperature before placing in the bath. The stirring tubes were maintained at a constant temperature in a water-bath controlled to ±0.01°. The time used for stirring and allowing the suspended solid to settle was varied, although one hour of stirring and one hour for settling was found to be sufficient. Four runs were made in which samples were withdrawn at half hour intervals after stirring was stopped. Duplicate samples of solution were withdrawn from each tube, one through a one inch, tightly packed, cotton plug and the other simply pipetted. No significant difference was found between the samples which were filtered and those which were not. Samples of the solutions were pipetted into deep, glass-stoppered weighing bottles. The samples were weighed, evaporated to dryness in an oven at 115–120° and the residues weighed. The residues which contained both potassium perrhenate and potassium chloride were analyzed for rhenium by a colorimetric method[5] using a wave length of 400 m. μ. on a Coleman Spectrophotometer. Check determinations on the solubility of potassium perrhenate at 0° were also made colorimetrically. Since the colorimetric method involves the addition of rather high concentrations of potassium thiocyanate and hydrochloric acid it was assumed that the presence of potassium chloride with potassium perrhenate would not interfere with the determination. The weight of potassium chloride was determined by difference. The solids in equilibrium with the solutions were not analyzed. The compositions of these solids were assumed on the basis that potassium chloride and potassium perrhenate are not isomorphous and that chloride-free potassium perrhenate is precipitated by the addition of potassium chloride to a solution of potassium perrhenate. No check determinations used varied more than 0.5% from the mean.

Summary

The solubility of potassium perrhenate in water has been determined from 0 to 50°. There is good agreement with published data with the exception of a deviation[2] of 6% at 0°.

The system potassium perrhenate–potassium chloride–water has been investigated at 0 and 30°. The advantages of recovering potassium perrhenate at the lower temperature are presented.

KNOXVILLE, TENN. RECEIVED AUGUST 2, 1945

---

(5) Hiskey and Meloche, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 505 (1940).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Fundamental Studies with the Dropping Mercury Electrode. IV. Empirical Modification of the Ilkovic Equation

BY JAMES J. LINGANE AND BRIAN A. LOVERIDGE

According to the Ilkovic equation the diffusion current constant, $i_d/Cm^{2/3}t^{1/6}$, of a given substance in a given supporting electrolyte should be a function of only the number of electrons associated with a molar unit of the electrode reaction, the temperature, and the diffusion coefficient of the reducible substance, and it should be independent of the characteristics (*i. e.*, $m^{2/3}t^{1/6}$) of the dropping electrode. However, it was demonstrated in a previous study[1] that the diffusion current constant of lead ion varies significantly and regularly with the value of $m^{2/3}t^{1/6}$, as shown by curve *a* in Fig. 1.

The rapid increase in $i_d/Cm^{2/3}t^{1/6}$ which occurs when $m^{2/3}t^{1/6}$ is increased beyond about 3.5 mg.$^{2/3}$sec.$^{-1/2}$ is not surprising. When $m^{2/3}t^{1/6}$ is large the drop time is necessarily quite small, and since rapid dropping causes stirring of the solution near the electrode, the normal diffusion layer is disturbed and transfer of the reducible substance to the electrode surface is accelerated.

On the other hand, the values of $i_d/Cm^{2/3}t^{1/6}$ also increase regularly with decreasing values of $m^{2/3}t^{1/6}$ below 3.5. The possibility that this left branch of the curve is simply a reflection of an instrumental peculiarity can be dismissed, because it was demonstrated that different methods of measurement with many different capillaries yield agreeing data and that the observed diffusion current is independent of the characteristics of the current-measuring galvanometer within wide limits.[1] Hence the left branch of curve *a* points to a real failure of the Ilkovic equation.

In the derivation of the Ilkovic equation[2,3,4] several simplifying assumptions were introduced. One of these is that the mercury drop is perfectly spherical throughout its life and that its entire surface is exposed to the solution; actually when the drop is very young an appreciable fraction of its area is screened off by the lumen of the capillary, and as the drop grows it loses its perfect sphericity and becomes very slightly tear shaped. These effects are observable in the motion picture photographs in Fig. 2 of a recent paper by MacNevin and Balis.[5] Therefore the average area is not exactly proportional to $m^{2/3}t^{1/6}$ as assumed.[4] It has also been assumed that the rate of mercury

---

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

(2) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934); *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, 1941, p. 30 *et. seq.*

(5) W. M. MacNevin and E. W. Balis, THIS JOURNAL, **65**, 660 (1943).

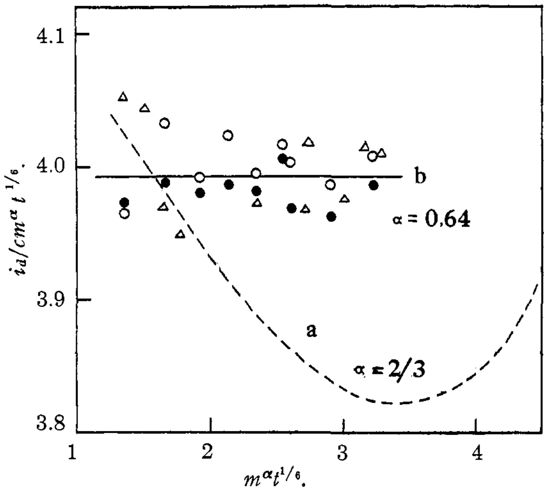

Fig. 1.—Plots of $i/Cm^{\alpha}t^{1/6}$ *versus* $m^{\alpha}t^{1/6}$ with α equal to the theoretical 2/3 (curve *a*) and equal to 0.64 (line *b*). See ref. 1 for the complete curve *a* with experimental points; the curve continues to increase rapidly above $m^{2/3}t^{1/6} = 4.5$. The experimental points pertain to $\alpha = 0.64$. Points denoted by open circles were obtained by the resistance–potentiometer method, the solid circles were obtained by galvanometric measurement, and the triangles were obtained by measurement with the Sargent–Heyrovsky Polarograph; see data in Tables I and II.

flow *m* is constant during the life of a drop, which is not strictly true. The interfacial tension at the mercury–solution interface produces a "back pressure" which opposes the applied pressure, and since this back pressure is inversely proportional to the radius of the drop it decreases as the drop grows so that the effective pressure is increased and *m* increases slightly.[1,4] Consequently the exponents of *m* and *t* in the Ilkovic equation are slightly erroneous.

The most conclusive procedure for determining which of the two exponents is the most faulty, and the correct empirical value of each, would be to perform two series of measurements, in one of which *m* is kept constant while *t* is varied, and the other with *t* constant and varying values of *m*. Unfortunately it is not experimentally feasible to fabricate various capillaries with identical values of *m* and widely different values of *t*, and *vice versa*, so recourse was had to the following less direct but more practical method.

The Ilkovic equation may be written in two logarithmic forms

$$\log (i_d/Ct^{1/6}) = \log 605nD^{1/2} + \alpha \log m \qquad (1)$$

$$\log (i_d/Cm^{2/3}) = \log 605nD^{1/2} + \beta \log t \qquad (2)$$

where α and β would be equal to $^2/_3$ and $^1/_6$, respectively, if the Ilkovic equation were strictly correct. Using data previously described,[1] plots of each of these equations were constructed, and it was found that the experimental points in the plot of Eq. 1 showed much less scatter about a straight line than those in the plot of Eq. 2. Although admittedly not conclusive proof this is at least a good indication that the exponent of *m* is more in error than that of *t*, and that a satisfactory empirical modification of the Ilkovic equation can be obtained by retaining $^1/_6$ as the exponent of *t* and modifying only the exponent of *m*.

Accordingly the quantity $i_d/Cm^{\alpha}t^{1/6}$ was tested with various assumed values of α until a value of α was found which led to the most constant value of $i_d/Cm^{\alpha}t^{1/6}$. The method of least squares was employed in deciding the best value of α. Data pertaining to values of $m^{2/3}t^{1/6}$ between 1 and 3.5 (the left branch of curve *a* in Fig. 1) only were used, because this is the extent of the useful range in practical polarographic measurements. The value of α found in this way is 0.64, compared to the theoretical 0.667. The modified Ilkovic equation then becomes

$$i_d = 605nD^{1/2}Cm^{0.64}t^{1/6} \qquad (3)$$

Tables I and II present a comparison of the constancy of $i_d/Cm^{\alpha}t^{1/6}$ with α equal to the theoretical $^2/_3$ and to 0.64. Curve *b* in Fig. 1 is a plot of $i_d/Cm^{0.64}t^{1/6}$ *versus* $m^{0.64}t^{1/6}$. Details of the three methods of measurement have been described in the previous paper,[1] which also contains all the original data.

Table I

Data Obtained by the Resistance–Potentiometer Method and by Galvanometric Measurement with the Leeds and Northrup Galvanometer

All measurements were made at −0.75 v. *vs.* the S. C. E. at 25.00° with 1.995 millimolar lead ion in 1 *N* potassium chloride containing 0.01% gelatin. Capillary I consisted of "marine barometer tubing," and capillaries J and K were hand drawn. See Ref. 1 for complete details of the measurements.

				$\frac{i_d}{Cm^{2/3}t^{1/6}}$		$\frac{i_d}{Cm^{0.64}t^{1/6}}$	
Capillary	*h* cm.	*m* mg./sec.	*t* sec.	Res.-Pot.	Galv.	Res.-Pot.	Galv.
I	20	0.9026	8.86	3.976	3.984	3.965	3.973
	30	1.408	5.67	3.996	3.952	4.033	3.988
	40	1.902	4.30	3.925	3.912	3.992	3.980
	50	2.385	3.40	3.932	3.895	4.024	3.986
	60	2.881	2.86	3.884	3.870	3.995	3.981
	70	3.373	2.45	3.889	3.878	4.017	4.006
J	20	3.392	2.90	3.875	3.841	4.003	3.968
	30	5.239	1.96	3.835	3.814	4.008	3.986
K	20	4.269	2.28	3.835	3.812	3.986	3.962
					Av.	4.003	3.981
					Av. dev.	±0.016	±0.009

Although the value of $i_d/Cm^{2/3}t^{1/6}$ varies by about 6% over a range of *m* values from 0.9 to 6.2 mg./sec., and a range of drop times from 1 to 9 sec., the value of $i_d/Cm^{0.64}t^{1/6}$ is very satisfactorily constant over the same wide range of capillary characteristics. The measurements with the Leeds and Northrup galvanometer are seen to be the most precise, the average deviation from the mean being only ±0.2%, and the resistance–potentiometer data are next in order

TABLE II

DATA OBTAINED WITH THE SARGENT–HEYROVSKY POLAROGRAPH

All measurements made at −0.75 v. *vs.* the saturated calomel electrode at 25.00°, with 2.000 millimolar lead ion in 1 *N* potassium chloride. Capillaries F, G and H were hand-drawn. See ref. 1 for complete details of the measurements.

Capillary	h, cm.	m, mg./sec.	t, sec.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	$\frac{i_d}{Cm^{0.64}t^{1/6}}$
F	40.0	1.072	4.49	4.045	4.053
	50.0	1.354	3.60	3.990	4.022
	60.0	1.642	2.92	3.918	3.970
	70.0	1.922	2.56	3.880	3.948
G	30.0	2.988	2.50	3.864	3.973
	40.0	4.050	1.82	3.823	3.968
	50.0	5.113	1.41	3.807	3.976
	60.0	6.174	1.18	3.821	4.011
H	30.0	4.146	1.79	3.868	4.018
	40.0	5.617	1.31	3.834	4.015
					Av. 3.995
					Av. dev. ±0.028

with an average deviation from the mean of ±0.4%. As expected from the relatively short scale on the instrument (15 cm.) the data obtained with the Sargent–Heyrovsky Polarograph are least precise (average deviation from the mean ±0.7%), but the average value of $i_d/Cm^{0.64}t^{1/6}$ with the Polarograph agrees almost exactly with the mean of the other two methods.

These data constitute conclusive proof that these three commonest methods of measuring the diffusion current yield practically identical results. They also show that the diffusion current observed with the dropping electrode is reproducible to a few parts per thousand, and that under optimum conditions the polarographic method is inherently capable of greater accuracy than is usually assumed.

In view of the fact that the foregoing results were obtained with only one reducible substance they should not be construed as proof of the general validity of Eq. 3. However, the polarographic behavior of lead ion is normal in all respects, which leads us to expect that a value of α equal to 0.64 probably will be generally applicable. We plan to obtain data with several reducible and oxidizable substances to test the general validity of Eq. 3.

Summary

The diffusion current constant $i_d/Cm^{\alpha}t^{1/6}$ of lead ion in 1 *N* potassium chloride decreases by about 6% as m increases from 0.9 to 6.2 mg./sec., and t decreases from 8.9 to 1.3 sec., if the theoretical value of $\alpha = 2/3$ is used. When the empirical value $\alpha = 0.64$ is employed the diffusion current constant of lead ion is truly constant to a few tenths of a per cent. over the same wide range of capillary characteristics. The value $\alpha = 0.64$ probably is generally applicable, but it should not be so assumed until confirmatory data are available.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 26, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Polymeric Compounds Formed by the Decomposition of 2,4,6-Tribromo-3-fluorophenol Bromide and the Sodium Salt of 2,4,6-Tribromo-3-fluorophenol[1,2]

BY L. CHAS. RAIFORD[3] AND ARTHUR L. LEROSEN[4]

In a previous paper[5] we have mentioned the formation of 2,4,6-tribromo-3-fluorophenol bromide (or hypobromite) in the bromination of *m*-fluorophenol. We report below some interesting reactions in which both this compound and the sodium salt of 2,4,6-tribromo-3-fluorophenol take part to yield a series of polymers of the composition $(C_6HOBr_2F)_n$. For comparison tribromophenol bromide, 2,4,6-tribromo-3-chlorophenol bromide, and the sodium salt of tribromophenol have also been studied.

The formation of amorphous compounds from tribromophenol bromide by the loss of bromine was reported by Benedikt.[6] These substances have been studied by Olivier,[7] Kastle and coworkers,[8] and by Hunter and his students. Hunter and his associates[9–14] have noted that the same type of polymer may be obtained from various salts of trihalogenated phenols by the effect of heat in benzene, or the catalytic effects of ethyl

---

[1] From a Thesis submitted by Arthur L. LeRosen in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate College of the State University of Iowa, June, 1940.

[2] Presented before the Regional Meeting of the American Chemical Society at Baton Rouge, Louisiana, October, 1945.

[3] Deceased January 8, 1944.

[4] Present address: Chemistry Department, Louisiana State University, Baton Rouge 3, Louisiana.

[5] L. C. Raiford and A. L. LeRosen, THIS JOURNAL, 2080 (1944).

[6] R. Benedikt, *Ann.*, **199**, 127 (1879).

[7] S. C. J. Olivier, *Rec. trav. chim.*, **28**, 359 (1909).

[8] J. H. Kastle, A. S. Loevenhart, R. Speyrer and J. W. Bilbert, *Am. Chem. J.*, **27**, 31 (1902).

[9] H. A. Torrey and W. H. Hunter, *Ber.*, **40**, 4333 (1907); THIS JOURNAL, **33**, 200 (1911).

[10] W. H. Hunter, E. A. Daniells, A. O. Olson and L. Karatz, Orig. Comm. 8th Intern. Congr. Appl. Chem. (Appendix), **25**, 393; *cf. C. A.* **7**, 2189 (1913).

[11] W. H. Hunter and F. E. Joyce, THIS JOURNAL, **39**, 2640 (1917).

[12] W. H. Hunter and G. H. Woollett, *ibid.*, **43**, 131, 135 (1921).

[13] W. H. Hunter and R. B. Whitney, *ibid.*, **54**, 1167 (1932).

[14] W. H. Hunter and Miles A. Dahlen, *ibid.*, **54**, 2456 (1932).