

TABLE VI
PHENYL UREAS^a

Reacting base	Phenylureido derivative	M. p., °C.		% N Kjeldahl	
		corr.	Calcd.	I	II
Acetylenediamine	1-Acetyl-2-phenylcarbonamidoethylenediamine	191	19.00	18.84	18.88
Propionylethylenediamine	1-Propionyl-2-phenylcarbonamidoethylenediamine	180	17.87	17.78	17.81
Benzoylethylenediamine	1-Benzoyl-2-phenylcarbonamidoethylenediamine	215	14.84	14.95	14.89
2-Phenyl-4,5-dihydroimidazole	2-Phenyl-3-phenylcarbonamido-4,5-dihydroimidazole	156	15.85	15.73	15.99
<i>p</i> -Tolylethylenediamine	1- <i>p</i> -Tolyl-2-phenylcarbonamidoethylenediamine	191	14.14	14.19	14.28
2- <i>p</i> -Tolyl-4,5-dihydroimidazole	2- <i>p</i> -Tolyl-3-phenylcarbonamido-4,5-dihydroimidazole	157	15.05	15.09	15.12

^a All phenyl ureas were made in acetone and recrystallized from acetone or 95% alcohol. All phenyl ureas are insoluble in water, ether, and hydrocarbon solvents.

TABLE VII
PHENYL THIOUREAS^{a,b}

Reacting base	Phenylthioureido derivative	M. p., °C.		% N Kjeldahl	
		corr.	Calcd.	I	II
Acetylenediamine	1-Acetyl-2-phenylthiocarbonamidoethylenediamine	172	17.72	17.77	17.65
Propionylethylenediamine	1-Propionyl-2-phenylthiocarbonamidoethylenediamine	143	16.73	16.76	16.50
Benzoylethylenediamine	1-Benzoyl-2-phenylthiocarbonamidoethylenediamine	150	14.05	14.10	14.12
2-Phenyl-4,5-dihydroimidazole	2-Phenyl-3-phenylthiocarbonamido-4,5-dihydroimidazole ^c	104	14.95	14.84	14.99
<i>p</i> -Tolylethylenediamine	1- <i>p</i> -Tolyl-2-phenylthiocarbonamidoethylenediamine	173	13.42	13.45	13.57

^a All thioureas except 1-acetyl-2-phenylthiocarbonamidoethylenediamine were made and recrystallized in acetone; all are insoluble in water, ether, and hydrocarbons. ^b 2-*p*-Tolyl-4,5-dihydroimidazole and phenyl isothiocyanate would not react even when refluxed together in benzene solution for three hours. ^c This compound formed readily in cold acetone, but it was yellow colored in contrast with the other thioureas, and on long standing it slowly decomposed with evolution of C₆H₅NCS.

unknown aromatic monoacylethylenediamines has been developed.

3. The conversion of monoacylethylenediamines into pure 2-alkyl- and 2-aryl-4,5-dihydroimidazoles has been effected in nearly quantita-

tive yields.

4. The cyclic and acyclic bases prepared in this study have been fully characterized as picrates, hydrochlorides, phenyl ureas and phenyl thioureas.

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Fundamental Studies with the Dropping Mercury Electrode. I. The Ilkovic Equation of Polarographic Diffusion Currents¹

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Introduction

The most important characteristic of the current-voltage curves, or "polarograms," obtained by electrolyzing solutions of electro-reducible or electro-oxidizable substances with the dropping mercury electrode, is that the current does not increase indefinitely with increasing applied e. m. f. after the decomposition potential is exceeded, but reaches a more or less constant limiting value. Under optimum conditions, such a limiting current is directly proportional to the concentration of the electro-reducible substance,

(1) This paper is based on a thesis submitted by James J. Lingane to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1938.

(2) J. T. Baker Fellow in Analytical Chemistry, 1937-1938.

and this fact is the basis of quantitative polarographic analysis.³

The limiting current is caused by an extreme state of concentration polarization at the dropping electrode, and its magnitude is determined by the rate at which the reducible substance migrates up to the surface of the mercury drops from the body of the solution. In general, re-

(3) For general reviews of the polarographic method see: (a) J. Heyrovsky, "Polarographie," in W. Böttger, "Physikalische Methoden der analytischen Chemie," Bd. 2, Akad. Verlagsgesellschaft, Leipzig, 1936; *Mikrochem.*, **12**, 25 (1932). (b) H. Hohn, "Chemische Analysen mit dem Polarographen," Verlag von Julius Springer, Berlin, 1937; *Z. Elektrochem.*, **43**, 127 (1937); (c) W. Kemula, *ibid.*, **37**, 779 (1931); (d) I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, in press (1939). A complete bibliography of the polarographic literature, with subject titles, up to 1937 inclusive, has been compiled by J. Heyrovsky and J. Klumpar, *Coll. Csech. Chem. Comm.*, **10**, 153 (1938).

ducible ions migrate up to the dropping electrode under the influence of two more or less independent forces: a diffusive force, proportional to the concentration gradient between the depleted region at the electrode surface and the body of the solution, and an electrical force, proportional to the electrical potential gradient near the electrode.^{3d,4-6} According to Heyrovsky and Ilkovic,⁴ the total limiting current, i_l , can be regarded as the algebraic sum of a part i_d due to diffusion, and a part i_m due to electrical migration or transference. The migration current i_m is equal to the product $T_i i_l$, where T_i is the transference number of the reducible ions,^{3d,4-6,7} By adding an excess of an indifferent⁸ salt to the solution, T_i is reduced to a negligibly small value, and hence the migration current is practically eliminated.⁴⁻⁶ Under these conditions, the limiting current for a given capillary is governed practically entirely by the rate of diffusion of the reducible ions up to the dropping electrode, and hence is called a "diffusion current."

From purely theoretical considerations, Ilkovic⁴ derived the following equation for the diffusion current with an excess of foreign salt in the solution

$$i_d = 0.627nFD^{1/2}Cm^2/it^{1/2} \quad (1)$$

In this equation, the diffusion current i_d is expressed in amperes, n is the number of faradays of electricity required for the electroreduction of one mole of the substance in question, F is the faraday (96,500 coulombs), D is the diffusion coefficient of the reducible substance (cm^2/sec), C its concentration in moles per ml., m the weight of mercury in g. flowing from the dropping electrode capillary per sec., and t the time in seconds for the formation of each drop (drop time). The fundamental theory underlying the derivation of this equation has been discussed recently in detail by MacGillivray and Rideal.⁷ The constant 0.627 is a combination of numerical and geo-

(4) D. Ilkovic, *Coll. Czech. Chem. Comm.*, **6**, 498 (1934).

(5) D. MacGillivray, *Rec. trav. chim.*, **56**, 1039 (1937); **57**, 33 (1938).

(6) J. J. Lingane, Ph.D. Thesis, University of Minnesota, June, 1938.

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

(8) An indifferent salt is one that is reduced at a more negative potential than the reducible substance in question, and one that does not form complexes, or react specifically in other ways, with the reducible substance. Because of their very negative reduction potentials, the salts of the alkalis and alkaline earths, and ammonium salts, are usually used as "supporting electrolytes." Tetra-substituted alkyl ammonium salts, and hydroxides, are commonly used in the polarographic analysis for the alkali and alkaline earth ions.

metrical constants; it is based entirely on theoretical considerations, and is not empirical.

It is evident from eq. 1 that, with all other factors (*i. e.*, temperature, concentration of foreign salts, and pressure on the dropping mercury) constant, the diffusion current of a given reducible substance should be directly proportional to its concentration, that is

$$i_d = KC \quad (2)$$

This simple linear relation is the basis of quantitative polarographic analysis, and it has been verified by many investigators.^{3,6,9} Maas⁹ found that eq. 2 was not obeyed strictly when the drop time was shorter than about four seconds, but with a longer drop time it was valid within about $\pm 1\%$ over a range of concentrations from about 10^{-4} to 10^{-2} molar in the case of cadmium. From his results, and our own experience, it appears that the optimum drop time is between three and six seconds. The proportionality constant K may be called the "diffusion current constant,"⁶ and it is expressed most conveniently in the units microamp./ millimole/liter. When i_d is expressed in microamperes, C in millimoles per liter, D in cm^2/sec ., m in mg./sec., t in seconds, and F in coulombs, eq. 1 becomes

$$i_d = 605nD^{1/2}Cm^2/it^{1/2} \quad (3)$$

or

$$K = 605nD^{1/2}m^2/it^{1/2} \quad (4)$$

The quantities m and t in this equation, and hence K , depend on the characteristics of the particular capillary that is used, and on the pressure on the dropping mercury.

Maas⁹ has shown that the amount of mercury flowing from the capillary per sec. under the pressure P , can be expressed fairly accurately by the familiar hydrodynamical equation of Poiseuille

$$m = w/t = \pi\rho Pr^4/8L\eta \quad (5)$$

in which w is the weight of mercury flowing in t sec. from a capillary of radius r , and length L , ρ is the density of mercury, and η the viscosity of mercury. P is usually expressed as the difference in height between the tip of the dropping electrode and the mercury level in the reservoir. According to this equation, m should be directly proportional, and t should be inversely proportional, to P , so that eq. 4 can be written as

$$K = knD^{1/2}P^{1/2} \quad (6)$$

This relation has been verified experimentally by Ilkovic,⁴ and particularly by Maas.⁹ It is very

(9) J. Maas, Dissertation, Amsterdam, 1937; *Coll. Czech. Chem. Comm.*, **10**, 42 (1938).

useful in practical work for correlating diffusion currents obtained with the same capillary under different pressures.

From eq. 4 the relation between K for a given substance and the geometrical properties of the capillary should be given by

$$K = k'm^{2/3}t^{1/6} \quad (7)$$

Therefore, the various diffusion current constants of a given substance obtained with different capillaries, or with the same capillary at different pressures, under otherwise identical conditions, should bear the same relation to each other as the values of the product $m^{2/3}t^{1/6}$ for the different capillaries. Maas⁹ tested eq. 7 with many different capillaries, and he found with cadmium that it was obeyed with an accuracy of about $\pm 2\%$ when the drop time was greater than about three seconds. The importance of this relation in quantitative polarographic analysis is at once evident, since it makes possible a simple correlation of diffusion currents obtained with different capillaries.^{3d,6}

Ilkovic⁴ and Lingane⁶ have shown that the amount of mercury flowing from the capillary per sec. is practically constant, and independent of the potential of the dropping electrode, provided the temperature and pressure on the dropping mercury are kept constant (see Table I). Furthermore, Kolthoff and Lingane^{3d} have shown that, at constant pressure and temperature, m is also practically independent of the medium in which the drops form. In other words, at constant temperature and constant pressure on the dropping mercury, m is practically constant and independent of the interfacial tension at the mercury-solution interface.

On the other hand, the drop time t is practically directly proportional to the interfacial tension, and since the latter depends on the potential of the dropping electrode (electro-capillary curve of mercury), and also on the medium in which the drops form, t also depends on these factors. Since K is proportional to $t^{1/6}$, it will depend on the potential of the dropping electrode and the medium in which the drops form.

K also depends on the temperature. Nejedly,^{10a} and Majer,^{10b} have shown experimentally that the diffusion currents of most metal ions increase by about 2 to 2.5% per degree increase in tem-

perature. Ilkovic¹¹ and Lingane⁶ showed that the observed temperature coefficient was due chiefly to the increase in the diffusion coefficient of the reducible ion with increasing temperature, and to a lesser degree to the decrease in the viscosity of mercury and the corresponding increase in m (eq. 5). In practical work, the temperature should be controlled to at least $\pm 0.5^\circ$, in order to keep variations due to the temperature effect within $\pm 1\%$.

From the investigations cited above, the correctness of the terms C , $m^{2/3}$, and $t^{1/6}$ in the Ilkovic equation has been established satisfactorily. The purpose of the present study was to investigate the influence of the diffusion coefficient term, $D^{1/2}$, and to obtain data for a direct test of the Ilkovic equation, and the validity of the constant 0.627. The only previous direct comparison of experimentally measured diffusion currents with those calculated by means of eq. 1 has been made by Ilkovic.⁴ However, Ilkovic tested eq. 1 with data from only two experiments, and a more thorough test is therefore very desirable. In the present investigation, we determined the diffusion current constants of various metal ions, and also of iodate and ferricyanide ions, in 0.1 *N* potassium chloride, and compared the data so obtained with the corresponding values calculated by means of the Ilkovic equation.

Experimental

Electrical Circuit.—At the time this study was started, a polarograph^{9,12} was not available and the c. v. (current-voltage) curves were therefore measured manually by means of the simple circuit shown in Fig. 1. The e. m. f. applied to the cell was regulated by means of a rheostat, consisting of two radio rheostats of the "potentiometer" type connected in series, and it was measured with a potentiometer. One rheostat for coarse adjustment had a resistance of 1000 ohms, and the other, for fine adjustment, 10 ohms. The current through the cell (usually less than 50 microamperes) was measured either by measuring the potential drop across the standard resistance R (four-dial precision resistance box) with a potentiometer, and applying Ohm's law or, more conveniently, by means of the calibrated galvanometer. The galvanometer was a moving coil mirror and scale instrument with a maximum sensitivity of 0.005 microamp./mm./m., and a period of about forty seconds. It was provided with a curved scale which was read with a telescope in the usual way. By means of the shunt closest to the galvanometer (radio "potentiometer" rheostat), the sensitivity was adjusted so that at full sensitivity 1 mm. on the scale corresponded to exactly 0.01 microamp. Then by means of the Ayrton

(10) (a) V. Nejedly, *Coll. Czech. Chem. Comm.*, **1**, 319 (1929);
(b) V. Majer, *Z. anal. Chem.*, **92**, 321 (1933).

(11) D. Ilkovic, *Coll. Czech. Chem. Comm.*, **10**, 249 (1938).

(12) J. Heyrovsky and M. Shikata, *Rec. trav. chim.*, **44**, 496 (1925).

shunt the sensitivity could be adjusted decimally from 0.01 microamp. to 1000 microamp. per mm. The galvanometer was calibrated carefully by impressing a small e. m. f. across both it and the standard resistance (10,000 ohms), measuring the potential drop across the standard resistance with the potentiometer, and applying Ohm's law. The relation between the galvanometer deflections and the current was found to be linear over a range of 30 cm. on the scale, within $\pm 0.5\%$. The resistance box was left permanently in series with the cell and galvanometer, in order to be able to frequently check the readings of the latter.

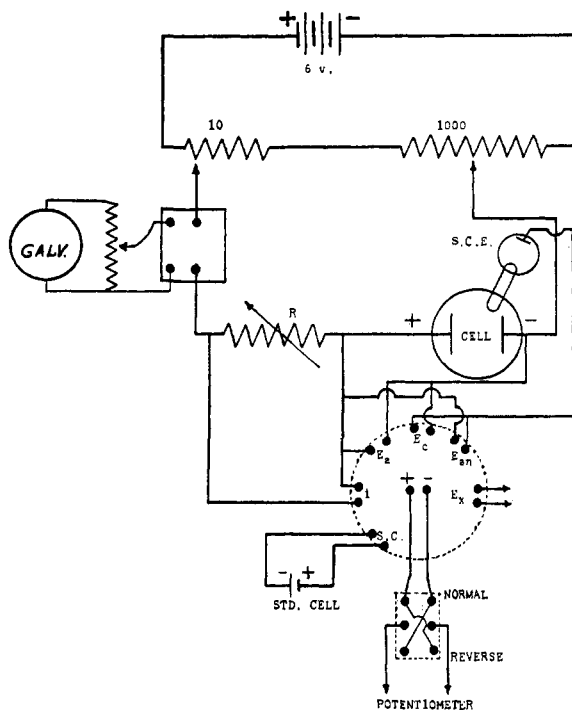


Fig. 1.—Principle of circuit for manually obtaining current-voltage curves.

With the particular shunts used the galvanometer was over-damped, but this was a distinct advantage since it reduced the magnitude of the oscillations caused by the periodic change in current during the formation of the mercury drops. During the formation of each mercury drop the current increases many fold, and the maximum current just before the drop falls from the capillary is usually several times greater than its minimum value at the very beginning of the drop formation, as Ilkovic,¹³ and Brdiccka,¹⁴ have demonstrated with a sensitive oscillograph. The Ilkovic equation (eq. 1) refers to the average current during the formation of each mercury drop, and hence in this study the average current (average of the galvanometer oscillations) was measured. With the galvanometer over-damped, the oscillations were quite small, usually only about $\pm 2\%$ of the average current, and the average current readily could be read with a precision of $\pm 1\%$ or better in most cases.

(13) D. Ilkovic, *Coll. Czech. Chem. Comm.*, **8**, 13 (1936).

(14) R. Brdiccka, *ibid.*, **8**, 419 (1936).

The e. m. f. applied to the cell, the potentials of the dropping electrode and the quiet electrode against a saturated calomel reference electrode (S. C. E. in Fig. 1), and the potential drop across the standard resistance, were all measured with a potentiometer. To facilitate these readings, a circular six-position double-pole selector switch was used as shown in Fig. 1.

Fabrication of the Dropping Electrode.—The capillaries were prepared by drawing out the end of 20 cm. lengths of Pyrex capillary tubing (ca. 1 mm. i. d. and 6 mm. o. d.) until the internal diameter of the tip was about 0.03 mm. The end of the tube was thickened in the flame before drawing so that the tip would not be too slender and fragile. The tip was then cut off until the length of the narrowest part was about 2 or 3 cm., and of uniform internal diameter. The exact dimensions must be decided by trial and error, until a capillary is obtained whose drop time in dilute potassium chloride solution can be adjusted to between three and six seconds by suitable adjustment of the pressure on the dropping mercury. The method of fabricating suitable capillaries has been discussed in detail by Heyrovsky,^{3a} Hohn,^{3b} and especially by Maas.⁹

Most previous workers with the dropping electrode connected the capillary to the mercury reservoir by means of rubber pressure tubing, and varied the pressure on the dropping mercury by simply raising or lowering the mercury reservoir. In order to avoid all possible contamination from rubber connections we sealed the capillary directly to the mercury reservoir (made from a 50-ml.

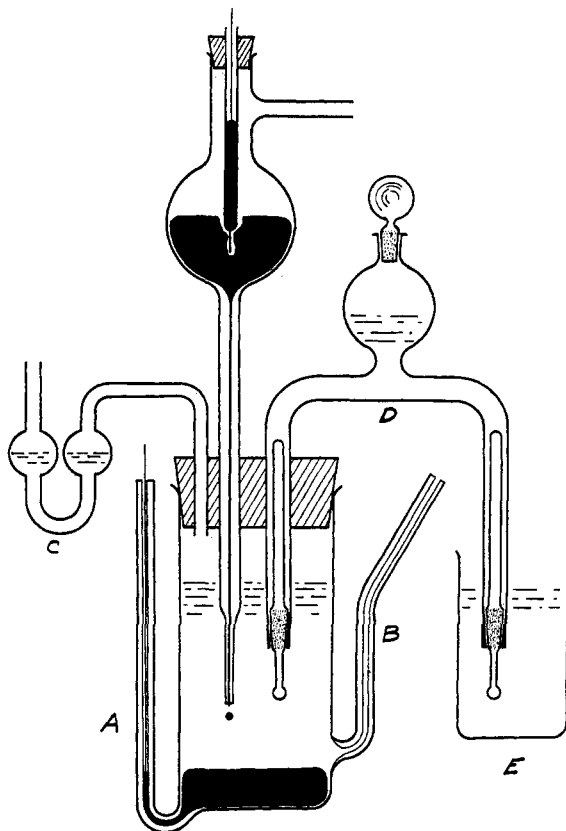


Fig. 2.—Dropping electrode and electrolysis cell.

Pyrex distilling flask) as shown in Fig. 2. Somewhat similar arrangements have been described recently by Müller, Garman, and Droz,¹⁵ and by Peracchio and Meloche.¹⁶ The pressure on the dropping mercury was regulated by means of the arrangement shown in Fig. 3. The total pressure was equal to the height of the mercury column in the dropping electrode itself, plus or minus the pressure indicated by the open-end mercury manometer.

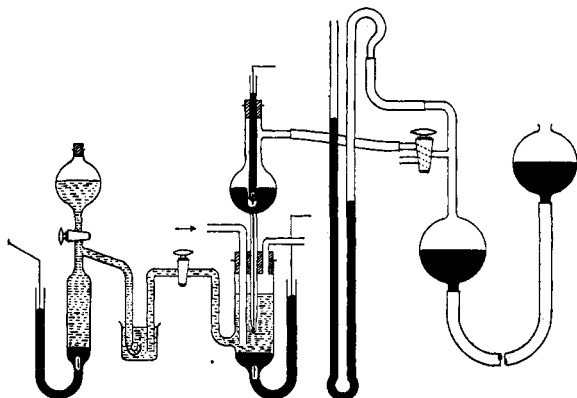


Fig. 3.—Arrangement for regulating the pressure on the dropping mercury.

When not in use the tip of the capillary was immersed in pure mercury, with the pressure reduced to prevent the mercury from draining out. Before being placed in a solution the pressure is increased so that the issuing mercury drops prevent the entrance of solution into the tip. After long use, the interior of the tip occasionally became dirty, causing an irregular flow of mercury. When this happened the capillary was cleaned with aqua regia, which always restored the original properties. With these simple precautions, we have used a single capillary for over a year. The same capillary, with the same pressure on the dropping mercury, was used in all the measurements recorded in this paper.

The Cell.—The most popular type of polarographic cell has the shape of an Erlenmeyer flask,⁸ but this style is not suitable for use in a thermostat, nor for measuring the potentials of the electrodes against an external reference electrode during the course of an experiment. We found that the cell shown in Fig. 2 was more suitable for these purposes. Mercury for the quiet electrode is poured into the cell until it rises part way into the capillary side tube A, and electrical connection is made by means of a platinum wire immersed in the mercury in this side tube. The capillary gas-inlet tube B is for the introduction of nitrogen or hydrogen to remove air from the solution, and C is a gas-outlet trap containing either pure water or a little of the cell solution.

The salt bridge D¹⁷ is for making electrolytic connection to a saturated calomel reference electrode, and it was usually filled with the same solution as in the cell.

(15) R. H. Müller, R. L. Garman, M. E. Droz and J. F. Petras, *Ind. Eng. Chem., Anal. Ed.*, **10**, 339 (1938).

(16) E. S. Peracchio and V. W. Meloche, *THIS JOURNAL*, **60**, 1770 (1938).

(17) G. W. Irving, Jr., and N. R. Smith, *Ind. Eng. Chem., Anal. Ed.*, **6**, 480 (1934).

The external end of the bridge dipped into an intermediate vessel E filled with concentrated potassium chloride solution, into which the side arm of the calomel reference electrode also dipped.

General Technique.—The cell was first assembled and flushed out with purified nitrogen, and the solution was then introduced from a pipet. The passage of nitrogen was continued for twenty to thirty minutes to remove dissolved air from the solution, because oxygen is easily reduced at the dropping electrode and interferes with the c. v. curves of the ions that we studied. The nitrogen stream was stopped before an experiment was begun, because its stirring effect causes the current to be erratic. All experiments were made without any stirring of the solution.

The pressure was adjusted to the desired value (21.8 cm.), and the drop time was measured with a stop watch by counting ten or more drops. The cell was then connected into the circuit, the applied e. m. f. was increased by steps and the corresponding current was measured at each value of the applied e. m. f. The potential of the dropping electrode (and occasionally that of the quiet anode) was measured against the calomel reference electrode at each value of the applied e. m. f. Hereinafter, the current is expressed in microamperes, designated by i , the total e. m. f. applied to the cell is designated by E_a , the potential of the dropping electrode by $E_{d.e.}$ or E_c (cathode), and that of the quiet electrode by $E_{q.e.}$ or $E_{an.}$ (anode). All potential values refer to the saturated calomel electrode as zero, and the signs of $E_{d.e.}$ and $E_{q.e.}$ were taken as positive when the electrode in question was positive to the calomel electrode, and *vice versa*.

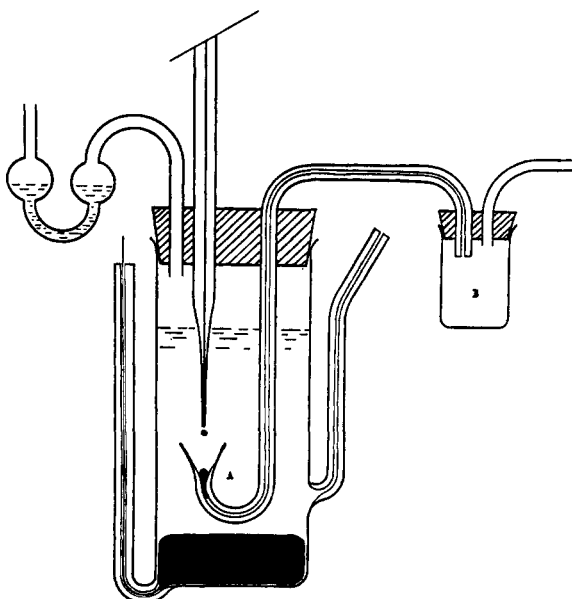


Fig. 4.—Arrangement for collecting mercury drops.

In order to determine the amount of mercury flowing from the capillary per second at various values of E_c without admitting air to the cell or removing it from the thermostat, a given number of mercury drops was collected by means of the simple arrangement shown in Fig. 4.

The drops were collected in the cup A, formed by enlarging the end of a 1 mm. i. d. capillary tube. The capillary tube was bent as shown so that the collected mercury could be sucked over into the small weighing bottle B. The capillary tube fitted loosely enough in the stopper so that it could be rotated to turn the collecting cup out of the way of the falling drops, but yet snug enough to prevent the ingress of air. The collecting cup was swung under the dropping electrode until the desired number of mercury drops was collected (usually 25), and was then rotated out of the way of the falling drops. The time required for the formation of the number of drops collected was measured simultaneously with a stop watch. The collected drops, together with three or four drops of solution, were then sucked over into the weighing bottle B. The globule of mercury was washed with water, then with acetone, and was weighed after drying for a few minutes in the air at room temperature.

All measurements were made with the cell and reference electrode in a water thermostat at $25.00 \pm 0.02^\circ$.

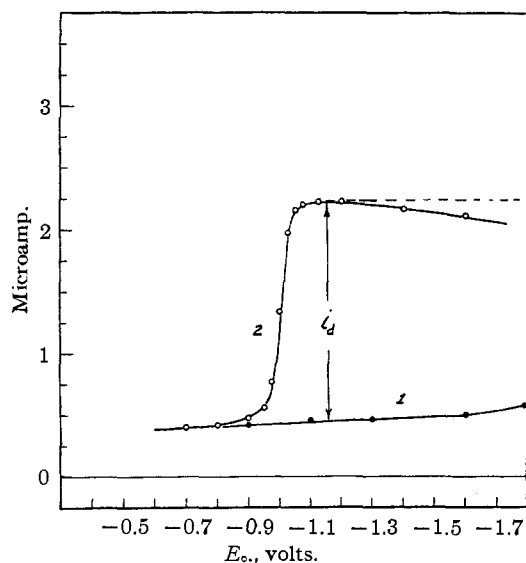


Fig. 5.—Typical current-voltage curve of zinc ions and method of measuring the diffusion current: curve 1, residual current of 0.1 *N* potassium chloride containing 2×10^{-6} molar sodium methyl red; curve 2, 2.15×10^{-4} molar zinc sulfate in 0.1 *N* potassium chloride containing 2×10^{-6} molar sodium methyl red.

Method of Measuring the Diffusion Currents.—When a solution of an indifferent salt, such as potassium chloride, is electrolyzed with the dropping electrode, a small “residual current,” which increases practically linearly with the applied e. m. f., is observed before the decomposition potential of the potassium ions is finally reached. In a very pure solution of an indifferent salt, such a residual current is due chiefly to the transfer of charges across the mercury-solution interface in the process of charging the dropping electrode to each particular value of the potential.^{8d,9,18} This current is analogous to the small current

that flows across an ordinary condenser in the process of charging or discharging (except that with the dropping electrode the current is continuous due to the continuously increasing area), and hence it is called a “charging current,” or “condenser current.” The residual current will also include a small “faradaic” current if traces of reducible impurities (*e. g.* oxygen) are present in the solution. In any event, the residual current must be subtracted from the observed diffusion current of a reducible substance in order to obtain the true diffusion current. This correction obviously becomes increasingly more important the smaller the concentration of the reducible substance being determined.

Several more or less empirical methods for graphically evaluating the diffusion current have been discussed by Hohn,^{3b} Maas,⁹ and Borchardt, Meloche and Adkins.¹⁹ In the present study we were concerned with the measurement of the diffusion current with only one reducible ion in the solution, and the following direct method of correcting for the residual current was found to be most satisfactory for our purpose. The residual current of the pure solution of the indifferent salt, with no reducible substance present, was determined at various potentials (Table I), and the values so obtained were subtracted from the observed diffusion currents. A typical c. v. curve, which illustrates this method of measuring the diffusion current, is shown in Fig. 5. The decrease in the diffusion current with increasing negative potential is due to the decrease in $m^{2/3} t^{1/6}$ (Table I).

Influence of the Potential of the Dropping Electrode on the Quantities m , t , and $m^{2/3} t^{1/6}$.—The influence of the potential of the dropping electrode on the quantities m , t , and the product $m^{2/3} t^{1/6}$, in air-free 0.1 *N* potassium chloride is demonstrated by the data in Table I.

TABLE I

THE PRODUCT $m^{2/3} t^{1/6}$ AS A FUNCTION OF THE POTENTIAL OF THE DROPPING ELECTRODE AND THE COMPOSITION OF THE SOLUTION

$P = 21.8 \pm 0.2$ cm. Temp. = 25° . 0.2 ml. of 0.1% sodium methyl red added per 50 ml. of solution.

E_c , vs. S. C. E., v.	i , microamp.	m , mg. sec. ⁻¹	t , sec.	$m^{2/3} t^{1/6}$, mg. ^{2/3} / sec. ^{-1/2}
(a) 0.1 <i>N</i> KCl				
0.0	-0.18	2.651	2.75	2.27
- .5	+ .10	2.621	3.08	2.29
- .8	.21	2.626	2.88	2.28
-1.1	.29	2.625	2.66	2.24
-1.5	.38	2.672	2.18	2.18
-1.9	.70	2.681	1.56	2.08
(b) 0.0011 <i>M</i> CdSO ₄ in 0.1 <i>N</i> KCl				
-0.8	8.90	2.605	2.86	2.26
(c) 0.0011 <i>M</i> CdSO ₄ in 1 <i>N</i> KCl				
-0.8	8.92	2.603	2.85	2.26
(d) 0.001 <i>M</i> TiCl ₃ . No other salt present				
-0.8	10.9	2.621	2.97	2.28
(e) (d) repeated after saturating solution with air				
-0.8	14.8	2.646	2.99	2.29

(19) G. T. Borchardt, V. W. Meloche and H. Adkins, *THIS JOURNAL*, **59**, 2171 (1937).

(18) D. Ilkovic, *Coll. Czech. Chem. Comm.*, **8**, 170 (1936).

It will be noted that the amount of mercury flowing from the capillary per sec. was virtually constant and independent of the potential of the dropping electrode. On the other hand, the drop time, t , first increased, passed through a maximum at about -0.5 v., and then decreased rapidly with increasing negative potential, according to the electrocapillary curve. Corresponding to the variation of t , the product $m^{2/3}t^{1/6}$ first increased slightly, passed through a very flat maximum, and then decreased with increasing negative potential. Since this product is a function of only the sixth root of t , its variation was of course much less than that of t . For practical purposes, the product $m^{2/3}t^{1/6}$ may be considered to be constant ($\pm 1\%$) over the potential range from zero up to about -1.0 v., but at more negative potentials its decrease must be taken into account (Fig. 5). These results agree with similar data obtained by Ilkovic.⁴

The remaining data in Table I show that the product $m^{2/3}t^{1/6}$ did not change appreciably during the discharge of cadmium ions, thallos ions, or oxygen, but remained the same as in the pure 0.1 N potassium chloride solution. The data also demonstrate that the product $m^{2/3}t^{1/6}$ is independent of the chloride ion concentration between 0.001 and 1 N .

Test of the Ilkovic Equation.—In order to obtain data for a direct test of the Ilkovic equation, we determined the diffusion currents of various concentrations of thallos, lead, cadmium, zinc, iodate, and ferricyanide ions in 0.1 N potassium chloride at 25° . A trace of methyl red (0.2 ml. of 0.1% sodium methyl red per 50 ml.) was added to the solutions to eliminate the maxima otherwise present, and to obtain well-defined diffusion currents. The characteristics and methods of eliminating maxima have been discussed in detail by Heyrovsky,^{3a,20} Ilkovic,²¹ and Koltzoff and Lingane.^{3d} A typical example of the elimination of a maximum by methyl red is given in Fig. 6. Methyl red itself is reducible at the dropping electrode, and hence contributes to the diffusion current. However, the concentration required to suppress maxima is so small (usually less than 2×10^{-5} molar) that its effect on the diffusion current is usually negligible or can be corrected for.

(20) J. Heyrovsky, "A Polarographic Study of the Electrokinetic Phenomena of Adsorption, Electroreduction, and Overpotential Displayed at the Dropping Mercury Cathode," *Actualités Scientifique et Industrielle*, No. 90, Hermann et Cie., Paris, 1934.

(21) D. Ilkovic, *Coll. Czech. Chem. Comm.*, **8**, 13 (1936).

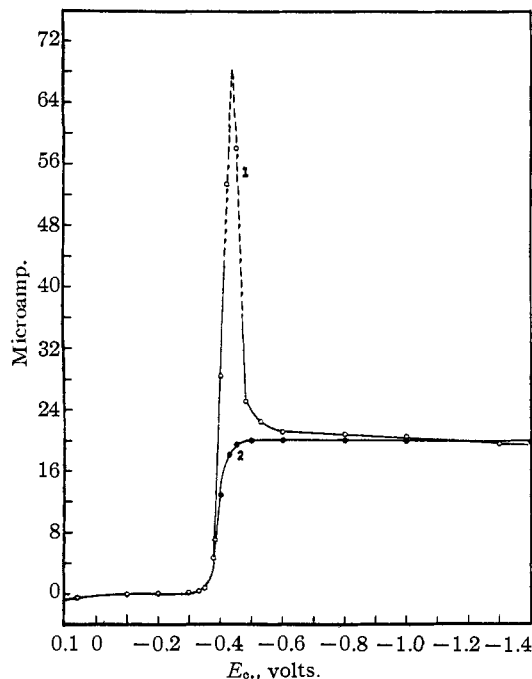


Fig. 6.—Suppression of a maximum by methyl red: curve 1, 55 ml. of 2.3×10^{-3} M lead nitrate in 0.1 N potassium chloride (open circles); curve 2, repeated after addition of 0.1 ml. of 0.1% sodium methyl red (solid circles).

We found that the diffusion currents of lead, thallos, cadmium, zinc, iodate, and ferricyanide ions were directly proportional to their concentrations in 0.1 N potassium chloride, when a trace of sodium methyl red was present and proper correction was made for the residual current. In the case of the metal ions the linear relation (eq. 2) was followed accurately over a concentration range from 10^{-4} up to 10^{-2} molar. This is demonstrated by the typical set of data obtained with lead ions given in Table II. The corrected values

TABLE II
DIFFUSION CURRENTS OF VARIOUS CONCENTRATIONS OF LEAD NITRATE IN 0.1 N POTASSIUM CHLORIDE

Air removed from the solutions with purified nitrogen, and 0.1 ml. of 0.1% sodium methyl red added per 50 ml. of solution. Temp. = 25° , $P = 21.8$ cm., $m^{2/3}t^{1/6} = 2.28$ mg.^{2/3} sec.^{-1/2}.

Pb(NO ₃) ₂ mmol. per liter	i_d obsd. microamp.	i_d corr. microamp.	K microamp./ mmol./l.
0.129	1.29 ^a	1.14	8.84
.392	3.60	3.45	8.80
.925	8.17	8.02	8.67
2.28	20.2	20.0	8.78
4.17	36.8	36.6	8.78
7.14	63.0	62.8	8.80
			Av. 8.78

^a Diffusion currents measured at $E_{d.} = -0.7$ v.

of the diffusion currents in the third column of this table were obtained by subtracting the residual current of the potassium chloride solution containing methyl red at -0.7 v. (Table I) from the observed diffusion currents.

In the case of iodate, we found that the linear relation between i_d and c was obeyed over a concentration range from 2×10^{-4} to 10^{-3} molar, and in the case of ferricyanide from 2×10^{-4} to 5×10^{-3} molar.

An external saturated calomel electrode, rather than the usual quiet pool of mercury on the bottom of the cell, was used as anode to obtain the current-voltage curves of ferricyanide ions. This was necessary because the ferricyanide ions were reduced partially by contact with the large mercury anode. Electrolytic connection between the external calomel anode and the cell was made by means of the salt bridge shown in Fig. 2. The electrolyses of the ferricyanide solutions were carried out in the cell shown in Fig. 4. The mercury drops from the dropping electrode were collected in the cup A and periodically sucked over into the weighing bottle B, to minimize contact of the solutions with mercury.

In Table III is given a comparison of the observed diffusion current constants of the foregoing ions with the corresponding values calculated from eq. 4.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED DIFFUSION CURRENT CONSTANTS

Determined in 0.1 *N* potassium chloride containing 0.1 to 0.2 ml. of 0.1% sodium methyl red per 50 ml. Air was removed from the solutions with purified nitrogen. $P = 21.8 \pm 0.2$ cm. Temp. = 25° .

Ion	$m^2/s_1^{1/2}$ mg. ² / ₃ sec. ^{-1/2}	D^0 cm. ² sec. ⁻¹ $\times 10^5$	<i>K</i>		Diff., %
			microamp./mmol./l. Obsd.	Calcd.	
Tl ⁺	2.28	2.00	6.13	6.16	+0.7
Pb ⁺⁺	2.28	0.98	8.78	8.67	-1.3
Zn ⁺⁺	2.24	.72	7.65	7.27	-5.2
Cd ⁺⁺	2.28	.72	8.00	7.40	-8.0
IO ₃ ⁻	2.18	1.09	26.3	26.2	-0.4
Fe(CN) ₆ ⁼	2.28	0.89	3.78	4.12	+8.3

In order to calculate the diffusion current constants it was necessary to know the diffusion coefficients of the various ions in the presence of an excess of potassium chloride. Since such data are not available in the literature for the reducible ions in question, we calculated the diffusion coefficients by means of eq. 9 below.

When a single pure salt is diffusing its constituent positive and negative ions are not free to

diffuse independently according to their characteristic diffusion coefficients. The *tendency* for unequal rates of diffusion, due to the different intrinsic mobilities of the positive and negative ions, causes the accumulation of space charges in the diffusion layer, and the resulting diffusion potential acts as a balancing force constraining the positive and negative ions to diffuse at the same net rate. However, if a sufficiently large excess of some foreign salt is present at the same concentration on both sides of the diffusion layer, the restraining diffusion potential is practically eliminated, and the ions of the diffusing salt are then more or less free to diffuse independently according to their characteristic diffusion coefficients.^{6,22-24} This is the condition obtaining in the present experiments in which the reducible ions were present in small concentrations in a large excess of potassium chloride, and hence the diffusion coefficient in eq. 4 is the characteristic or individual diffusion coefficient of the reducible ions.

In general, the diffusion coefficient per mole of a substance is given by

$$D = RT\delta \quad (8)$$

where δ is the absolute mobility of the diffusing particles, that is, their velocity under unit force. In the case of ions, the velocity under unit potential gradient is given by the familiar relation λ_1^0/F , where λ_1^0 is the equivalent conductance of the ions at infinite dilution, and F is the faraday. When the potential gradient is unity, the force on a mole of z -valent ions is equal to zF . Hence, the characteristic molar diffusion coefficient of an ionic species at infinite dilution and 25° can be calculated by means of the following equation, originally derived by Nernst²⁵

$$D_1^0 = \frac{RT\lambda_1^0}{z_1 F^2} = 2.67 \times 10^{-7} \frac{\lambda_1^0}{z_1} \text{ (cm.}^2 \text{ sec.}^{-1}) \quad (9)$$

This equation is strictly valid only at infinite dilution. The diffusion coefficient of an ion at any finite concentration will differ more or less from the value given by eq. 9 because of inter-ionic forces. It might be thought that the diffusion coefficient of an ion could be computed from its equivalent conductance at a particular ionic strength,^{4,7} but this is not true, because, as McBain and Liu²⁶ have pointed out, the equiva-

(22) Abegg and Bose, *Z. physik. Chem.*, **30**, 545 (1899).

(23) G. Jander and A. Winkel, *ibid.*, **A149**, 97 (1930).

(24) Haskell, *Phys. Rev.*, **27**, 145 (1908).

(25) W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(26) J. W. McBain and T. H. Liu, *THIS JOURNAL*, **53**, 59 (1931).

lent conductance of an ion is a measure of its mobility only at infinite dilution. At any finite concentration the equivalent conductance is governed by the magnitude of interionic forces, in addition to the intrinsic mobility of the ions. The effect of interionic forces is much smaller in the case of diffusion, than in the more complicated process of electrolytic conduction,²⁶⁻²⁸ and hence the diffusion coefficients of salts decrease much less than their equivalent conductances with increasing ionic strength.^{27,28}

We assumed in interpreting our experimental results that the diffusion coefficients of the various reducible ions in 0.1 *N* potassium chloride were the same as at infinite dilution given by eq. 9. The diffusion coefficients at infinite dilution given in the third column of Table III were calculated by means of eq. 9, using data for the equivalent ionic conductances from the "International Critical Tables." The equivalent conductance of the ferricyanide ion at infinite dilution was taken from the recent paper of Hartley and Robinson.²⁹

The diffusion current constants in the fifth column of Table III were calculated by means of eq. 4, using the calculated values of D^0 in column three and values of the product $m^{2/3}t^{1/6}$ from Table I at the potential at which the diffusion currents were measured. For example, the calculated diffusion coefficient of the lead ion at infinite dilution is 0.98×10^{-5} cm.² sec.⁻¹, and from Table I the product $m^{2/3}t^{1/6}$ at -0.7 v. for the particular capillary used was 2.28 mg.^{1/3} sec.^{-1/3}. Since n is 2 in the discharge of lead ions, the calculated diffusion current constant is $K = 605 \times 2 \times (0.98 \times 10^{-5})^{1/2} \times 2.28 = 8.67$ microamp./millimole/liter.

Discussion

It will be observed from the data in Table III that the agreement between the observed and calculated values of K for thallos, lead, and iodate ions is within the limits of experimental error. In the cases of zinc and cadmium ions the observed values of K are, respectively, 5 and 8% greater than the calculated values. This may be due to the existence of a considerable fraction of the cadmium and zinc in the form of ions of the type $CdCl^+$ and $ZnCl^+$ in the presence of the excess of chloride ions. Such ions, being univalent

and probably less highly hydrated than divalent ions, probably have a much larger diffusion coefficient, and hence produce a larger diffusion current than simple (hydrated) divalent cadmium and zinc ions at the same concentration.

It will be noted that the observed diffusion current constant of ferricyanide ions is 8% smaller than the calculated value. This may have been caused by an appreciable amount of direct "chemical" interaction of ferricyanide ions with the mercury of the dropping electrode, which would decrease the number of ferricyanide ions available for the electro-reduction, and therefore decrease the diffusion current.

It may be mentioned that the only previous direct experimental test of the Ilkovic equation to be found in the polarographic literature is in the original paper of Ilkovic.⁴ Ilkovic tested his equation in only two cases: in the discharge of 0.001 *M* cadmium ions from 0.1 *N* sulfuric acid, and in the discharge of 0.001 *M* hydrogen ions from 0.1 *N* potassium chloride. He concluded that the observed diffusion current of the cadmium ions was 9% smaller than the calculated value; just the opposite of our results. However, in calculating the diffusion coefficient of cadmium ions, he overlooked the valence factor in eq. 9. He also employed the equivalent conductance of the cadmium ion at 0.001 *M* rather than at infinite dilution, which as we have pointed out is not justified. Hence his calculated value of the diffusion coefficient of the cadmium ions (1.20×10^{-5} cm.² sec.⁻¹) was incorrect.

In view of the complexity of the diffusion and discharge processes at the dropping electrode the agreement between the observed and calculated values of K in Table III is gratifying. It is evident that the Ilkovic equation, and the postulates on which it is based, are essentially correct.

Heyrovsky^{3a} has stated that the diffusion currents of the same equivalent concentration of various reducible substances, with the exception of hydrogen ions and a few complex ions, will be the same when all other conditions are constant. It is evident from the foregoing discussion and the data in Table III that this is only a very rough approximation, and it is not a general rule. The diffusion currents at the same equivalent concentration of two substances, determined under identical conditions, can only be equal in the special case that their diffusion coefficients are equal, and in general this will not be the case.

(27) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(28) P. Van Rysselberghe, *THIS JOURNAL*, **60**, 2326 (1938).

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

Summary

1. The significance of the various terms in the Ilkovic equation for the diffusion currents obtained with the dropping mercury electrode is discussed. The term "diffusion current constant" is introduced to characterize the diffusion current obtained with a solution containing one millimole per liter of the reducible substance. The significance and method of computing the diffusion coefficient term in the Ilkovic equation is discussed.

2. A simple apparatus for manually obtaining current-voltage curves with the dropping mercury electrode is described.

3. The diffusion current constants of thallos, lead, cadmium, zinc, iodate, and ferricyanide

ions were determined in 0.1 *N* potassium chloride at 25°, and compared with the corresponding values calculated from the Ilkovic equation. In the cases of thallos, lead, and iodate ions the agreement between the observed and calculated diffusion current constants was within the limits of experimental error (about ±1%). In the cases of zinc and cadmium ions the observed diffusion current constants were, respectively, 5 and 8% larger than the calculated values. The observed diffusion current constant of ferricyanide ions was 8% smaller than the calculated value.

It is concluded that the Ilkovic equation is essentially correct.

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The Reaction of Sulfur Trioxide with Sodium Chloride

BY D. J. SALLEY

Sulfur trioxide and sodium chloride interact in two ways, depending on the temperature region in which the reaction is carried out. From room temperature to about 100° an addition complex of uncertain composition is formed.^{1,2} Above about 200°, a profound change occurs, but investigators differ as to the products. Some claim that only chlorine and sodium sulfate are formed,³ others include sulfur dioxide,⁴ while still others suggest that oxygen affects the reaction course.⁵ Since several possible over-all reactions involving these reactants and resultants may be written down, all of them apparently thermodynamically permissible, it was of interest to identify with certainty the products of the high temperature reaction and to ascertain the relative amounts produced. From such knowledge, it might be decided whether a single simple reaction was occurring or whether several were taking place simultaneously.

Identification of Reaction Products

The identity of the products and the quantitative methods of their analysis were established in preliminary flow experiments. In these, the low

temperature addition complex, made by passing sulfur trioxide over salt at about 90°, was held at several temperatures between 220 and 444°; nitrogen was used as the carrier gas. The volatile products were frozen out at -78 and -180°, and by fractional distillation in vacuum between these low temperatures, they were separated into several fractions. In this manner, unchanged sulfur trioxide was found; sulfur dioxide and chlorine were each identified by color and smell, and in aqueous solutions of these fractions by qualitative test. Substitution of oxygen as the carrier gas or decomposition of the addition complex in vacuum gave only these same products. None of the various possible sulfur-chlorine or sulfur-oxygen-chlorine compounds was detected.

When the gaseous decomposition products were led into a single large trap filled with glass beads, all could be frozen out at -180° and then dissolved without loss in aqueous alkali. The solutions so formed did not give a test for free chlorine (production of iodine from acidified potassium iodide) or sulfur dioxide (decolorization of iodine in acidified potassium iodide), although naturally chloride and sulfate ion tests were strongly positive. Such a result could be obtained, of course, only if the sulfur dioxide and chlorine had been formed in exactly equivalent quantities and were

(1) Schultz-Sellack, *Ann.*, 193 (1871).

(2) Traube, *Ber.*, 46, 2513 (1913).

(3) Schmidt, British Patent 249,474 (1926).

(4) Deacon, British Patent 1908 (1871).

(5) Clemm, British Patent 15,152 (1899).