molecule at the dropping mercury electrode. The values of n_{SE} (Table IX) are certainly unreliable. However, the values of n_m as calculated from the average of three experimental values of D are definitely 2, 4, 6 and 8 for butyl nitrate, ethylene glycol dinitrate, glycerol trinitrate and pentaerythritol tetranitrate, respectively.

From the polarographic data and the number of electrons involved in the reduction of one molecule (as calculated from Ilkovic equation with experimentally determined values of D) of a polynitrate ester, it appears that each ONO_2 group in the molecule reduces in a 2-electron step. This has been shown to give an alcohol and nitrite ion as the products

$$RONO_2 + 2e^- \longrightarrow RO^- + NO_2^-$$
$$RO^- + H_2O^- \longrightarrow ROH + OH^-$$

Thus, for glycerol trinitrate the following over-all reduction probably takes place at the dropping mercury electrode in neutral or slightly acidic solutions.

$$C_3H_5(ONO_2)_3 + 6e^- + 3H_2O \longrightarrow C_3H_5(OH)_3 + 3NO_2^- + 3OH^-$$

It may be postulated that in alkaline solution the secondary ONO_2 group is readily attacked by the large concentration of hydroxyl ion and thus a more complicated process is involved. Polynitrate esters are certainly less resistant to attack by hydroxyl ion at room temperature than a simple nitrate ester such as *n*-butyl nitrate. Work now in progress on the alkaline decomposition of glycerol trinitrate may lead to an understanding of the reactions at the dropping mercury electrode in alkaline solution.

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[Contribution from the Oak Ridge National Laboratory, Chemistry Division]

The Polarography of Thallium(III)[1]

By Gilbert W. Smith and Frederick Nelson

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The polarography of thallium(III) in chloride solutions has been investigated. Two diffusion current plateaus were found in Tl(III) polarograms; the first plateau can be interpreted to correspond to the reduction Tl(III) to Tl(I) and the second to the reduction Tl(III) to Tl(0)(Hg). The magnitude of both diffusion current plateaus is apparently controlled by the rate of diffusion of Tl(III). The diffusion current constants for the two-electron and three-electron reductions Tl(III) to Tl(I) and Tl(III) to Tl(0), were found to be 3.83 ± 0.03 and 5.72 ± 0.08, respectively, in 0.6 M HCl corresponding to a diffusion coefficient, D Tl(III) of 1.00×10^{-5} cm.^{2} sec.$^{-1}$. The diffusion current constant for Tl(I) in 0.6 M HCl was determined from separate experiments with Tl(I) solutions and found to be 2.65 ± 0.03, corresponding to D Tl(I) = 1.91×10^{-5} cm.^{2} sec.$^{-1}$, in reasonably good agreement with previously reported values. Polarograms from solutions containing both Tl(I) and Tl(III) were found to be suitable for analytical determination of Tl(I) and Tl(III). The half-wave potential of the "Tl(I)/(0) wave" for Tl(III) solutions was practically the same as that for Tl(I) in the same supporting electrolyte.

Although the polarography of thallium(I) has been studied extensively,[2-4] apparently only one note, by Hughes and Hush,[5] discusses the polarography of thallium(III). These authors found that for perchloric acid solutions, polarograms of Tl(III) had a "reproducible and well defined" diffusion current plateau which merged with the anodic dissolution current of mercury. This plateau is followed by a wave which on the basis of its half-wave potential was identified with the Tl(I)/(0) wave. The first diffusion current plateau was thus assumed to result from the reduction of Tl(III) to Tl(I), and the second plateau was assumed to result from the reduction of Tl(III) to Tl(0). Since mercury dissolution occurs at a more negative potential than the Tl(III)/(I) reduction potential[6] a polarographic "half-wave" for the Tl(III)/(I) reduction is not observed. No values were given for the diffusion current constants of Tl(III).

The present investigation was primarily concerned with the measurement of diffusion current constants of Tl(III) from the Tl(III)/(I) and the Tl(III)/(0) reduction currents in chloride solution to test the possibility of utilizing polarographic methods for the determination of Tl(I) and Tl(III) in Tl(III)-(I) mixtures. Half wave potentials of the Tl(I)/(0) wave in Tl(III)-(I) mixtures were also measured and compared with previously reported values for Tl(I) solutions.

Experimental

Tl(I) stock solutions (*ca.* 10^{-3} M Tl) were prepared by dissolving recrystallized nitrate-free[7] thallous chloride in 0.1, 0.6 and 1.0 M HCl or 0.1 M KCl containing 5×10^{-3} M HCl. Tl(III) stock solutions were prepared from Tl(I) solutions by oxidation with chlorine gas. Thallium concentrations were determined by iodometric[8,9] titration after removal of the excess chlorine with phenol.

Polarograms were recorded in an air conditioned room at 25 ± 1° with a Sargent Model XXI recording polarograph. A polarographic cell having a capacity of about 20 ml. was used in conjunction with a KCl-agar bridge and a saturated calomel reference electrode. Oxygen (or excess chlorine) was purged from the solutions with nitrogen purified by passing through a train of ammoniacal cuprous chloride or, in some cases, through copper turnings at 500°. When the solutions contained chlorine, the dropping mercury electrode was introduced after the chlorine had been expelled, to

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(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) J. J. Lingane, This Journal, **61**, 2099 (1939).

(3) L. Meites, *ibid.*, **73**, 4257 (1951).

(4) "Bibliography of Polarographic Literature," Leeds and Northrup Co., Philadelphia, Pa., 1950.

(5) G. K. Hughes and N. S. Hush, *Aust. J. Sci.*, **10**, 184 (1948).

(6) The potential of the Tl(I)/(III) couple is −1.25 v. (*vs.* H_2 electrode); W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 2nd Ed., 1952.

(7) By brucine sulfate test—F. Feigl, "Spot Tests," Elsevier Press, New York, N. Y., 3rd Ed., 1946.

(8) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Rev. Ed., The Macmillan Co., New York, N. Y., 1947.

(9) C. W. Sill and H. E. Peterson, *Anal. Chem.*, **21**, 1268 (1949).

avoid oxidation of the mercury. To obtain reproducible diffusion currents with Tl(III) solutions, it was necessary to begin measurements as soon as the dropping mercury electrode was introduced since it was found that Tl(III) slowly reduces upon contact with the mercury pool in the cell. Maxima were not usually observed; however, when they did appear gelatin (0.01%) was added as suppressor.

Half wave potentials of the Tl(I)/(0) waves were usually taken from plots of log $i/(i_d - i)$ *vs.* potential E (corrected for iR drop). The current i was obtained at several points along the wave after stopping the bridge to obtain a constant current. The total limiting current, i_d, was measured at −0.7 v. *vs.* S.C.E. and both i and i_d were corrected for residual current. At each point on the wave, the applied potential was measured with a Leeds and Northrup potentiometer. Since, as mentioned, Tl(III) slowly reduces on contact with mercury, measurements were made rapidly and a second polarogram was usually run immediately to determine whether the bulk Tl(III) concentration had remained essentially constant.

Results and Discussion

A. Polarograms of Tl(III) and Tl(I).—A typical polarogram of Tl(III) in 0.6 *M* HCl is shown in Fig. 1 (curve A). The reduction current of Tl(III) merges without break with the anodic dissolution current of mercury near zero volts (*vs.* S.C.E.), rises to a constant current, $i_{(\text{III})/(\text{I})}$ (corrected for residual current), and then rises again near −0.45 v. *vs.* S.C.E. to a second constant current, $i_{(\text{III})/(0)}$. The current $i_{(\text{III})/(\text{I})}$ may be assumed to result from the reduction of Tl(III) to Tl(I) and the current $i_{(\text{III})/(0)}$ can be assumed to represent the reduction of Tl(III) to Tl(0) (Tl-amalgam). The current, $i_{(\text{III})/(\text{I})}$, was measured over the range 0.02 to 1.0 × 10^{-3} *M* Tl(III) and found to be proportional to Tl(III) concentration.

The diffusion currents, $i_{(\text{III})/(\text{I})}$ and $i_{(\text{III})/(0)}$, were measured at −0.26 and −0.70 v. *vs.* S.C.E., respectively. It was found by averaging the results for several Tl(III) solutions in 0.6 *M* HCl that the ratio, $i_{(\text{III})/(0)}$ to $i_{(\text{III})/(\text{I})}$, was 1.51 ± 0.01. This value is in accordance with the assumption that these currents result from three-electron and two-electron reductions, respectively, and that the diffusion rate of Tl(III) controls the magnitude of both diffusion currents. This observed value for the ratio is in excellent agreement with the expected value of 1.516, which takes into account small differences in current arising from differences in characteristics of the capillary electrode at the above potentials, *i.e.*, $m^{2/3}t^{1/6} = 2.161$ and 2.184 m.g.$^{2/3}$ sec.$^{-1/2}$, at −0.26 and −0.70 v. *vs.* S.C.E., respectively. The drop times, t, at these potentials were 4.34 and 4.42 seconds, respectively.

It was shown that by varying the mercury height $i_{(\text{III})/(\text{I})}$ was very nearly proportional to the square root of the mercury pressure (expressed in cm. of mercury) over the range *ca.* 28 to 79 cm. of mercury. This observation and the fact that the Tl(III)/(I) diffusion current plateau was very nearly parallel to the residual current may be taken as evidence that the reduction of Tl(III) to Tl(I) occurs practically instantaneously at the dropping mercury electrode.

For comparison a polarogram of Tl(I) at the same thallium concentration (3.33 × 10^{-4} *M* is also shown in Fig. 1 (curve B). It can be seen that $i_{(\text{I})/(0)}$ corrected for residual current in curve B is about 40% larger than the corresponding reduction current $i_{(\text{III})/(0)} - i_{(\text{III})/(\text{I})}$ of curve A. This large difference indicates that the diffusion coefficient of Tl(I) is considerably larger than that of Tl(III).

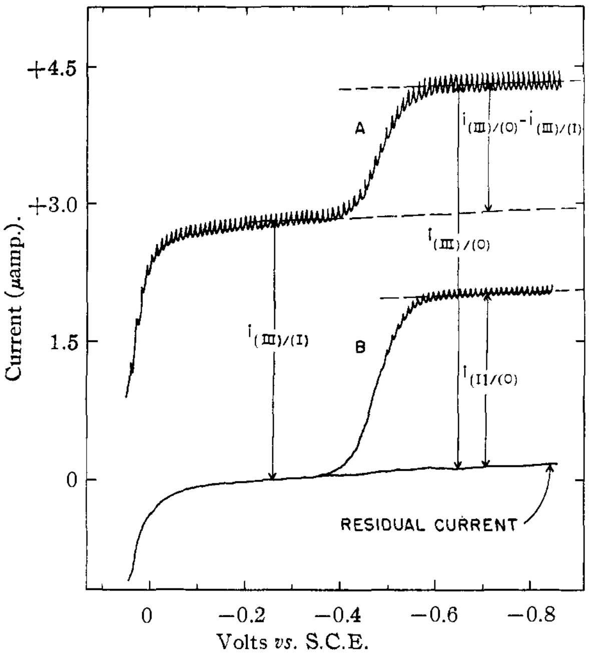

Fig. 1.—Polarograms of thallium(III) and- (I) solutions 25°, 0.6 *M* HCl; A, 3.33 × 10^{-4} *M* Tl(III); B, 3.33 × 10^{-4} *M* Tl(I).

Diffusion current constants, $I_{(\text{III})/(\text{I})}$ and $I_{(\text{I})/(0)}$ for Tl(III) and Tl(I) solutions, respectively, were calculated in the usual way, by substituting values of $i_{(\text{III})/(\text{I})}$ and $i_{(\text{I})/(0)}$ in the equation $I = i_d/cm^{2/3}t^{1/6}$ (*cf.* Ilkovič equation, $i_d = 607nD^{1/2}\cdot cm^{2/3}t^{1/6}$ where n, D, c, m and t have their usual definition.[10] For 0.6 *M* HCl solution, $I_{(\text{III})/(\text{I})} = 3.83 \pm 0.03$, $I_{(\text{III})/(0)} = 5.72 \pm 0.08$, and $I_{(\text{I})/(0)} = 2.65 \pm 0.03$.[11] Each of these values is based on measurements of currents from at least nine separate polarograms of pure Tl(III) or Tl(I) solutions. Diffusion coefficients corresponding to these diffusion current constants were calculated with the Ilkovič equation and found to be 1.00 and 1.91 × 10^{-5} cm.^{2} sec.$^{-1}$ for Tl(III) and Tl(I), respectively.

B. Polarograms of Tl(III)-Tl(I) Mixtures.—Polarograms were run on several solutions containing varying amounts of Tl(III) and Tl(I) in 0.6 *M* HCl. The total thallium concentration (0.332 × 10^{-4} *M*) was held constant while the concentration of Tl(I) was increased from 0 to 0.315 × 10^{-3} *M*. The results are summarized in Fig. 2.

At a potential −0.27 v. *vs.* S.C.E. the current $i_{(\text{III})/(\text{I})}$ observed for solutions containing Tl(III) and Tl(I) results from the reduction of Tl(III) to Tl(I) and as shown in Fig. 2 is proportional to Tl(III) concentration. The total current at −0.7 v. *vs.* S.C.E., however, may be considered to represent the sum of two reduction currents, $i_{(\text{I})/(0)}$ and

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

(11) This value is in good agreement with literature values (a) I = 2.69 for 0.1 *N* HCl, J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939); (b) I = 2.71 in 0.1 *N* KCl, F. Buckley and J. K. Taylor, *J. Research Natl. Bur. Standards*, **34**, 106 (1945); and (c) I = 2.693 in 0.613 *N* HCl, L. Meites, THIS JOURNAL, **73**, 4257 (1951).

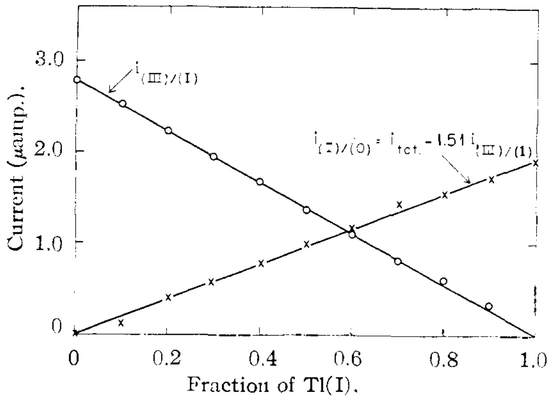

Fig. 2.—Diffusion currents of Tl(III) and Tl(I) in 0.6 M HCl; total Tl = 0.332×10^{-3} M, 25°, no maximum suppressor.

$i_{(III)/(0)}$. By substituting the measured current, $i_{(III)/(I)}$, in the relationship, $i_{(III)/(0)} = \alpha\, i_{(III)/(I)}$ where α = a proportionality constant, the Tl(I) current, $i_{(I)/(0)}$ may be calculated by the expression

$$i_{(I)/(0)} = i_{tot} - \alpha i_{(III)/(I)} \qquad (1)$$

where i_{tot} = total current corrected for residual current at −0.7 v. *vs.* S.C.E. Figure 2 also shows a plot of $i_{(I)/(0)}$ calculated by equation 1 (using the experimental value $\alpha = 1.51$) *vs.* fraction of Tl(I). It can be seen that $i_{(I)/(0)}$ is proportional to Tl(I) concentration. At small fractions of Tl(I), $i_{(I)/(0)}$ values were, of course, subject to greater errors because of difficulty of measuring small differences between two relatively large reduction currents. A similar series of measurements with solutions containing a total thallium concentration of 1.00×10^{-3} M gave essentially similar results.

It can be concluded from these experiments that diffusion current constants for Tl(I) and Tl(III) are independent of the Tl(I)/Tl(III) ratio in Tl(I)–Tl(III) mixtures and hence analysis of such mixtures may be carried out rather easily, by utilizing the linear relationship expressed in equation 1. Certain reducible substances, such as Fe(III) which also produce a constant reduction current in the region 0 to −0.45 v. *vs.* S.C.E. must of course be taken into consideration in analytical applications.

C. Half-wave Potential of Tl(I).—The most precise measurements of the Tl(I)/(0) half-wave potential (*vs.* S.C.E.) reported in the literature appear to be those by Lingane[2] who found $E_{1/2}$ = −0.458 ± 0.003 v. in 0.10 M KCl and $E_{1/2}$ = −0.480 v. in 1.0 M KCl. The average of three determinations in this Laboratory in 0.10 M KCl was $E_{1/2}$ = 0.458 ± 0.003 and a single measurement in 0.1 M KCl, 0.005 M HCl gave $E_{1/2}$ = −0.462, in reasonable agreement with Lingane's value for 0.1 M KCl. In 1.0 M HCl, $E_{1/2}$ was found to be −0.491 v., considerably more negative than Lingane's value for 1.0 M KCl. This more negative value probably is due, in part, to the fairly large liquid junction potential which exists between 1 M HCl and the saturated calomel reference electrode.

Half-wave potentials of the wave appearing in the polarograms of pure Tl(III) solutions were found to be essentially the same[12] as those for pure Tl(I) solution in the same supporting electrolyte. For example, $E_{1/2}$ = −0.463 ± 0.003 and −0.495 ± 0.003 in 0.10 M KCl, 0.005 M HCl and 1.0 M HCl, respectively. Each measurement was based on at least three separate determinations with pure Tl(III) solutions. All waves were tested for reversibility, plotting log $(i - i_{(III)/(I)})/(i_{(III)/(0)} - i)$ *vs.* E_{cor}, and the resulting slopes were found to agree within ±0.004 v. with the expected Nernst slope, −0.059 v. at 25°.

Acknowledgment.—The authors are indebted to Dr. Kurt A. Kraus for helpful criticisms and advice during the course of the work.

[12] This wave is thus associated with the Tl(I) to Tl(0) reduction as pointed out previously by Hughes and Hush (ref. 5).

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Transference Numbers in Aqueous Zinc and Cadmium Sulfates[1]

BY ROBERT E. LANG AND CECIL V. KING

RECEIVED FEBRUARY 26, 1954

Transference numbers of zinc and cadmium ions in aqueous solutions of the sulfates at 25° have been determined from the electromotive force of concentration cells with lead amalgam-lead sulfate electrodes. The results for zinc ion agree with those found by Purser and Stokes,[3] and values for cadmium ion are similar.

Transference numbers of the sulfate ion in aqueous zinc and cadmium sulfates were calculated by Wolten and King[2] from the e.m.f. of concentration cells with zinc and cadmium amalgam electrodes. The measurements with zinc sulfate were repeated by Purser and Stokes,[3] who pointed out that the experimental e.m.f. values of Wolten and King were not adequate for the purpose, and that the mathematical treatment and interpretation were improper. The present authors agree with these conclusions, and have made new measurements in order to establish transference numbers in both systems with certainty. The values obtained for zinc ion agree closely with those found by Purser and Stokes, and those for cadmium ion are similar.

Transference numbers of the metal ions were determined directly with the aid of the cells

$$\underset{\text{two phase}}{\text{Pb–Hg}} \mid \text{PbSO}_4(s),\ \text{MSO}_4(m) \mid \text{MSO}_4(\text{ref}),\ \text{PbSO}_4(s) \mid \underset{\text{two phase}}{\text{Pb–Hg}}$$

MSO_4(ref) indicates a constant molality for all

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[1] From a Ph.D. thesis submitted to the Graduate School of New York University by Robert E. Lang.

[2] G. M. Wolten and C. V. King, THIS JOURNAL, **71**, 576 (1949).

[3] E. P. Purser and R. H. Stokes, *ibid.*, **73**, 5650 (1951).