$\mathfrak{D}'$ in these equations is defined by

$$\mathfrak{D}' = \frac{\mathfrak{D}}{1000\nu\, RT(\overline{\mathfrak{M}}/c)} - 1 \qquad (3)$$

where $\mathfrak{D}$ is the diffusion coefficient and $(\overline{\mathfrak{M}}/c)$ is the mobility term.[5]

Table I contains details of the calculation of $(\overline{\mathfrak{M}}/c)$ and subsequently $\mathfrak{D}'/c^{1/2}$ for lithium nitrate and values for these quantities for cesium nitrate. The values of the limiting conductances and other quantities employed in the calculations are appended at the bottom of Table I.

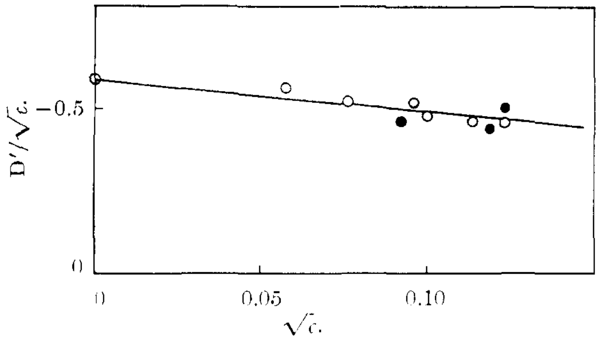

Fig. 1.—Plot for the computation of the activity coefficients of lithium and cesium nitrates at 25°: ○, lithium nitrate; ●, cesium nitrate.

The plot of $\mathfrak{D}'/c^{1/2}$ *vs.* $c^{1/2}$ used for the computation of the activity coefficients is shown in Fig. 1. Here the circles represent the results for lithium nitrate and the dots those for cesium nitrate. The graph is a straight line. Individual plots were used in evaluating the activity coefficients given in Table II from which it appeared that the activity of cesium nitrate is slightly less than lithium nitrate.

TABLE II

ACTIVITY COEFFICIENTS OF ALKALI METAL NITRATES IN DILUTE AQUEOUS SOLUTIONS AT 25°

			$\gamma_\pm$			
c(moles/l.)	$LiNO_3$	$NaNO_3$	KNO_3	$CsNO_3$	$LiClO_4$	$KClO_4$
0.0005	0.9746	0.9746	0.975	0.975	0.975	0.975
.001	.9646	.9646	.964	.964	.966	.966
.002	.9508	.9508	.950	.950	.954	.954
.005	.9251	.9251	.924	.924	.932	.934
.01	.8983	.8983	.896	.896	.913	.915
.015	.8793	.9793	...	...	...	...
.020	.8643	.8643	...	...	...	...

Similar calculation of the activity coefficients of lithium and potassium perchlorates leads to the results recorded in the last two columns of Table II. It is safe to conclude from these results that the activity coefficients of the perchlorate are greater than those of the nitrates. The result of this determination that potassium perchlorate appears to have a greater activity coefficient than the lithium salt at 0.005 and 0.01 seems unusual and may be due to experimental error.

This investigation was supported in part by the Atomic Energy Commission under contract AT-(30-1)-1375.

[5] The equations for computing $(\overline{\mathfrak{M}}/c)$ are given by H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., p. 121-122, equations (4-4-19), (4-4-20) and (4-4-21), Reinhold Publ. Corp., New York, N. Y., 1958. See also refs. 3 and 4.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Voltammetric Membrane Electrodes. I. Basic Theory and Characteristics of Thallous and Cadmium Reduction

BY RICHARD C. BOWERS AND ARTHUR M. WILSON[1]

RECEIVED SEPTEMBER 9, 1957

A new type of voltammetric mercury electrode is described. It is constructed in a manner such that linear finite diffusion of the reducible or oxidizable species takes place across a cellophane membrane. The theoretical equations for diffusion across the membrane are given and a method is outlined for the determination of diffusion coefficients in the membrane. Excellent agreement between theory and experiment is observed for diffusion currents due to the reduction of thallous ion. Adsorption in the membrane markedly affects the apparent diffusion characteristics of cadmium at low concentrations. The experimental results indicate a "homogeneous" phase rather than a porous structure for the cellophane membranes used.

Introduction

Clark, *et al.*,[2] have reported the use of a platinum electrode covered with a film of collodion or cellophane for the determination of oxygen in whole blood. These workers observed that the film prevented poisoning of the electrode while allowing oxygen access to the electrode. An electrode employing mercury as the electrode material and cellophane as an ion permeable diffusion layer has been described briefly by the authors.[3] In theory the membrane should act as a well defined diffusion layer when the electrode is placed in a stirred solution. Due to the finite thickness of the diffusion layer, a steady state is obtained.

The present investigation was initiated to evaluate theoretically the currents obtained with voltammetric membrane electrodes and to characterize more fully the behavior of this type of electrode.

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[1] Taken from the research by the junior author in partial fulfillment for the Ph.D. degree.

[2] L. C. Clark, R. Wolf, D. Granger and Z. Taylor, *J. Appl. Physiol.*, **6**, 189 (1953).

[3] R. C. Bowers and A. Wilson, "Third National Symposium on Instrumental Methods of Analysis," Chicago, Illinois, 1957.

Theoretical

The current at an electrode when the rate-controlling step is the diffusion of the electroactive species to the electrode surface is given by

$$i = n\,FAD\left(\frac{\partial c}{\partial x}\right)_{x\,=\,0} \qquad (1)$$

where n is the number of electrons transferred in the electrode process, F the faraday, A the cross sectional area through which diffusion takes place, D the diffusion coefficient and $(\partial C/\partial x)_{x\,=\,0}$ the concentration gradient at the electrode surface. In order to obtain an expression for the concentration gradient at the electrode surface, the fundamental diffusion equation

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) \qquad (2)$$

must be solved.

Steady-state Limiting Current.—At potentials where essentially instantaneous reduction (or oxidation) of the electroactive species takes place, the boundary conditions for diffusion across the membrane are $C_{(0,\,t)} = 0$ and $C_{(1,\,t)} = C_1$. At the steady state, $\partial C/\partial t = 0$, and it follows immediately that

$$i_\infty = nFADC_1/l \qquad (3)$$

C_1 is the concentration of the electroactive species at the interface of the membrane and the body of the solution and l is the thickness of the membrane.

Instantaneous Currents.—Experimentally, the steady-state current can be approached from either direction. In case A, the electroactive species is present in solution at the time when the potential is applied. Thus, the initial concentration, $C_{(x,\,0)}$, in the membrane is equal to C_1. In case B, the electroactive species is injected into the stirred solution after a potential, sufficient to cause reduction, has been applied. Under these circumstances, the initial concentration within the membrane is zero.

Equation 2 can be solved under the above conditions by using the Laplace transformation. The solution in both cases can be written in two possible forms[4] which result in the following alternate equations for the instantaneous current

Case A:

$$[C_{(x,\,0)} = C_1]$$

$$i_t = nFADC_1/l\left[1 + 2\sum_{m\,=\,1,\,2,\,3\ldots}^{m\,=\,\infty} \exp(-m^2\pi^2Dt/l^2)\right] \qquad (4)$$

or

$$i_t = nFAC_1\sqrt{D/\pi t}\left[1 + 2\sum_{m\,=\,1,\,2,\,3\ldots}^{m\,=\,\infty} \exp(-m^2l^2/Dt)\right] \qquad (5)$$

Case B:

$$[C_{(x,\,0)} = 0]$$

$$i_t = nFADC_1/l\left[1 + 2\sum_{m\,=\,1,\,2,\,3\ldots}^{m\,=\,\infty} (-1)^m\exp(-m^2\pi^2Dt/l^2)\right] \qquad (6)$$

or

$$i_t = 2nFAC_1\sqrt{D/\pi t}\sum_{m\,=\,1,\,2,\,3\ldots}^{m\,=\,\infty} \exp(-m^2l^2/4Dt) \qquad (7)$$

Equations 4 and 6 are generally the more useful forms since their series terms converge rapidly except at short times. However, at times less than 0.19 l^2/D, the magnitude of the series term in (5) is less than 0.01 and this equation reduces to that for linear infinite diffusion.[5,6]

Experimental

Reagents.—1.0 M solutions of recrystallized potassium nitrate were used as supporting electrolyte in all experiments. Stock solutions of thallous chloride were prepared from recrystallized thallous chloride. Cadmium nitrate solutions were prepared from reagent grade chemicals and standardized according to the procedure of Wiley.[7] The mercury employed in the electrode was purified by treatment with a 10% nitric acid solution followed by distillation at reduced pressure.

Electrode.—The electrode was constructed by placing a piece of cellophane membrane, previously swollen in water, over one end of a piece of glass tubing. A polyethylene ring was used to hold the membrane in place, a water-tight seal being obtained between the ring and the glass using Apiezon wax. Prior to assembling, the inside of the glass tube was treated with a silicone. The thickness of the membrane was determined after swelling in water by measuring several thicknesses with a micrometer. The average deviation of a series of such measurements was less than ±1%. A small pool of mercury was placed on top of the membrane and electrical contact made with a platinum or tungsten wire.

Apparatus.—A jacketed cell was used to maintain a constant temperature of 25.0 ± 0.1° except where otherwise stated. Stirring was accomplished using a magnetic stirrer. The solutions were deaerated with Linde H. P. nitrogen. All current–voltage curves and current–time curves were recorded using a Sargent Model XXI polarograph, the pen response of the recorder being approximately four seconds full scale.

Results and Discussion

Residual Currents.—An electrode constructed from commercially available cellophane which has been swollen in water exhibits a somewhat erratic cathodic residual current. This initial residual current can be eliminated by applying a potential of about −1.5 volt *vs.* S.C.E. for a few minutes. After this treatment, the residual current is less than 0.10 μamp. in the potential range of zero to −1.2 v. *vs.* S.C.E. in 1.0 M potassium nitrate. The residual current exhibits a rapid increase as the potential is made more negative than this. In 0.1 M potassium nitrate as well as in 0.1 M tetramethylammonium bromide, the residual current remains negligible out to about −1.5 volt *vs.* S.C.E.

Current–Voltage Curves.—Typical current–voltage curves for the reduction of thallous and cadmium are shown in Fig. 1. A normal appearing wave is obtained upon scanning the potential from left to right; however when scanned in the reverse direction, a shift of the wave to more negative potentials and an anodic stripping current are observed. Both of these effects are due to an accumulation of the reduced species in the mercury. An additional effect of this accumulation is that the "half-wave" potentials are shifted to more negative values with decreasing rate of potential scan (Table I).

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(4) See, for example: J. Crank, "The Mathematics of Diffusion," Oxford University Press, London, 1956, p. 17–22.

(5) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishing Co., New York, N. Y., 1952.

(6) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishing Co., New York, N. Y., 1954.

(7) R. C. Wiley, *Ind. Eng. Chem., Anal. Ed.*, **3**, 14 (1931).

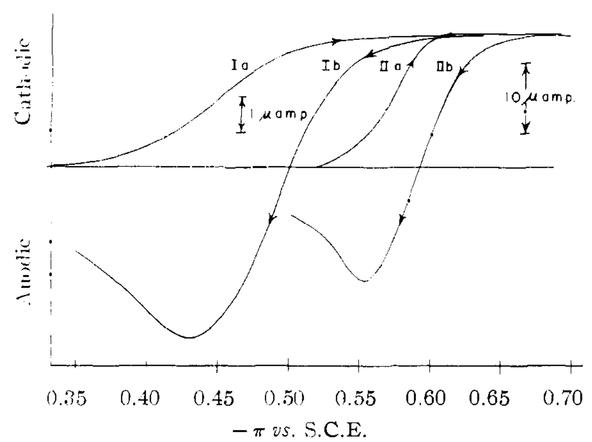

Fig. 1.—Current-voltage curve of 0.244 × 10^{-3} M TlCl (I) and 2.36 × 10^{-3} M $Cd(NO_3)_2$ (II): (a) potential scan from left to right; (b) potential scan from right to left.

A similar phenomenon has been observed with the rotated mercury electrode[8] and the convection mercury electrode.[9] In both of the above cases adequate theoretical treatments of this phenomenon have been given. A more detailed description and a theoretical discussion of the characteristics of current-voltage curves at membrane electrodes will be given in a subsequent publication.

TABLE I

EFFECT OF RATE OF POTENTIAL SCAN ON "HALF-WAVE" POTENTIAL OF 0.244 × 10^{-3} M TlCl

Scan rate (v./sec.)	$\pi_{1/2}$ vs. S. C. E.
0.00250	−0.435
.00125	− .452
.000625	− .463

Limiting Currents.—The form of equation 3 was tested by a series of experiments in which the concentration, area of the electrode and thickness of the membrane were varied independently. Table II summarizes the results obtained.

TABLE II

EFFECT OF CONCENTRATION, AREA AND MEMBRANE THICKNESS ON STEADY-STATE LIMITING CURRENTS

A. Concentration dependence

TlCl C_1 (mmolar)	TlCl i (μamp.)	TlCl i/C_1	$Cd(NO_3)_2$ C_1 (mmolar)	$Cd(NO_3)_2$ i (μamp.)	$Cd(NO_3)_2$ i/C_1
0.00993	0.081	8.2	0.0236	0.111	4.70
.0446	.366	8.21	.119	0.577	4.83
.0938	.772	8.24	.359	1.75	4.86
.289	2.39	8.27	.835	4.09	4.89
.948	7.87	8.30	3.15	15.3	4.86

B. Area dependence

0.0989 mM. TiCl; l = 0.82 × 10^{-2} cm.

A (cm.^{2})	i (μamp.)	i/A
0.408	1.31	0.321
1.09	3.66	.297
2.53	7.88	.311

C. Thickness dependence

0 566 mM TlCl

l × 10^2, cm.	i (μamp.)	il × 10^2
0.81	8.37	6.8
1.62	4.67	7.6
2.47	2.87	7.1

The deviations in i/A and il are of the order of 3 to 5% which is larger than the experimental error associated with the measurement of the current. This much deviation in current also was found in successive experiments using different pieces of cellophane of the same measured thickness and area, and it is felt that the cellophane membrane is somewhat non-uniform both with respect to thickness and diffusion properties. In the concentration dependence experiments, the same membrane was used throughout and excellent results were observed over a wide range of concentrations.

Evaluation of Diffusion Coefficients.—Diffusion coefficients in the membrane can be calculated from observed steady-state limiting currents (equation 3). Two assumptions are inherent in this method however. The cross sectional area through which diffusion occurs will be equal to the area of the electrode only if the membrane is considered to be a "homogeneous" phase.[10,11] If access to the electrode is limited to pores, the area through which diffusion actually occurs will be much smaller than the measured area. In addition, it must be assumed that the concentration of diffusing species at the interface of the membrane and the solution is equal to that in the body of the solution.

The rate of steady-state attainment offers a second method of evaluating the diffusion coefficients. Dividing equations 4 and 6 by equation 3 one obtains

Case A:

$$i_t/i_\infty = 1 + 2 \sum_{m\,=\,1,\,2,\,3\,\ldots}^{m\,=\,\infty} \exp(-m^2\pi^2Dt/l^2) \quad (8)$$

Case B:

$$i_t/i_\infty = 1 + 2 \sum_{m\,=\,1,\,2,\,3\,\ldots}^{m\,=\,\infty} (-1)^m \exp(-m^2\pi^2Dt/l^2) \quad (9)$$

The above equations predict that the rate of steady-state attainment is independent of the area through which diffusion takes place and of the concentration of the electroactive species.

The solid lines in Fig. 2 were constructed from values of the quantity π^2Dt/l^2 which is designated as Θ. The circles represent experimental values from the current–time curves in the reduction of thallous. The time axis for these experimental

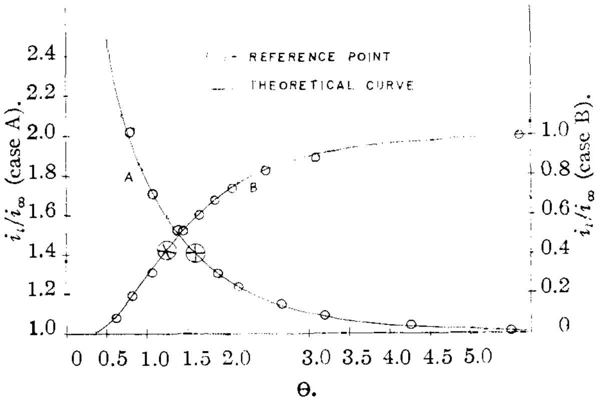

Fig. 2.—Theoretical and experimental steady-state attainment: case A, 1.19 × 10^{-3} M TlCl; case B, $C_{t=0}$ = 0.0742 × 10^{-3} M TlCl, ΔC = 0.0246 × 10^{-3} M TlCl; $\Theta = \pi^2 Dt/l^2$.

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(8) T. S. Lee, THIS JOURNAL, **74**, 5001 (1952).

(9) I. M. Kolthoff, J. J. Jordan and S. Prager, *ibid.*, **76**, 5221 (1954).

(10) J. Wilbrandt, *J. Gen. Physiol.*, **18**, 933 (1935).

(11) T. Teorell, *Disc. Faraday Soc.*, **21**, 9 (1956).

points has been adjusted so that one experimental point from each curve coincides with the theoretical curve.

The values of Θ corresponding to experimental values of i_t/i_∞ can be obtained from these theoretical curves. The quantity Θ/t is a constant equal to π^2D/l^2 and diffusion coefficients can be evaluated from this quantity. An alternate procedure of calculating the diffusion coefficient in case A is to use only the initial portion of the current–time curves since at short times

$$i_t\sqrt{t} = nFAC_1\sqrt{D/\pi} \qquad (10)$$

This method requires the same assumptions with regard to A and C_1 as discussed previously. However, it is to be noted that the use of equation 10 does not necessitate a knowledge of l, the thickness of the membrane.

Table III lists the values of Θ/t and $i_t\sqrt{t}$ obtained from the current–time curves for the reduction of thallous.

TABLE III

ATTAINMENT OF STEADY STATE

$A = 0.424$ cm.^{2}, $l = 2.7 \times 10^{-2}$ cm.

Case A ($C_{t=0} = C_1$) 1.19 mM TlCl					Case B ($C_{t=0} = 0$) 0.0246 mM TlCl			
t (sec.)	i_t (μamp.)	i_t/i_∞	Θ/t	$i\sqrt{t}$	t (sec.)	i_t	i_t/i_∞	Θ/t
15	13.45	2.02	0.051	52.3	12	0.011	0.079	0.052
20	11.38	1.71	.053	51.0	16	.028	.197	.051
25	10.18	1.53	.054	51.0	20	.044	.314	.051
30	9.36	1.41	.053	51.2	24	.061	.432	.052
35	8.75	1.31	.053	50.9	28	.074	.525	.051
40	8.26	1.24	.053	52.2	32	.086	.607	.050
50	7.68	1.15	.052	54.3	36	.096	.683	.051
60	7.29	1.09	.052	56.5	40	.1038	.736	.051
80	6.95	1.04	.049	62.2	48	.1165	.827	.051
∞	6.67	1.00			∞	.1410	1.00	

$D_\infty = 3.70 \times 10^{-6}$ cm.^{2}/sec. $D_\infty = 3.78 \times 10^{-6}$ cm.^{2}/sec.
$D_{\Theta/t} = 3.84 \times 10^{-6}$ cm.^{2}/sec. $D_{\Theta/t} = 3.76 \times 10^{-6}$ cm.^{2}/sec.
$D_{i\sqrt{t}} = 3.51 \times 10^{-6}$ cm.^{2}/sec.

Within experimental error, Θ/t is constant over the entire range of times and $i_t\sqrt{t}$ is constant at short times. The agreement between the diffusion coefficients calculated by the different methods is excellent in both cases A and B.

Tables IV and V summarize the values of the diffusion coefficients obtained for thallous and cadmium over a wide range of concentrations.

TABLE IV

DIFFUSION COEFFICIENTS OF THALLOUS ION AT VARIOUS CONCENTRATIONS

$A = 0.404$ cm.^{2}, $l = 1.8 \times 10^{-2}$ cm.^{2}

Concn. (mM)	$D_\infty \times 10^6$ (cm.^{2}/sec.)	$D_{\Theta/t} \times 10^6$ (cm.^{2}/sec.) Case A	Case B
0.00993	3.78	..	3.7
.0198	3.70	3.1	3.7
.0446	3.79	3.8	3.5
.0692	3.79	..	3.7
.1138	3.80	3.7	..
.282	3.82	3.8	3.2
.519	3.76	..	..
.948	3.83	3.8	3.5

TABLE V

DIFFUSION COEFFICIENTS OF CADMIUM ION AT VARIOUS CONCENTRATIONS

A = 0.404 cm.^{2}; $l = 1.8 \times 10^{-2}$ cm.

Concn. (mM)	$D_\infty \times 10^6$ (cm.^{2}/sec.)	$D_{\Theta/t} \times 10^6$ (cm.^{2}/sec.) Case A	Case B
0.0236	0.97	0.19	0.30
.0715	.97	.43	.50
.119	.99	.47	.65
.359	1.00	.78	1.02
.598	1.00	.93	1.04
.835	1.00	.97	1.10
3.15	1.00	.95	1.17
6.23	0.96	1.10	1.07

The agreement between D_∞ and $D_{\Theta/t}$ for thallous is within experimental error over the entire concentration range. However at low cadmium concentrations large deviations are observed between these two quantities. At higher concentrations good agreement is obtained and it is reasonable to take the value of 1.0×10^{-6} cm.^{2}/sec. as the correct one for the diffusion coefficient of this ion. The low values observed for $D_{\Theta/t}$ reflect a slower rate of steady-state attainment than predicted on the basis of D_∞. It is believed that adsorption of cadmium occurs within the membrane and that this accounts for the discrepancy between $D_{\Theta/t}$ and D_∞.

Initially the amount of adsorbed cadmium will be uniform throughout the membrane. When a potential sufficient to cause reduction is applied, the concentration of "free" cadmium decreases throughout the membrane until the steady state is established. Since the amount of adsorbed cadmium at any point in the membrane will be a function of the concentration of "free" cadmium at that same point, a desorption must take place during the time of attainment of the steady state. This desorbed cadmium diffuses to the electrode surface where it is reduced and a larger current than predicted is observed. Therefore, the area between the experimental and theoretical current–time curves is equal to the number of coulombs corresponding to the cadmium which has been desorbed. When no cadmium is initially present in the membrane (case B), a portion of that which enters during the establishment of the steady state is adsorbed and never reaches the electrode surface. Thus the current is less than theoretical and again the difference between the experimental and theoretical curves is a measure of the cadmium adsorbed. At the steady state, only the "free" cadmium is able to diffuse through the membrane and the theoretical current is observed at all concentrations.

It is expected that the adsorption of cadmium will follow a typical adsorption isotherm. Therefore, as the concentration of cadmium in the solution is increased, the relative amount of adsorbed cadmium decreases and the value obtained for $D_{\Theta/t}$ increases until it is very nearly equal to D_∞.

Temperature Dependence of Diffusion Coefficients.—The diffusion coefficients of thallous and cadmium in the membrane were determined at several temperatures between 15 and 45°. Plots of log D *vs.* $1/T$ gave straight lines indicating an exponential dependence of the diffusion coefficient on the temperature. According to the theory of absolute reaction rates as applied to diffusion,[12]

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[12] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," Chapter IX, McGraw-Hill Book Co., New York, N. Y., 1941.

the diffusion coefficient can be expressed by the equation

$$D = A\exp(-E/RT) \qquad (11)$$

where E is the activation energy for diffusion and

$$A = e\lambda^2 \frac{kT}{h} \exp(\Delta S^{\ddagger}/R) \qquad (12)$$

λ being the distance between two successive equilibrium positions.

In Table VI, the values of A, E and $\lambda[\exp(\Delta S^{\ddagger}/R)]^{1/2}$ for diffusion in the membrane are compared with values of these quantities calculated from literature data[13] on the temperature dependence of diffusion currents at the dropping mercury electrode.

It is apparent that the entropy factor is largely responsible for the difference between the diffusion coefficients of these ions in aqueous solution and in the cellophane membrane. Due to its structure, a considerable fraction of the membrane is blocked insofar as diffusion is concerned even though the diffusion is not restricted to rigorously defined pores. The smaller entropy factor is in accord with this model.

TABLE VI

ENERGY OF ACTIVATION AND ENTROPY FACTOR FOR DIFFUSION

Diffusion system	$A \times 10^3$ (cm.^{2}/sec.)	E(kcal.)	$\lambda[\exp(\Delta S^{\ddagger}/R)]^{1/2}$ (A)
Tl^+ in aqueous soln.	24	4.2	3.8
Tl^+ in cellophane membrane	3.2	4.0	1.4
Cd^{++} in aqueous soln.	41	5.0	4.9
Cd^{++} in cellophane membrane	6.6	5.2	2.0

Acknowledgment.—The authors are indebted to Professor D. D. DeFord for many valuable suggestions and discussions.

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(13) V. Nejedly, *Collection Czechoslov. Chem. Communs.*, **1**, 319 (1929).

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

The Cyanogen–Oxygen Flame under Pressure

BY J. B. CONWAY[1] AND A. V. GROSSE

RECEIVED DECEMBER 20, 1957

The cyanogen–oxygen flame yields one of the highest flame temperatures obtainable by chemical means. The experimental flame temperature (4640°K.) at atmospheric pressure is in good agreement with the calculated flame temperature (4835°K.) providing additional evidence in favor of the high value for the dissociation energy of nitrogen. A technique is described for operating this flame at elevated pressures to give increased flame temperatures. Flashback velocities at various pressures are reported and are very sensitive to pressure changes. A generalized plot is presented for calculating theoretical adiabatic flame temperatures for various CO/N_2 ratios.

The equation

$$C_2N_2(g) + O_2(g) \longrightarrow 2CO(g) + N_2(g) \qquad (1)$$

represents the simplest possible stoichiometric relation describing the combustion of cyanogen. The heat of the reaction at 298°K. is equal to 126,680[2] cal. which when coupled with the fact that the reaction products are extremely stable suggests the production of very high flame temperatures by this reaction.

The reactions of cyanogen with air and oxygen have been studied for many years. Dixon[3] studied the explosion rates of various mixtures of cyanogen and oxygen at several pressures. Smithells and Ingel[4] and Smithells and Dent[5] described the structure of the cyanogen–air flame as obtained with a cone-separating apparatus and also indicated the gaseous composition of the various cones of the flame. The kinetics of the oxidation of cyanogen have been studied by Hadow and Hinshelwood[6] and Pannetier[7] discussed the mechanism by which various additives decrease the luminosity of the cyanogen–oxygen flame. The inflammability of mixtures of cyanogen and air has been studied by Pannetier and Lafitte.[8] Dolique[9] investigated the combustion of cyanogen and reported that it does not entirely follow the theoretical chemical equation. Reis[10] made a thorough study of the cyanogen–oxygen flame, analyzed the gaseous products of combustion and also analyzed the flame spectrum. A theoretical flame temperature of 4740° was reported, but no experimental flame temperature was measured. Thomas, Gaydon and Brewer[11] have reported recent work on the cyanogen–oxygen flame in which the flame temperature was measured by determining the vibrational intensity distribution of the cyanogen bands. The vibrational temperature was found to be 4800 ± 200°K. for the stoichiometric composition. The theoretical flame temperature for the stoichiometric composition was calculated to be 4850°K. using the high value (ΔH_0^0 = 226,000 cal. per mole) for the dissociation energy of nitrogen. A temperature of 4325°K. was obtained when the low value (ΔH_0^0 = 170,240 cal. per mole) was used. From these results the authors concluded that the high value is correct.

As is the case with all flames the cyanogen–oxygen flame temperature is limited by the dis-

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(1) General Electric Company, Aircraft Nuclear Propulsion Department, Evendale, Ohio.

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(3) H. Dixon, *J. Chem. Soc.*, **49**, 384 (1886).

(4) A. Smithells and H. Ingle, *ibid.*, **61**, 204 (1892).

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