# THE MOLAL REDUCTION POTENTIAL OF SELENIUM AND THE FREE ENERGY OF SELENIOUS ACID FROM EQUILIBRIUM MEASUREMENTS

Thesis

by

Hermann F. Schott

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## Purpose

As there is among the free energy values recorded in literature no record of any values for the compounds of selenium, it was thought advisable to determine the free energy for one of the more important of these compounds.

## Theory

Thermodynamics leads to the following relation between the molal electrode potential of a cell and the equilibrium constant of the reaction taking place when the cell is in operation : $ENF = RT \ln K$ . Making use of the fact that the potential $E$ is equal to the difference of the potentials $E_1$ and $E_2$ , respectively , of the two half cells , $E_1$ may be calculated , given $E_2$ , and the equilibrium constant K, at a definite temperature, T, according to the following equation in which the values of the various constants have been substituted, and common logarithims are used :

$$E_1N = 0.5915 \log K + E_2N$$

The molal free energy decrease is then obtainable from the following relation:

$$-\Delta F_1^\circ = E_1NF$$

And from this the free energy of the oxidized compounds can be calculated , if the free energy in the reduced state is known .

## Choice of Reaction

It was necessary to find a reaction in which selenium and selenious acid were brought into equilibrium by some suitable oxidizing agent, the molal reduction potential of which is already known . A further requirement was that no other compound of selenium would be formed during the reaction .

From some work done last year by Mr. Nordquist, in this laboratory, and from the known properties of the element , it was concluded that its reduction potential in acid solution would not differ greatly from that of silver . The search for a suitable oxidizing agent in this neighborhood, which would not combine with selenium, resulted finally in the choice of iodine . Beckman and Faust, ( Z. anorg. Chem. 84, 103) have shown that iodine and selenium form no compounds or solid solutions whatever .

The reaction of selenious acid with hydriodic acid has been studied for analytical purposes by Muthmann and Schäfer , in 1893( Ber. 26, 1008 ), and again in 1895 by Gooch and Reynolds ( Z. fur anorg. Chem 10,248), and further by Gooch and Pierce, 1896( Z. anorg. Chem. 11, 249 ).

From this work it is evident that the reaction proceeds to completion only in strongly acid solutions, if at all, and apparently does not take place in neutral solutions. The reversibilityof the reaction was readily demonstrated , As may be seen from the equation,

$$Se(s) + 3H_2O(l) + 2\ I_2(s) = H_2SeO_3 + 4H^+ + 4I^-$$

the reaction is very sensitive to change in acidity or in iodine concentration, and therefore the equilibrium conditions can be adjusted, without great difficulty, to give analytically suitable quantities of the various constituents .

## Preliminary Experiments

Last Spring several solutions of varying compositions were prepared, and the equilibrium products were subjected to analysis . The analyses, for various reasons, were not satisfactory . However, sufficient data were available for the approximate evaluation of an equilibrium constant in two of the solutions, having widely different hydrogen ion concentration ( 1 N and .06 N ) . About $10^{-13}$ was found as the value for this constant for both of the solutions. The best analytical conditions as to concentration of all the constituents were those in the .06 N solutions .

## Analytical Methods

In order to facilitate the analysis of such dilute solutions, it was decided to search for a volumetric method . The scheme of analysis finally chosen is based on the hydrazine method for selenium, which was perfected by Strecker and Schartow ( Z. anal. Ch. 64 ,218 )

It seemed best to make up solutions with known iodide, selenious acid, and hydrogen ion concentration, so that the equilibrium value of the last could be indirectly determined from the measured change in the other concentrations , without the necessity of an actual acidimetric titration in the dark colored equilibrium solution . It was found that the iodine could be titrated directly in the neutralized equilibrium mixture with either hydrazine sulphate, or sodium thiosulphate solutions , without any reduction of $H_2SeO_3$ provided that the titration as performed at room temperature and in a reasonable amount of time . An excess of hydrazine sulphate could then be added to the solution , which after acidification would then be heated on the water bath until no mor e selenimm precipitated. The solution would then be filtered, neutralized, and the excess hydrazine determined , from which the amount of selenium reduced could be calculated. The excess hydrazine could be determined by a nmber of different methods. The results here were obtained by titrating the standard iodine solution in the presence of a buffer , according to Stollé ( J. pr. Ch.(2) 66 ,332 (1902) C-B 1903 (2) 1340 ).

The detailed procedure was as follows :

Definite quantities of previously standardized solutions of $HClO_4$, KI, and $H_2SeO_3$, were introduced by means of burettes into a 250 cc. volumetric flask, and the solution diluted to the mark with distilled water. The solution was then poured into a bottle containing and excess of solid phases of selenium and iodine , in an atmosphere of carbon dioxide . The bottle was sealed , and shaken for several days at constant temperature ( 25°C) . Two 50 cc. portions were then pipetted out ,. One portion was then titrated with deci-normal thiosulphate solution in the presence of a buffer . The second portion was treated with 50 cc. of hydrazine sulphate solution (.15N) sufficient buffer was added to cause disappearance of the iodine color, and the solution heated for several hours on the water bath . More buffer was then added , and the solution filtered , and titrated with iodine , until the appearance of the yellow color . More reproducible results could be obtained in this last titration without the use of the starch indicator . This is in accordance with the results of Kolthoff ( J. Amer.Ch. Soc. 46, 2009 (1924) ) . T

Both the hydrogen ion and the iodide ion concentrations were at first determined by noting the change in selenious acid content, and assuming that this all represented an oxidation or reduction , in accordance with the equilibrium reaction. However, the high values for the iodide/tri-iodide ratio, obtained in this way showed that this was not the case, but that some atmospheric oxidation had taken place, necessitating a different basis of calculation . As the solutions were saturated with respect to iodine the values of the iodide/tri-iodide ratio should be nearly constant and equal to the values to be found in the literature for the same concentrations . In this way the iodide concentration could be determined from the experimentally found iodine concentration , and the change in hydrogen ion assumed to be equal to the change in iodide .This assumption is justified by the fact that the loss in iodide from atmospheric oxidation, as well as in accordance with the equilibrium reaction is just equivalent to the loss in hydrogen ion .

$$H_2O + Se + O_2 = H_2SeO_3$$

$$4HI + O_2 = 2I_2 + 2H_2O$$

## Preparation of Materials

### $HClO_4$

Two perchloric acid solutions were prepared by diluting the 60% C.P. acid . They were standardized against a sodium carbonate, prepared by heating very pure sodium bicarbonate ( Kahlbaum's"zur Analyse ") in a platinum crucible at 300 C. for about half an hour, and drying over anhydrous calcium chloride .

### KI

Merck C.P. KI was weighed out after powdering and drying at 100°C. , and cooling over calcium chloride . It was put into a volumetric flask, and made up to 250cc. with boiled water . Solution was calculated to be .3749 N in KI on the basis of 99.88% purity.

### $I_2$

Approximately deci-normal iodine solutions were made up and standardized against arsenious oxide. These were compared with the thiosulphate solution which was later used as a standard for other iodine solutions.

### $N_2H_6SO_4$

Approximately sixth normal was made up from some of the salt prepared last summer by Mrs Stone in this laboratory. The ratio of iodine to hydrazine was determined and the strength of the hydrazine calculated from the known strength of the iodine. As a buffer $Na_2HPO_4$ was chosen. This is preferable to $NaHCO_3$ as it does not become basic upon boiling, and does not produce a gas, which might increase the loss of iodine from the solution.

### $H_2SeO_3$

Se "Perlen", were dissolved in concentrated nitric acid, the solution evaporated to dryness, the residue redissolved in water, filtered, reevaporated, and sublimed onto a round bottomed flask filled with cold water. Approximately 4.5 grams of the white needles of $SeO_2$ thus obtained, wre then dissolved in one half liter of water. Ten cc. portions were then analysed with the use of excess hydrazine as previously described.

### Se

The solid selenium was prepared by dissolving some $SeO_2$, prepared as described above, in water, adding HCl, and reducing with $SO_2$. The black amorphous precipitate thus obtained was then filtered in a Büchner funnel, and washed with water and alcohol.

### $I_2$

Commercially obtained, re-sublimed C.P. iodine was used. From the approximate equilibrium constant found last year the following sets of solutions were calculated:

| | Final Concentrations | | | Initial Concentrations | | |
|---|---|---|---|---|---|---|
| | $SeO_2$ | $H^+$ | $I^- + I_3^-$ | $SeO_2$ | $H^+$ | $I^- + I_3^-$ |
| 1a | .010 | .064 | .055 | 0.0 | .023 | .015 |
| 1b | .010 | .064 | .055 | .012 | .072 | .063 |
| 2a | .013 | .064 | .052 | 0.0 | .011 | .0 |
| 2b | .013 | .064 | .052 | .015 | .072 | .060 |
| 3a | .016 | .064 | .049 | 00.004 | .012 | .0 |
| 3b | .016 | .064 | .049 | .018 | .072 | .057 |

It will be noted that each pair of solutions represents the same equilibrium conditions approached from opposite sides of the reaction . They were a rranged in this way in order to prove q uantitatively the establishment of equilibrium . The actual initial compositions and those of the eq uilibrium are shown in the following tables: The concentrations are in mmols, per L.

| | 1a | 1b | 2a | 2b | 3a | 3b |
|---|---|---|---|---|---|---|
| .3576N $HClO_4$ cc. | ----- | 50.00 | ----- | 50.00 | ----- | 50.00 |
| .1486N $HClO_4$ cc. | 39.19 | 24.--- | 18.96 | ----- | 20.19 | ----- |
| $HClO_4$ mmls/l. | 23.29 | 71.53 | 11.27 | 71.53 | 12.00 | 71.53 |
| .3749M KI cc. | 10.09 | 43.09 | 0 | 40.32 | 0 | 38.23 |
| KI mmls/l. | 15.13 | 64.62 | 0 | 60.47 | 0 | 57.33 |
| .0806 M $H_2SeO_3$ | 0 | 37.97 | 0 | 46.22 | 12.34 | 55.55 |
| $H_2SeO_3$ mmls/l. | 0 | 12.237 | 0 | 14.90 | 3.98 | 17.94 |

Analyses of equilibrium samples:

| | 1a | 1b | 2a | 2b | 3a | 3b |
|---|---|---|---|---|---|---|
| Volume in cc. | 45.96 | 45.95 | 45.95 | 45.95 | 45.94 | 45.94 |
| Weight in grams | 46.51 | 46.77 | 46.48 | 46.72 | 46.50 | 46.75 |
| .0995N $Na_2S_2O_3$ cc. | 21.73 | 21.68 | 20.60 | 21.13 | 20.81 | 18.64 |
| $\Sigma I_2$ mmls./l. | 23.52 | 23.47 | 22.30 | 22.87 | 22.54 | 20.19 |
| $\therefore I_3^-$ mmls./l. | 22.19 | 22.14 | 20.97 | 21.54 | 21.21 | 19.86 |
| .1523N $NaH_6SO_4$ cc. | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |
| .0992N $I_2$ | 33.08 | | | | | |
| .1034N $I_2$ | | 32.17 | 29.60 | 28.93 | 22.13 | 24.49 |
| $\Sigma$oxid.ml.eq. | 4.332 | 4.287 | 4.561 | 4.623 | 5.326 | 5.082 |
| $\Sigma I_2$ ml.eq. | 2.162 | 2.157 | 2.050 | 2.102 | 2.071 | 1.855 |
| $\therefore H_2SeO_3$ mmls/l. | 11.70 | 11.59 | 13.68 | 13.72 | 17.72 | 17.59 |

Assuming no atmospheric oxidation:

| | 1a | 1b | 2a | 2b | 3a | 3b |
|---|---|---|---|---|---|---|
| $\Delta H_2SeO_3$ ml.eq./l. | 46.80 | -2.60 | 54.32 | -2.25 | 54.91 | -1.57 |
| $\Sigma I^-$ " " " | 61.93 | 62.02 | 54.32 | 58.22 | 54.91 | 55.76 |
| $I^-$ " " " | 39.74 | 39.88 | 33.35 | 36.68 | 33.70 | 35.90 |
| $H^+$ " " " | 70.09 | 68.93 | 65.59 | 59.28 | 66.91 | 69.96 |
| $(I^-)/(I_3^-)$ | 1.79 | 1.80 | 1.59 | 1.70 | 1.59 | 1.81 |

This table also shows the iodide/ tri-iodide ratios, obtained on the assumption that none of the oxidation was due to air .

## Calculations

As one of the samples from each solution w as weighed before analyzing, the concentrations could be converted to molality - that is, from mols per liter to mols per 1000 grams of solvent . The activities of HI were found by using the activity coefficients found by Pearce and Fortsch (J. Amer. Chem. Soc. [illegible] 45 2852 ) They give two sets of values, one based on the Lewis and Randall value of the mean activation of HCl st .005 mol , and the other on the Noyes and McInnes cvalue . For the sak e og consistency, the Lewis and Randall values were used , a as most of the other thermodynamic constants used were those of Lewis and Randall . The activation in each solution was obtained by graphic interpolation of the ionic strength from the table above referred to . This point is important , as the activation must be raiseed to the eighth power.

The dissociation of selenious acid is calculated from the hyrgoen ion concentration and the constant g given by Blanc . (J. de Ch. Phys. 18 40 ) According to the work of Blanc, $K_1 = 2.7 \times 10^{-15}$ , $K_2 = 5.1 \times 10^{-15}$ .

The tri-iodide concentration is found by subtracting from the analytically determined iodine, the solubility of iodine . Lewis and Randall give the following table

| | | | |
|---|---|---|---|
| Total iodine salt concentration : | .10m | .02m | .10m |
| K (KI)/($KI_3$) : | .99 | 1.04 | 1.06 |

Bray and McKay (J. Amer. Chem. Soc. 32 1207 (1910) ) have shown that the value of this constant does not depend upon the total iodine concentration, but only upon that of the iodide . ~~The~~

The iodide concentrations are then first approximately determined from the tri-iodide by assuming the value 1.02 for K in all solutions . From these values the total iodide concentration ( that is, $\Sigma I = I^- + I_3^-$) , is readily determined for each solution , by interpolating these into the above table, K may be more exactly determined , and the iodine recalculated from this value .

The following table gives the results of these calculations

The concentrations in mmols per liter .

| | 1a | 1b | 2a | 2b | 3a | 3b |
|---|---|---|---|---|---|---|
| $I_3^-$ | 22.19 | 22.84 | 20.97 | 21.54 | 21.21 | 19.86 |
| $\Sigma I^-$ (approx) | 44.8 | 44.7 | 42.4 | 43.6 | 42.9 | 40.2 |
| $K = (I^-)/(I_3^-)$ | 1.019 | 1.019 | 1.020 | 1.020 | 1.020 | 1.022 |
| KI (init) | 15.13 | 64.62 | 0 | 60.47 | 0. | 57.33 |
| $\Delta \Sigma I$ | +29.67 | -19.92 | +42.36 | -16.96 | +42.84 | -17.07 |
| $HClO_4$ (init) | 23.29 | 71.53 | 11.27 | 71.53 | 12.00 | 71.53 |
| $H^+$ ( uncor ) | 52.96 | 51.61 | 53.63 | 54.57 | 54.84 | 54.46 |
| | | | | | | |
| Wt. solutes/l. | 17.2 | 23.8 | 13.96 | 22.6 | 14.7 | 21.9 |
| Wt. solution | 1012. | 1018. | 1012. | 1018. | 1012. | 1017. |
| g.aq./liter | 994.8 | 994.0 | 997.5 | 995.0 | 997.5 | 994.8 |
| | | | | | | |
| Ionic strth. | 68.6 | 116.8 | 54.28 | 115.7 | 55.66 | 112.6 |
| Activation | .859 | .842 | .866 | .842 | .867 | .843 |
| | | | | | | |
| $HSeO_3^-$ | .66 | .68 | .75 | .76 | .95 | .98 |
| $H_2SeO_3$ (undis) | 11.04 | 10.91 | 12.95 | 12.96 | 16.77 | 16.61 |
| $H^+$ | 53.62 | 52.29 | 54.38 | 55.33 | 55.79 | 55.44 |
| | | | | | | |
| log (H) + 2 | .7293 | .7184 | .7354 | .7430 | .7466 | .7438 |
| log (I) +2 | .3543 | .3533 | .3303 | .3418 | .3351 | .3075 |
| 2 log $\alpha$ +1 | .8680 | .8506 | .8750 | .8506 | .8760 | .8516 |
| log (H)(I) $\alpha^2$ +4. | 9516 | .9223 | .9406 | .9354 | .9577 | .9029 |
| log($H_2SeO_3$) +2 | .0430 | .0378 | .1116 | .1126 | .2245 | .2204 |
| 9 colog [illegible] | .0203 | .0235 | .0096 | .0196 | .0098 | .0203 |
| 3 colog a | .0020 | .0030 | .0015 | .0030 | .0011 | .0030 |
| log K + 15 | .8718 | .7445 | .8853 | .8768 | 1.0669 | .8553 |
| 4 log (H)(I)$\alpha^2$+13 | .8064 | .6802 | .7624 | .7416 | .8308 | .6116 |

mean log K = -14.1166 K = 76 x $10^{-15}$ Aver. K = 7.83 x $10^{-14}$

$E_1 - E_2$ = -.2087 volts

$E_1^-$ = .7444 volts

## Subsequent Work

In view of the high degree of dependence of these results on thr iodide concentration, it was deemed advisable to determine the latter directly . For this-p purpose the method of Bray and McKay (J. Amer. Ch. Soc 32 1193 (1910) ) seems to be well adapted.

The following scheme of analysis was tried : The sample is made neutral with a buffer, titrated to disappearance of the yellow color with hydrazine sulphate. An excess of hydrazine sulphate is added , the solution slightly acidified, heated, and filtered as before. A small excess of potassium permanganate is added, the solution allowed to stand for a minute or two, made neutral with a buffer, and the excess iodine titrated with more hydrazine sulphate solution . The solution, after evaporating to a suitable volume, is then acidified, titrated with permanganate, and the iodine formed removed with carbon tetrachloride, and then determined with thiosulphate according to the scheme of Bray and McMcKay.

Some solutions were made up, and analyzed by this method . As yet, however, sufficient data for recalculation has not been collected. The results do show, howeverm that, due to the evaporation of iodine, or some other cause, as much as one or two percent difference may occur in the iodine determination of two supposedly identical samples.

This would account for the rather considerable variation of K in the previous results, since K is so largely dependent upon the iodine concentration, as far as calculations are concerned.

## Conclusions

This work shows that the method of equilibrium measurements may be applied to such problems, and that fairly consistent results may be obtained, even with an inferior analytical method. This implies that the use of a more accurate procedure should yield very exact va values for the electrode potential .

Much aid was derived from the advise and suggestiions of Dr. Earnest H. Swift, under whom the work was started, and Dr. Don M, Yost , unde whose direction the majpr part of the work was carried on.

## Summary

The equilibrium constant of the reaction was de-

$3H_2O\ (l) + 2I_2(s) + Se(s) \rightleftharpoons H_2SeO_3\ 4HI$

termined by direct analysis. A mean value of log K was -14.1166, from which the electrode reduction potential for selenium of -.7444 volts, based on the standard hydrogen cell. The free energy of $H_2SeO_3$ was found to be 100,975 calories at 25 C.