

0.025 cm. and with increased wall surface. The reaction was found to be homogeneous and unimolecular at all pressures.

The heat of activation as given by the Arrhenius expression for the temperature coefficient of reaction rate is 40,900 cal. per mole. The rate constant is given by the expression $K = 5.6 \times 10^{13} \times e^{-\frac{40,900}{RT}}$

A discussion of these results in relation to various theories of reaction rate is given. Theory II of Rice and Ramsperger would require that the rate constant of the reaction become smaller at pressures below 0.025 cm. if the *azo-isopropane* molecule had 45 to 50 degrees of freedom. It is thought likely that the specific heat of *azo-isopropane* would be large enough to permit this number of degrees of freedom.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 162]

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

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RECEIVED DECEMBER 5, 1927

PUBLISHED MARCH 7, 1928

Introduction

The fact that selenous acid, H_2SeO_3 , is reduced to elementary selenium by iodides in acid solutions is well known and is made use of in analytical methods for the determination of selenium.¹ The reduction, however, is quantitative only in moderately strong acid solutions. It was found, as a result of a number of preliminary experiments, that in more dilute acid solutions the substances taking part in the reaction are present in measurable amounts when equilibrium is attained.

In this paper are described equilibrium measurements at 25° for the following reaction, together with the thermodynamic quantities calculated from them, $\text{Se}(s) + 2\text{I}_2(s) + 3\text{H}_2\text{O}(l) = \text{H}_2\text{SeO}_3(\text{aq}) + 4\text{H}^+ + 4\text{I}^-$.

We wish to express here our appreciation of the many useful suggestions made by Professor A. A. Noyes. The investigation was aided on the financial side by funds granted to him by the Carnegie Institution of Washington.

Outline of the Investigation

The reaction mixtures were prepared by mixing standard solutions of selenous acid, potassium iodide, perchloric acid and water in 250cc. volumetric flasks and transferring the contents to glass-stoppered bottles

¹ Muthman and Schäfer, *Ber.*, **26**, 1008 (1893); Gooch and Reynolds, *Z. anorg. Chem.*, **10**, 248 (1895).

containing solid iodine and black selenium.² Some precautions were taken to exclude atmospheric oxygen, but it was never entirely eliminated, as will appear below. The bottles were rotated in a thermostat at 25° for at least one week, the preliminary experiments having shown that equilibrium is attained within this time.

Preparation of the Materials

Selenium.—Pure, sublimed selenium dioxide was dissolved in a slight excess of dilute sodium hydroxide solution, and the resulting mixture was treated with sodium thiosulfate and heated to boiling for several hours. The precipitate of elementary selenium which formed was filtered off, washed with water and alcohol, and finally dried in a current of air. This procedure yields the black selenium, which is stable at ordinary temperatures.³

Selenous Acid.—Commercial black powdered selenium was dissolved in nitric acid, evaporated to dryness and heated until the yellow color disappeared. The residue was then dissolved in water, the solution filtered, evaporated to dryness and the residue sublimed.⁴ The stock solution of selenous acid was prepared by dissolving the fine, needle-like crystals in water.

Hypochlorous Acid.—This was prepared by passing chlorine through a mixture of water and solid mercuric oxide for about one hour and distilling in a current of air the resulting solution, after removing the excess of mercuric oxide.⁵ The distillate containing the hypochlorous acid was absorbed in ice-cold water.

Other Materials.—The iodine, potassium iodide and perchloric acid used were the purest trade preparations.

Analysis of the Equilibrium Mixtures

Samples of the liquid phase, free from any solid, were removed from the bottles by forcing the solutions into a 50cc. pipet equipped with an asbestos filter, compressed air being used which had been passed over solid iodine.

Two samples were required for a complete analysis of each equilibrium mixture. One of them was used for the determination of the iodine and selenous acid, the other for the determination of the acid. The standard solutions were all about 0.1 *N*. The two methods of analysis used were as follows.

Determination of Iodine and Selenous Acid.—A 50cc. sample, immediately after its removal from the reaction mixture, was run into a glass-stoppered flask containing 10–30 cc. of standard hydrazine sulfate solution and 13–16 millimoles of Na_2HPO_4 . The excess of iodine remaining

² Beckmann and Grünthal, *Z. anorg. chem.*, **84**, 97 (1913), have shown that selenium and iodine form no compounds, mixed crystals or solid solutions.

³ See Abegg-Auerbach-Kappel, "Handbuch der anorganischen Chemie," Band IV, 1 Abt., 1 Hälfte, S. Hirzel, Leipzig, 1927. The product used here was a fine black powder.

⁴ Sacc, *Ann. chim. phys.*, [3] **21**, 119 (1847); Janneck and Meyer, *Z. anorg. allgem. Chem.*, **83**, 51 (1913).

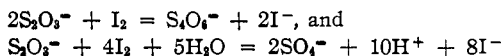
⁵ Bray and Cuy, *THIS JOURNAL*, **46**, 858 (1924).

was then titrated with more of the standard hydrazine solution.⁶ In this mixture, which is practically neutral, the iodine is reduced quantitatively to iodide by the hydrazine, while selenous acid is not appreciably affected by either the iodide or hydrazine during the time required for the analysis.

To the sample after the hydrazine titration, there was added 4-4.5 cc. of 6 *N* sulfuric acid and an excess (35-60 cc.) of the standard hydrazine, and the resulting mixture was kept at about 100° for three to four hours.⁷ After cooling and filtering the solution it was made neutral with 4-6 cc. of 4 *N* sodium hydroxide, and excess (10-25 cc.) of standard hypochlorous acid added and after five minutes the liberated iodine was titrated with the standard hydrazine. In this process selenous acid is reduced to elementary selenium by the hydrazine and iodide in the hot acid solution. The hypochlorous acid added to the neutral solution quantitatively oxidizes the excess of hydrazine and also liberates iodine, the latter then being determined with the standard hydrazine.

Determination of the Strong Acid.—To determine in the equilibrium mixtures the "strong acid" present (that is, the acid in other forms than selenous acid) a 50cc. sample of the equilibrium mixture was introduced into a flask containing 10-25 cc. of standard thiosulfate and an excess (25-55 cc.) of standard hydrocarbonate solution. The rest of the iodine present was then just decolorized by titrating it with more of the standard thiosulfate. The resulting solution was titrated with standard hydrochloric acid, using a mixture of methyl red and methylene blue as indicator. A blank containing only selenous acid in the same amount that was present in the sample was treated with an excess of standard hydrocarbonate and the excess determined with standard hydrochloric acid.

It was necessary to decolorize the iodine in order to see the color changes of the indicator. The reaction between iodine and thiosulfate in hydrocarbonate solution produces not only tetrathionate, but also some sulfuric acid according to the reaction⁸



It was possible to make a correction for the acid formed by the second reaction, since the total amount of iodine present was known from the results of the hydrazine titration, namely, since for each equivalent of iodine that reacts in the second way there would be a decrease of $\frac{7}{8}$ mole in the thiosulfate consumed, and since this reaction produces $\frac{10}{8}$ equivalent of hydrogen ion for each equivalent of iodine, the acid produced is $\frac{10}{7}$ times the difference between the equivalents of iodine present and the mole of thiosulfate used. Making this correction and also that resulting from

⁶ Stolle, *J. prakt. Chem.*, [2] 66, 332 (1902); *Chem. Zent.*, 1903, II, 1340.

⁷ Strecker and Schartow, *Z. anal. Chem.*, 64, 218 (1924).

⁸ Abel, *Z. anorg. Chem.*, 74, 395 (1912); Topf, *Z. anal. Chem.*, 26, 184 (1887).

the blank analyses of the selenous acid alone, the concentration of the strong acid in the equilibrium mixture was calculated. Duplicate analyses always agreed within 1%.

Density Measurements.—In order that the volume concentrations might be converted into weight concentrations, a definite volume of each equilibrium mixture (free from solid) was weighed.

Calculation of the Equilibrium Concentrations

The concentration of strong acid and the total concentration of selenous acid were calculated directly from the analytical data. To obtain the concentration of hydrogen ion due to both the free acid and the dissociated selenous acid it was necessary to employ the first ionization constant of 56–60 selenous acid. This has been determined by Blanc⁹ to be 2.7×10^{-3} . The second ionization constant (5×10^{-8} , according to Blanc) is small enough to be neglected at this point. The concentration of undissociated selenous acid was obtained as follows. If a is the concentration of strong acid, b the total concentration of selenous acid and x that of the dissociated selenous acid, then $a + x$ is the concentration of H^+ in the solution, x that of $HSeO_3^-$, and $b - x$ that of the undissociated selenous acid, H_2SeO_3 . Substituting these quantities in the expression $(H^+)(HSeO_3^-) = 2.7 \times 10^{-3} (H_2SeO_3)$, the value of (H_2SeO_3) is obtained.

The concentration of iodide ion was obtained by first subtracting from the total iodine concentration as determined by analysis the solubility of iodine in water and then multiplying the difference, which is the concentration of tri-iodide ion, I_3^- , by the known value of the iodide-tri-iodide ratio for a solution saturated with respect to iodine and having the same total iodide (iodide plus tri-iodide) concentration as the equilibrium mixture. The value of the ratio for each mixture was interpolated from the results given by Bray and MacKay,¹⁰ which are in part as follows.

Total iodide (I^-) + (I_3^-)	0.1000	0.020	0.010
Ratio (I^-):(I_3^-)	0.99	1.04	1.06

Their value for the solubility of iodine in water (1.33 millimolal) was also used.

The activity of the undissociated selenous acid was taken equal to its concentration. The activity coefficient of the hydriodic acid was found by interpolating the activity coefficient corresponding to the ionic strength of each equilibrium mixture from the table given by Pearce and Fortsch,¹¹ some of whose results are as follows.

Molality of HI	0.050	0.100	0.200
Activity coefficient, γ	0.868	0.846	0.834

⁹ Blanc, *J. chim. phys.*, **18**, 28 (1920).

¹⁰ Bray and MacKay, *THIS JOURNAL*, **32**, 914 (1910).

¹¹ Pearce and Fortsch, *ibid.*, **45**, 2852 (1923).

The ionic strengths of the equilibrium mixtures were taken as the total molality of the cations since all ions present at appreciable concentrations were univalent.

Composition of the Equilibrium Mixtures

The initial compositions of the mixtures, expressed in millimoles per liter, are given in Table I. Solid iodine and solid black selenium were always present initially and when equilibrium was attained.

TABLE I
INITIAL CONCENTRATIONS OF THE MIXTURES

Expt.	1	2	3	4	5
KI	4.15	87.88	0.00	0.00	58.88
HClO ₄	50.15	39.67	.00	9.87	26.50
H ₂ SeO ₃	0.00	10.00	.00	14.00	25.00

In Table II are given the concentrations of the various constituents present when equilibrium was attained. The auxiliary data necessary to calculate the equilibrium constant are also included. All concentrations are expressed in millimoles per liter. The values for the equilibrium constant, K , were calculated by the expression

$$K = (\text{H}_2\text{SeO}_3)(\text{H}^+)^4(\text{I}^-)^4\gamma^3/w^9$$

In this expression (H_2SeO_3) is the concentration of undissociated selenous acid, γ the activity coefficient of hydriodic acid and w the weight of water per liter of solution. This last factor served to change the values of the equilibrium concentrations given in the table from millimoles per liter of solution to moles per kilogram of water.¹²

TABLE II
FINAL CONCENTRATIONS OF THE EQUILIBRIUM MIXTURES AT 25°

Expt.	1	2	3	4	5
(ΣI_3) (deter.)	21.42	43.93	27.23	22.57	34.86
(I_3^-) (calcd.)	20.15	42.60	25.99	21.24	33.53
Ratio, (I^-)/(I_3^-)	1.022	0.996	1.014	1.020	1.006
(I^-) (calcd.)	20.59	42.43	26.35	21.67	33.73
Strong acid (deter.)	74.34	34.02	51.62	50.78	31.94
(H^+) (calcd.)	74.66	34.86	52.26	52.09	34.19
($\Sigma\text{H}_2\text{SeO}_3$) (deter.)	9.33	11.65	13.03	26.62	30.82
(H_2SeO_3) (calcd.)	9.00	10.81	12.37	25.31	28.57
G. solution per liter	1008.26	1019.66	1008.78	1008.90	1016.10
G. solute per liter solution	17.03	30.87	15.29	15.61	26.30
G. water per liter of solution	991.2	988.8	993.5	993.3	989.8
Concentration of cations	78.81	122.7	52.26	52.09	93.07
Activity coeff. of HI	0.853	0.841	0.866	0.865	0.848
$K \times 10^{14}$	1.525	1.433	1.492	1.369	1.482

Mean 1.46

¹² Owing to the fact that oxygen was always present initially and this caused the liberation of some iodine in the acid-iodide mixtures, the final acid concentrations cannot be estimated from the changes in the concentrations of selenous acid. In all cases the true equilibrium concentrations were taken to be those determined by analysis.

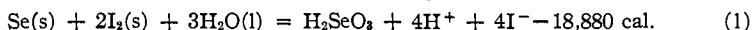
The Equilibrium Constant

The agreement among the values for the equilibrium constant is very satisfactory, especially when it is considered that the large exponents occurring in the mass action expression cause small errors (always less than 1%) in the analytical results to be greatly magnified in the values for the equilibrium constant.

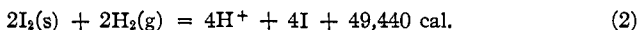
As the best value of the equilibrium constant $K = (\text{H}_2\text{SeO}_3)(\text{H}^+)^4(\text{I}^-)^4$ the mean value 1.46×10^{-14} may be adopted. In this value the concentrations are expressed in moles per 1000 g. of water, and activities of H^+ and I^- are used in place of their concentrations.

Free Energies and Reduction Potential

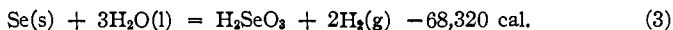
From the equilibrium constant of the reaction the free energy decrease accompanying it was calculated by the well-known expression $-\Delta F^\circ = RT \ln K$. The result is expressed by the equation



Now, according to Lewis and Randall,¹³ at 25°

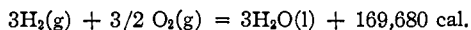


Subtracting we get



This is, however, the reaction that occurs in the cell $\text{Se(s)}, \text{H}_2\text{SeO}_3 \parallel \text{H}^+, \text{H}_2(\text{g})$. Its free energy decrease therefore corresponds to the reduction potential of $\text{Se(s)} + 3\text{H}_2\text{O(l)} = \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^-$. Multiplying the free energy value by 4.185 (to change it to joules) and dividing by $4 \times 96,500$ coulombs, we get for this reduction potential the value -0.740 volt.

We may find also the free energy of 1 *M* H_2SeO_3 (un-ionized) by adding to Equation (3) the following¹³

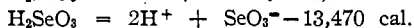
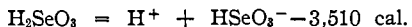


Hence

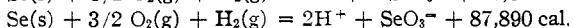
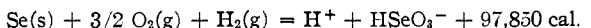


That is, ΔF_{298}° for H_2SeO_3 (un-ionized) is $-101,360$ cal.

From the first and second ionization constants of selenous acid, which are 2.7×10^{-3} and 5×10^{-8} according to Blanc,⁹ we get



Adding separately each of these equations to Equation (4) gives



That is, ΔF_{298}° is $-97,850$ cal. for HSeO_3^- , and $-87,890$ cal. for SeO_3^{2-} .

¹³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 607.

Summary

In this paper are described determinations of the equilibrium of the reaction $\text{Se}(\text{black}) + 2\text{I}_2(\text{s}) + 3\text{H}_2\text{O} = \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{I}^-$ at 25° . The equilibrium constant $K = (\text{H}_2\text{SeO}_3)(\text{H}^+)^4(\text{I}^-)^4$ was found to be 1.46×10^{-14} , expressing the concentrations in moles per 1000 g. of water and using the activities of H^+ and I^- in place of their concentrations.

From this constant and existing thermodynamic data the reduction potential of $\text{Se}(\text{black}) + 3\text{H}_2\text{O}(\text{l}) = \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{E}^-$ was calculated to be -0.740 volt, showing that the reducing power of selenium (at $1 M$ H^+ concentration) is about the same as that of Fe^{++} , Fe^{+++} (-0.747), and intermediate between those of I^- , $\text{I}_2(\text{s})$ (-0.536) and Ag , Ag^+ (-0.800).

The corresponding free energies (ΔF°) at 25° of H_2SeO_3 , HSeO_3^- , and SeO_3^{2-} at $1 M$ were found to be $-101,360$, $-97,850$ and $-87,890$ calories, respectively.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NON-RESIDENT LECTURESHIP
IN CHEMISTRY, BAKER LABORATORY, CORNELL UNIVERSITY]

TRANSITION CELLS OF THE SIXTH CLASS

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RECEIVED DECEMBER 5, 1927

PUBLISHED MARCH 7, 1928

A transition cell may be defined broadly as any reversible galvanic element containing a solid substance which may exist in a number of modifications.

While five different classes of such elements have been treated theoretically as well as experimentally by Ernst Cohen and his co-workers,¹ transition cells of the sixth class have not, as yet, been experimentally realized. Such an element is to contain a depolarizer which possesses a transition point. This paper deals with a transition cell of this type, the depolarizer being silver iodide.

Experimental

It was thought best to use a cell with a standard electrode, rather than two electrodes of silver iodide, one stable and the other metastable. With the former type of cell the temperature-e.m.f. curve may be run over a wide range of temperatures, the transition temperature being indicated by a sudden change in the temperature coefficient of e.m.f. The choice of an electrolyte afforded some difficulty. The use of aqueous solutions was impractical, since the temperatures to be used were as high as 175° . The solvent finally chosen was fused calcium chloride hexahydrate. The boiling point of this substance was within the temperature range over

¹ Ernst Cohen, "Physico-chemical Metamorphosis and Some Problems in Piezochemistry," McGraw-Hill Book Co., New York, 1926, p. 151 ff.