were predicted from, experimental data on the catalytic decomposition of hydrogen peroxide.

4. Balint's earlier measurements at 0°, which hitherto have been overlooked, are summarized. When the activity correction is applied χ_2 is equal to 0.00062.

5. The hypobromite ion mechanism suggested by Christiansen is shown to be unsatisfactory.

6. The hypobromous acid mechanism for the reaction between hydrogen peroxide and bromine and for the catalytic decomposition of hydrogen peroxide is in excellent agreement with the known experimental facts.

7. A satisfactory iodimetric method of determining hydrogen peroxide is described.

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THE REDUCTION POTENTIAL OF SELENOUS ACID AND THE FREE ENERGY OF AQUEOUS SELENIC ACID

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Introduction

It is well known that selenic acid may be prepared by oxidizing an aqueous solution of selenous acid with chlorine, and that selenic acid may be reduced to selenous acid by treatment with concentrated hydrochloric acid. This at once leads to the conclusion that, for the reaction $Cl_2 + H_2SeO_3 + H_2O = H_2SeO_4 + 2HCl$, there should be a concentration of hydrochloric acid at which a measurable amount of both selenic and selenous acids would be present when the pressure of chlorine is approximately one atmosphere.

The equilibrium conditions of this reaction were investigated for the purpose of determining, with the aid of the known chloride–chlorine potential, the reduction potential of the reaction H_2SeO_3 (1 m.) + H_2O = $HSeO_4^-$ (1 m.) + $3H^+$ (1 m.) + $2E^-$. The thermodynamic relations involved are indicated below.

The reaction, written in the ionic form $Cl_2\ (g) + H_2O + H_2SeO_3 = 3H^+ + HSeO_4^- + 2Cl^-$ takes place in the hypothetical voltaic cell

$$\text{Pt}\left\{\begin{matrix} H_2SeO_3 & (1\text{ m.}) \\ HSeO_4^- & (1\text{ m.}) \\ H^+ & (1\text{ m.}) \end{matrix}\right. \,\|\, Cl^-\ (1\text{ m.}),\ Cl_2\ (1\text{ atm.}) + \text{Pt}$$

The free energy decrease ($-\Delta F$) attending the change in state in this cell, corresponding to the passage of two faradays, may be calculated either from the electromotive force E of the cell, or from the equilibrium constant K of the reaction by the following well-known equations

$$-\Delta F = 2\text{E}F = RT \ln K$$

The total electromotive force E is, however, equal to the difference $E_1 - E_2$ between the two separate electrode potentials. Since the chloride–chlorine potential E_2 is known at 25° to be equal to −1.359 volt,[1] the desired reduction potential E_1 is given by the equation

$$E_1 = -1.359 + \frac{RT}{2F} \ln K = -1.359 + 0.02957 \log K$$

In order to verify the value of E_1 obtained in this way a study was also made of the corresponding oxidation-reduction reaction with bromine and hydrobromic acid in place of chlorine and hydrochloric acid. In this investigation the activity and concentration of the bromine in the equilibrium solution was conveniently regulated and determined by distribution into carbon tetrachloride. The thermodynamic relations involved are the same as those above. In this case the reduction potential E_1 was calculated by the equation

$$E_1 = -1.087 + 0.02957 \log K$$

in which −1.087 volts[2] is the potential of the bromide–bromine electrode at 25°.

Preparation and Purification of the Chemicals

The chemicals used are listed below, together with the method of preparation or purification.

Selenous Acid.—At the start of the work a small amount of C. P. crystalline selenous acid which had been obtained from the General Chemical Company was available. It was further purified by recrystallizing from water several times. After this supply was exhausted the acid was prepared from a sample of commercial selenium. The method used was that suggested by Dennis and Koller,[3] which consists of dissolving the selenium in nitric acid, evaporating to dryness several times with water to remove the nitric acid, then recrystallizing the resulting acid from water four times. A very pure sample of selenous acid may be obtained in this way.

Selenic Acid.—At first a small amount of selenic acid solution (approx. 43%) obtained from the General Chemical Company was also available. Later the acid was prepared from the purified selenous acid, using the method suggested by Meyer and Moldenhauer,[4] which consists in oxidizing the selenous acid to selenic acid by means of chloric acid, prepared from barium chlorate, and then concentrating the resulting solution *in vacuo*. An 85% acid prepared in this way showed the presence of only a trace of selenous acid.

Chlorine.—The chlorine was prepared by dropping concentrated hydrochloric acid on C. P. potassium permanganate in a glass generating flask. The resulting chlorine was washed by passing it through a solution of hydrochloric acid of approximately the same concentration as the acid in the equilibrium chamber.

Hydrochloric Acid.—All solutions were made up from C. P. concentrated hydrochloric acid of specific gravity 1.19.

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 426.

[2] Lewis and Randall, Ref. 1, p. 427.

[3] Dennis and Koller, THIS JOURNAL, **41**, 949–970 (1919).

[4] Meyer and Moldenhauer, *Z. anorg. Chem.*, **116**, 193–200 (1921).

Bromine.—U. S. P. bromine was further purified by allowing it to stand for several days over finely powdered, recrystallized potassium bromide and then distilling in an all glass apparatus. The middle portion of the distillate (about one-third of the total) was then used.

Hydrobromic Acid.—All solutions were made up from C. P. constant boiling hydrobromic acid prepared in the usual way.

Carbon Tetrachloride.—Eastman's C. P. sulfur-free carbon tetrachloride was refluxed with bromine for six hours in an all glass apparatus. The bromine was removed by repeated washing with dilute sodium hydroxide and finally with water. The product was then dried over anhydrous calcium chloride for two weeks and distilled. The fraction boiling between 76.71 and 76.81° was used.

Preparation of the Equilibrium Mixtures

Chlorine System.—Merewether[5] has shown that when selenic acid is dissolved in 2.06 *N* hydrochloric acid and the solution saturated with chlorine at room temperature, no selenous acid can be detected even after long standing; also that when selenous acid is dissolved in 12 *N* hydrochloric acid and the solution saturated with chlorine no selenic acid is formed. However, he found measurable quantities of both selenic and selenous acids present in a solution from 7–9 molal in hydrochloric acid with a chlorine pressure of one atmosphere. In view of these facts the present work was carried out with solutions ranging from 7–8.5 molal in hydrochloric acid and the chlorine pressure between 650 and 900 mm.

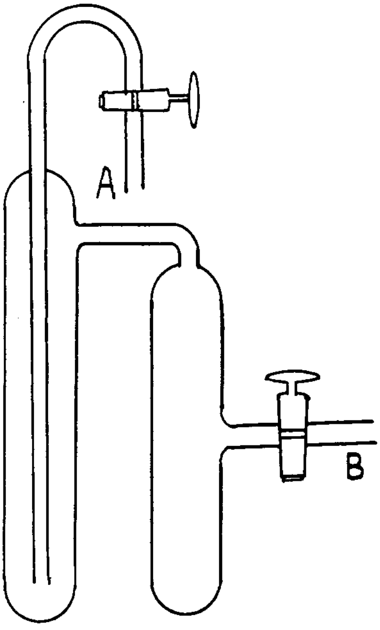

Fig. 1.

The hydrochloric acid solution, containing in some cases selenic acid, in other cases selenous acid and in still other cases both selenic and selenous acids, was placed in the glass apparatus shown in the figure. Chlorine, prepared as previously described, was then bubbled through the solution until all air was expelled and the solution saturated with the gas at a pressure somewhat greater than one atmosphere. The apparatus was then placed in a horizontal position in a thermostat at 25.00 ± 0.01° and gently rocked until equilibrium was reached. In most cases the chlorine pressure was adjusted so that at equilibrium the pressure would be approximately one atmosphere. In other cases the pressure was allowed to adjust itself and was measured by means of a mercury manometer. With a manometer

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[5] Merewether, M. I. T. *Thesis*, **1925**, unpublished.

connected to the apparatus it served as a fairly delicate method of indicating when equilibrium had been reached. When there was no further change in pressure the apparatus was shaken for twelve to twenty-four hours longer to insure equilibrium. By applying pressure to the apparatus at B, the solution was forced out at A, directly into the weighing bottle. Weighed samples were then analyzed for the various constituents.

No attempt was made to determine the rate of the reaction in either direction, but from the length of time (four to seven days) necessary to establish equilibrium it is known to be very slow.

Bromine System.—The reduction potential obtained in the chlorine system indicated that the equilibrium constant in a bromine system should be near unity. Since the bromine concentration could be kept low, this meant that the concentration of hydrobromic acid could be kept below one molal.

Equilibrium was established in the system in the following way: about 40 cc. of a solution of bromine in carbon tetrachloride (mole fraction 0.0005–0.005) was placed in a glass-stoppered cylinder of 100cc. capacity; then about 60 cc. of a hydrobromic acid solution (molality 0.10–0.40) containing either selenous acid or selenic acid, and in some cases both selenous and selenic acid, was added. The cylinder was stoppered and sealed with paraffin, placed in a thermostat at $25.00 \pm 0.01°$ and shaken until equilibrium was established. The water layer was then analyzed for hydrobromic, selenous and selenic acids and the carbon tetrachloride layer for bromine.

As in the chlorine system no attempt was made to determine the rate of the reaction in either direction, but it must be extremely slow since from fifty to seventy days were necessary for equilibrium to be established.

Methods of Analysis of the Equilibrium Mixtures

The concentrations of hydrochloric, hydrobromic, selenous and selenic acids and that of chlorine and bromine in the equilibrium mixtures were determined as follows.

Hydrochloric Acid.—A weighed sample was diluted with ice water and shaken over mercury for thirty minutes to remove the chlorine. The mercury was then removed with a separatory funnel and the mercurous chloride by filtration. The hydrochloric acid in the filtrate was determined by the silver thiocyanate method, as modified by Drecksel.[6]

Selenous Acid.—A weighed sample was diluted with ice water and chlorine or bromine removed as before. The selenous acid was then determined by the method of Norris and Fay,[7] which is based on the reaction

$$SeO_2 + 4HCl + 4Na_2S_2O_3 \longrightarrow Na_2S_4SeO_6 + Na_2S_4O_6 + 4NaCl + 2H_2O$$

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[6] See Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1914**, p. 707.

[7] Norris and Fay, *Am. Chem. J.*, **23**, 119–128 (1900).

The solution (usually about 200 cc.) was cooled to 0°; then, after addition of 10 cc. of concentrated hydrochloric acid, sodium thiosulfate was added in slight excess, this excess being titrated with iodine, using starch as indicator.

Selenic Acid.—A weighed sample was placed in a long-necked, round-bottomed flask of 250cc. capacity, 75 cc. of concentrated hydrochloric acid added and the mixture refluxed on a water-bath for eight to ten hours, using a glass tube placed inside the neck of the flask as a condenser. The solution was then cooled to 0° and the selenous acid determined as before. The selenic acid was determined by difference.

It is known that in hot solution hydrochloric acid and selenous acid react to form selenium tetrachloride and that some of the tetrachloride escapes with the vapors. However, it was found by very careful experimentation that with the system of refluxing used no selenium was lost, even after long boiling.

Chlorine.—Although the activity of the chlorine in the equilibrium mixture is definitely determined by the pressure of the chlorine, it was nevertheless necessary to determine the amount of dissolved chlorine in order to compute the concentrations of the other substances as formula weights per 1000 g. of water. As no method presented itself for the direct determination of chlorine in the presence of selenous acid, these concentrations of chlorine were obtained by graphical interpolation from the values given in the following section for the solubility of chlorine in hydrochloric acid of varying composition. In these hydrochloric acid solutions the chlorine was determined by titrating a weighed sample, after addition of potassium iodide, with sodium thiosulfate.

Hydrobromic Acid.—A weighed sample was diluted with water and the bromine removed by shaking with mercury under conditions previously described for removing chlorine. The hydrobromic acid in the filtrate was then determined by the silver thiocyanate method.

Bromine.—A weighed sample of the carbon tetrachloride layer was added to potassium iodide and the liberated iodine titrated with sodium thiosulfate. The total bromine in the hydrobromic acid solutions was determined by titrating a weighed sample of the aqueous layer, after addition of potassium iodide, with sodium thiosulfate.

Solubility of Chlorine in Hydrochloric Acid Solutions

Jakowkin[8] has shown that chlorine is more soluble in hydrochloric acid solutions than in pure water. He attributed the increase in solubility to the reaction, $Cl_2 + Cl^- = Cl_3^-$. As his results do not cover the range of concentrations needed in this investigation, it was necessary to make a series of direct determinations of the solubility of chlorine in solutions of

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[8] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

hydrochloric acid, not only to find the total amount of dissolved chlorine in the equilibrium mixtures, but also to be able to estimate the proportion of chloride in such mixtures converted to trichloride ion. The equilibrium was established as described above for the cases in which selenic and selenous acids were also present.

The results of these solubility determinations are given in Table I. The solubility of chlorine was reduced to the basis of one atmosphere pressure of chlorine gas by applying Henry's law, which is valid over the narrow range of pressure involved. The partial pressure of chlorine saturating the solution was found by deducting from the observed barometric pressure the sum of the partial vapor pressures of water and of hydrochloric acid in the solution. The latter were obtained from vapor-pressure measurements of hydrochloric acid solutions containing no dissolved chlorine. As no direct determinations of the total vapor pressure of such solutions were available, it was necessary to combine Dobson and Masson's[9] measurements of the partial vapor pressure of water with Bates and Kirschman's[10] measurements of the partial vapor pressure of hydrochloric acid in solutions of varying acid content. The desired values for the total vapor pressure were obtained from these measurements by graphical interpolation.

TABLE I

SOLUBILITY OF CHLORINE GAS IN HYDROCHLORIC ACID AT 25° AND ONE ATMOSPHERE

	Concentration of			Ratio
ΣHCl	ΣCl_2	(Cl_3^-)	(Cl^-)	$(Cl_3^-)/(Cl^-)$
4.903	0.0978	0.0360	4.867	0.00739
7.016	.1150	.0532	6.963	.00764
8.163	.1219	.0601	8.102	.00742
8.854	.1281	.0663	8.788	.00754
9.805	.1326	.0709	9.734	.00727

The concentrations in the table are expressed as formula weights (or moles of the molecular species) per 1000 g. of water. The concentration of the trichloride ion in the third column was computed under the assumption that the acids are completely ionized and that the concentration of Cl_2 as such is 0.0618 M, the value derived by Lewis and Randall[11] from Jakowkin's data for this saturation concentration in dilute aqueous solutions when the (partial) pressure of Cl_2 is 1 atm. Under this assumption, the ratio $(Cl_3^-)/(Cl^-)$ given in the last column corresponds to the equilibrium constant of the reaction $Cl_2\ (g) + Cl^- = Cl_3^-$. In consideration of the fact that the actual solubility of the molecular species Cl_2 is almost certainly less than the assumed value (0.0618 M), the value of the constant is to be regarded only as a rough approximation. Its average value

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[9] Dobson and Masson, *J. Chem. Soc.*, **125**, 668 (1924).

[10] Bates and Kirschman, THIS JOURNAL, **41**, 1991 (1919).

[11] Ref. 1, p. 502.

(0.0074) was used to compute the small proportion of chloride converted to trichloride in the equilibrium mixtures containing selenous and selenic acids. The value evidently corresponds to 0.74% conversion at all concentrations of hydrochloric acid.

Distribution of Bromine between Carbon Tetrachloride and Aqueous Solutions of Hydrobromic Acid

Jakowkin,[12] and Lewis and Storch[13] have shown from the distribution of bromine between carbon tetrachloride and aqueous solutions of potassium bromide or hydrobromic acid that bromine dissolved in the aqueous layer is partly converted to a tribromide ion by the reaction $Br_2 + Br^- = Br_3^-$. Lewis and Storch have computed the equilibrium constant of this reaction to be approximately 16.4 at 25°, which does not differ greatly from the value obtained by Jakowkin. As their measurements were limited to a single concentration of acid, 0.1 formal HBr, it seemed desirable to make a series of determinations at varying acid concentrations. The results are shown in Table II.

The equilibrium conditions were established and analyses made by the methods described in the preceding section. The total concentration of bromine, given in Col. 2, was kept low in order to reduce the tendency to form a pentabromide, or higher bromide ion.

TABLE II

EQUILIBRIUM CONCENTRATIONS IN SOLUTIONS OF HYDROBROMIC ACID AND BROMINE AT 25°

Formula weights per 1000 g. of water			Molality		
ΣHBr	ΣBr_2	(Br_2)	(Br_3^-)	(Br^-)	$K = \frac{(Br_3^-)}{(Br_2)(Br^-)}$
0.10408	0.0018675	0.0006847	0.001183	0.10290	16.80
.10408	.003290	.001209	.002081	.10200	16.87
.10408	.004303	.001591	.002712	.10137	16.81
.10408	.006467	.002406	.004061	.10002	16.88
.3216	.004944	.0007671	.004177	.31747	17.15
.4408	.01578	.001867	.01391	.4269	17.45
.4408	.02172	.002594	.01913	.4217	17.48
.5204	.01779	.001799	.01599	.5044	17.62
.5204	.03855	.00404	.03451	.4859	17.58

The molality of bromine recorded in the third column was calculated from the analysis of the tetrachloride layer with the aid of the distribution ratio of bromine between water and carbon tetrachloride given by Lewis and Storch. In dilute solution this ratio is $c/x = 0.371$, where c is the molality of bromine in the water solution and x is its mole fraction in the tetrachloride solution.

The values of the equilibrium constant shown in the last column are all somewhat higher than the value given by Lewis and Storch, and increase

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[12] Jakowkin, *Z. physik. Chem.*, **18,** 583 (1895); **20,** 19 (1896).

[13] Lewis and Storch, THIS JOURNAL, **39,** 2544 (1917).

with increasing concentration of the hydrobromic acid. In computing the amount of bromide converted to tribromide ion in the equilibrium mixtures containing selenous and selenic acids, a value of the equilibrium constant was chosen which corresponded to the total concentration of hydrobromic acid present.

Tabulation and Discussion of Results

Chlorine System.—The values given in Cols. 2 to 5 of Table III represent the total concentrations of the respective substances as determined from the analyses and from graphical interpolation of the solubility data for chlorine. Ratios (p/p_0) of the vapor pressure of water in the solutions to the vapor pressure of pure water are recorded in the seventh column as the activity $[H_2O]$ of water. The values for the molality of the hydrogen ion and that of the chloride ion were computed from the total concentration of acid under the assumption that hydrochloric acid, and selenic acid, with respect to its first hydrogen, are completely ionized, and that selenous acid, and selenic acid, with respect to its second hydrogen, are in these solutions of high hydrogen ion activity un-ionized. In computing the chloride ion concentration a correction was made for the small proportion of chloride converted to trichloride.

TABLE III

COMPOSITION OF THE EQUILIBRIUM MIXTURES AT 25°

	Formula weights per 1000 g. of water				Pressure atm.	Activity of water	Molality of		Ion activa-	Con- stant,	Reduction potential,
Expt.	ΣHCl	ΣCl_2	H_2SeO_4	H_2SeO_3	of Cl_2,	$[H_2O]$	(H^+)	(Cl^-)	tion (γ)	$K \times 10^{-9}$	E_1
1[a]	6.886	0.1118	0.2380	0.0467	1.000	0.5921	7.124	6.836	4.554	1.297	−1.0899
2[a]	7.412	.11346	.2310	.1813	.9784	.5577	7.643	7.539	5.314	1.272	−1.0902
3[a]	7.623	.11587	.1003	.1014	.9849	.5530	7.723	7.568	5.440	1.242	−1.0905
4	7.682	.11511	.0723	.0777	.9823	.5513	7.754	7.627	5.491	1.274	−1.0902
5[a]	7.706	.11691	.1821	.2156	.9856	.5429	7.888	7.650	5.71	1.571	−1.0875
6[a]	7.836	.12472	.1018	.1636	1.0473	.5400	7.938	7.776	5.805	1.273	−1.0902
7	7.132	.11166	.8342	.9510	0.9815	.5379	7.966	7.081	5.84	1.595	−1.0873
8[a]	7.854	.14965	.1199	.1688	1.2565	.5370	7.974	7.782	5.85	1.295	−1.0900
9[a]	7.981	.09937	.0837	.1982	0.8312	.5311	8.065	7.981	5.91	1.346	−1.0895
10	8.374	.12001	.0612	.3009	.9710	.5093	8.435	8.314	6.725	1.615	−1.0871
11	8.447	.12182	.0719	.3761	.9842	.5034	8.519	8.386	6.90	1.81	−1.0857
									Mean	1.42	1.088

[a] Equilibrium approached from the chlorine side.

The equilibrium constant was calculated under the assumption that the mean activity coefficient of selenic acid (regarded here as a univalent acid) is the same as that of hydrochloric acid. The values employed in the calculation are tabulated in Col. 10. They were taken equal to the mean activity coefficient of hydrochloric acid as given by Randall and Young[14] at a concentration equal to that of (H^+) in the equilibrium mixture. Under these assumptions the equilibrium constant is given by the equation

$$K = \frac{(H^+)^3(HSeO_4^-)(Cl^-)^2\gamma^6}{(H_2SeO_3)\ [H_2O]\ p_{Cl_2}}$$

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[14] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

In the last two columns of the table are recorded the value of this constant, and the corresponding values for the reduction potential E_1 of the reaction H_2SeO_3 (1 m.) + H_2O = $3H^+$ (1 m.) + $HSeO_4^-$ (1 m.) + $2E^-$ computed by the equation previously given. The error in the equilibrium constant due to the assumptions that H_2SeO_3 and $HSeO_4^-$ are not appreciably ionized is probably very small. It can be shown to be so in the case of selenous acid by reference to its ionization constant, which is given by Blanc[15] to be equal to 0.0027.

The ionization relations of selenic acid are not definitely known, but are almost certainly similar to those of sulfuric acid. This is indicated not only by its chemical behavior but also by the fact that the change in its equivalent conductance with concentration closely parallels that of sulfuric acid.[16] Furthermore Small[17] has shown that the electromotive force of a voltaic cell of the type H_2, H_2SO_4 (c. f.), H_2SeO_4 (c. f.), H_2 is substantially zero, when the concentrations of the two acids in the cell are made equal to each other. (It was not possible to carry such measurements to concentrations above 1.0 *f*, since at these higher concentrations reduction to selenium takes place at the platinized electrode.)

Sherrill and Noyes[18] have derived the value 0.0115 for the ionization constant of the second hydrogen of sulfuric acid under the assumption that the first hydrogen is completely ionized. Adopting this same value as the ionization constant of the $HSeO_4^-$, the ratio $[SeO_4^=]/[HSeO_4^-]$ of the activity of $SeO_4^=$-ion to that of $HSeO_4^-$-ion in the equilibrium mixtures may be computed from the activities of the H^+-ion. Thus in Expt. 1, $[SeO_4^=]/[HSeO_4^-] = 0.0115/32.4 = 0.00035$. The small values thus obtained for these activity ratios make plausible the assumption that the concentration of $SeO_4^=$-ion is negligibly small in comparison with that of the $HSeO_4^-$-ion.

The assumption that the mean activity coefficient of selenic acid is equal to that of hydrochloric acid is not exact but is the simplest assumption to make under the circumstances.

The mean values for the equilibrium constant and for the reduction potential obtained are **1.4** × 10^9 and **−1.088** volts, respectively.

Bromine System.—The concentrations of the various substances present in the aqueous solution at equilibrium are given in Table IV. The ion activation values in Col. 9 were taken equal to the mean activity coefficient of hydrobromic acid, as given by Livingston,[19] at a concentration equal to the total hydrogen ion concentration recorded in Col. 7. The

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[15] Blanc, *J. chim. phys.*, **18,** 28 (1920).

[16] Landolt-Börnstein, "Phys. Chem. Tabellen," pp. 1081 and 1093.

[17] Small, M. I. T. *Thesis,* 1927.

[18] Sherrill and Noyes, THIS JOURNAL, **48,** 1861 (1926).

[19] Livingston, *ibid.,* **48,** 45 (1926).

TABLE IV

COMPOSITION OF THE EQUILIBRIUM MIXTURES AT 25°

Expt.	Formula weights per 1000 g. of water					Molality		Ion-Activation (γ)	Constant K	Reduction potential E_1
	ΣHBr	ΣBr_2	H_2SeO_4	H_2SeO_3	(Br_2)	(H^+)	(Br^-)			
1	0.1725	0.0005233	0.08547	0.08475	0.0001333	0.2579	0.1721	0.7887	0.944	−1.0877
2[a]	.2779	.001520	.03244	.07493	.0002802	.3104	.2767	.7865	.837	−1.0892
3[a]	.2875	.001551	.02647	.05876	.0003016	.3120	.2860	.7864	.878	−1.0887
4	.2955	.001390	.02821	.09460	.0002302	.3237	.2943	.7862	.899	−1.0884
5[a]	.1059	.002593	.2225	.02669	.0009334	.3284	.1042	.7861	.810	−1.0897
6[a]	.2362	.002999	.09511	.06818	.0006992	.3315	.2339	.7861	.938	−1.0878
7[a]	.2445	.004176	.1158	.1026	.0008169	.3603	.2411	.7863	.888	−1.0885
8	.2952	.005557	.08447	.1158	.000927	.3797	.2906	.7863	.860	−1.0889
9[a]	.1860	.002347	.1966	.1922	.0005674	.3824	.1841	.7864	.808	−1.0897
10	.3047	.005747	.08334	.1166	.000947	.3880	.2999	.7870	.942	−1.0878
								Mean	.88	−1.088

[a] Equilibrium approached from the bromine side.

values of the equilibrium constant tabulated in Col. 10 were calculated under assumptions entirely analogous to those made in the case of the chlorine equilibrium except that in these more dilute solutions the activity of water was taken equal to unity. The values for the equilibrium constant were thus calculated by the equation $K = \dfrac{(H^+)^3(HSeO_4^-)(Br^-)^2\gamma^6}{(H_2SeO_3)(Br_2)}$.

The assumption that H_2SeO_3 and $HSeO_4^-$ are not appreciably ionized is less justified here than in the case previously considered. It may, however, be noted that, since the ratio of the concentration of these two substances occurs in the expression of the equilibrium constant, there is a tendency for the two errors introduced by the assumption to counterbalance each other.

The mean values for the equilibrium constant and the reduction potential are **0.88** and **−1.088** volts, respectively. It is fortuitous that this value for the reduction potential is identical with that obtained from a study of the chlorine equilibrium, considering the approximate assumptions that were necessarily made.

The Free Energy of Aqueous Selenic Acid

From the value of the reduction potential (−1.088 volts) the free energy decrease attending the corresponding change in state may be calculated by the familiar equation $-\Delta F = \text{ENF}$. The result is shown by the following free energy equation

$$H_2SeO_3 + H_2O(l) = H^+ + HSeO_4^- + H_2(g) - 50210 \text{ cal.} \qquad (1)$$

According to Schott, Swift and Yost,[20] at 25°

$$Se(s) + \frac{3}{2}O_2(g) + H_2(g) = H_2SeO_3 + 101360 \text{ cal.} \qquad (2)$$

According to Lewis and Randall,[21] at 25°

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O\ (l) + 56560 \text{ cal.} \qquad (3)$$

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[20] Schott, Swift and Yost, THIS JOURNAL, **50,** 721 (1928).

[21] Ref. 1, p. 485.

By addition of these three free energy equations there results

$$Se(s) + 2\ O_2(g) + H_2(g) = H^+ + HSeO_4^- + 107710 \text{ cal.} \qquad (4)$$

That is, $\Delta F_{298} = -107710$ cal. for $HSeO_4^-$ (or for one formula weight of aqueous H_2SeO_4).

Summary

The equilibrium conditions of the reactions

$$Cl_2(g) + H_2SeO_3 + H_2O = 3H^+ + HSeO_4^- + 2Cl^- \text{ and}$$
$$Br_2 + H_2SeO_3 + H_2O = 3H^+ + HSeO_4^- + 2Br^-$$

were determined at 25°. The values of the corresponding equilibrium constants were found to be 1.42×10^9 and 0.88, respectively. From each of these constants and known thermodynamic data the reduction potential of the reaction $H_2SeO_3 + H_2O\ (l) = 3H^+ + HSeO_4^- + 2E^-$ was calculated to be −1.088 volts. From this value and existing free energy data, the free energy (ΔF) at 25° of $HSeO_4^-$ (or of one formula weight of aqueous H_2SeO_4) was calculated to be −107,710 cal.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. IV. THE POTENTIOMETRIC TITRATION OF VANADYL ION ALONE OR IN THE PRESENCE OF FERRIC AND CHROMIC IONS. NOTE ON THE STABILITY OF VANADYL SOLUTIONS[1]

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This communication reports further progress in a study of the direct uses of standard ceric sulfate solutions in volumetric analysis. The apparatus and technique have been described in a former paper.[2]

Experimental

Approximately 0.05 *M* solutions of ceric sulfate in dilute sulfuric acid were prepared and standardized by potentiometric titration with oxalic acid (exactly 0.05 *N*) that had been prepared by dissolving pure, dry sodium oxalate in water acidified with 10 cc. of sulfuric acid (sp. gr. 1.84) per liter.

Note on the Stability of Vanadyl Solutions.—During the course of the investigation observations were made on the stability of vanadyl solutions. The author's findings are in agreement with the conclusions of Stout and Whitaker[3] who stated that vanadyl solutions are stable for six months or more.

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[1] Presented at the spring meeting of the American Chemical Society at St. Louis, Missouri, April, 1928.

[2] Furman, THIS JOURNAL, **50,** 755 (1928).

[3] Stout and Whitaker, *Ind. Eng. Chem.*, **20,** 210 (1928).