

with the complex. The amount of boron trichloride adsorbed never exceeded 0.2 mole BCl_3 per mole of complex, whereas boron trifluoride was absorbed to the extent of about 0.85 mole of BF_3 per mole of complex.

Thermal decomposition of ethylenediamine- BF_3 at 260° in a sealed tube produced ammonium fluoborate. *Anal.* Calcd. for NH_4BF_4 : HBF_4 , 84.30; N, 13.60; H, 3.81. Found: HBF_4 , 83.70; N, 13.35; H, 3.84. In addition small amounts of ammonia and ethylenimine were found in

the decomposition products and were identified by their infrared spectra.

Acknowledgment.—The authors are indebted to Dr. Benjamin W. Howk of the Chemical Department, E. I. du Pont de Nemours & Co., for a sample of pure hexamethylenediamine.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE REFINING TECHNICAL AND RESEARCH DIVISIONS, HUMBLE OIL AND REFINING COMPANY]

Diffusion Currents at Cylindrical Electrodes. A Study of Organic Sulfides

BY M. M. NICHOLSON

RECEIVED NOVEMBER 23, 1953

A theory of diffusion currents at stationary cylindrical electrodes with linear variation of applied potential is presented. Ferro- and ferricyanide ions approach closely the behavior predicted for a reversible electrochemical system. In general, these results justify the conclusion that convection effects can be reduced to minor importance in conventional polarographic operation without elaborate precautions and that the current-voltage curves obtained in the manner described are amenable to theoretical interpretation. Evidence of irreversibility is found in anodic polarograms of a series of organic sulfides. The reaction is shown to be a 2-electron process, corresponding to formation of the sulfoxide. Diaryl sulfides are more difficult to oxidize electrolytically than other types.

The theory of diffusion currents at plane electrodes with linear variation of applied potential has been developed in papers on oscillographic polarography.¹⁻³ The same equations are valid approximately for stationary spherical and cylindrical electrodes if the time of electrolysis is sufficiently short. Specifically, the error in calculated maximum current at a cylindrical electrode does not exceed 5% when $D/ta^2 \leq 3 \times 10^{-3}$, where D is the diffusion coefficient of the current-controlling species, t the time of electrolysis, and a the radius of the cylinder.³ Ordinary polarographic conditions correspond to values of this term about one thousand times greater, and in such cases it becomes necessary to consider the curvature of the surface in an accurate theoretical treatment.

In the present investigation, current-voltage curves of good reproducibility, resembling qualitatively those obtained by the oscillographic technique, were observed at wire electrodes with an automatic voltage change of a few millivolts per second. It is known, however, that the steady state currents measured manually at constant voltage on stationary wires depend upon convection effects due to density gradients produced by the electrode reaction and, therefore, are greater than those which would result from diffusion in an unstirred solution.^{4,5} Some workers with stationary electrodes have approached this steady state by slow automatic change of voltage⁶; others have employed usual rates of polarographic recording⁷ but have not made an exact theoretical study of the results.

The following discussion of cylindrical electrodes

- (1) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948).
- (2) A. Sevcik, *Collection Czechoslov. Chem. Commun.*, **13**, 349 (1948).
- (3) T. Berzins and P. Delahay, *THIS JOURNAL*, **75**, 555 (1953).
- (4) H. A. Laitinen and I. M. Kolthoff, *ibid.*, **61**, 3344 (1939).
- (5) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061 (1941).
- (6) D. B. Julian and W. R. Ruby, *THIS JOURNAL*, **72**, 4719 (1950).
- (7) L. B. Rogers, H. H. Miller, R. B. Goodrich and A. F. Stehney, *Anal. Chem.*, **21**, 777 (1949).

extends the theory to take into account the curvature of the electrode surface.

Theory of Diffusion Currents at Cylindrical Electrodes

The fundamental differential equation for cylindrical diffusion is

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \left(\frac{\partial C}{\partial r} \right) \right] \quad (1)$$

in which C is concentration and r is distance from the axis of the cylinder.

Boundary Conditions.—A numerical solution of equation 1 is sought for boundary conditions corresponding to a reversible reaction at a cylindrical electrode of radius a , with reactants and products soluble in the supporting electrolyte medium. It is assumed that none of the principal electrolysis product is present before the reaction, but that the current-controlling species has an initial concentration c^0 .

The fact that the flux of material diffusing to the electrode surface must be equal and opposite to that leaving it leads to the expression

$$(c_{\text{ox}})_a + (c_{\text{red}})_a = c^0 \quad (2)$$

for surface concentrations if the ratio of diffusion coefficients $D_{\text{ox}}/D_{\text{red}}$ is taken equal to unity.¹

The electrode potential E is given by

$$E = E_i \pm \alpha t \quad (3)$$

in which E_i is the initial potential and α is the magnitude of the rate of change of E with time. According to polarographic convention, the *plus* sign applies to an anodic reaction, the *minus* to a cathodic one. It is convenient to represent the conventional expression $nF(E - E^0)/2.3RT$ by the symbol τ . Equation 2 and the Nernst equation yield

$$\tau = \pm \log [(c^0 - c)/c] \quad (4)$$

where c is concentration of the current-controlling species and the signs are designated as for equation

3. The dimensionless quantity τ specifies an interval on the time and voltage scales.

Method of Solution.—Equation 1 may be solved numerically by means of the corresponding finite difference equation⁸

$$C(r, t + \delta t) = \frac{1}{2} [C(r + \delta r, t) + C(r - \delta r, t)] + \frac{\delta r}{2r} [C(r + \delta r, t) - C(r, t)] \quad (5)$$

which is a simplified form derived by choosing the increments so that $(\delta r)^2 = 2D\delta t$. For the symbol C the ratio c/c^0 is understood. At 25° $\delta t = 0.05915 \cdot \delta t/n\alpha$. A suitably small $\delta\tau$ interval is selected for the spacing of a network of points extending from the surface outward to the region of unchanged concentration, and covering a range of several integers in the values of τ . Surface concentrations are known from equation 4, and to start the numerical process a series of c/c^0 ratios at distances $\delta r, 2\delta r, 3\delta r \dots$ can be guessed at some τ value where the ratio is almost unity. Concentrations at subsequent points are evaluated by repeated application of equation 5 until the traverse of the entire network is completed. A closer approximation is achieved by use of a smaller $\delta\tau$. The value of 0.1 was used throughout the present work, and calculations were made arithmetically; an equivalent graphical method was used by Randles¹ in solving the problem of linear diffusion.

The immediate result of such a series of calculations, in which $\delta\tau = 0.1$, $a = 0.0254$ cm., $\delta r = 0.00489$ cm., $D = 1.00 \times 10^{-5}$ cm.²/sec., $n = 2$, and $\alpha = 0.00247$ v./sec., is presented in Fig. 1.

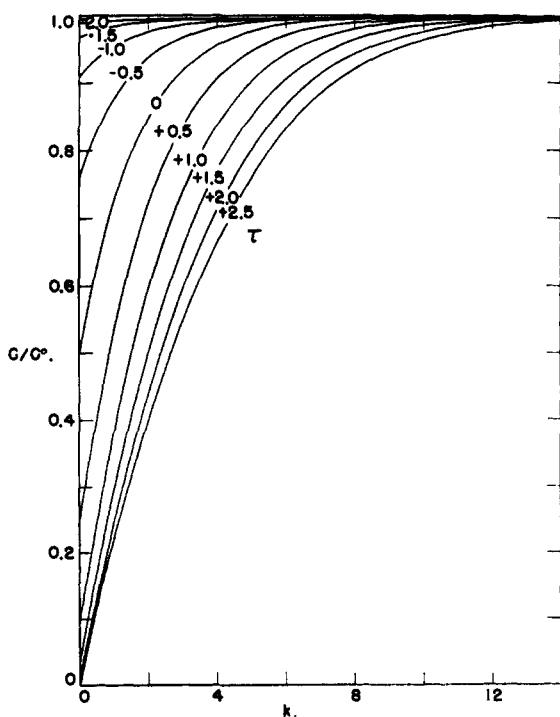


Fig. 1.—Distribution of concentration at different values of τ : $\frac{1}{a} \left(\frac{D}{n\alpha} \right)^{1/2} = 1.77$; distance from surface = $0.192ka$.

(8) J. B. Scarborough, "Numerical Mathematical Analysis," The Johns Hopkins Press, Baltimore, Md., 1930, p. 309.

The applicability of each numerical solution is limited by dependence of the term $\delta r/2r$ on the electrode radius. Noting that

$$\delta r/r = \frac{\delta\tau/a}{1 + k\delta\tau/a} \quad (6)$$

where k is an integer, it is apparent from relations between δr , δt and $\delta\tau$ that $(1/a)(DT/n\alpha)^{1/2}$ is the experimental parameter which fixes the numerical values of c/c^0 in the network. After the completion of one network, the labor of additional ones is shortened by estimating the starting c/c^0 points nearer to $\tau = 0$, on the basis of the previous set.

All calculations are reported for 25° ; hence temperature is not indicated as a variable in the figures.

Concentration Gradients and Current-Voltage Curves.—The concentration gradients per unit δr at the electrode surface were evaluated by numerical differentiation

$$\delta(c/c^0)_a = \delta^2(c/c^0)_a - \frac{1}{2} \delta^2(c/c^0)_a + \frac{1}{3} \delta^3(c/c^0)_a \quad (7)$$

where

$\delta^m(c/c^0)_a$ is the m th diagonal difference.

Figure 2 shows a series of curves obtained in this manner. These plots are general representations of theoretical current-voltage curves, since

$$i = nFAD \left(\frac{\partial c}{\partial r} \right)_a \quad (8)$$

in which i is the diffusion current, A the electrode area, and $(\partial c/\partial r)_a = c^0[\delta(c/c^0)_a/\delta r]$. Coordinates of the maxima are given in Table I.

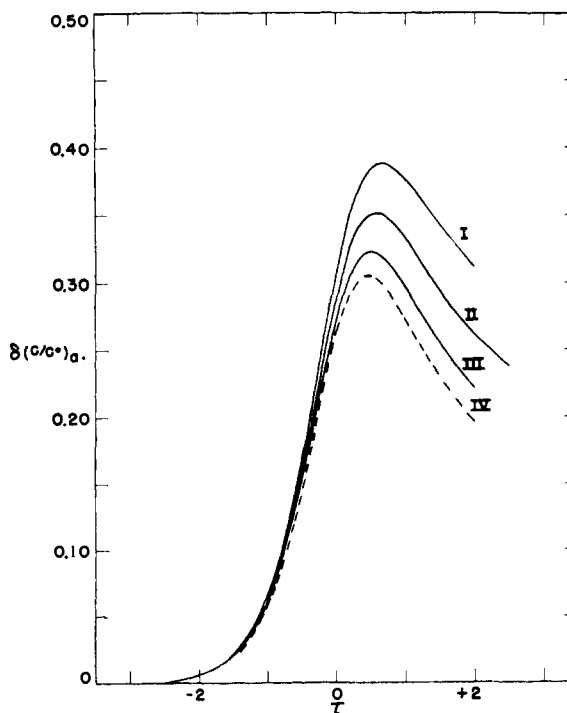


Fig. 2.—Surface concentration gradient as function of τ : I, $\frac{1}{a} \left(\frac{D}{n\alpha} \right)^{1/2} = 3.62$; II, 1.77; III, 0.648; IV, 0 (extrapolated).

Gradients derived from the three calculated networks are plotted vs. $(1/a)(D/n\alpha)^{1/2}$ in Fig. 3.

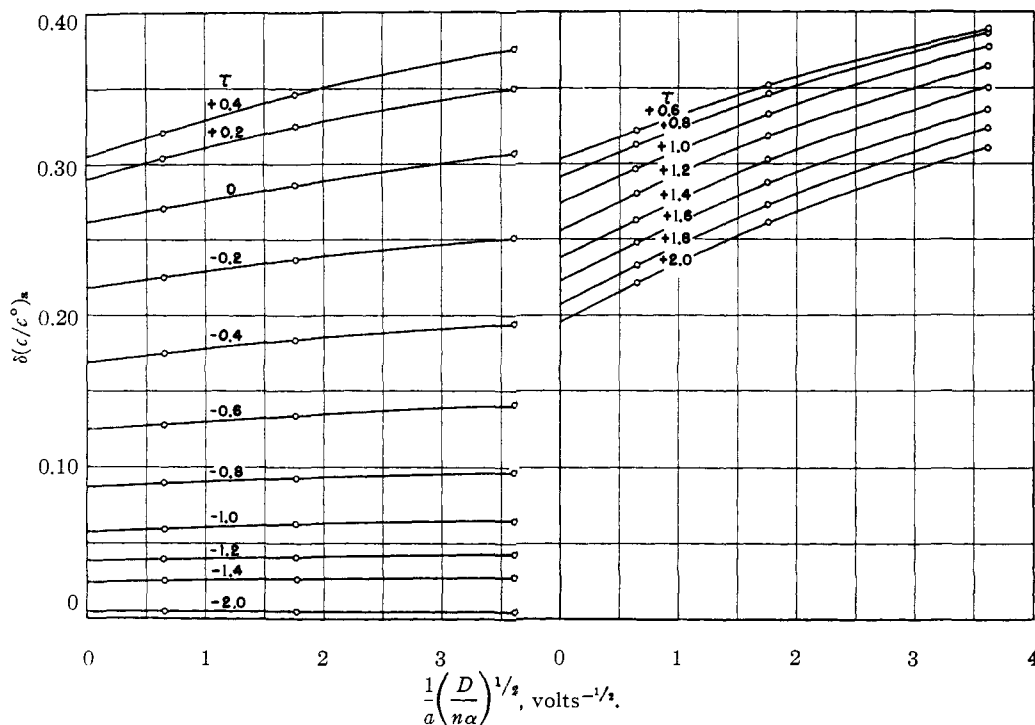


Fig. 3.—Surface concentration gradients at various values of τ : circles are calculated points.

TABLE I

MAXIMUM CONCENTRATION GRADIENTS

$(1/a)(D/n\alpha)^{1/2}$	$\delta(c/c^0)_a \text{ max}$	τ_{max}
3.62 v. $^{-1/2}$	0.388	0.65
1.77	.352	.57
0.648	.324	.51
0	.306 ^a	.48
0	.310 ^b	..

^a Extrapolated. ^b Randles.

The intercepts of these curves on the vertical axis correspond to $\alpha = \infty$, or to the case of linear diffusion. Accordingly, the extrapolated curve of Fig. 2 coincides with that found by Randles for a plane electrode. By interpolation on Fig. 3, current-voltage curves for various experimental conditions can be constructed.

A detailed expression for current at both plane and cylindrical electrodes is

$$i = \pm \frac{n^{3/2} F^{3/2} A D^{1/2} \alpha^{1/2} \delta(c/c^0)_a}{(2\delta\tau \times 2.3RT)^{1/2}} c^0 \quad (9)$$

with the subscript a designating a surface value, and the *minus* sign indicating an anodic reaction. In the case of the cylinder a simple proportionality between maximum current and $n^{3/2}\alpha^{1/2}$ is prevented by dependence of $\delta(c/c^0)_a$ on these variables. The maximum current is still greatly increased by increase in n but not by a factor as large as $n^{3/2}$. The theoretical curves in Fig. 8 provide a basis for comparison of plane and cylindrical electrodes with respect to variation of maximum current with α .

Transformation to the voltage coordinate is made through the relation $E = E^0 + (2.3RT/nF)\tau$, from which it is seen that with a large n a given range of τ covers a small voltage span, resulting in a sharp peak in the current-voltage curve.

Experimental

Materials.—Dimethyl and pentamethylene sulfides were obtained from the American Petroleum Institute, diethyl sulfide from the National Bureau of Standards. These samples were pure within a few hundredths mole per cent. Methyl phenyl sulfide was available only as a 0.05 M solution in a benzene-2,2,4-trimethylpentane mixture, which had been prepared three months earlier from a 99.9 mole per cent. sample supplied by American Petroleum Institute Project 48. Dibenzyl sulfide, an Eastman White Label product, was recrystallized three times from a 10:1 ethanol-water mixture. The maximum diffusion current of a 0.001 M solution increased 6% with the first crystallization and remained constant within 0.6% thereafter. The final m.p. was 48.3–48.7° (lit. 49°). Eastman White Label diphenyl sulfide and di- n -butyl and di- t -butyl disulfides were tested without purification. A 95% dibenzyl sulfoxide sample was furnished by Dr. F. G. Bordwell.

Nitrogen and hydrogen were freed from oxygen by passage over copper turnings at 450°. All other materials were reagent grade chemicals which were not further purified.

Solutions.—The liquid sulfides were weighed in sealed glass bulbs. The "methanolic 0.1 M HCl" contained the required volume of standardized aqueous 2.50 M hydrochloric acid to yield a cell solution 0.1 M in acid, 2.1 M in water. The 0.001 M methyl phenyl sulfide solution contained in addition 2 ml. of the hydrocarbon solvent per 100 ml. of cell solution. Because acidified sulfide solutions were found to decrease in concentration about 0.5% per day, the acid was put into the cell solutions immediately before measurement. The ferrocyanide solution also was freshly prepared. Dilutions for the cell were made at rounded concentrations from 0.006 M stock solutions by the usual volumetric techniques.

Cell and Electrodes.—The cell was an all glass H type with electrode compartments 20 mm. in diameter, separated by an agar plug saturated with potassium chloride.

The cylindrical platinum electrode used throughout the investigations was a vertical wire of 20 mils diameter sealed at the upper end into a 6-mm. o.d. soft glass tube and attached at the lower end to a glass bead about 2 mm. in diameter to eliminate edge effects. Measured dimensions were: diameter, 0.0510 ± 0.0004 cm.; length, 0.44 ± 0.02 cm.

In the coulometric experiment a platinum sheet electrode of 6 cm.² area was used. The wires for potentiometric hydrogen electrode measurements were platinized.

A saturated calomel electrode prepared directly in the cell served as a working and reference electrode. The cell resistance, measured on a 1000-cycle conductance bridge, was 250 ohms with the aqueous solutions, 650 ohms with the alcoholic ones.

Polarographic Procedure.—The cell was placed in a water-filled thermostat controlled to $25.0 \pm 0.1^\circ$. To minimize mechanical disturbances the bath was mounted on large rubber stoppers and stirred by an air bubbler. A period of 20 minutes was allowed after filling the cell to attain thermal equilibrium and complete drainage of solution from the walls of the cell. Without this precaution, erratic waves of abnormal height often were observed on the first recordings. At least two agreeing curves were obtained on each solution.

Current-voltage curves were recorded on a Sargent Model XXI Polarograph without damping. Except for some points in Fig. 6, all curves were obtained on a 2.00 v. span, for which $\alpha = 0.00247$ v./sec. The direction of polarization was positive for an anodic wave, negative for a cathodic one. The voltage settings of the instrument were checked against a Beckman Model G pH Meter, and the average uncertainty of the values observed polarographically is estimated at ± 0.01 volt.

The platinum wire electrode was cleaned usually once each day in 1:1 nitric acid. In the case of the organic sulfides, a definite tendency was observed toward decreasing wave height on consecutive recordings, accompanied by a shift of the current maximum to more positive voltages, an effect which was only partially eliminated by stirring the solution with the electrode between measurements. It was found that by application of a small a.c. voltage to the cell for a few minutes after each run, curves of excellent reproducibility, usually better than $\pm 1\%$ at the maximum current, could be obtained repeatedly. This procedure had no special effect in the ferricyanide solutions, where the electrode returned to its original condition after stirring. Voltage for the electrolytic cleaning technique was conveniently supplied by a conductance bridge at 1.6 v. and 1000 cycles/sec.

Oxygen was removed from the ferro- and ferricyanide solutions by passage of water-saturated purified nitrogen. The polarographic behavior of the sulfides was unaffected by oxygen, and the currents were recorded in the presence of air.

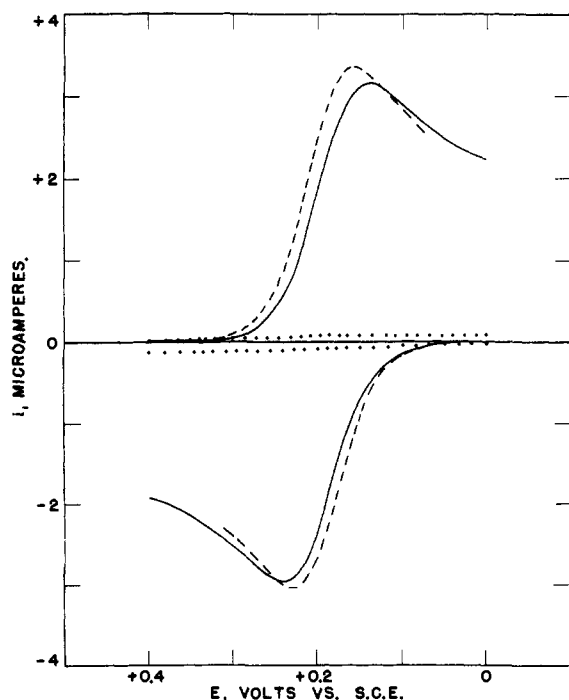


Fig. 4.—Polarograms of ferro- and ferricyanides in 0.2 *M* KCl: —, experimental; ---, theoretical;, residual current; upper curves, 1 millimolar $K_3Fe(CN)_6$; lower curves, 1 millimolar $K_4Fe(CN)_6$.

Corrections for residual current were made by subtraction of "blank" recordings on the supporting electrolyte media, assuming that the currents were directly additive. Dimethyl sulfide was dissolved in J. T. Baker methanol; all others were in the Mallinckrodt product. The corresponding blanks were applied, the slight differences being significant at the three lowest sulfide concentrations.

Hydrogen Electrode Measurements.—A platinized wire electrode was placed in the sample compartment of the H cell containing the methanolic 0.1 *M* HCl. A constant voltage with respect to the aqueous saturated calomel electrode was indicated on the Beckman Model G pH meter after passage of purified solvent-saturated hydrogen for a few minutes. Identical readings were observed on duplicate platinized electrodes. Smooth platinum electrodes failed to reach a constant potential in two hours.

Coulometric Procedure.—A 15-ml. sample of 5×10^{-4} *M* diethyl sulfide in methanolic 0.1 *M* HCl was electrolyzed two hours at a platinum anode of 6 cm.² area, with current recorded on the polarographic chart. The potential with respect to the calomel electrode was maintained at 0.90 v. after correction for *iR* drop in the cell. A blank run was carried out by the same procedure, and both current-time curves were replotted on a sheet of convenient size. The quantity of electricity used in the oxidation was equivalent to the difference in areas under the two curves, measured with a planimeter, and the amount of sulfide reacted was determined from polarograms taken on the standardized wire electrode before and after electrolysis.

Results and Discussion

The Ferrocyanide-Ferricyanide System.—Theoretical and observed current-voltage curves are shown in Fig. 4 for the reduction of ferricyanide ion and oxidation of ferrocyanide at 25° with $\alpha = 0.00247$ v./sec. The experimental curves have been corrected for residual current and *iR* drop. The diffusion coefficients used were those listed for infinite dilution by Kolthoff and Lingane.⁹ The maximum occurred at +0.14 v. vs. the saturated calomel electrode at all ferricyanide concentrations. Corrected values of the maximum current are reproduced by the expression $i_{\max} = 3.13c$ with a maximum deviation of 2% and an average of $\pm 1\%$, where i_{\max} is in microamperes and *c* is in millimoles per liter.

Agreement between observed and predicted currents is within the limit of accuracy imposed by the various experimental quantities which enter into the calculations. Direct proportionality of maximum current to concentration is in accordance with equation 9. The calculated increase of 6% in i_{\max} was observed in 1 millimolar potassium ferricyanide on increasing the temperature from 25 to 30° . The voltage separating anodic and cathodic maxima is slightly greater in the case of the experimental curves, which may be interpreted as a tendency toward irreversibility. In comparison of studies with stationary and rotating electrodes, Laitinen and Kolthoff¹⁰ concluded that while the oxidation current of ferrocyanide ion was diffusion-controlled at a stationary electrode with manual application of voltage, a slow step in the reaction became evident when the electrode was rotated.

In general, the results in this system justify the conclusion that convection effects can be reduced to minor importance in conventional polarographic operation without elaborate precautions and that current-voltage curves obtained in the manner de-

(9) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, p. 52.

(10) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1944).

TABLE II
MAXIMUM OXIDATION CURRENTS OF ORGANIC SULFIDES IN METHANOLIC 0.1 M HCl
25°; $\alpha = 0.00247$ v./sec.; E_{\max} in volts vs. S.C.E.; i_{\max} in microamps.; c in mmoles/l.

c	Dimethyl		Diethyl		Pentamethylene		Methyl phenyl ^a		Dibenzyl	
	E_{\max}	$-i_{\max}$	E_{\max}	$-i_{\max}$	E_{\max}	$-i_{\max}$	E_{\max}	$-i_{\max}$	E_{\max}	$-i_{\max}$
0.05	0.83	0.72	0.79	0.66	0.81	0.68	0.81	0.48
.1	.83	1.41	.79	1.34	.81	1.3381	0.97
.2	.83	2.80	.78	2.71	.81	2.6981	1.93
.5	.84	7.06	.79	6.66	.82	6.7783	4.73
1	.86	14.1	.81	13.3	.84	13.2	0.89	12.0	.84	9.68
2	.88	27.5	.85	25.8	.86	25.186	18.5
3	.89	40.2	.86	38.3	.86	37.689	26.3
4	.91	53.6	.86	50.4	.87	48.889	34.5
5	.93	66.1	.86	62.0	.88	59.993	42.0

^a Hydrocarbon content of solution is indicated in Experimental section.

scribed are amenable to quantitative theoretical interpretation.

The use of potassium ferricyanide as a standard for calibration and comparison of electrode areas is recommended.

Organic Sulfides.—The platinum wire electrode offers a suitable means of studying the electrolytic oxidation of a series of organic sulfides. The experimental curve for diethyl sulfide shown in Fig. 5 is typical of the anodic currents observed for these compounds.

In the coulometric experiment it was found that 0.685 coulomb was required to oxidize 3.27×10^{-6} mole of diethyl sulfide, giving a loss of 2.2 electrons per mole, which corresponds to formation of the sulfoxide. Wave heights of all of the sulfides measured form a smooth function of molecular weight, indicating the same number of electrons transferred in each case.

Oxidation current data, corrected for iR drop and residual current, for several sulfides are given in Table II. A current increase beginning near +0.9 v. was observed in 1 millimolar diphenyl sulfide solution, but any maximum was obscured by the oxidation current of the medium. A similar interference was encountered in tests of di-*n*-butyl and di-*t*-butyl disulfides, whose maxima were estimated to occur near +1.0 v.

The maximum currents of the sulfides are expressed as functions of concentration by least squares equations of the form $-i_{\max} = Ac + Bc^2$, for which the constants are recorded in Table III. Current is expressed in microamperes and concentration in millimoles per liter.

TABLE III
CONSTANTS OF THE EQUATION $-i_{\max} = Ac + Bc^2$

Sulfide	$\Delta = i_{\text{obs.}} - i_{\text{calc.}}$		Δ , av., %	Δ_{\max} , %
	A	B		
Dimethyl	14.20	-0.208	± 0.6	1
Diethyl	13.41	- .206	$\pm .6$	2
Pentamethylene	13.48	- .311	$\pm .7$	2
Dibenzyl	9.71	- .267	$\pm .7$	2

The data of Table II are presented graphically in Fig. 6 in the form $-i_{\max}/c$ vs. c . The straight lines are plots of the least squares equations.

The theoretical curve in Fig. 5 is based on the values $n = 2$ and $D = 1.95 \times 10^{-5}$ cm.²/sec. The diffusion coefficient of diethyl sulfide was estimated

by application of a viscosity correction to that of diethyl ether in pure methanol at 15°, the necessary data being found in the "International Critical Tables." Because of the uncertainty in D it is important to compare the shapes of the curves as well as the heights. For this purpose the peaks were made to coincide on the voltage coordinate.

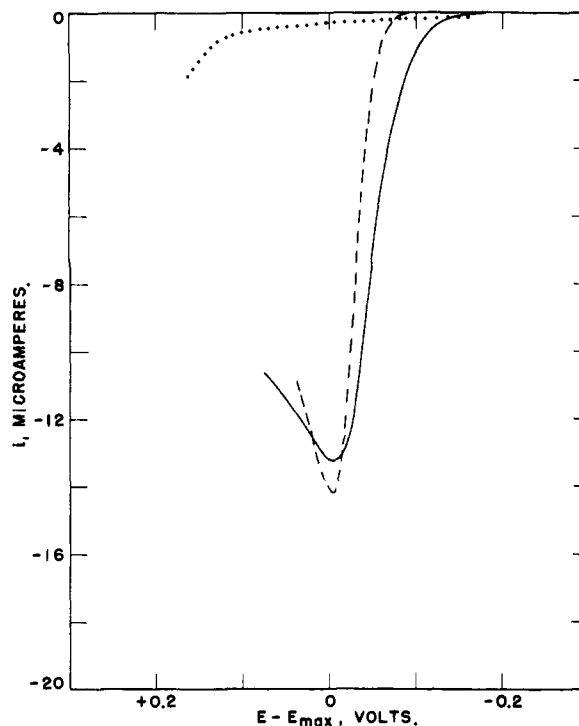


Fig. 5.—Polarograms of 1 millimolar diethyl sulfide in methanolic 0.1 M HCl: —, experimental; ---, theoretical for reversible reaction; . . . , residual current.

For experimental convenience, measurements of potential were made against an aqueous saturated calomel electrode and include an unknown liquid junction potential. An alternate reference system, without liquid junction, was established by potentiometric measurement of the calomel half-cell vs. a hydrogen electrode in the same methanol-hydrochloric acid solution. The calomel electrode was 0.265 v. positive after correction to a hydrogen pressure of one atmosphere. If +0.265 v. is added to the E_{\max} values reported in Table III, the result is a measure of the relative ease of oxidation of hy-

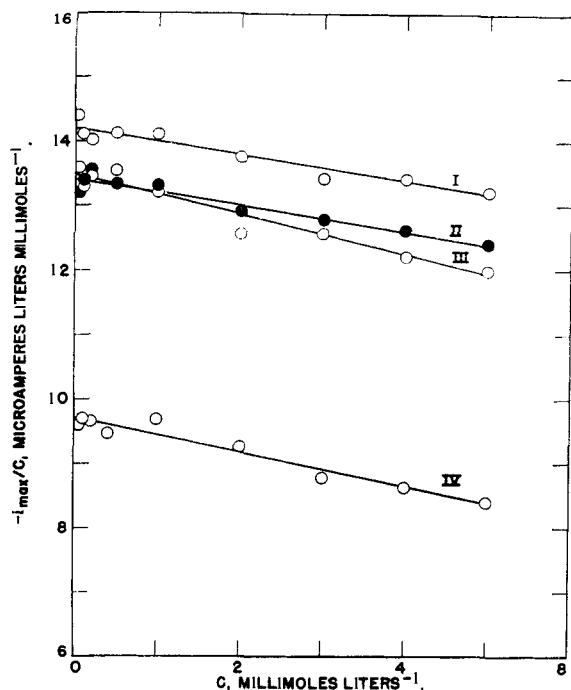


Fig. 6.—Maximum oxidation currents of organic sulfides; straight lines are plots of least squares equations: I, dimethyl sulfide; II, diethyl; III, pentamethylene; IV, dibenzyl.

drogen and the organic sulfide in the 0.1 *M* HCl medium. If the sulfide-sulfoxide system behaved reversibly, its thermodynamic potential with respect to the standard hydrogen electrode in this solvent could be estimated directly.

There is evidence for an influence of reaction rate on the sulfide oxidation currents. A broadening of the current peak is characteristic of irreversible electrode reactions.¹ More conclusive was an attempt to reduce an air-free 1 millimolar solution of dibenzyl sulfoxide in the same medium. No current was detected in the usable voltage range, +0.9 to -0.2 v. vs. the calomel electrode. A similar result was reported by Stone¹¹ on dropping mercury in dioxane-water solutions. If the system were reversible, there should be a separation of only 0.03 v. between anodic and cathodic peak currents.

When the temperature was increased from 25 to 30°, the observed increases in wave heights in 1 millimolar solutions were: dimethyl sulfide, 5%; diethyl, 3; pentamethylene, 5; dibenzyl, 1. A theoretical increase of 5% is estimated for diethyl sulfide on the basis of viscosity changes. Since a low energy of activation governs the maximum value, the current apparently approaches diffusion control in the vicinity of E_{\max} .

The necessity for special cleaning of the electrode after each recording suggests that the variation of E_{\max} and i_{\max}/c with concentration might be caused by an adsorption effect.

Figure 7 is an empirical plot of A vs. molecular weight of the sulfide. The constant B for methyl phenyl sulfide was estimated by analogy from the lines in Fig. 6.

(11) K. G. Stone, *THIS JOURNAL*, **69**, 1832 (1947).

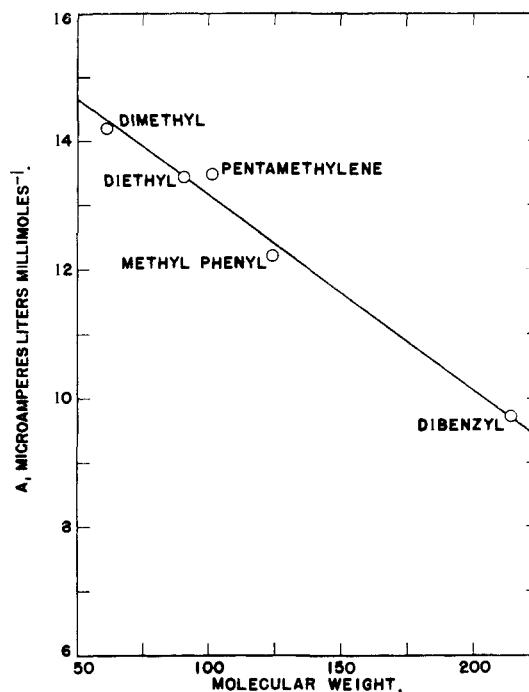


Fig. 7.—Dependence of constant A on molecular weight of organic sulfide.

Effects of n and α .—The values of $\delta(c/c^0)_a$ for ferricyanide ion and diethyl sulfide are almost identical. This coincidence permits direct comparisons of 1-electron and 2-electron curves in Fig. 8. Similar deviation of experimental points

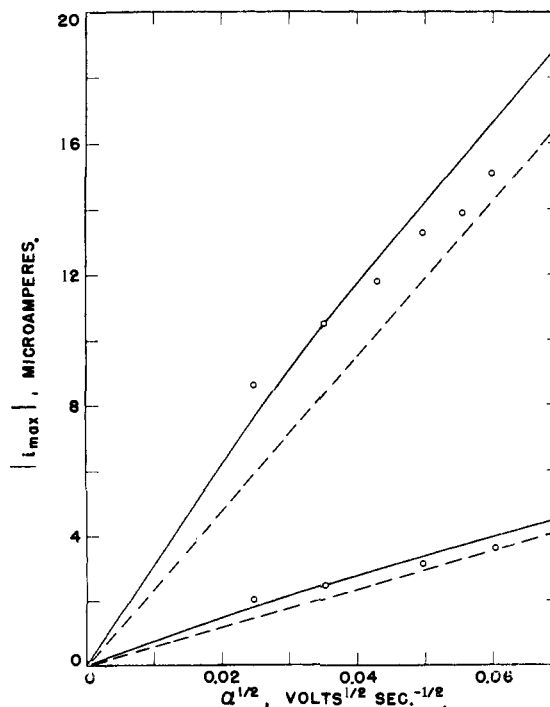


Fig. 8.—Effect of α on maximum current: —, theoretical for cylindrical electrode; ---, for plane of equal area, circles, experimental values; upper curves, 1 millimolar $(C_2H_5)_2S$ in methanolic 0.1 *M* HCl; lower curves, 1 millimolar $K_3Fe(CN)_6$ in aqueous 0.2 *M* KCl.

as α increases has been observed oscillographically.¹ Convection effects appear to become oper- able near $\alpha = 0.0012$ v./sec. BAYTOWN, TEXAS

[CONTRIBUTION No. 298 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]¹

The Separation of Rare Earths by Ion Exchange. VII. Quantitative Data for the Elution of Neodymium

BY F. H. SPEDDING AND J. E. POWELL

RECEIVED AUGUST 17, 1953

The elution of neodymium from Nalcite HCR resin beds with 0.1% citric acid-ammonium citrate solutions was investigated and quantitative measurements were made to determine the distribution of constituents between the aqueous and resin phases. The data obtained in the pH range 5.0 to 8.0 have led to a much clearer understanding of the fundamental mechanisms involved when rare earths are separated by the ion-exchange method. Several basic correlations of the experimental data have been presented.

I. Introduction

It has been shown, by this Laboratory, that excellent separations of rare earths in high purity and good yields can be obtained by eluting the mixed rare earths from Nalcite HCR beds with 0.1% citric acid in the pH range 5.0 to 8.0.^{2,3} Since it was clear from this earlier work that the columns could be operated under nearly equilibrium conditions, it was considered desirable to obtain quantitative data for the behavior of individual rare earth bands under equilibrium conditions. It was hoped that such information would lead to a better understanding of the fundamental mechanisms involved when rare earths are separated on ion-exchange columns with citrate solutions. We believe this objective has been fulfilled, since it has been possible to explain in a quantitative fashion all the phenomena which are observed by using only the ordinary laws of chemical thermodynamics.

The theoretical part of this discussion is being presented in a companion article⁴; this paper will deal with the experimental results and empirical relationships which were observed concerning variables of the system (part of the results already have been announced⁵). Since that time much more extensive experiments have been carried out and the pH range extended. The almost linear relationships described previously were found to deviate somewhat at higher and lower pH values, but the chemical thermodynamic theory accounts for these deviations.

A number of frustrating experimental difficulties were encountered, during this work, which we believe to be worthwhile mentioning, since they may save other experimentalists considerable time in future work of this sort.

While a plot of the ammonia in the eluant *versus* the rare earth in the eluate seemed to reproduce from experiment to experiment, a plot of hydrogen

ion in the eluate *versus* the rare earth in the eluate gave different results each time the experiment was performed. The erratic behavior was finally traced to three different origins: (1) The citric acid is an excellent medium for the culture of molds. Since the experiments extend over a period of one or two months, this mold growth can be troublesome. Long before mold can be observed visually it will affect the results by upsetting the pH balance in the eluate. It was found, in general, that mold growth could be prevented by the addition of 1 gram of phenol per liter of eluant, and that below a pH of 6.5 in the eluate the phenol acted as an inert diluent and did not upset the equilibria. For a narrow range above 6.5 the equilibria could be corrected successfully for the presence of phenol. (2) It is necessary to use considerable quantities of pure water in these experiments and since in this Laboratory, as in many others, such quantities of distilled water are not readily available, it was thought that condensed steam would suffice if it were passed first through cation and anion exchangers in order to deionize the water. However, most condensed steam contains appreciable quantities of iron rust from the plumbing, and while cation and anion exchangers remove from ions fairly efficiently they do not remove colloidal iron. Such iron was present in our condensed steam and could be observed readily when this water was illuminated by a beam of light in a darkened room. The colloidal iron dissolved when citric acid was added, and since ferric iron forms strong citrate complexes, the equilibria under observation were upset. The difficulty was circumvented by first passing the condensed steam through packed columns of Pyrex glass wool, which removed the colloidal iron fairly efficiently. The water was then passed through cation and anion exchangers. (3) Citric acid solutions are also good media for the growth of bacteria and it was found, in one of our runs, that the apparatus had become contaminated with an organism similar to acetic acid bacteria. These bacteria seemed to grow even in 0.1% phenol solution and definitely upset the hydrogen-ion equilibria. While the disturbance was not too serious for ordinary separations, it was serious in experiments designed to determine thermodynamic constants. It was, therefore, necessary to sterilize all the equipment to

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) (a) F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, *THIS JOURNAL*, **72**, 2354 (1950); (b) F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffe, *ibid.*, **73**, 4840 (1951).

(3) F. H. Spedding and J. E. Powell, ISC-349, Iowa State College (1953).

(4) F. H. Spedding and J. E. Powell, *THIS JOURNAL*, **76**, 2550 (1954).

(5) F. H. Spedding and J. E. Powell, *ibid.*, **74**, 856, 867 (1952).