by the prescribed test using catalyst prepared by the precipitation of nickel on kieselguhr[6] had an iodine number of 48 to 55, while under the same conditions of testing, the nickel–chromic oxide catalyst consistently gave hardened fats of iodine number of 29 to 35. With the promoted catalysts, using one of the promoting substances, sulfur, selenium or tellurium in its optimum concentration, it was possible to obtain, consistently, hardened fats of iodine number 2 to 7 under the same conditions as to concentration of catalyst, time, temperature and degree of agitation. It is a generally accepted fact that even the most minute quantities of compounds of sulfur, selenium or tellurium are extremely deleterious to the activity of hydrogenation catalysts, and especially so when those compounds are associated with the catalysts at high temperatures, as during the reduction. Such is true in higher concentrations as exemplified by catalysts 13, 15, 19 and 20 above. However, when the concentration is less there is actually an increase of activity over that of catalysts prepared in exactly the same way but with the strict exclusion of all traces of the so-called promoter elements. Further as the concentration is made still less the activity of the catalysts diminishes and approaches that of the unpromoted catalysts. The same degree of enhancement of activity is produced by each of the promoting elements sulfur, selenium and tellurium but at slightly different concentrations of each of the three due to the difference in solubility of the compounds in the mother liquor from the preparation of the nickel ammonium chromate. Catalysts 11 and 12 indicate that the promotion by a sulfur compound can be brought about by the addition of the sulfur compound after the decomposition of the nickel ammonium chromate and that it is not entirely necessary to have the sulfur compound incorporated at the time of the precipitation.

No explanation for the promotion of the activity of hydrogenation catalysts by substances usually considered to be virulent catalyst poisons can be offered now.

Summary

1. Catalysts composed of nickel and chromic oxide have been shown to be of high activity for the hydrogenation of an oil.

2. The use of small quantities of the compounds of sulfur, selenium and tellurium for the promotion of the activity of nickel–chromic oxide catalysts for the hydrogenation of an oil has been described.

BALTIMORE, MD. RECEIVED JANUARY 28, 1936

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[6] Reid and Rather, THIS JOURNAL, 37, 2116 (1915).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 358]

The Oxidation Potential of Thallous and Thallic Salts

BY MILES S. SHERRILL AND ARTHUR J. HAAS, JR.

Introduction

The ease of oxidation of thallous to thallic salt varies greatly with the nature of the anion present. Thus thallous chloride in hydrochloric acid solution is much more easily oxidized than is thallous sulfate or thallous nitrate in solutions of sulfuric or nitric acid. This difference is due mainly to the fact that the thallic ion, which is the primary oxidation product of thallous ion, is more or less converted into a complex anion with a consequent displacement of the equilibrium conditions of the thallous–thallic ion reaction of oxidation. The extent of such complex-ion formation, and hence the magnitude of the effect, varies with the nature of the anion of the salt and acid present.

Spencer and Abegg[1] have studied this effect of complex-ion formation quantitatively by measuring the oxidation potential of the reaction of reduction of the thallic salt for the cases cited above. Later Grube and Hermann[2] made a more careful determination at 18° of the oxidation potential of thallic to thallous sulfate in sulfuric acid solution. They showed that the oxidation potential is nearly independent of the concentration of the sulfuric acid, and that, when referred to the molal hydrogen electrode, it varies with the ratio, $(\Sigma \mathrm{Tl}^{+++})/(\Sigma \mathrm{Tl}^{+})$, of the two salt concentrations, expressed as formula weights per liter, in accordance with the simple equation

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[1] Spencer and Abegg, *Z. anorg. Chem.*, 44, 379 (1905).

[2] Grube and Hermann, *Z. Elektrochem.*, 26, 291 (1920).

$$E = 1.211 + 0.029 \log \frac{(\Sigma \mathrm{Tl}^{+++})}{(\Sigma \mathrm{Tl}^{+})} \qquad (1)$$

On the basis of this investigation the value 1.211 volt is often regarded as the molal oxidation potential at 18° of the ion reaction $\mathrm{Tl}^{+++} + 2E^- = \mathrm{Tl}^+$. This cannot be the correct value, however, since it is very improbable that the ratio of the *formal* ion constituent concentrations is identical with the ratio of the *molal* ion activities in the solutions investigated. For this reason the value 1.211 volt may be preferably called the *formal* oxidation potential of the reaction.

Partington and Stonehill[3] investigated the variation of this formal oxidation potential with the concentration of the sulfuric acid through measurement of the electromotive force at 25° of cells of the type

$$\mathrm{H_2(g),\ H_2SO_4(}c_1\mathrm{),}\ \begin{array}{c}\mathrm{Tl_2SO_4(}c_2\mathrm{)}\\ \mathrm{H_2SO_4(}c_1\mathrm{),\ Pt}\\ \mathrm{Tl_2(SO_4)_3(}c_2\mathrm{)}\end{array} \text{ and}$$

$$\mathrm{H_2(g),\ H_2SO_4(}c_1\mathrm{),\ H_2SO_4(}c_1\mathrm{),\ Hg_2SO_4(s)} + \begin{array}{c}\mathrm{Tl_2SO_4(}c_2\mathrm{)}\\ \mathrm{Hg(l),\ H_2SO_4(}c_1\mathrm{),\ Pt}\\ \mathrm{Tl_2(SO_4)_3(}c_2\mathrm{)}\end{array}$$

The concentration of the sulfuric acid is seen to be the same throughout each cell, and the ratio $(\Sigma\mathrm{Tl}^{+++})/(\Sigma\mathrm{Tl}^{++})$ is made equal to unity. For each concentration of sulfuric acid investigated (from 1 to 0.0125 f.wt. H_2SO_4 per liter) the actual thallium salt concentrations were progressively decreased by suitable dilution, and the value approached by the electromotive force as these salt concentrations approached zero was obtained. By this means the liquid potentials were eliminated. The authors deduce from their results by theoretical considerations the value 1.2207 volts for the true *molal* oxidation potential at 25° of the ion reaction $\mathrm{Tl}^{+++} + 2\mathrm{E}^- = \mathrm{Tl}^+$.

In this paper are presented the results of measurements at 25° of the electromotive force of cells of the type

$$\mathrm{H_2(g),\ HClO_4(}c_1\mathrm{).}\ \begin{array}{c}\mathrm{TlClO_4(}c_2\mathrm{)}\\ \mathrm{HClO_4(}c_1\mathrm{),\ Pt}\\ \mathrm{Tl(ClO_4)_3(}c_3\mathrm{)}\end{array}$$

The perchlorates were chosen as there is little likelihood of complex ion formation in such solutions, and the liquid potential may be regarded as negligibly small.

There are also presented the results of measurements of the oxidation potential of thallic–thallous–sulfate mixtures in solutions of sulfuric acid by means of similar cells.

Experimental Methods

Preparation of Materials.—Lead-free thallous nitrate recrystallized three times from water and dried at 120° was the source of all thallium salts. In preparing the thallous perchlorate (or sulfate) this purified nitrate was treated with a slight excess of perchloric (or sulfuric) acid and evaporated to strong fuming. The residue was dissolved in a little water and again evaporated. After three such evaporations, the thallous perchlorate (or sulfate) was recrystallized three times from water, and subsequently dried at 120° for an hour. In these preparations Mallinckrodt "Analytical Reagent" grades of perchloric acid and sulfuric acid were used.

The thallic salts were obtained in solution by dissolving thallic hydroxide in the required acid. The thallic hydroxide was prepared as follows. Precipitated thallous chloride, formed by the addition of hydrochloric acid to a solution of thallous nitrate, was suspended in a solution 1 *N* in hydrochloric acid, and after heating to about 60° the thallous salt was oxidized with potassium bromate. The solution was then made alkaline with ammonium hydroxide, and the precipitated thallic hydroxide was washed by decantation until the supernatant liquid gave no test for chloride or bromide with silver nitrate. The precipitate was filtered and left moist.

The hydrogen was prepared by electrolyzing a 10% solution of sodium hydroxide. For purification it was passed first through a bubbling tower containing 10% sodium hydroxide solution, then to a tube filled with glass wool to remove spray, next over platinized asbestos electrically heated to about 300°, and beyond this through a cooling spiral, then through a bubbling tower containing a solution of the acid being used in the cell and finally through 3 mm. copper tubing to the acid half of the cell.

Preparation and Analysis of the Cell Solutions.—Conductivity water was used in making up all solutions. The titrations were made with weight burets, and correspondingly all concentrations are expressed as weight formalities, or formula weights of substance per kilogram of water.

For each series of measurements a sufficient quantity of acid solution of the desired concentration was prepared at the start to meet the needs of both of the half cells. This original acid solution was divided into two equal parts. Thallic hydroxide in excess was added to one portion, and the solution allowed to stand with frequent shakings for several days. It was finally filtered from the excess of thallic hydroxide. This stock solution, containing a relatively small quantity of dissolved thallic salt, was analyzed by the following method.[4]

Standard carbonate-free sodium hydroxide solution was added to a weighed quantity of the solution until it was only very slightly acid. The solution was then heated, whereby the precipitated thallic hydroxide was converted to the easily filterable thallic oxide. After standing for twelve hours, the precipitate was filtered on a weighed Gooch crucible, washed thoroughly with hot water, and finally heated to 200° in a carbon dioxide-free atmosphere for an hour. It was weighed as Tl_2O_3.

The acid remaining in the filtrate and washings from the precipitated thallic oxide was determined by titration with the standard sodium hydroxide solution. The total

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[3] Partington and Stonehill, *Trans. Faraday Soc.*, **31**, 1365 (1935).

[4] Meyer, *Z. anorg. Chem.*, **24**, 321 (1900).

amount of sodium hydroxide required is equivalent to the acid actually present plus that produced by the hydrolysis of the thallic salt.

When the concentration of thallic salt was very small, the precipitated thallic oxide was dissolved in a solution 1 *N* in hydrochloric acid and determined volumetrically as follows. Sulfur dioxide was passed into the solution for about ten minutes to reduce the dissolved salt to the thallous state. The solution was then boiled for fifteen minutes to expel the excess of sulfur dioxide, and titrated for its content of thallous salt by a method described briefly by Kolthoff[5] and by Zintl and Rienäcker,[6] and in greater detail by Noyes, Pitzer and Dunn[7] (from investigations by Mr. C. D. Coryell). This consists in titrating at about 60° a thallous salt in an acid solution 1 *N* in chloride ion, using methyl orange as an oxidation–reduction indicator. The procedure followed was essentially that described by the last named investigators.

This solution, containing the acid ($HClO_4$ or H_2SO_4) and the thallic salt ($Tl(ClO_4)_3$ or $Tl_2(SO_4)_3$) at known concentrations, was then divided into a number of parts, and to each part a small but known quantity of thallous salt ($TlClO_4$ or Tl_2SO_4) was added. By this means the ratio of thallic to thallous salt was varied in the series of acid–thallous–thallic mixtures required in one-half of the cell.

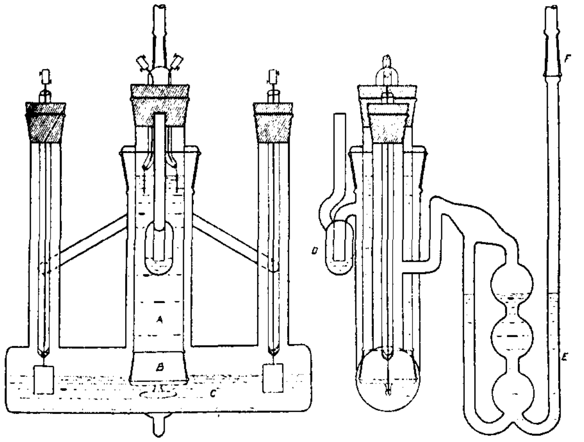

Fig. 1.

The second portion of the original acid solution, after careful determination of its acid content by direct titration with the standard sodium hydroxide solution, was used to make up the corresponding series of solutions in the other half of the cell at the hydrogen electrode. The necessary quantities of water (and of thallous salt in certain specified cases) were added to weighed portions of the original acid solutions so as to produce a final concentration of acid (and of thallous salt in the specified cases) equal to that in the acid–thallous–thallic mixtures.

Description of the Cell and Technique of Operation.—The cell, shown in Fig. 1, was of ground-glass stopper type[8] containing two independent platinized platinum electrodes in each half. The cell was held permanently in a brass frame which was clamped to an oscillating shaft in the thermostat to impart a gentle rocking motion. The female part of the ground glass joint F was "piceined" to the copper tubing from the hydrogen purification train, and was securely fastened to the oscillating shaft. When the cell was placed in the thermostat the two parts engaged, and with a little grease could be made gas-tight.

In operating the cell, the acid solution was placed in the hydrogen half-cell C, the trap D, and to saturator E to the levels as indicated. During this operation the vertical tube A, closed at its lower end by the ground glass stopper B, but unstoppered at the top, was empty. The two platinum electrodes were placed in position in compartment C, and the whole cell was suspended in the thermostat, regulated to 25 ± 0.02°. The purified hydrogen was allowed to pass slowly through the cell. Meanwhile enough of the acid–thallous–thallic mixture to fill the half-cell A was placed in a separate tube in contact with the other two electrodes. This tube was likewise suspended in the thermostat.

When the solutions had come to the temperature of the thermostat, the acid–thallous–thallic mixture was pipetted into the cell and the two electrodes inserted as shown in the figure. Half an hour later the potentials corresponding to the four combinations of electrodes were measured on a Leeds and Northrup Type K potentiometer in conjunction with a Leeds and Northrup high sensitivity galvanometer and an Eppley standard cell whose electromotive force in international volts was accurately known. At the same time the barometric pressure was read. Potentials were measured for five hours thereafter. The results varied less than 0.05 millivolt after the first reading. At the end of each experiment, the acid–thallous–thallic mixture was analyzed for its thallous content by titration with standard potassium bromate solution. In no case was a change in composition of the solution during the experiment detected.

Tabulation and Discussion of Results

Solubility of Thallic Hydroxide.—Some preliminary determinations at 25° of the solubility of the moist thallic hydroxide in perchloric and sulfuric acid solutions were made to serve as a guide in the selection of suitable concentrations of acid to be used in the cells to be investigated. The results are shown in Table I.

Table I

Solubility of Thallic Hydroxide at 25°

In Presence of Perchloric Acid

Concn. acid, wgt. formality	Solubility, wgt. formality	Equilib. constant $(Tl^{+++})/(H^+)^3$
1.9297	0.08881	0.0123
1.4943	.04424	.0132
0.9912	.01485	.0152
.5246	.00221	.0153
In Presence of Sulfuric Acid		
0.6215	0.05038	
.5267	.03294	
.4676	.02402	
.2871	.006880	
.2084	.002753	
.1590	.001255	

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[5] Kolthoff, *Rec. trav. chim.*, **41**, 189 (1922).

[6] Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, **153**, 278 (1926).

[7] Noyes, Pitzer and Dunn, This Journal, **57**, 1232 (1935).

[8] Jones and Baeckstrom, *ibid.*, **56**, 1524 (1934).

Assuming no complex-ion formation in the presence of the perchloric acid, the solubility of the thallic hydroxide may be attributed entirely to the reaction

$$Tl(OH)_3(s) + 3HClO_4 = Tl(ClO_4)_3 + 3H_2O$$

The equilibrium constant of this reaction recorded in the third column was accordingly calculated, regarding the activity coefficients of the perchlorates as unity. The value increases with decreasing concentration of perchloric acid, becoming constant in solutions 1.0 to 0.5 formal in perchloric acid. Accepting 0.0155 as the true value of this constant, the solubility product of the thallic hydroxide may be calculated from it through multiplication by the ionization constant of water (10^{-14}) raised to the third power. The solubility product thus calculated is 1.55×10^{-44}, a value of the same order of magnitude as that obtained by Spencer and Abegg[1] from determinations of the solubility of thallic hydroxide in the presence of nitric acid. It is evident that the value of the solubility product will depend on the nature of the thallic hydroxide, which must vary with the conditions under which it is precipitated.

The solubility of the thallic hydroxide is considerably greater in sulfuric acid than in perchloric acid solutions, even at the same normal concentration. This increased solubility is probably due largely to the conversion of the thallic ion to a complex anion. No further attempt is made to interpret the results, since the ionization relations of thallic sulfate and sulfuric acid are complicated and unknown.

Electromotive Force Measurements with Perchlorates

The results of the measurements of the electromotive force of the cells containing mixtures of the perchlorates of thallium in perchloric acid solution are shown in Table II.

The values recorded in the fourth column for the observed electromotive force of the cell correspond to a pressure of hydrogen at the electrode equal to one atmosphere. The actual pressure of hydrogen in each cell investigated was obtained by deducting from the observed barometric pressure the vapor pressure of the solution obtained from data of Pearce and Nelson.[9]

The ionic strength μ of each mixture in the thallic–thallous half-cell, given in the third column, was calculated by the relation $\mu = c_1 + 6c_2 + c_3$.

TABLE II

OXIDATION POTENTIALS OF $Tl(ClO_4)_3$–$TlClO_4$ MIXTURES IN $HClO_4$ SOLUTION AT 25°

$(TlClO_4)$ c_3	$(\Sigma Tl^{+++})/(\Sigma Tl^{+})$ c_2/c_3	$^1/_2\Sigma(cz^2)$ μ	E. m. f. $E_{obsd.}$	Oxidation potentials E	E^0_μ
Series 1. $HClO_4(c_1 = 1.2205$ wf.) $(\gamma_1 = 0.895)$				$Tl(ClO_4)_3$ $(c_2 = 0.01051$ wf.)	
0.002285	4.6004	1.2857	1.28234	1.28460	1.26500
.005494	1.9191	1.2890	1.27100	1.27326	1.26489
.01079	0.9744	1.2943	1.26240	1.26466	1.26499
.02430	.4935	1.3049	1.25358	1.25584	1.26491
.05243	.2005	1.3360	1.24217	1.24443	1.26507
.07895	.1331	1.3625	1.23704	1.23930	1.26520
.1052	.1000	1.3887	1.23353	1.23579	1.26536
Series 2.[a] $HClO_4(c_1 = 0.9465$ wf.) $(\gamma_1 = 0.781)$				$Tl(ClO_4)_3$ $(c_2 = 0.005808$ wf.)	
0.001379	4.2117	0.9827	1.2850	1.2772	1.2588
.002085	2.7856	.9834	1.2799	1.2721	1.2590
.002081	2.7909	.9833	1.2800	1.2722	1.2591
.007783	0.7465	.9891	1.2631	1.2553	1.2591
.02501	.2323	1.0063	1.2480	1.2402	1.2590
.04057	.1432	1.0219	1.2418	1.2340	1.2590
.07195	.08072	1.0533	1.2351	1.2273	1.2597
.1610	.03607	1.1423	1.2251	1.2173	1.2600
Series 3. $HClO_4(c_1 = 0.7160$ wf.) $(\gamma_1 = 0.722)$				$Tl(ClO_4)_3$ $(c_2 = 0.002138$ wf.)	
0.000597	3.5812	0.7294	1.28829	1.27134	1.25496
.002228	0.9596	.7310	1.27115	1.25420	1.25473
.01081	.19778	.7396	1.25093	1.23398	1.25479
.02156	.099165	.7504	1.24212	1.22517	1.25485
.05352	.039947	.7823	1.23066	1.21371	1.25506
Series 4. $HClO_4(c_1 = 0.5000$ wf.) $(\gamma_1 = 0.709)$				$Tl(ClO_4)_3$ $(c_2 = 0.001493$ wf.)	
0.0004169	3.5812	0.5094	1.29453	1.26789	1.25151
.001556	0.9596	.5105	1.27778	1.25114	1.25167
.007549	.19778	.5165	1.25784	1.23120	1.25201
.01506	.099165	.5240	1.24901	1.22237	1.25205
.03737	.039947	.5463	1.23751	1.21087	1.25222

[a] In Series 2, the first studied, the acid concentrations in the two half-cells were not quite equal. The measured potentials were therefore corrected for the small liquid potential by the familiar equation $E_L = (\Lambda_{H^+} - \Lambda_{ClO_4^-})/(\Lambda_{H^+} + \Lambda_{ClO_4^-})\ 0.05915 \log (c_1/c_1')$, c_1 and c_1' being the acid concentrations on each side of the boundary. The required conductance and transference data were found in "I. C. T.," Vol. VI, p. 242.

The values recorded in the fifth column for the observed oxidation potential E of the thallic–thallous mixtures in the cell are referred to the molal hydrogen electrode potential as zero. For each mixture investigated this oxidation potential was calculated from the observed electromotive force of the whole cell under the assumption that the activity coefficient of the hydrogen ion in the hydrogen half-cell is equal to the mean activity coefficient of the ions of perchloric acid. This mean activity coefficient, obtained from data of

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(9) Pearce and Nelson, THIS JOURNAL, 55, 3075 (1933).

Pearce and Nelson,[9] is recorded for each series as γ_1, corresponding to the acid concentration c_1. No correction was applied for the liquid potential in the cell.

If the principle be accepted that the activity coefficients, γ_2 and γ_3, of the thallic and thallous ion constituents in the acid–thallic–thallous perchlorate mixtures are determined by the ionic strength of the solution, the oxidation potential E of any mixture of known ionic strength μ may be calculated by the equation

$$E = E^0_\mu + 0.02957 \log c_2/c_3 \qquad (2)$$

The values for the formal oxidation potential, E^0_μ, computed by this equation are recorded in the last column of the table.

In each series the above principle is subjected to experimental test by maintaining the ionic strength approximately constant, and varying greatly from 50 to 100 fold, the ratio of c_2 to c_3. The slight variation in the values of E^0_μ for each series may be reasonably attributed to the correspondingly slight variation in the ionic strength of the mixtures.

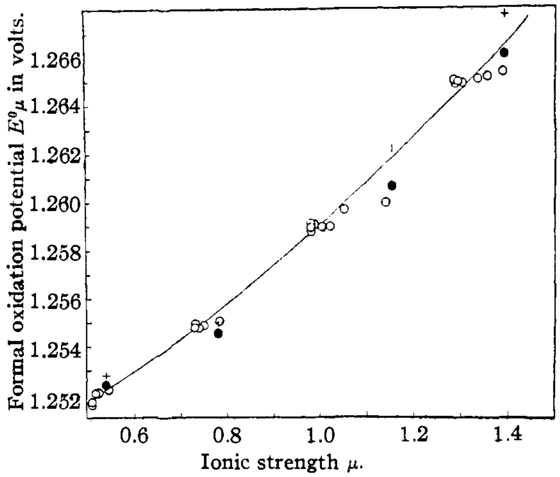

Fig. 2.—Formal oxidation potentials of $Tl(ClO_4)_3$–$TlClO_4$ mixtures in $HClO_4$ solutions.

In Fig. 2 the observed values of E^0_μ in all four series of measurements are plotted as circles against the ionic strength of the mixtures, and a best representative line is drawn through these points. The corresponding empirical equation, showing the variation of the formal oxidation potential with the ionic strength is

$$E^0_\mu = 1.2466 + 0.0076\,\mu + 0.00482\,\mu^2 \qquad (3)$$

The experimental values deviate from those calculated by the equation on an average of about 0.3 millivolt. Somewhat larger deviations are observed at the higher concentrations of thallous perchlorate.

The oxidizing potential of any acid–thallic–thallous perchlorate mixture can be computed by combining equations (2) and (3). It should be noted, however, that equation (3) is, strictly speaking, limited to the range of ionic strength, 0.5 to 1.4, covered by the experiments. For this reason the term 1.2466 does not represent the limiting molal oxidation potential of the reaction corresponding to zero ionic strength.

A fifth series of experiments was carried out to measure any change in the electromotive force of a given cell produced by adding to the hydrogen half-cell sufficient thallous perchlorate to give a uniform concentration of this salt throughout the whole cell. The cells selected for this series correspond approximately to the last cell, the one with the maximum concentration of thallous perchlorate, in each of the four series of Table II. Assuming the liquid potential in the cell to be reduced to zero by such addition, the observed change in the electromotive force may be taken as a measure of the liquid potential in the original cell.

The results of the measurements are shown in Table III. The values, $E_{\text{obsd.}}$ and $E'_{\text{obsd.}}$, of the observed electromotive force recorded in the fifth and sixth columns correspond to the cell without and with addition of thallous perchlorate to the hydrogen half-cell. The differences between these two values, which are recorded in the next column as the liquid potential of the original cell, are seen to be less than 0.5 millivolt.

This estimate of the liquid potential is, however, in error due to the tacit assumption that the added thallous sulfate has no effect on the activity co-

TABLE III

LIQUID POTENTIALS IN CELLS

$HClO_4$ c_1	$Tl(ClO_4)_3$ c_2	$(TlClO_4)$ c_3	$^1/_2\Sigma(cz^2)$ μ	E. m. f. $E_{\text{obsd.}}$	 $E'_{\text{obsd.}}$	Liquid potential $E_{\text{obsd.}} - E'_{\text{obsd.}}$	Oxidation E^0	Potentials E'^0
1.2270	0.009230	0.1090	1.391	1.23184	1.23187	−0.00003	1.26611	1.26742
0.9496	.005804	.1682	1.153	1.22437	1.22431	+ .00006	1.26064	1.26210
.7160	.002119	.0533	0.782	1.23008	1.23029	− .00021	1.25456	1.25504
.4948	.001474	.0383	.542	1.23789	1.23824	− .00035	1.25240	1.25279

efficient of the hydrogen ion in the hydrogen half-cell. The magnitude of this effect may be judged by comparing the values of the formal oxidation potentials, E^0 and E'^0 given in the last two columns at the prevailing ionic strength, shown in column four, of the acid–thallic–thallous perchlorate mixture. In calculating the second value, E'^0, the activity coefficient of the hydrogen ion in the hydrogen half-cell was regarded equal to the mean activity coefficient of the perchloric acid alone at a concentration equal to the total perchlorate concentration, $c_1 + c_3$, in the hydrogen half-cell. These values, corrected in this way for the liquid potential, are plotted in Fig. 2 as crosses. The corresponding uncorrected values are plotted as dots. The corrected values show no better agreement with equation (3) than do the uncorrected ones.

Electromotive Force Measurements in Solutions of Sulfuric Acid

Thallous and thallic sulfates in the presence of excess sulfuric acid are largely converted to the corresponding hydrosulfates with a consequent reduction in the concentration of the sulfuric acid in the solution. Due to such reactions a cell of the type

$$H_2(g),\ H_2SO_4(c_1),\ \overset{Tl_2SO_4(c_3)}{\underset{Tl_2(SO_4)_3(c_2)}{H_2SO_4(c_1)}},\ Pt$$

may have an appreciable liquid potential. Since the concentration of the thallic salt is relatively small, this potential can be largely reduced by adding thallous sulfate to the hydrogen half-cell until its concentration there becomes equal to that in the other half of the cell.

This effect was investigated by using for each experiment two cells, one with and the other without such addition of thallous sulfate to the hydrogen half-cell. The results of the measurements are presented in Table IV. The second cell in each experiment contains no thallous sulfate in the hydrogen half-cell. The weight formalities of H_2SO_4, $Tl_2(SO_4)_3$, and Tl_2SO_4 in such cells are indicated by the superscript *a*.

The values for the observed electromotive force in column five were corrected, as in the previous experiments, to a hydrogen pressure of one atmosphere.

The concentration of the hydrogen ion in the hydrogen half-cell, recorded in column four, was calculated in each case under the inexact assumption that sulfuric acid is completely ionized into H^+ and HSO_4^- with no secondary ionization of the HSO_4^-. For those cells in which thallous sulfate was also present, the further assumption was made that this salt was quantitatively converted by the sulfuric acid into the hydrosulfate. Although the hydrogen-ion concentration thus estimated is too small, it may, as an approximation, be regarded as equal to the hydrogen-ion activity, since the activity coefficient of hydrogen ion is less than unity. Accordingly, the electrode potentials in the sixth column, which are referred to the molal hydrogen electrode, were computed by the simple equation

$$E = E_{\text{obsd.}} - 0.05915 \log 1/(H^+) \qquad (4)$$

The formal oxidation potentials in the seventh column are related to the corresponding oxidation potentials of the thallic–thallous mixtures in the cells by the equation

$$E = E^0 + 0.02957 \log c_2/c_3 \qquad (5)$$

The liquid potentials recorded in the last column are based on the assumption that the addition of thallous sulfate to the hydrogen half-cell reduces the liquid potential in any such cell to zero. This assumption obviously disregards entirely the effect of the thallic sulfate on the liquid potential. The small negative values obtained for the cells with the higher ratios, c_2/c_3, of the thallic to thallous salt concentrations indicate that such an effect is not negligible. In the cells with the higher concentrations of thallous salt, the liquid potentials, without addition of thallous sulfate to the hydrogen half-cell, are in all cases positive and of significant magnitude.

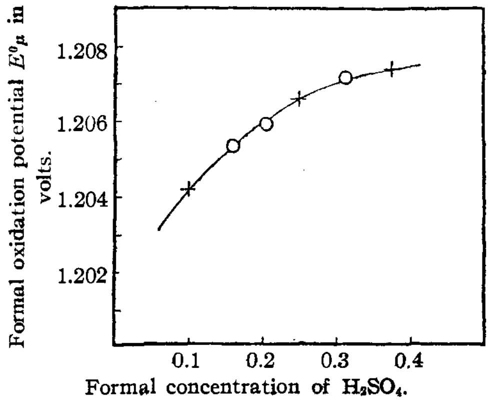

Fig. 3.—Formal oxidation potentials of $Tl_2(SO_4)_3$–Tl_2SO_4 mixtures in H_2SO_4 solutions.

In each series the values for the formal electrode potential calculated by equation (5) in-

TABLE IV

OXIDATION POTENTIALS OF $Tl_2(SO_4)_3$–Tl_2SO_4 MIXTURES IN H_2SO_4 SOLUTION AT 25°

Expt. no.	(Tl_2SO_4) c_3	(ΣTl^{+++})/(ΣTl^{+}) c_2/c_3	H^+-Concn. (H^+)	E. m. f. $E_{obsd.}$	Oxidation potentials E	Oxidation potentials E^0	Liquid potential E_L
Series 1.		H_2SO_4 $c_1 = 0.3049$ wf. $c_1^a = 0.3139$ wf.			$Tl_2(SO_4)_3$ $c_2 = 0.00430$ wf. $c_2^a = 0.00499$ wf.		
1	0.001427	2.8931	0.3035	1.25194	1.22130	1.20765	0.00000
	.001807[a]	2.7607	.3139	1.25022	1.22046	1.20742	−.00023
2	.004138	0.9981	.3008	1.23815	1.20733	1.20736	.00000
	.005010[a]	.9960	.3139	1.23692	1.20716	1.20721	−.00015
3	.02063	.2002	.2843	1.21708	1.18476	1.20541	.00000
	.02498[a]	.1998	.3139	1.21565	1.18587	1.20658	+.00117
4	.04120	.1002	.2637	1.20790	1.17365	1.20320	.00000
	.05535[a]	.09015	.3139	1.20436	1.17460	1.20550	+.00230
5	.06155	.06710	.2434	1.20241	1.16611	1.20081	.00000
	.07450[a]	.06698	.3139	1.19967	1.16991	1.20463	+.00382
Series 2.		H_2SO_4 $c_1 = 0.2049$ wf. $c_1^a = 0.2047$ wf.			$Tl_2(SO_4)_3$ $c_2 = 0.002269$ wf. $c_2^a = 0.002317$ wf.		
6	0.001126	2.0155	0.2038	1.25665	1.21581	1.20681	0.00000
	.001228[a]	1.8856	.2047	1.25500	1.21425	1.20610	−.00071
7	.002222	1.0214	.2027	1.24785	1.20686	1.20659	.00000
	.002443[a]	0.9482	.2047	1.24603	1.20528	1.20596	−.00063
8	.01120	.2026	.1937	1.22682	1.18468	1.20518	.00000
	.01184[a]	.1957	.2047	1.22519	1.18444	1.20539	+.00021
9	.02157	.1052	.1833	1.21820	1.17465	1.20356	.00000
	.02199[a]	.1054	.2047	1.21662	1.17587	1.20477	+.00121
10	.05375	.04222	.1511	1.20567	1.15717	1.19782	.00000
	.05900[a]	.03927	.2047	1.20191	1.16116	1.20273	+.00491
Series 3.		H_2SO_4 $c_1 = 0.1607$ wf. $c_1^a = 0.1603$ wf.			$Tl_2(SO_4)_3$ $c_2 = 0.001238$ wf. $c_2^a = 0.001267$ wf.		
11	0.000658	1.8815	0.1600	1.26118	1.21416	1.20604	0.00000
	.000681[a]	1.8618	.1603	1.26045	1.21347	1.20549	−.00055
12	.001301	0.9512	.1594	1.25245	1.20530	1.20594	.00000
	.001325[a]	.9600	.1603	1.25233	1.20530	1.20535	−.00059
13	.01281	.09664	.1479	1.22264	1.17355	1.20355	.00000
	.01272[a]	.09961	.1603	1.22213	1.17510	1.20472	+.00117
14	.03210	.03856	.1286	1.21027	1.15761	1.19941	.00000
	.03142[a]	.04033	.1603	1.20907	1.16204	1.20327	+.00386
15	.06420	.01928	.0965	1.20074	1.14067	1.19137	.00000
	.06350[a]	.01995	.1603	1.19791	1.15088	1.20115	+.00978

[a] Concentrations in cells without addition of Tl_2SO_4 to the hydrogen half-cell.

creases appreciably with the concentration ratio c_2/c_3, but remains nearly constant when the concentration ratio exceeds unity.

In Fig. 3 is presented a comparison of the results with those obtained by Partington and Stonehill.[3] The formal electrode potentials of the second cell of experiments 2, 7 and 12 is plotted as a circle against the corresponding concentration of sulfuric acid. These cells contained no thallous sulfate in the hydrogen half-cell, and substantially equi-formal quantities of the two thallium salts in the other half. The crosses indicate formal electrode potentials for similar cells calculated on the same basis from the results of Partington and Stonehill at somewhat different concentrations of sulfuric acid. The concentration of each thallium salt in these cells is 0.0025 formula weight per liter, which is approximately equal to the mean of the thallic salt concentration in the cells of experiments 2, 7 and 12. The values shown for the formal oxidation potential at this particular concentration of thallic salt were obtained by graphical interpolation from the experimental values at other concentrations. The two investigations appear to be in agreement within 0.1 millivolt.

Summary

The oxidation potential of mixtures of thallic and thallous perchlorate in perchloric acid solution, and of thallic and thallous sulfate in sulfuric acid solution, were obtained by electromotive force measurements at 25° against a hydrogen electrode.

For the acid–thallic–thallous perchlorate mixtures, covering an acid concentration range 0.5 to 1.22 weight-formal $HClO_4$, the oxidation potential was found to be determined by the ionic strength μ of the solution, and by the concentration ratio $(\Sigma Tl^{+++})/(\Sigma Tl^{+})$ as shown by the two equations

$$E = E^0 + 0.02957 \log (\Sigma Tl^{+++})/(\Sigma Tl^{+}) \text{ and}$$
$$E^0 = 1.2466 + 0.0076\,\mu + 0.00482\,\mu^2$$

in which E^0 is the formal oxidation potential of the reaction $Tl^{+++} + 2E^- = Tl^+$.

For the acid–thallic–thallous sulfate mixtures, covering an acid concentration range 0.16 to 0.30 weight-formal H_2SO_4, the formal electrode potential computed by the first of the above equations was found to vary appreciably at the lower concentration ratios $(\Sigma Tl^{+++})/(\Sigma Tl^{+})$, but to remain nearly constant when the concentration ratio exceeded unity. This limiting value varied slightly with the acid concentration, from 1.205 volts in 0.16 formal to 1.207 volts in 0.30 formal sulfuric acid solution. The results of these measurements were shown to be in good agreement with those of Partington and Stonehill.[3]

The potential at the liquid junction

$$H_2SO_4(c_1),\ H_2SO_4(c_1) + Tl_2SO_4(c_3) + Tl_2(SO_4)_3(c_2)$$

which occurs in the type of cell investigated, was estimated by determining the change in the electromotive force produced by dissolving sufficient thallous sulfate in the sulfuric acid to give uniform concentration of this salt throughout the cell.

Incidentally the solubility at 25° of moist thallic hydroxide in solutions of perchloric acid and of sulfuric acid of varying concentration was determined. The solubility product of thallic hydroxide was estimated to be 1.5×10^{-44}.

CAMBRIDGE, MASS. RECEIVED APRIL 9, 1936

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Activity Coefficients of Some Bivalent Metal Sulfates in Aqueous Solution from Vapor Pressure Measurements

BY ROBERT A. ROBINSON AND RONALD S. JONES

Continuing our investigations on the activity coefficients of salts in aqueous solutions, measurements by the isopiestic vapor pressure method[1] have now been extended to solutions of some bivalent metals, *viz.*, copper, magnesium, zinc, cadmium, manganese and nickel. These salts were selected because it was felt desirable to obtain accurate data for salts other than those of the uni-univalent type and yet to retain that symmetry in the ion valences which renders theoretical treatment comparatively easy. The investigation proved more tedious than the previous work because a much larger number of determinations was necessary to cover the concentration range 0.1 *M* to the saturated solution. All measurements were made at 25° using pure recrystallized salts, except in the case of cadmium sulfate, which was prepared by the method of La Mer and Parks.[2]

Instead of tabulating the concentrations of isopiestic solutions of potassium chloride and metal sulfate, we shall record[3] values of the osmotic coefficient at round concentrations. These were obtained by first calculating the osmotic coefficient of potassium chloride, $\varphi' = (55.51/2m') \ln p_0/p$, from the molal vapor pressure lowerings of this salt previously recorded.[1a] Since p_0/p is the same for two isopiestic solutions, the osmotic coefficient of the sulfate, $\varphi = (55.51/2m) \ln p_0/p$, can be calculated from the concentration data. These values were plotted on a large-scale graph and no difficulty was experienced in drawing a smooth curve through the experimental points. The osmotic coefficients are recorded in Table I at sufficient concentrations to enable the curve of φ against $\sqrt{m}$ to be reproduced.

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(1) (a) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934); (b) Robinson, *ibid.*, **57**, 1161, 1165 (1935).

(2) La Mer and Parks, *ibid.*, **53**, 2040 (1931).

(3) Measurements on the sulfates of magnesium, zinc and cadmium were made by both observers; on magnesium sulfate 44 measurements were made by R. S. J. and 25 by R. A. R. In the case of cadmium sulfate the figures were 25 and 37, respectively, and in the case of zinc sulfate, 31 and 31. For the data on the sulfates of copper, manganese and nickel one of us (R. A. R.) must take full responsibility, the number of determinations being 30, 61 and 40, respectively.