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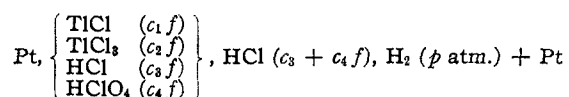
The Formal Oxidation-Reduction Potentials of Thallous-Thallic Salts in Aqueous Hydrochloric Acid Solutions. Formation of Chlorothallate Complex Ions¹

BY RICHARD H. HUGHES AND CLIFFORD S. GARNER

The oxidation-reduction potentials of thallous-thallic salts have been investigated in aqueous solutions of hydrochloric,² sulfuric,^{2,3,4} nitric^{2,5} and perchloric⁶ acids. These studies have shown that the formal potentials⁷ differ in the presence of various anions, suggesting the formation of anion complexes with thallic ion.

In particular, the experiments of Spencer and Abegg² have indicated the probable formation of one or more chloride complexes of thallic ion. However, their data are not easily interpreted for several reasons: (1) because a 0.1 *N* calomel half-cell was used as a reference electrode, the results were complicated by the presence of relatively large liquid junction potentials which were not taken into account; (2) since the thallous-thallic solutions were always less than 0.2 *f* in hydrochloric acid, considerable hydrolysis of the thallic salts must have occurred in many of their solutions; and, (3) the chloride ion concentration was not varied independently of the hydrogen ion concentration and the ionic strength.

Since it seemed desirable to have more accurate values of the formal potentials in hydrochloric acid solutions and to study the formation of chloride complexes of thallic ion, the measurement of the electromotive forces of cells of the type



has been undertaken. Conditions of concentration were chosen such that the difficulties referred to in the above paragraph were eliminated almost entirely.

For the above cell, the formal potential, E^0 (for the reaction $\text{Tl}^{\text{I}} = \text{Tl}^{\text{III}} + 2e^-$) has been de-

(1) Based on a thesis presented by R. H. Hughes to the Graduate Faculty of the University of Texas in partial fulfillment of the requirements for the degree of Master of Arts, June, 1942.

(2) Spencer and Abegg, *Z. anorg. Chem.*, **44**, 379 (1905).

(3) Grube and Hermann, *Z. Elektrochem.*, **26**, 291 (1920).

(4) Partington and Stonehill, *Trans. Faraday Soc.*, **31**, 1357 (1935).

(5) Noyes and Garner, *THIS JOURNAL*, **58**, 1268 (1936).

(6) Sherrill and Haas, *ibid.*, **58**, 952 (1936).

(7) The "formal potential" is the potential, referred to the standard molal hydrogen electrode, when the total concentrations of the reduced and oxidized substances (without reference to their possible incomplete ionization, hydrolysis, formation of complexes, etc.) are both 1.0 *f*.

rived by adding to the observed potential, $E_{\text{obsd.}}$, the two following quantities

$$E_C = (RT/2F) \ln(c_2/c_1) \quad (\text{A})$$

to provide for equiformal concentrations of thallic and thallic salts, and

$$E_H = (RT/F) \ln(\sqrt{p}/\gamma(c_3 + c_4)) \quad (\text{B})$$

to refer the values to the molal hydrogen electrode, γ being the mean ionic activity coefficient of hydrogen ions in $c_3 + c_4 f$ hydrochloric acid, and p being the partial pressure of hydrogen in atmospheres. The liquid junction potential was made negligibly small by keeping the total salt concentration ($c_1 + c_2$) less than 1% of the total acid concentration, which was the same in both half-cells.⁸ This low salt concentration also made possible the maintenance of constant ionic strength in a given series of experiments. Hydrolysis of the thallic salts was reduced to a minimum by having the acid concentration 1 *f* or greater.

Since thallic ion appears to have no tendency to form chloride complexes,⁹ the variation of the formal potential with changes in concentration of thallic ions or chloride ions may be interpreted in terms of the formation of chloride complexes of thallic ion.

Hence, two types of experiment were planned. In one (Series 1 and 2) the ratio of thallic to thallic salt concentration, c_2/c_1 , was varied, and in the other (Series 3, 4 and 5) the ratio of hydrochloric to perchloric acid concentration, c_3/c_4 , was altered, in both cases $c_3 + c_4$ and all other factors being held constant in a particular series.

Experimental

Preparation and Analysis of the Solutions.—"Chemically pure" thallic nitrate was recrystallized from water solution three times, dried in an oven at 120° and stored in

(8) Although there is a liquid junction between hydrochloric and hydrochloric-perchloric acid solutions in some of the cells, the junction potential is negligible, for these two acids possess at 25° closely agreeing activity coefficients and almost identical equivalent conductances over the concentration range 1 to 4 *f*. See, for example, Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 323, and "International Critical Tables," Vol. VI, McGraw-Hill Book Co., New York, N. Y., 1929, p. 241.

(9) Noyes, *Z. physik. Chem.*, **9**, 603 (1892), has shown that the solubility of thallic chloride in solutions of potassium chloride or hydrochloric acid at 25° decreases substantially in accordance with the solubility product principle, at least up to 0.8 *f* potassium chloride solution.

a desiccator. Analysis by the iodate method using the iodine monochloride end-point¹⁰ showed the product to be 99.5% pure. It was used without further purification.

Thalious nitrate was dissolved in water, and a slight excess of hydrochloric acid was added. The precipitated thalious chloride was washed with water until the washings gave a negative test for nitrate ion with sulfuric acid and ferrous sulfate. A portion of this thalious chloride was dissolved in water. The resulting solution was standardized by the above iodate method, using a 0.01 *N* potassium iodate solution which had been prepared by weight and checked by titration against samples of Bureau of Standards arsenious oxide. The stock solution thus prepared was 0.004032 *f* in thalious chloride. All other thalious chloride solutions were made from it by weight dilution.

To prepare a stock thallic chloride solution a suspension of thalious chloride in hydrochloric acid was heated with an excess of c. p. potassium bromate. Thallic hydroxide was then precipitated by the addition of ammonium hydroxide, and was washed until the washings failed to give a positive test for bromide or chloride ion with nitric acid and silver nitrate. The moist thallic hydroxide was suspended in water and just enough hydrochloric acid added to dissolve it. Concordant analyses, made by methods described in an earlier paper,⁵ showed the resulting stock solution to be 0.02508 *f* in thallic chloride and 0.0002403 *f* in thalious chloride (this small amount of thalious chloride was always taken into account in the preparation of the cell solutions). The amount of free hydrochloric acid was negligible. Other stock thallic chloride solutions were prepared in a similar way. Both the thalious and thallic stock solutions were checked at the end of this investigation and found to have undergone no appreciable change.

The hydrochloric and perchloric acid solutions were obtained by dilution of reagent grade concentrated acids, the impurities in which were stated to be negligible. These solutions were standardized by titrating portions of a sodium hydroxide solution which had been just standardized against Bureau of Standards potassium hydrophthalate.

Tank (electrolytic) hydrogen was purified by passing it successively through concentrated solutions of sulfuric acid, potassium hydroxide and sodium plumbite, then over electrically-heated platinized asbestos.

The Cell.—The assembled cell is shown in Fig. 1. A 180-ml. electrolytic beaker served as a container (A) for the thalious-thallic mixture, in which was immersed the hydrogen half-cell and two bright platinum wire electrodes (B). In some of the early experiments one of these electrodes was cathodically polarized and the other anodically polarized in 1 *f* hydrochloric acid; our experience, unlike that of Spencer and Abegg,² indicated that equilibrium was more quickly attained with non-polarized electrodes. The hydrogen half-cell vessel was made from a 25 × 200 mm. test-tube equipped with a standard taper ground-glass joint (C) which prevented appreciable liquid diffusion while allowing electrolytic contact. The liquid junction was made inside this joint by diffusion. Inside this vessel was the hydrochloric acid solution into which dipped two platinized platinum-foil electrodes (D) and the hydrogen entrance tube (E). Before entering the half-cell the hydro-

gen from the purification train passed through a long "bubbler" trap containing hydrochloric acid of the same concentration as that used in the half-cell. A small "bubbler" trap (F) was also provided at the hydrogen outlet.

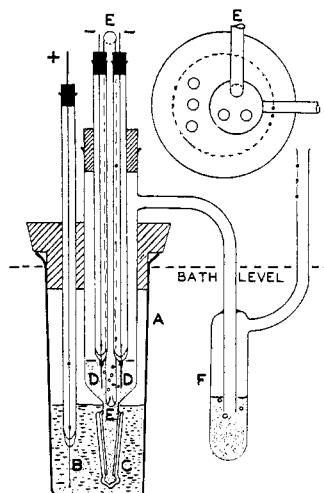


Fig. 1.—Cell for e. m. f. measurements.

All rubber stoppers and tubing were boiled in sodium hydroxide solution and rinsed well to remove sulfur.

The cell and "bubbler" traps were immersed in a kerosene-bath thermostated at the desired temperature to within $\pm 0.05^\circ$.

Method of Potential Measurements.—A Leeds and Northrup Type K-1 potentiometer and Type R galvanometer were used for the e. m. f. measurements.¹¹ The Eppley standard cell used was checked several times during the investigation against a cell which had just been certified by the National Bureau of Standards.

Solutions of thalious chloride and of thallic chloride, both in 0.9952 *f* hydrochloric acid, were prepared by weight from the stock solutions, and mixed in varying proportions for the cells of Series 1 and 2. The cells of Series 3, 4 and 5 were prepared using a stock solution containing both thalious and thallic chlorides in water or in 4 or 2 *f* perchloric acid. To a given weight of one of these solutions was added a constant weight of water obtained by mixing in the desired proportion hydrochloric and perchloric acid solutions of the same concentration.

After the cells had attained thermal equilibrium (about half an hour was allowed), the potentials were measured at intervals over a period of two to fifty hours. In practically all cases equilibrium appeared to be reached within three hours, and thereafter readings were generally constant to 0.4 mv. or better. With rare exceptions, the readings taken with the duplicate electrodes in the same cell agreed to 0.1 mv. Occasionally some of the cells were agitated by hand, and this seldom produced an appreciable effect.

All volumetric apparatus, weights and thermometers employed in this research were calibrated, and all weighings were corrected to vacuum conditions. Distilled water was used in the preparation of all the solutions.

(11) The authors wish to thank Professor W. A. Felsing for his kindness in making available to them this equipment.

(10) Swift and Garner, *THIS JOURNAL*, 58, 113 (1936).

TABLE I
ELECTROMOTIVE FORCES AT 25 AND 15° IN HYDROCHLORIC ACID SOLUTION

Series 1. 0.9952 <i>f</i> HCl ($\gamma = 0.808$) at 25°, $\mu = 1.00$							
TlCl, c_1	TlCl, c_2	$Tl^I + Tl^{III}$, $c_1 + c_2$	Tl^{III}/Tl^I , c_2/c_1	$E_{obsd.}$	E_C	E_H	$E^{0'}$
0.0001814	0.00001886	0.0002001	0.1040	-0.7593 (1)	-0.0291	+0.0049	-0.7835
.0001016	.00009430	.0001959	0.9281	-.7862 (2)	-.0010	+.0049	-.7823
.0001556	.0004715	.0006271	3.030	-.8019 (2)	+.0142	+.0051	-.7826
.0001097	.0009430	.001053	8.596	-.8148 (3)	+.0276	+.0049	-.7823
.00006390	.001415	.001479	22.14	-.8272 (4)	+.0398	+.0051	-.7823
.0001962	.004715	.004911	24.03	-.8289 (2)	+.0408	+.0050	-.7831
.0001452	.004715	.004861	32.32	-.8328 (1)	+.0446	+.0050	-.7832
.00001806	.001886	.001904	104.4	-.8468 (3)	+.0597	+.0049	-.7822
.00004515	.004715	.004760	104.4	-.8474 (1)	+.0597	+.0050	-.7827
.0001806	.01886	.01904	104.4	-.8489 (2)	+.0597	+.0049	-.7843
Mean							-.7829
Series 2. 0.9952 <i>f</i> HCl ($\gamma = 0.822$) at 15°, $\mu = 1.00$							
0.0001814	0.00001886	0.0002001	0.1040	-0.7585 (1)	-0.0281	+0.0045	-0.7821
.0001016	.00009430	.0001959	.9281	-.7844 (2)	-.0010	+.0045	-.7809
.00001806	.001886	.001904	104.4	-.8422 (1)	+.0577	+.0045	-.7800
.0001806	.01886	.01904	104.4	-.8456 (2)	+.0577	+.0045	-.7834
Mean							-.7816

Results and Discussion

Potentials in Hydrochloric Acid Solution.—

In Table I are presented the results of measurements made at 25 and 15° with cells in which perchloric acid was not present. The hydrochloric acid concentration was kept at 0.9952 *f*, corresponding to an ionic strength (μ) of 1.00. All concentrations have been expressed as weight formalities, *f* (formula weights per kilogram of water). Usually check cells were made up and measured. The values of $E_{obsd.}$ given in the table represent average values based on the number of cells indicated in the parentheses immediately following each value.¹² The values of $E^{0'}$ were calculated as indicated earlier in this paper, the values of the activity coefficient of hydrochloric acid (given in parentheses following the concentration of the acid) being interpolated from the data of Harned and Ehlers,¹³ and the partial pressure of hydrogen being computed from the corrected barometric pressure by subtraction of the vapor pressure of the acid solution at the given temperature¹⁴ and addition of the hydrostatic head.

From the third, fourth and last columns of Table I it may be seen that the formal potential is not materially altered by changing the ratio c_2/c_1 or the formal concentration of the thallic salt one

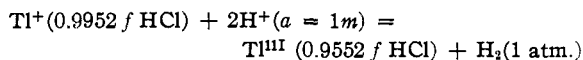
(12) The spread between extreme values was less than 0.5 mv. as a rule, but in a number of cases it was greater, becoming 3.7 mv. in the worst case.

(13) Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933).

(14) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 301.

thousand-fold in the range indicated. One requirement of this constancy of $E^{0'}$ is that there be only one thallium atom per thallic complex present in appreciable concentration.¹⁵

The cells of Series 1 and 2 give the average values of -0.7829 ± 0.0015 and -0.7816 ± 0.0015 volt for $E^{0'}$ at 25 and 15°, respectively. From these values there are calculated for the cell reaction



values of $\Delta F_{298}^0 = 36.12$ kcal., $\Delta H_{298}^0 = 34.48$ kcal., and $\Delta S_{298}^0 = -0.0055$ kcal./deg.¹⁶

Potentials in Mixtures of Hydrochloric and Perchloric Acid Solutions.—The measurements of Series 3, 4 and 5 were carried out with mixtures of hydrochloric and perchloric acid solutions so that the chloride ion concentration could be varied independently of hydrogen ion concentration and ionic strength. The results, together with the concentration conditions under which they were obtained, are given in Table II. Reference to columns one and six shows that the formal poten-

(15) If complexes of the type $Tl_2Cl_x(\nu - 3x)^{\pm}$ are important and stable in the solutions studied, then

$$E^{0'} = (RT/2F)(1 - 1/x) \ln c_2 + \text{constant}$$

where x is the average number of thallium atoms per complex. For example, if x were 2, the thousand-fold variation in c_2 would have produced a change of 44 mv. in $E^{0'}$ at 25°.

(16) From the relatively large variation in the values of $E^{0'}$ at 15° it would appear that the entropy change is unreliable. However, by taking the temperature coefficients of the six cells involved and averaging them the value -0.00012 volt per degree was obtained, the mean deviation from the mean being 0.00002 volt per degree.

TABLE II
ELECTROMOTIVE FORCES AT 25° IN MIXTURES OF HYDROCHLORIC AND PERCHLORIC ACID SOLUTIONS

HCl, c_1	Log ₁₀ c_1	$E_{\text{obsd.}}$	E_C	E_H	$E^{0''}$	$E^{0'''}$
Series 3. Total acid concentration, 4.007 f ($\gamma = 1.762$), $\mu = 4.01$ ($c_1 = 2.070 \times 10^{-4} f$, $c_2 = 4.520 \times 10^{-4} f$, $c_2/c_1 = 2.184$)						
1.003	+0.0013	-0.7260 (2)	+0.0100	-0.0506	-0.7666	-0.7667
0.8020	- .0958	- .7357 (2)	+ .0100	- .0506	- .7763	- .7664
.6017	- .2206	- .7472 (1)	+ .0100	- .0508	- .7880	- .7652
.4013	- .3965	- .7682 (2)	+ .0100	- .0509	- .8091	- .7681
.2010	- .6968	- .8008 (4)	+ .0100	- .0507	- .8415	- .7694
						Mean - .7672
Series 4. Total acid concentration, 2.000 f ($\gamma = 1.010$), $\mu = 2.00$ ($c_1 = 2.070 \times 10^{-4} f$, $c_2 = 4.520 \times 10^{-4} f$, $c_2/c_1 = 2.184$)						
1.001	+0.0004	-0.7691 (2)	+0.0100	-0.0188	-0.7779	-0.7779
0.8006	- .0966	- .7785 (2)	+ .0100	- .0188	- .7873	- .7773
.6006	- .2214	- .7912 (2)	+ .0100	- .0189	- .8001	- .7772
.5006	- .3005	- .7991 (1)	+ .0100	- .0188	- .8079	- .7768
.4006	- .3973	- .8091 (2)	+ .0100	- .0189	- .8180	- .7769
.2006	- .6977	- .8413 (2)	+ .0100	- .0189	- .8502	- .7780
						Mean - .7774
Series 5. Total acid concentration, 0.9952 f ($\gamma = 0.808$), $\mu = 1.00$ ($c_1 = 2.099 \times 10^{-4} f$, $c_2 = 1.866 \times 10^{-4} f$, $c_2/c_1 = 0.8890$)						
0.9952	-0.0021	-0.7871 (1)	-0.0015	+0.0050	-0.7836	-0.7834
.7464	- .1270	- .7991 (2)	- .0015	+ .0051	- .7955	- .7824
.4976	- .3031	- .8204 (2)	- .0015	+ .0050	- .8169	- .7855
.3483	- .4581	- .8348 (1)	- .0015	+ .0050	- .8313	- .7839
.2488	- .6042	- .8465 (2)	- .0015	+ .0049	- .8431	- .7806
.1742	- .7590	- .8644 (1)	- .0015	+ .0051	- .8608	- .7822
.0995	-1.002	- .8938 (1)	- .0015	+ .0049	- .8904	- .7867
						Mean - .7835

tial, $E^{0''}$, is a function of chloride ion or perchlorate ion concentration. Since the work of Sherrill and Haas⁶ has indicated that perchlorate ions have little or no tendency to form complexes with thallic ion over the range 0.5 to 1.2 f perchloric acid, this variation in $E^{0''}$ may be interpreted in terms of the formation of complexes involving chloride and thallic ions.

Conceivably, a solution of thallic chloride in hydrochloric acid may contain complexes such as TiCl^{++} , TiCl_2^+ , TiCl_3 , TiCl_4^- , . . . , $\text{TiCl}_i^{(i-3)-}$, having equilibrium dissociation constants K_1 , K_2 , K_3 , . . . , K_i , respectively. Assuming that the relatively high acid concentrations employed in these studies prevent the formation of hydrolytic complexes such as TlOH^{++} and $\text{Tl}(\text{OH})_2^+$, and that the concentration of free (hydrated) Tl^{+++} is very small compared to that of the complexes,¹⁷ then

$$c_2 = (\text{TiCl}^{++}) + (\text{TiCl}_2^+) + \dots + (\text{TiCl}_i^{(i-3)-}) \quad (1)$$

In terms of the dissociation constants, (1) becomes

(17) The latter assumption seems justified in view of the fact that the formal potentials in hydrochloric acid solutions are about 0.5 volt more positive than the corresponding potentials in perchloric acid solution.

$$c_2 = (\text{Ti}^{+++}) \sum_{i=1}^n (\text{Cl}^-)^i / K_i \quad (2)$$

Now, the formal potential is related to the molal thallos-thallic potential, E^0 , by the equation

$$E^{0''} = E^0 - (RT/2F) \ln (\gamma_{\text{Ti}^{+++}} / \gamma_{\text{Ti}^+}) + (RT/2F) \ln c_2 / (\text{Ti}^{+++}) \quad (3)$$

Substitution of (2) into (3) and the collection of all terms which are constant under the conditions of Series 3, 4 or 5, leads to the following relation for the variation of $E^{0''}$ with chloride ion concentration:

$$E^{0''} = (RT/2F) \ln \sum_{i=1}^n (\text{Cl}^-)^i / K_i + \text{constant} \quad (4)$$

Within the accuracy of the results described in this paper, the sum term may be replaced by the term $(\text{Cl}^-)^y / K_y$, where y is a weighted average of the number of chlorine atoms per complex.¹⁸ Equa-

(18) The condition for the replacement is that

$$(\text{Cl}^-)^y = \frac{a(\text{Cl}^-) + b(\text{Cl}^-)^2 + \dots + n(\text{Cl}^-)^n}{ab \dots n}$$

where the coefficients are products of suitable dissociation constants. Consequently, the value of y is a function of chloride ion concentration as well as of the exponents, but for our experiments the change in y for a ten-fold change in (Cl^-) is less than 10%. This change in slope cannot be detected in our graphs, and for all practical purposes y is a constant.

tion (4) then becomes

$$E^{0''} = y(RT/2F) \ln(\text{Cl}^-) + \text{constant} \quad (5)$$

Accordingly, a straight line should be obtained if $E^{0''}$ is plotted against $\log c_3$, the slope being $2.303 (RT/2F)y$.

In order to investigate this power dependence of $E^{0''}$ upon the chloride ion concentration, plots were made of the data from Series 3, 4 and 5, and these are given in Fig. 2. Within the experimental error the points fall on straight lines the slopes of which are almost identical. The average number of chlorine atoms per thallic complex was thus found to be 3.5 ± 0.2 , indicating that chlorothallate anions exist in appreciable concentrations under the given conditions. Definite conclusions regarding the formulas of such complex ions cannot be deduced from these data, however.¹⁹

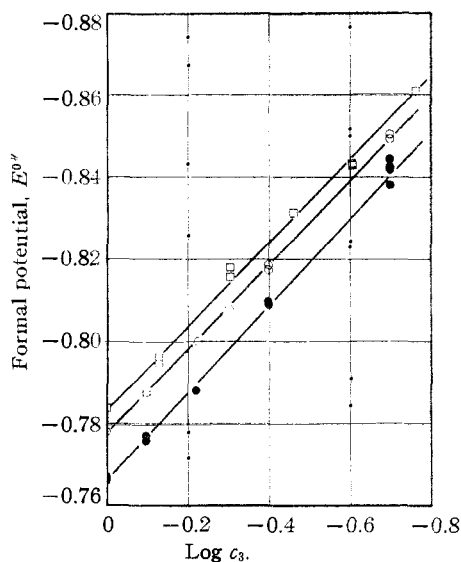
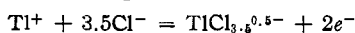


Fig. 2.—Power dependence of formal potential upon the chloride ion concentration: ●, $\mu = 4.01$; ○, $\mu = 2.00$; □, $\mu = 1.00$.

In the last column of Table II are given values of $E^{0'''}$, the formal potential for the reaction



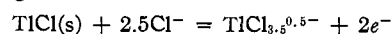
(19) It has been reported that a solid with the composition $\text{TlCl}_{3.5}$ may be prepared from thallic and thallic chlorides (see, for example, Spencer and Abegg, *loc. cit.*). If this solid is a compound it may be thallic hexachlorothallate, in which event TlCl_6^{3-} ions presumably could exist in solution as well as in the crystal lattice. Covalent complexes of this type could probably be formed by use of the $6s$ and $6p$ orbitals (TlCl_4^- , sp^3) or with the $6s$, $6p$ and two $6d$ orbitals (TlCl_5^{2-} , sp^3d^2); these two complexes would then resemble SnCl_4 and SnCl_5^{2-} , since it is likely that the latter make use of the corresponding $5s$, $5p$ and $5d$ orbitals in bond formation. There would probably be an appreciable amount of ionic character to such bonds.

Using the average of the values at each ionic strength, the following relation has been derived for the temperature of 25°

$$E^{0'''} = -0.7880 + 0.00508 \mu \quad (6)$$

Equation (6) reproduces within 1 mv. the values of $E^{0'''}$ over the range $\mu = 1$ to $\mu = 4$.

Equation (6) may be combined with the standard free-energy of ionization of solid thallic chloride²⁰ to give for the reaction



the formal potential, $E^{0''''}$, at 25°

$$E^{0''''} = -0.8902 + 0.00508 \mu \quad (7)$$

This value should replace that estimated by Latimer.²¹

Summary

1. The formal oxidation-reduction potential, $E^{0''}$, of thallic-thallic salts in 0.9952 *f* hydrochloric acid has been determined at 25 and 15° . $E^{0''} = -0.7829 \pm 0.0015$ volt for the reaction $\text{Tl}^I = \text{Tl}^{III} + 2e^-$ at 25° in the above acid solution and for a thousand-fold variation of thallic salt concentration. The thermodynamic constants for the reaction $\text{Tl}^+ (0.9952 \text{ } f \text{ HCl}) + 2\text{H}^+ (a = 1m) = \text{Tl}^{III} (0.9952 \text{ } f \text{ HCl}) + \text{H}_2 (1 \text{ atm.})$ were found to be: $\Delta F_{298}^0 = 36.12$ kcal., $\Delta H_{298}^0 = 34.48$ kcal., and $\Delta S_{298}^0 = -0.0055$ kcal./deg.

2. Measurements have been made of the potentials in mixtures of hydrochloric and perchloric acid solutions of constant total acid concentration and constant ionic strength. The results were interpreted in terms of the formation of chlorothallate anions of the type TlCl_4^- and TlCl_6^{3-} . Most of the thallic ions are bound in the form of such complexes, there being one thallium atom and, on the average, 3.5 chlorine atoms per complex in the range of hydrochloric acid concentration from 0.1 to 1 *f*.

3. For the half-cell reaction $\text{Tl}^+ + 3.5\text{Cl}^- = \text{TlCl}_{3.5}^{0.5-} + 2e^-$, the formal potential at 25° was found to be given by the relation $E^{0'''} = -0.7880 + 0.00508 \mu$, over the range of ionic strength from $\mu = 1$ to $\mu = 4$. The corresponding formal potential, $E^{0''''}$, for the reaction $\text{TlCl}(s) + 2.5\text{Cl}^- = \text{TlCl}_{3.5}^{0.5-} + 2e^-$ is $E^{0''''} = -0.8902 + 0.00508 \mu$.

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(20) $\text{TlCl}(s) = \text{Tl}^+(aq.) + \text{Cl}^-(aq.)$; $\Delta F_{298}^0 = 5.086$ kcal. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1928, p. 152.

(21) Latimer, *ibid.*, p. 154.