

amalgam containing 1.27% of silver. Raoult's law was found to be obeyed within the limit of experimental error.

Measurements with gold amalgams at concentrations up to 23.7% of gold showed the separation of a solid phase at an approximate composition of 16.5%. In the more dilute amalgams the vapor pressures were found to be greater than those calculated from the simple form of Raoult's law. The deviation is such that to explain it on the basis of Raoult's law one would have to assume a rather complex gold molecule. The observations are very well expressed by the equation:

$$\frac{P}{P_0} = \frac{N}{N+I} 10^{\frac{0.23}{(1+0.23N)^2}}$$

This equation corresponds in form to one derived by van Laar, but with values assigned to the constants which are purely empirical.

Bismuth amalgams of all concentrations are liquid at this temperature, and, like gold amalgams, gave vapor pressures higher than those calculated from Raoult's law. If the validity of that law is assumed the deviations from its simple form could be explained by assuming the two equilibria:



This would give an equation containing but two constants, but complicated in form. The equation of van Laar, which permits deviations from Raoult's law without assuming association or other chemical changes, again expresses the observations very accurately when numerical values are chosen as follows:

$$\frac{P}{P_0} = \frac{N}{N+I} 10^{\frac{0.1425}{(1+0.234N)^2}}$$

It is pointed out, however, that too much stress should not be placed upon this agreement on account of the entirely empirical nature of the constants assumed.

To decide to what extent deviations from the simple Raoult's law should be accounted for by either of the two methods, it is shown that recourse must be had to other methods for distinguishing between normal and associated liquids.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]
THE MEASUREMENT OF OXIDATION POTENTIALS AT MERCURY ELECTRODES. I. THE STANNIC-STANNOUS POTENTIAL.

BY GEORGE SHANNON FORBES AND EDWARD PAYSON BARTLETT.

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The existing data on oxidation potentials are neither so abundant nor so concordant as the importance of the subject would warrant. This remains true of the stannic-stannous potential, for instance, in spite of

careful investigations by Bancroft,¹ Fredenhagen,² Dolch,³ and Foerster and Yamasaki.⁴ Thus, Fredenhagen, working in solutions tenth-normal with respect to both hydrochloric acid and tin, the stannic concentration being twenty-four times the stannous, noted potentials varying two-tenths of a volt, and not approaching constant or agreeing values after days of waiting. Dolch, working in several concentrations of sodium hydroxide, fared better, but did not record enough results to draw sweeping conclusions as to the reproducibility of his figures, or the effect of the variable concentrations. Yamasaki gives seven determinations, three with pink salt, three with half-normal acid, and one with twice normal acid where the concentration ratio of the tin salts is not recorded. Both of the last-mentioned investigators waited from five to twenty days before sufficient constancy was attained to justify recording measurements.

It appeared that improvement would be impossible if platinum electrodes were used as in the above researches. Fredenhagen has pointed out the difficulties arising from solutions which do not react readily with oxygen, and which thus fail to come into equilibrium with the hypothetical platinum oxides which are supposed to carry over the potential to the platinum itself.

Of other electrode materials, gold and palladium were tried by Peters.⁵ Abegg⁶ was probably the first to suggest the use of base metals, especially copper, though he did not publish any results. Mazzucchelli,⁷ in his research on the chromic-chromous potential, used copper, silver, and mercury. His difficulties, as will be shown in a paper shortly to be published, lay in the decomposition of his solutions rather than in his electrodes, at least where mercury was used. This metal possesses the great advantages of a free surface on which hydrogen has a high overvoltage. Hydrogen undoubtedly deposits on platinum immersed in powerful reducing agents, and we have found that the potentials of such solutions are much more electronegative on mercury than on platinum, a strong point in favor of mercury electrodes. The effects of air on the two electrodes were studied in a stannic-stannous cell of the type described below, but provided with a platinum as well as a mercury electrode. This was brought to equilibrium as pure carbon dioxide, then air was passed in for a time, then carbon dioxide again. The single potentials were recorded as follows:

¹ *Z. physik. Chem.*, 10, 399 (1892).

² *Z. anorg. Chem.*, 29, 445 (1902).

³ *Z. Elektrochem.*, 16, 602 (1910).

⁴ *Ibid.*, 17, 361 (1911).

⁵ *Z. physik. Chem.*, 26, 198 (1898).

⁶ *Z. Elektrochem.*, 13, 34 (1907).

⁷ *Zentralblatt*, 76, II, 294 (1905).

Conditions.	Time. Min.	Mercury. Volt.	Platinum. Volt.
Equilibrium, CO ₂	0	0.411	0.488
Air passed in.....	3	0.465	0.541
Air passed in.....	29	0.449	0.542
Air passed in.....	66	0.453	0.546
Air off, CO ₂ on.....	74	0.424	0.520
Air off, CO ₂ on.....	155	0.408	0.461
Air off, CO ₂ on.....	234	0.409	0.474

The air evidently disturbs the potential on the platinum much more than on the mercury, and its effects are almost impossible to eliminate from the platinum, while the mercury quickly recovers. Hydrogen, on the other hand, was proved in a similar experiment to have very little effect on the potential at mercury electrodes.

The assumption is made, and verified below, that when constant potential is attained the oxidizing potential of the extremely dilute mixture of mercury salts present is equal to that of the stannic-stannous solution.

The single potential difference between mercury and its normal salts, 1.07 volts, sets a limit to its use in the study of oxidizing solutions. Solutions approaching this degree of oxidizing power would have to contain sufficient mercury salts at the start to avoid oxidation of metallic mercury, and as anion only perchlorate would be suitable. Perchlorate yields mercury salts freely soluble, and excess of the acid can be added to check hydrolysis without danger of oxidation due to the decomposition of the anion. In the presence of chloride, 0.56 volt, and in the presence of sulfate, 0.97 volt, the potentials of the corresponding standard electrodes, would be about the limits, if oxidation of mercury to insoluble salts is to be avoided.

Preparation of Materials and Solutions.—One-quarter of a gram atom of tin was dissolved in a known quantity of redistilled constant boiling hydrochloric acid in a flask provided with a ground-in reflux condenser terminating in a bent tube sealed with water to prevent entrance of air or escape of acid vapors. This water was added to the solution in the flask, and the whole made up to a liter, so that both the concentration of tin and of acid could be calculated. For a part of the work, reagent tin containing traces of carbon, but no iron, was used. For some of the determinations in twice normal hydrochloric acid (Solution 5) a sample was electrolyzed from an anode of this tin in a solution of stannous chloride made by dissolving another portion in acid. The agreement in potential noted upon plotting the results on the curves shows the equivalence of the two samples within one or two millivolts. Mercury, already quite pure, was passed repeatedly through a tower containing mercurous nitrate, and then distilled *in vacuo*. Carbon dioxide was freed from oxygen in Emmerling towers containing cuprous or chromous chloride, and in the later work on solutions twice normal in acid, as an additional precaution, the gas was dried with phosphorus pentoxide and passed through elec-

trically heated tubes containing copper gauze. It was in every case finally bubbled through a solution of essentially the same composition as that in the cell, to avoid concentration changes in the latter. Chlorine was prepared by the action of hydrochloric acid on potassium permanganate.

The Cells.—These were made from wide-mouthed bottles of 250 cc. capacity, closed with rubber stoppers pierced with five holes. Through these holes respectively, passed a glass tube with a sealed-in platinum wire to dip into the mercury on the bottom of the cells; a centrifugal stirrer; a tube for the delivery of carbon dioxide; a tube through which a pipet could be introduced; and a capillary emptying into an indifferent solution. This connecting liquid was saturated potassium chloride except in the case of part of the measurements with normal acid, where 24% of potassium nitrate was substituted for the same amount of chloride. The indifferent electrolyte was changed at frequent intervals.¹ It was connected by another capillary with the normal calomel electrode made up in a 125 cc. bottle, and checked at frequent intervals against a standard electrode carefully guarded from contamination. Connecting tubes gelatinized with agar agar were rejected as giving inconstant results. The whole system was immersed in a thermostat electrically regulated at 25.0°.

Both a potentiometer made by us from calibrated manganin resistance boxes and an elaborate Wolff potentiometer were used in making measurements. The compensation method was employed, a d'Arsonval galvanometer serving as a zero instrument, and several cadmium cells carefully made up serving as standards. Connections were carried in air lines or through glass tubes and other usual precautions observed. The cells, constantly swept out with pure carbon dioxide, were first filled with a solution of stannous chloride nearly free from stannic. After some hours the potential assumed a value which remained constant for days within 0.002 volt, provided no leakage of air or serious temperature change occurred. In the determination with Solution 1a, equilibrium was approached from the other side, by adding a trace of mercuric salt, which was reduced to mercurous salt and mercury until the oxidizing potential, due to mercury salts, was exactly equal to that of the stannic-stannous mixture. This conclusion, verified by the fact that these points also lie on the curve, demonstrates another point of superiority of mercury over platinum electrodes, where no corresponding experiment can be performed. All points on the curves were found with stationary though well mixed solutions, but figures noted on subsequent vigorous stirring are added in the tables.

Few workers in this field have taken the trouble to analyze their solu-

¹A. C. Cumming and E. Gilchrist, *Trans. Faraday Soc.*, 9, 174 (1913), while urging the frequent formation of new boundaries, recommend that capillaries be not used at all.

tions after each potential measurement. In the present research 10 cc. were always pipetted off into a flask swept out with carbon dioxide, diluted generously with air-free water, and titrated with 0.2 equivalent normal permanganate standardized at intervals with sodium oxalate from the

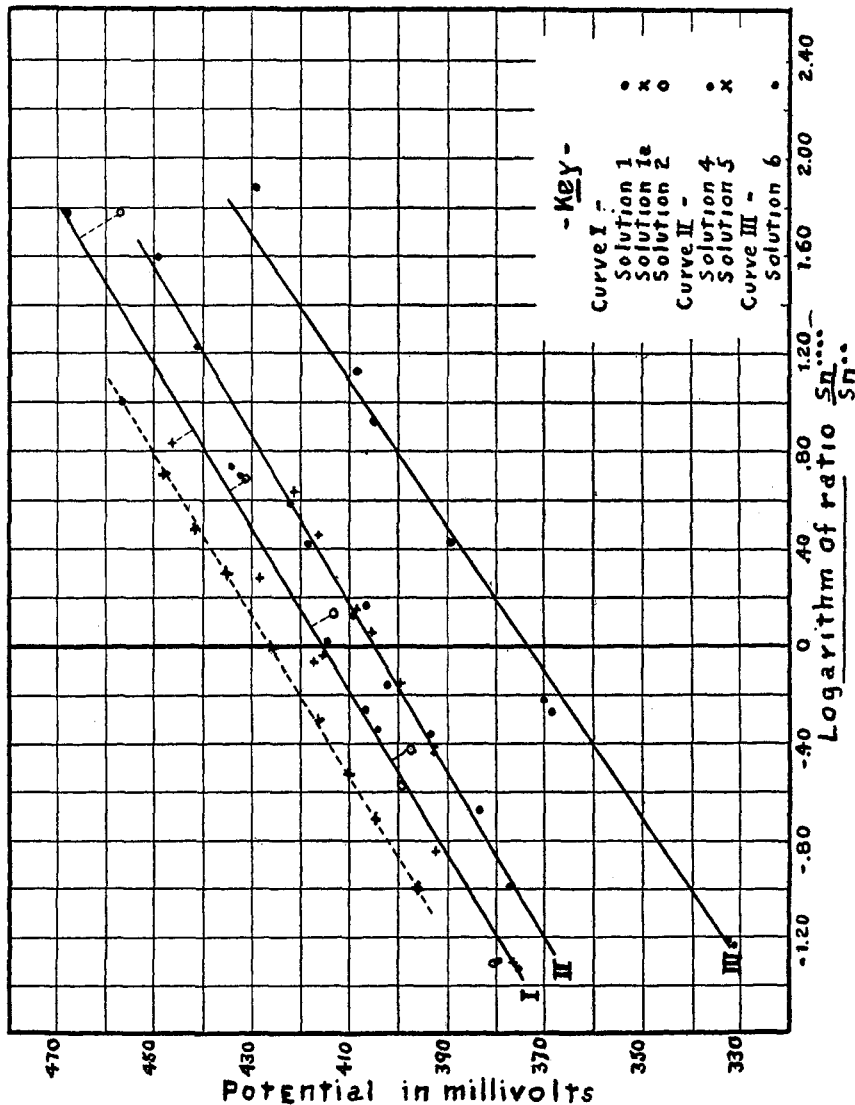


Fig. 1.

Bureau of Standards. It was shown by adding iodide and starch that no chlorine is set free previous to the last drop of permanganate, if only the solution is agitated. The addition of ferric chloride¹ and manganous

¹ Olsen, "Quantitative Chemical Analysis," 1904, p. 312.

salts had no effect on the results, and these reagents were in general omitted. End points were sharp and permanent. The amount of stannous salt thus found was subtracted from the total tin to find the stannic content. Next chlorine was passed in to change the concentration ratio, the acid concentration remaining constant; new measurements were then made, and so on until little stannous tin remained. As expected, the sharpest results were noted when neither valence was present in minimal concentration.

In the following tables each single potential as given results by subtracting the potential of the cell from the value assumed for the normal calomel electrode, namely 0.560 volt. This electrode always formed the positive pole of the cell. The correction for the potential at the

TABLE I.

Solution No. 1.

28.78 g. tin per liter. 1.016 *N* hydrochloric acid.

Cell No.	$\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Log $\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Time. Hrs.	π in millivolts.	
				At rest.	Stirring.
2	0.0462	-1.34	92	375	376
1	0.0500	-1.30	92	379	383
1	0.4540	-0.34	48	404	405
2	0.5440	-0.26	48	406	406
1	1.035	0.01	20	414	414
1	5.008	0.70	23	432	432
2	5.435	0.74	20	434	434
2	60.15	1.78	24	468	...

Solution No. 1a.

The same solution as in No. 1, but each equilibrium was attained after addition of mercuric chloride.

2	0.0485	-1.31	26	376	377
1	0.0504	-1.30	67	376	380
1	0.1444	-0.84	14	392	394
1	0.8600	-0.07	44	417	423
2	0.9145	-0.04	19	415	415
2	1.897	0.28	24	428	429
1	6.735	0.83	49	446	447

Solution No. 2.

29.69 g. tin per liter. 0.998 *N* hydrochloric acid.

Cell No.	$\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Log $\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Time. Hrs.	π .	
				At rest.	Stirring.
2	0.0298	-1.52	89	374	379
1	0.0481	-1.31	89	380	385
1	0.2690	-0.57	23	399	399
2	0.3740	-0.42	23	397	398
2	1.390	0.14	21	413	414
1	4.860	0.69	21	431	436
2	60.90	1.78	21	457	462

Solution No. 4.

29.69 g. tin per liter. 2.000 *N* hydrochloric acid.

Cell No.	$\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Log $\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Time. Hrs.	π .	
				At rest.	Stirring.
1	0.1033	-0.99	22	377	377
3	0.2118	-0.67	25	383	385
3	0.4420	-0.36	22	393	393
2	0.6879	-0.16	21	402	402
2	1.332	0.13	23	409	409
3	1.518	0.18	21	406	407
1	2.657	0.42	27	...	418
2	3.916	0.59	24	422	424
2	17.10	1.23	72	441	440
2	39.93	1.60	22	449	449

Solution No. 5.

Of same composition as solution No. 4, but prepared with electrolytic tin.

2	0.3651	-0.44	72	392	391
1	0.3900	-0.41	72	392	392
2	0.7014	-0.15	20	399	399
1	1.142	0.06	29	405	405
2	1.456	0.16	29	408	407
2	2.909	0.46	26	416	417
1	4.408	0.64	26	421	422

Solution No. 6.

29.69 g. tin per liter. 5.257 *N* hydrochloric acid.

Cell No.	$\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Log $\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Time. Hrs.	π .	
				At rest.	Stirring.
1	0.0584	-1.23	86	331	...
2	0.0622	-1.21	95	332	331
3	0.1233	-0.90	28	342	343
2	0.5333	-0.27	23	368	368
1	0.6012	-0.22	19	371	372
3	2.622	0.43	42	390	391
2	8.479	0.93	21	405	406
1	13.41	1.13	21	408	409
1	77.76	1.89	23	427	429

liquid junction between the potassium chloride and the acid is not applied because of the great uncertainty as to the nature, concentration, and degree of dissociation of the numerous compounds and complex ions that may be present. It will be shown that the best method to eliminate this uncertainty is to extrapolate to zero concentration of acid. The data in the table are plotted on the lines found in Fig. 1. Time elapsed, in hours, from the last alteration of concentration to the given observation is noted; in practically every case the potential was sensibly constant for the last twelve hours of this period. The work in normal acid (Curve 1) was carried out first, before experimental difficulties had been thoroughly overcome, so that the points in this series are somewhat less satisfactory than in the others.

Unless considerable acid is present, the hydrolytic equilibrium of stannic chloride is very slowly established, as indicated by Kowalewsky's conductivity measurements,¹ which we checked at 25°. For each con-

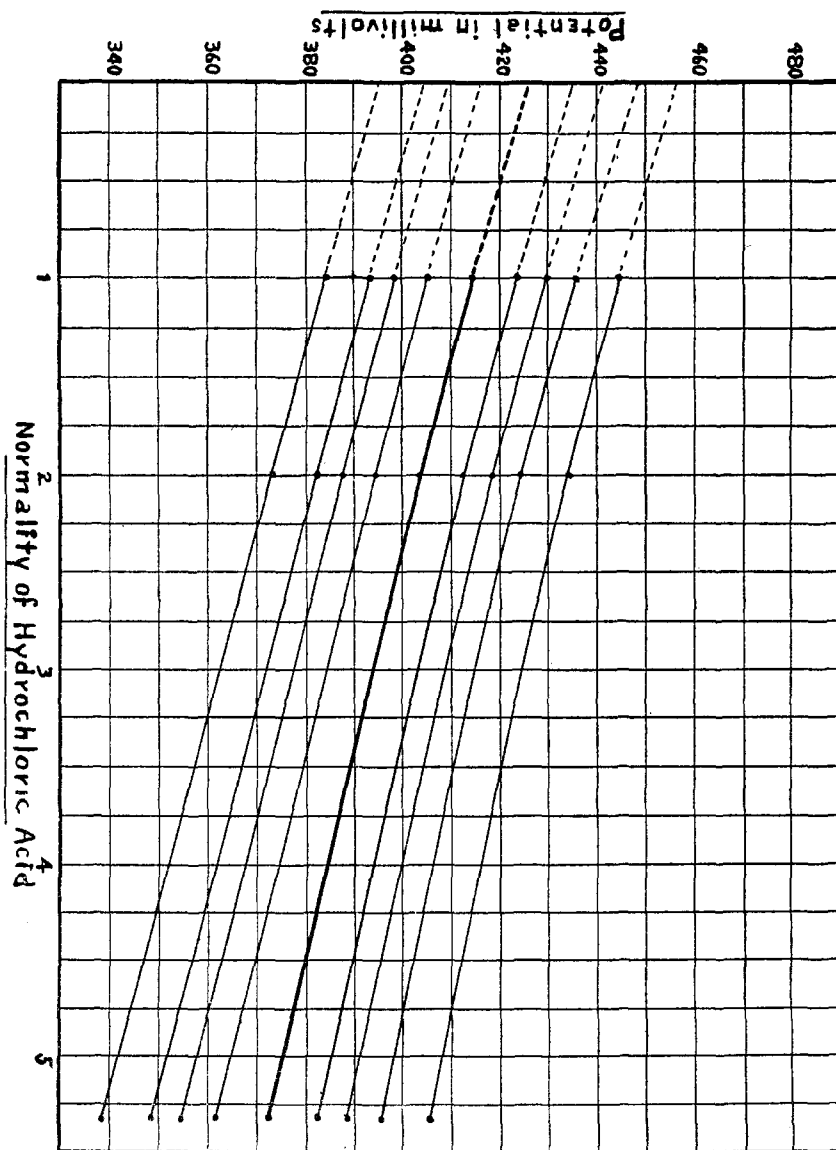


Fig. 2.

centration of acid used as a medium the curves show a relation, almost linear, between potential and the logarithm of the concentration ratio.

¹ *Z. anorg. Chem.*, 23, 1 (1900).

To find what values ought to be observed if acid could be eliminated without appearance of hydrolysis, we have in Fig. 2 plotted potentials for selected values of the concentration ratio against the several concentrations of acid employed, and extrapolated to zero concentration of acid. Values taken from the smoothed curves are used in preference to experimental points, and are given in Table II.

TABLE II.

$\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Log $\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Potential in millivolts.		
		1.00 <i>n.</i>	2.00 <i>n.</i>	5.26 <i>n.</i>
0.10	—1.00	385	374	339
0.20	—0.70	394	383	342
0.30	—0.52	399	388	355
0.50	—0.30	406	395	362
1.00	0.00	415	404	373
2.00	0.30	424	413	383
3.00	0.48	430	419	389
5.00	0.70	436	425	396
10.00	1.00	445	434	406

The graphs are nearly straight lines, so that no unusual risk is involved in the extrapolation to zero acid concentration. The dotted line in Fig. 1 shows these ideal stannic-stannous potentials, which can never be realized experimentally.

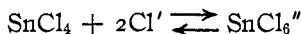
It is instructive to calculate the slopes of the several lines, considering the whole length in each case, and to compare them with the ideal slope of the line representing the equation $\pi = a + 0.029 \log \frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$, where

$\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}} = \frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}} \cdot \frac{\alpha^{\text{IV}}}{\alpha^{\text{II}}}$, assuming $\frac{\alpha^{\text{IV}}}{\alpha^{\text{II}}}$, the ratio of the dissociation constants,

to be invariable, a condition which is almost realized, apparently.

Concentration of HCl.	0 <i>n.</i>	1.0 <i>n.</i>	2.0 <i>n.</i>	5.26 <i>n.</i>	Ideal
Slope, $\Delta\pi/\Delta \log \frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	0.030	0.030	0.030	0.033	0.0295

Hydrochloric acid represses the ionization of stannic chloride and also of such complex ions as $\text{SnCl}_6^{\prime\prime}$ formed by the reaction



more than the ionization of the corresponding stannous compounds.¹

As there is no hydrolysis to check, increasing acid concentration causes $\frac{\alpha^{\text{IV}}}{\alpha^{\text{II}}}$, and, therefore, $\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$, to fall off, which is demonstrated by the in-

creasing slope obtained from the quotient $\Delta\pi/\Delta \log \frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$.

¹ See Young, *THIS JOURNAL*, 23, 21 (1901), and Engel, *Ann. chim. phys.*, 17, 338 (1889).

Effect of Varying Total Tin Concentration.—Cells were also observed containing but half the usual concentration of tin, that is, one-eighth of a gram-atom of tin per liter of normal hydrochloric acid.

TABLE III.

Solution No. 3.

14.85 g. tin per liter. 0.999 *N* hydrochloric acid.

Cell No.	$\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Log $\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$	Time. Hrs.	ϵ in millivolts.	
				At rest.	Stirring.
2	0.0487	-1.31	67	374	384
1	0.0668	-1.18	67	379	389
1	0.2865	-0.54	42	393	400
2	0.3560	-0.45	42	397	400
2	1.365	0.14	24	413	...
1	2.375	0.38	24	427	...
2	5.975	0.78	24	438	439

These values, if plotted as points in Fig. 1, would mingle with those found for twice this concentration of tin in normal acid. By subtracting from a number of potentials the quantity $0.029 \log \frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$ all are reduced to a hypothetical condition where the concentration ratio equals unity.

	Average.							
28.8 g. per l.....	415	414	417	419	416	420	414	415
14.4 g. per l.....	413	414	409	410	409	416	415	412

Thus it is shown that slightly more electronegative values result in the more dilute tin solution. Here the excess of chloride ions left free to repress the ionization of the stannic chloride and of its complexes is greater, and so the ratio $\frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}}$ is decreased. The difference, however, does not greatly exceed the limit of error of observation, and more exhaustive study would be necessary to settle the question even qualitatively, much more so quantitatively.

Until the degree of dissociation of the several stannic and stannous compounds involved, such as SnCl_4 , SnCl_6^{2-} , H_2SnCl_6 , SnCl_2 , SnCl_3^+ , HSnCl_3 , are known, it is impossible to unravel the various factors influencing the potentials. Were even a part of these known the above measurements would help to evaluate the rest. Meanwhile, mathematical treatment is altogether uncertain.

The work described in this paper was carried out in the spring of 1913, with the exception of the measurements in twice normal acid, which were made in the summer of 1914.

Summary.

Mercury is preferable to platinum in the measurement of oxidizing potentials of low intensity. Results are more quickly obtained, and

suffer less from irregularities in surface energy of the electrode and the presence of traces of oxygen.

The potentials of mixtures of stannic and stannous chlorides containing one-quarter of a gram-atom of tin per liter in hydrochloric acid of three concentrations were measured at mercury electrodes at 25°. The probable error is about two millivolts.

Halving the total tin concentration makes the potential very slightly more electronegative; it seems to be nearly independent of the total tin concentration, other things being equal.

By extrapolation to zero concentration of acid, results are obtained which should be largely unaffected by uncertainties due to hydrolysis and to the single potential at the boundary between the cell liquid and the indifferent electrolyte.

Up to two moles of hydrochloric acid per liter, the potentials are quite accurately expressed by the formula

$$\pi = 0.426 + 0.030 \log \frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}} - 0.011 \times \text{conc. HCl},$$

provided sufficient acid is added to check hydrolysis.

Curves showing the relations existing among the several variables are discussed in the light of present knowledge of solutions of stannic and stannous chlorides.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH, NEW YORK. DEPARTMENT OF EXPERIMENTAL BIOLOGY.]

STUDIES ON A NEW KIND OF E. M. F.

By REINHARD BEUTNER.

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1. Introductory Remarks.

1. It was shown by the author¹ in previous communications that it is possible to compose galvanic cells of water-immiscible organic substances and aqueous solutions without metals, which, in certain points, exhibit properties like the well-known galvanic cells of which metals are the most essential component. The most important aim of a systematic study of these phenomena is the artificial reproduction and the explanation of the electrical properties of living tissues, since it is well known that these also produce e. m. f. resembling e. m. f. of metals. This fact was well established by electrophysiologists long ago, for the magnitude of the e. m. f. produced by tissues resembles that of ordinary galvanic cells; the same is found to hold for the cell-systems described here.

An experimental investigation undertaken at the suggestion of Dr. J. Loeb by the author² had shown this similarity of e. m. f. produced by

¹ THIS JOURNAL, 35, 344 (1913); *Z. Electrochem.*, 19, 467 (1913).

² *Science*, 34, 884 (1911); *Biochem. Z.*, 41, 1 (1912).