undoubtedly real. These values if divided by the concentration of mercury dimethyl in molecules/cc. should give $k_2/k_1^{1/2}$. The results are as follows: 5.5, 5.0, 4.8, 4.8, 4.1 all times 10^{-13} molecules$^{-1/2}$ cc.$^{1/2}$ sec.$^{-1/2}$. The average value is 4.8×10^{-13} in this respect in good agreement with the Rebbert and Steacie value of 4.6×10^{-13} at the same temperature. The trend in the results in Table I could be due to several causes, such as "volume effect," walls, or possibly a method of ethane formation in addition to 1.

There are reasons for suspecting that a second ethane forming step may not be real,[9] but one argument in favor of such a step needs to be examined. Evidently at 175° (Table I) more than two methyls appear as methane and ethane per quantum absorbed. This might be due to some reaction which could be written either as the single step

$$CH_3 + Hg(CH_3)_2 = C_2H_6 + Hg + CH_3 \qquad (3)$$

or as a sequence of steps[3] with the same over-all result. However, the quantum yield of ethane formation is nearly independent of the amount of methane formed. This makes one suspect that formation of methane is accompanied by regeneration of methyl radicals at 175°, possibly by decomposition of CH_2HgCH_3. Ethylene is observed at temperatures over 200° so that CH_2HgCH_3 may decompose to give CH_3, CH_2 and Hg. At 175° the fate of $HgCH_2$ is unknown. Further speculation about the mechanism is not warranted. Suffice to say that short chains evidently occur, in agreement with the work of Linnett and Thompson.[10]

The formation of "hot" methyls has been postulated for this reaction by several authors.[11] If the steric factor for reaction 2 for "hot" methyls is the same as for "cold" methyls, it would be exceedingly difficult to obtain evidence either for or against them. At most 1% of the initially formed methyls would form methane because they are "hot," *i.e.*, the quantum yield of methane from this source would be not over 0.01 to 0.02 and would escape notice under most experimental conditions. At 175° where some of the methyls are formed from a chain propagating step an even smaller fraction would appear to be "hot" and the conclusion of Rebbert and Steacie[7] that "hot" methyls can be neglected in obtaining activation energies for the methane forming steps is undoubtedly correct under most experimental conditions.

It may be stated, therefore, that there is no conclusive evidence for an ethane forming step other than 1 and that evidence either for or against "hot" methyls could be obtained in this system only under exceptional circumstances and with data of very high precision.

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On the Theory of the Polarographic Diffusion Current. II. Diffusion of Small Amount of Thallium Ion in Aqueous Potassium Chloride Solutions[1]

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Previous results on the tracer-diffusion coefficients of Pb(II) and Zn(II) ions in solution of various supporting electrolytes show that there is considerable disagreement between the observed "diffusion current constant" and the theoretical values computed from the Ilkovič and Lingane–Loveridge equations, respectively.[1] Values of the "diffusion current constant" calculated from the Strehlow–von Stackelberg equation lie closer to the experimental values for Pb(II) ion in 0.1 *F* HCl + 0.1 *F* KCl solution and for Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution, respectively, but the agreement is not satisfactory enough for us to conclude definitely that the Strehlow–von Stackelberg equation is correct.

In the present work the tracer-diffusion coefficients of Tl(I) ion in aqueous potassium chloride solutions were determined. The results were discussed in the light of Onsager's theory for tracer-diffusion in dilute solutions. The "diffusion current constant" of Tl(I) ion in 0.1 *F* KCl solution was then calculated from the present data by means of the Ilkovič, Strehlow–von Stackelberg and Lingane–Loveridge equations, respectively, and compared with experimental data.

Experimental

Tracer Solution.—Tl^{204} was used as tracer for Tl(I) ion. This was obtained from the Isotopes Division of the U. S. Atomic EnergyCommission at Oak Ridge, Tennessee. In order to eliminate possible adsorption errors,[1] all solutions used in the present work were made from 0.0005 to 0.002 in TlCl.

Diffusion Measurement.—The experimental method of tracer-diffusion measurement has been described previously.[2] All measurements were carried out at 25.00 ± 0.01°.

Results and Discussion

The tracer-diffusion coefficients of Tl(I) ion in aqueous potassium chloride solutions at 25° as determined in the present work are summarized in Table I. Each value of *D* listed in Table I is the average result of six measurements.

TABLE I

TRACER-DIFFUSION COEFFICIENTS OF Tl(I) ION IN AQUEOUS KCl + TlCl SOLUTIONS AT 25°

Concn. of KCl, formula wt./l.	Concn. of TlCl, formula wt./l.	$D \times 10^5$, cm.^{2}/sec.
0.005	0.0005	1.92 ± 0.02
.02	.002	1.90 ± .03
.05	.002	1.86 ± .02
.10	.002	1.84 ± .02
.20	.002	1.79 ± .02

Using appropriate units the Onsager equation[3] can be written as

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[1] Paper I, THIS JOURNAL, **76**, 1528 (1954).

[2] J. H. Wang, C. V. Robinson and I. S. Edelman, THIS JOURNAL, **75**, 466 (1953).

[3] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

$$D_j = \frac{RT\lambda^0{}_j}{|Z_j|\mathfrak{F}^2} - \frac{\lambda^0{}_j|Z_j|\mathfrak{F}}{3N\mathfrak{D}} \times$$
$$2.694 \times 10^{16} \sqrt{\frac{4\pi}{\mathfrak{D}RT}}\,[1 - \sqrt{d(\omega_j)}\,]\sqrt{\sum_i c_iZ_i{}^2} \quad (1)$$

where D_j is the tracer-diffusion coefficient of ionic species j in a dilute solution containing other kinds of ions i, Z_i is the charge in electronic units and c_i the concentration in moles per liter of ion i, $\lambda_j{}^0$ the limiting equivalent conductance of ion j, $\mathfrak{D}$ the dielectric constant of the solvent, k the Boltzmann constant, F the Faraday constant, T the solute temperature, and $d(\omega_j)$ a function given by

$$d(\omega_j) = \frac{1}{\sum_i c_iZ_i{}^2} \sum \frac{c_i|Z_i|\lambda^0{}_i}{(\lambda^0{}_i/|Z_i|) + (\lambda^0{}_j/|Z_j|)}$$

using $\lambda^0{}_{Tl^+} = 74.7$,[4] $\lambda^0{}_{K^+} = 73.5$ and $\lambda^0{}_{Cl^-} = 76.35$[5] for the present system, equation 1 can be simplified to

$$D \times 10^5 = 1.95 - 0.454\sqrt{c} \qquad (2)$$

Equation 2 is plotted in Fig. 1 together with values listed in Table I. The shaded point represents the limiting value of D at infinite dilution computed from conductance data.[4,5] Figure 1 indicates that as the concentration of the supporting electrolyte approaches zero the D *vs.* $\sqrt{c}$ curve approaches very closely to the straight line representing equation 2. This agreement is rather surprising since there appears to be some evidence that TlCl has a small dissociation constant in aqueous solutions and yet the measured values of D for Tl(I) ion in KCl(aq) agree with the theoretical values predicted by equation 2 better than those for the tracer-diffusion of the "normal" ions such as Na^+, Cl^-, Cs^+, etc., in KCl (aq).[6]

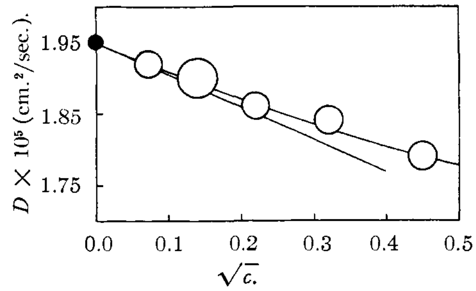

Fig. 1.—Tracer-diffusion coefficient of Tl(I) ion in KCl(aq) at 25°. The straight line represents equation 2.

If the evidence for the complex formation of Tl(I) ion in chloride solutions is valid,[7] we may take the values depicted in Fig. 1 as suggesting that the ion-complex, such as TlCl, diffuses somewhat slower than the simple Tl^+ ion in dilute solutions.

The equation for the polarographic diffusion current at the dropping mercury electrode is

$$i_d = 607nD^{1/2}cm^{2/3}t^{1/6}\left(1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}}\right) \qquad (3)$$

where $A = 0$ according to Ilkovič, $A = 17$ according to Strehlow–von Stackelberg, and $A = 39$ according to Lingane–Loveridge.[8] The diffusion current constant, $I = i_d/(cm^{2/3}t^{1/6})$, of Tl(I) ion in 0.1 F KCl solution containing 0.01% by weight of gelatin at 25° has been measured as a function of $t^{1/6}m^{-1/3}$ by Strehlow and von Stackelberg[9] and by Strehlow, Mädrich and von Stackelberg, respectively.[10] Their data are plotted in Fig. 2.

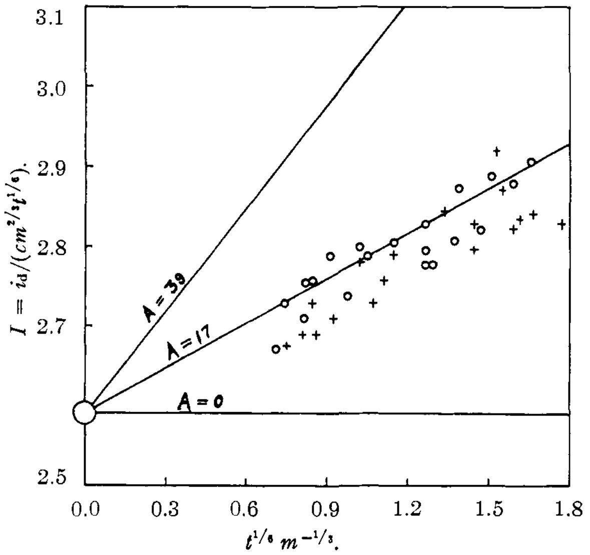

Fig. 2.—Comparison of equation 3 with polarographic diffusion current data for Tl(I) ion in 0.1 F KCl solution containing 0.01% by weight of gelatin at 25°: O, data from reference 9; +, data from reference 10.

The three straight lines in Fig. 2 represent equation 3 with $A = 0$, 17 and 39, respectively, computed from the present diffusion data with $D_{Tl(I)} = 1.827 \times 10^{-5}$ cm.²/sec. in 0.1 F KCl solution without gelatin as read from the curve in Fig. 1. Tanford[11] showed that the fraction of Tl(I) bound to bovine serum albumin is negligible at all experimental *p*H values. Consequently we may consider the effect of 0.01% gelatin on the tracer-diffusion coefficient of Tl(I) ion in 0.1 F KCl solution as negligible.

It is clearly shown in Fig. 2 that the deviations of equation 3 with A = 0 or 39 from the experimental values are much larger than those for A = 17, although the agreement for A = 17 cannot be consideerd as entirely satisfactory.

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