2. The distribution of phenol between water and five solvents has been studied in dilute solution at 25°.

3. In these solvents the phenol is shown to be present exclusively in single and double molecules.

4. A hitherto unreported inflexion has been observed in the curve connecting the distribution coefficient with the concentration.

5. The association constant of phenol in four of the solvents has been calculated.

6. Differences in the association constants are attributed to solvation of single molecules of phenol.

7. Substituents in the benzene ring of the solvent reduce (or increase) solvation in the following order: CH_3, Cl, (H), NO_2, OH.

8. This is shown to be in agreement with previous work, and is accounted for by a consideration of the mechanism of solvation and association.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Stannous-Stannic Oxidation-Reduction Potential

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Although the stannous-stannic electrode potential has been determined by Forbes and Bartlett[1] it was considered advisable to redetermine this constant, and extend the data over a wider range of acid concentration by a more accurate method developed since that time by Popoff and Kunz.[2] The electromotive force of cells of the following type was measured

$$\mathrm{Hg} \mid \mathrm{HCl \text{ and } SnCl_2 \text{ and } SnCl_4} \mid \mathrm{HCl} \mid \mathrm{H_2, Pt}$$

The treatment of these data is essentially the same as that by Popoff and Kunz.

Apparatus and Reagents

Two 150-cc. Pyrex flasks were used as electrode vessels, with proper fittings for gas inlet and outlet, electrode and flowing junction. Stock solutions were stored in Pyrex bottles and under carbon dioxide. The potential was read to ±0.01 mv. The temperatures used were 15, 25, and 35 ± 0.03°.

All reagents were of very pure materials. A "C. P. Analyzed" grade of tin was used. The hydrochloric acid was distilled. The water was conductivity water redistilled from alkaline permanganate. A good quality of mercury was thoroughly washed with dilute nitric acid containing mercurous nitrate, dried and distilled *in vacuo.*

Analytical Methods

Total Tin.—The gravimetric method in which the tin is precipitated with ammonia as the hydroxide[3] was found to be very satisfactory.

Ratio of Stannous to Stannic Tin.—This determination was made using a modification of the iodimetric method.[3] The stannous tin was first titrated and then the total tin was determined after reduction to the stannous condition. It was found necessary that the starch indicator be oxygen-free and that the time for reduction be extended to one hour for solutions in which the concentration of hydrochloric acid was less than 0.5 *M*.

Chlorides.—Volhard's method was used for the determination of chlorides. Sufficient nitric acid was added to make the solution 3 *N* with respect to this reagent at the end of the precipitation with silver nitrate. This accomplished the oxidation of the tin to the stannic form, thus preventing any reduction of the silver by the stannous ion, and also prevented the hydrolysis of stannic nitrate. The solubility of the silver chloride in this concentration of nitric acid was found to be not great enough to interfere with the reliability of the method.

Choice of Electrode Material

Several electrode materials were tried in the hope that at least two could be found that would be inert toward the potential, and thus afford comparison. Copper, gold, bismuth and platinum (bright and black) failed to give steady and reproducible potentials. Silver electrodes proved more promising and were tested exhaustively. Electrodes were made by coating silver wire with fine crystals electrolytically deposited and by covering the wire with spongy silver made from a coating of the carbonate decomposed at 445°.[4] The latter gave potentials that were quite steady, but they were not reproducible; the variations with a given solution covered a range of 100 mv. These results, in general, confirm the observations of previous investigators.[5]

Small quantities of various potential mediators[6] were tried, such as ferric chloride with the platinum electrode and silver nitrate with the silver electrode. In no case was the behavior of the electrode improved by this means.

The mercury electrode alone was found to give repro-

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(1) Forbes and Bartlett, THIS JOURNAL, **36**, 2030 (1914); **37**, 1201 (1915).

(2) Popoff and Kunz, *ibid.*, **51**, 382 (1929).

(3) Hillebrand and Lundell, "Applied Inorganic Analysis," J. Wiley and Sons, Inc., New York, 1929, p. 239.

(4) Lewis, THIS JOURNAL, **28**, 158 (1906).

(5) For a review of this literature, see Forbes and Bartlett, *ibid.*, **36**, 2030 (1914).

(6) Goard and Rideal, *Trans. Faraday Soc.*, **19**, 740 (1924).

ducible potentials; this corroborates the findings of Forbes and Bartlett.[5]

Experimental Methods and Calculations

Solutions were prepared by dissolving three grams of tin in the acid, and dividing this into two equal parts. One was placed in the storage bottle under carbon dioxide, and the other was saturated with chlorine to oxidize the tin to the stannic condition. This portion was then added to the storage bottle together with sufficient hydrochloric acid and water to make a liter of solution of approximately the desired acid concentration. This was analyzed by determining the ratio of stannous to stannic ion volumetrically, and then the chloride and total tin content, using weighed samples. From these data the amount of hydrochloric acid per kilogram of water was calculated. Next a solution of hydrochloric acid was prepared and adjusted to within 0.2% of the concentration of the free acid in the stannous–stannic solution.

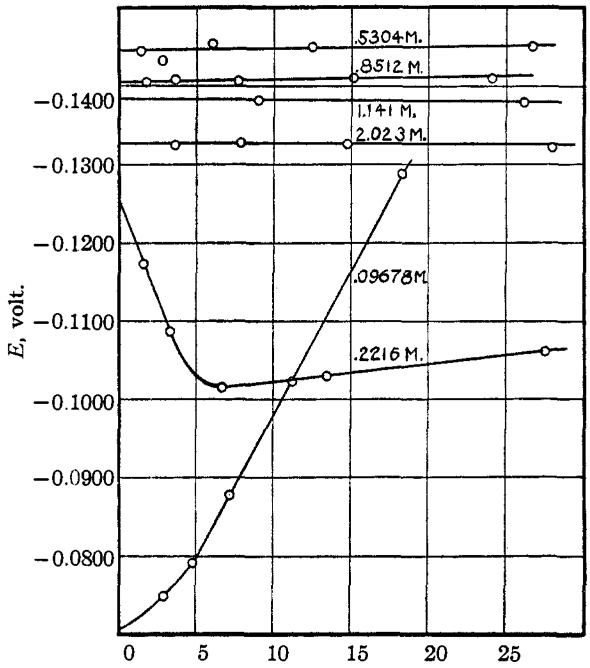

Fig. 1.—Plot of potential of stannous–stannic electrode against concentration of tin at several molalities of hydrochloric acid.

The half-cell for the tin solution was flushed out with carbon dioxide before the addition of the solution. A very slow stream of this gas was kept flowing over the solution and out through a water trap to protect against any leakage of air. After standing for about eight hours to reach equilibrium, the hydrogen electrode half-cell was connected by means of the flowing junction, and the potential read at half-hour intervals until the readings were constant for at least one hour. The hydrogen electrode was then replaced by another and the readings continued to constant value. The agreement of these cells with different hydrogen electrodes afforded an excellent check on the final equilibrium potential. The barometer reading was then taken and samples of the tin solution analyzed to determine the ratio of stannous to stannic ion at the end of each run.

The tin solution in the storage bottle was diluted one half by adding an equal volume of the oxygen-free hydrochloric acid. A new cell was set up containing this solution against the acid and the potential determined as described above. This procedure was repeated until the tin concentration was reduced to the point where the results were vitiated by experimental inaccuracies. The tin solution was weighed before and after each dilution so that from these data and the original tin concentration, the molality of the tin for each dilution could be calculated. These weights, as well as all others, were corrected by the proper buoyancy factors.

The temperature coefficient of the potential of the stannous–stannic electrode in 1.1 *M* hydrochloric acid was determined by taking cell potentials at 15, 25 and 35°. Since in acid of this strength the electromotive force was independent of the tin concentration, the temperature coefficient calculated from these data may be considered as that of the potential of the electrode at zero concentration of tin.

There are three sources of electromotive force in the cell

$$\underset{E_1}{\mathrm{Hg}\mid \mathrm{SnCl_4} + \mathrm{SnCl_2} + \mathrm{HCl}}\ \underset{E_j}{\mid}\ \mathrm{HCl}\ \underset{E_2}{\mid \mathrm{H_2},\mathrm{Pt}}$$

$$E_{\text{cell}} = E_1 + E_j + E_2$$

E_j cannot be calculated at finite concentrations of the tin chlorides. Including E_j with the normal oxidation–reduction potential and using the conventions of Lewis and Randall[7] we obtain

$$E_0' + E_j = E_{\text{cell}} - \frac{RT}{nF}\ln\frac{(A_{\mathrm{H^+}})^2}{(P_{\mathrm{H_2}})} - \frac{RT}{nF}\ln\frac{A_{\mathrm{Sn^{II}}}}{A_{\mathrm{Sn^{IV}}}}$$

The activity coefficients of the hydrogen ion were estimated from the data given by Harned and Ehlers[8] and the pressure of the hydrogen was taken as the barometric pressure less the vapor pressure of the water from the hydrochloric acid solution.[9] Since the activities of the stannous and stannic ions in the solutions were unknown, the ratio of the molalities was used instead, because the final extrapolation was made to zero concentration where the activity coefficients become unity.

For each series the calculated values for $E_0' + E_j$ were plotted against the molality of total tin and extrapolated to zero concentration to obtain E_0'. The values for E_0' were next plotted against acid molality and the curve extrapolated to zero concentration. This gives E_0 for the stannous–stannic electrode independent of the liquid junction potential and of the hydrochloric acid.

The cell readings for the temperature coefficient were treated in the same manner except for the extrapolations. The temperature coefficient for the stannous–stannic electrode was then calculated for the range 15 to 35° and the change in heat content for the reaction[10]

$$\mathrm{Sn^{II}} \longrightarrow \mathrm{Sn^{IV}} + 2e \text{ (in 1.1 } M \text{ HCl)}$$

computed by means of the Gibbs–Helmholtz equation.

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(7) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

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

(9) "International Critical Tables," Vol. III, 1928, p. 293.

(10) The stannous and stannic ions exist in the form of complexes, the nature and concentration of which are not definitely known, and the Roman numerals are used to indicate all the tin of that valency.

Experimental Data and Discussion

The experimental data together with the computed values are given in Table I. The graphic treatment of these data (Fig. 1) gives the normal electrode potentials recorded in Table II.

TABLE I

RESULTS OF ELECTROMOTIVE FORCE MEASUREMENTS

Expt.	HCl, molality	Sn, mml. per 1000 g. of soln.	Ratio: Sn^{II}/Sn^{IV}	Barometric pressure, mm. at 0°	E_{cell}, volt	$E_0' + E_j$, volt
Ia	0.09678	18.24	0.996	761.5	−0.1943	−0.1288
b		11.17	.986	766.4	.1682	.1024
c		7.019	.985	764.1	.1535	.0878
d		4.761	.993	761.0	.1445	.0790
e		2.990	.977	761.3	.1406	.0748
IIa	.2216	27.38	.992	755.9	− .1515	− .1062
b		13.38	.990	759.0	.1483	.1029
c		6.648	.981	763.3	.1470	.1014
d		3.305	.983	761.8	.1542	.1086
e		1.607	.975	756.5	.1628	.1172
IIIa	.5304	26.55	1.019	764.2	− .1679	− .1451
b		12.40	0.954	753.5	.1685	.1450
c		6.015	.999	763.7	.1685	.1454
d		2.830	.976	760.0	.1665	.1432
e		1.478	1.019	753.4	.1671	.1444
IVa	.8512	24.00	1.006	764.4	− .1508	− .1410
b		15.06	1.007	765.5	.1508	.1410
c		7.647	0.985	761.7	.1507	.1406
d		3.707	.984	764.4	.1508	.1407
e		1.759	.866	749.0	.1519	.1404
Va[a]	1.141	26.09	1.000	761.9	− .13516	− .13444
b		26.09	1.000	763.5	.13902	.13798
c[b]		26.09	1.000	763.0	.14211	.14085
d[a]		8.996	1.005	756.7	.13509	.13451
e		8.996	1.005	756.5	.13900	.13814
f[b]		8.996	1.005	756.5	.14212	.14105
VIa	2.023	56.09	1.005	758.4	− .1144	− .1333
b		27.87	0.992	762.3	.1136	.1323
c		14.70	.996	758.6	.1138	.1326
d		7.880	.998	760.2	.1139	.1327
e		3.672	.974	765.4	.1140	.1324

[a] Performed at 15°. [b] Performed at 35°. All other experiments were at 25°.

TABLE II

NORMAL ELECTRODE POTENTIALS IN DIFFERENT MOLALITIES OF HYDROCHLORIC ACID

HCl, molality	0.09678	0.2216	0.5304
E_0', volts	− .0702	− .1250	− .1444
HCl, molality	0.8512	1.141	2.023
E_0', volts	− .1404	−0.1382	−0.1325

A plot of these values is shown in Fig. 2 from which the normal oxidation–reduction potential was found to be −0.154 volt. This value is purely hypothetical, the potential of an electrode in a neutral solution in which no hydrolysis has occurred. For practical purposes the potentials shown in Fig. 2 are more useful because the oxidation–reduction system is nearly always used in acid solution.

At acid concentrations 0.53 *M* and higher the potential of the electrode was almost independent of the concentration of tin, indicating either that the activity coefficients of the stannous and stannic ions do not change greatly with the concentration, or that they change at the same rate. However, when the acid concentration was 0.22 *M* and lower, the potential was a function of the concentration of tin, and was considerably greater. This is the direction in which the potential would be expected to shift, considering that the hydrolysis of the stannic chloride would materially lower its activity. Owing to the fact that values in this range are so far out of line with the others, and supported by the findings of Collins and Wood[11] that stannic chloride is almost

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[11] Collins and Wood, *J. Chem. Soc.*, **121**, 441 (1922); **121**, 1122 (1922); **123**, 452 (1923).

completely hydrolyzed in acid of this range of concentration, the values in this range were not used in determining E_0.

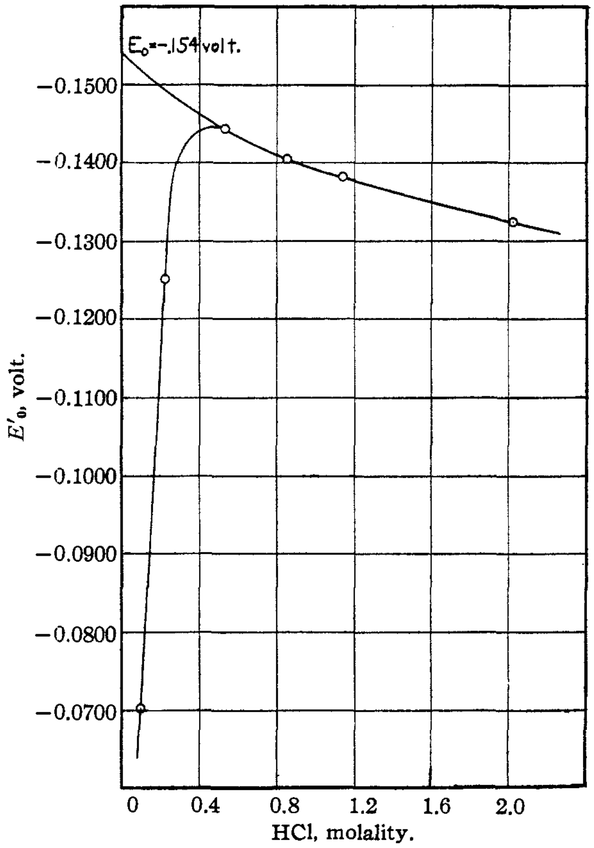

Fig. 2.—Plot of potential of stannous-stannic electrode against molality of hydrochloric acid.

From the data given in Table I, the change in heat content (ΔH) for the reaction, $Sn^{II} \longrightarrow Sn^{IV} + 2e$ is 1920 calories, in 1.1 *M* hydrochloric acid. Since the electrode potential does not change markedly with the concentration of acid, this value probably holds reasonably well in other solutions in which enough acid is present to prevent hydrolysis.

In a previous determination of the stannous–stannic electrode potential, Forbes and Bartlett obtained a value of −0.146 volt.[12] Three factors might account for the difference between the value given in this paper, and that of Forbes and Bartlett: (1) more complete data in the region from which the extrapolation to zero acid concentration was made, (2) lower concentration of tin employed, and (3) more complete elimination of the liquid junction potential.

Summary

1. The oxidation–reduction potential of the stannous–stannic system was measured at a mercury electrode.

2. The effect of the concentration of hydrochloric acid on this potential was studied over the range of 0.1 to 2 *M*.

3. Various electrodes were tried, but none other than mercury was found to be satisfactory.

4. The normal oxidation–reduction potential of the stannous–stannic electrode at 25° was found to be −0.154 volt.

5. For the reaction $Sn^{II} \longrightarrow Sn^{IV} + 2e$ (in 1.1 *M* HCl) the change in heat content was found to be 1920 calories.

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[12] The value given by Forbes and Bartlett was 0.430 volt, taking the potential of the normal calomel electrode to be 0.564 volt, and writing both potentials in the order: electrolyte, electrode. Reversing this order to conform with the conventions used in this paper, and using the value −0.280 volt for the potential of the normal calomel electrode, the above value of E_0 becomes −0.146 volt. In the "International Critical Tables," Vol. VI, p. 333, the value quoted from the same reference is erroneously given as −1.256 volts.