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THE HEAT, FREE ENERGY, AND ENTROPY
OF THE FERRATE (VI) AND SELENIDE IONS

BERKELEY, CALIFORNIA

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THE HEAT, FREE ENERGY, AND ENTROPY OF THE
FERRATE(VI) AND SELENIDE IONS

Robert H. Wood

(Thesis)

April 9, 1957

Printed for the U. S. Atomic Energy Commission

THE HEAT, FREE ENERGY, AND ENTROPY OF THE
FERRATE(VI) AND SELENIDE IONS

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THE HEAT, FREE ENERGY, AND ENTROPY OF THE FERRATE(VI) AND SELENIDE IONS

Robert H. Wood

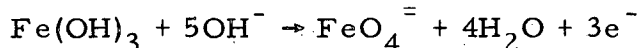
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

April 9, 1957

PART I: THE FERRATE ION

ABSTRACT

The heat of the reaction of aqueous K_2FeO_4 with $HClO_4$ (0.5 mole per kg of water) to give O_2 and Fe^{+3} has been measured at $25^\circ C$. From this datum the heat of formation of $FeO_4^{=}$ (aq) ($\Delta H_f^0 = -116 \pm 1$ kcal/mole) has been calculated. The entropy of $FeO_4^{=}$ (aq) has been estimated as 9 ± 4 eu. From these values the free energy of formation of $FeO_4^{=}$ (aq) has been calculated; it is $\Delta F_f^0 = -78 \pm 2$ kcal/mole. The standard potential of the half reaction



has been estimated as $E^0 = -0.71 \pm 0.03$ volts.

It has been verified that the ferrate ion at pH 10 is a dinegative species which decomposes only slowly.

The rate of decomposition of K_2FeO_4 in concentrated NaOH has been measured at $21^\circ C$. In 2.57 moles NaOH per kg of water the rate is given by

$$-\frac{dC_{FeO_4^{=}}}{dt} = 2.0 \times 10^{-3} C_{FeO_4^{=}}$$

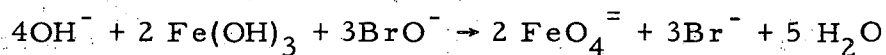
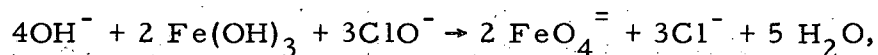
where t is the time in minutes. In 5.31 moles NaOH per kg. of water the rate of decomposition is 10^{-6} mole/liter min. if the concentration of $FeO_4^{=}$ is between 10^{-3} and 10^{-5} mole/liter. The decomposition in 0.9 mole NaOH per kg of water is quite rapid.

A method of analysis for aqueous K_2FeO_4 has been developed in which $Fe(OH)_3$ is removed by filtration and the total iron present is measured. This analysis has been shown to be accurate to better

than $\pm 1\%$ by comparison with the volume of O_2 liberated on acidifying an aqueous K_2FeO_4 solution. Other methods of analysis involving the oxidation in alkaline solution of I^- , $As(III)$, and $Cr(III)$ have been investigated.

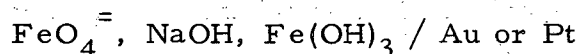
The absorption spectrum of K_2FeO_4 has been measured. The extinction coefficients in liters/mole cm are: at 3800 A, 341 ± 9 ; at 3900 A, 318 ± 9 ; at 5050 A, 1070 ± 30 ; at 5500 A, 967 ± 30 ; at 6750 A, 211 ± 6 .

The reactions



have been studied. In the forward direction steady-state concentrations of $FeO_4^{=2}$ are produced. In the reverse direction, no ClO^- or BrO^- was detected. The reactions do not reach equilibrium.

Measurements of the half cell



have shown that the electrode is irreversible in 10^{-4} , 2.5, 5, and 10 moles NaOH per kg of water.

INTRODUCTION

Although good methods for preparing and analyzing K_2FeO_4 have been described recently,^{1, 2, 3} no measurements of the thermodynamic constants of the aqueous ferrate ion have appeared in the literature. The purpose of this investigation was to measure the heat and free energy of the ferrate ion.

EXPERIMENTAL PROCEDURE

Preparation of K_2FeO_4

The samples of K_2FeO_4 were prepared by the method of Thompson, Ockerman, and Schreyer.¹ Their procedure consists of oxidizing some $Fe(OH)_3$ with $NaClO$ in strong $NaOH$; adding KOH to precipitate K_2FeO_4 ; dissolving the K_2FeO_4 in dilute $NaOH$; reprecipitating the K_2FeO_4 with KOH ; washing with benzene; washing with 95% ethyl alcohol; and finally drying with ether. The K_2FeO_4 was stored in a vacuum desiccator. One precaution should be noted in connection with this preparation. Because aqueous K_2FeO_4 reacts quite readily with ethanol, it is necessary to dry the K_2FeO_4 thoroughly before washing with ethanol. My experience has shown that the following procedure gives good results. After the last precipitation and filtration, air is pulled through the filter for about 5 minutes. The precipitate is washed with benzene, and again air is pulled through the filter for 5 minutes. The first portions of 95% ethyl alcohol are pulled through the filter as rapidly as possible.

Table I gives the amount of $Fe(NO_3)_3 \cdot 9H_2O$ taken for the preparation and the amount of K_2FeO_4 prepared.

The analyses follow the methods of Schreyer, Thompson, and Ockerman.³ In the As(III) method of analysis the K_2FeO_4 is added to 10 ml of an alkaline As(III) solution. The solution is titrated with Ce(IV) after addition of 100 ml H_2O and 100 ml 6 N H_2SO_4 . Some osmate is added to catalyze the oxidation of As(III) by the ceric ion, and orthophenanthroline ferrous sulfate is added to serve as the indicator. In the total-iron method of analysis the K_2FeO_4 is dissolved in 8 m $NaOH$ and the solution is filtered to remove

$\text{Fe}(\text{OH})_3$. * The filtrate is acidified to decompose the $\text{FeO}_4^{=}$, and the resulting Fe^{+++} is reduced with $\text{Sn}(\text{II})$ and titrated with a standard ceric sulfate solution. The inaccuracy in the analysis of sample No. 1 arises from an irreproducible blank. Sample No. 2 was analyzed by using a Jones reductor to reduce the Fe^{+++} . This method was found to give satisfactory results. The Fe_2O_3 content of the samples was found by analyzing the $\text{Fe}(\text{OH})_3$ left over from the total iron analysis.

Table I

Preparation and analysis of K_2FeO_4 samples.						
The yield is based on the amount of iron recovered as product. The analysis is given in percentage of K_2FeO_4 and percentage of Fe_2O_3 in the final product.						
Sample No.	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ taken	K_2FeO_4 found	Yield (percent of theoretical)	As(III) wt. % K_2FeO_4	Total iron wt. % K_2FeO_4	Fe(III) as wt. % Fe_2O_3
1	50 g 0.124 mole	9.5 g 0.048 mole	39	94.3±0.2	94.9±0.4	1.0
2	50 g 0.124 mole	4.4 g 0.022 mole	18		97.1±0.1	2.5

* Throughout this paper, the symbol M stands for "molar" (i.e., moles per liter of water at the temperature of measurement), the symbol m denotes "moles per kilogram of water."

Analysis of K_2FeO_4 Solutions

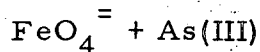
During the course of this project it was necessary to develop an analytical method for solutions of K_2FeO_4 dissolved in 10^{-4} M NaOH. The simplest and probably the most reliable method used was an analysis of the solutions for total iron after filtering out the $Fe(OH)_3$. The Fe^{+3} formed on acidifying the filtrate was reduced with a Jones reductor and titrated with standard Ce(IV) solution. In order to confirm the total iron analysis, several methods of analysis based on the oxidizing power of the ferrate were tried. A description of these methods and the results obtained are given below.

The $FeO_4^{=}$ solutions used in the trial analysis were prepared by dissolving K_2FeO_4 in 10^{-4} M NaOH. The solution was filtered and several samples were set aside for analysis by the total iron method.

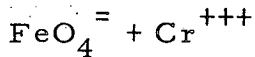
$FeO_4^{=} + I^-$

The first method tried was the oxidation of I^- . This analysis runs into difficulty because of the partial oxidation of the I^- by the Fe^{+3} ion formed. In one experiment 15 ml of 0.0186 M $FeO_4^{=}$ solution was added to solutions of KI in NaOH. The concentrations of KI and NaOH were varied from 1 to 7 M and from 0.4 to 10 M respectively. The volume of solution was varied from 11 to 31 ml. The solutions were analyzed by adding 50 ml of H_2O and then 10 ml of conc. H_3PO_4 . Ten seconds after the H_3PO_4 was added, 140 ml of a solution 0.07 M in $Fe(NH_4)_2(SO_4)_2$ and 0.6 M in H_2SO_4 was added. The solution was then titrated with standard $S_2O_3^{=}$. The H_3PO_4 and Fe^{++} were added to diminish the rate of oxidation of the I^- by the Fe^{+++} . The H_3PO_4 must be added before the Fe^{++} , or the IO_3^- present in the alkaline solution oxidizes the Fe^{++} to Fe^{+++} . A blank run in which equivalent amounts of $Fe(OH)_3$ and I_3^- were added to the KI and NaOH solution showed that the concentration of I_3^- was unchanged by this procedure. In all the trials of this method of analysis the oxidizing power of the ferrate was from 4% to 6% lower than expected on the basis of the total iron analysis. This result may be due to the comparatively slow oxidation of the I^- by $FeO_4^{=}$ in these solutions. (It takes from 2 to 5 minutes for the $FeO_4^{=}$ color to disappear). In experiments at a lower

OH^- concentration (pH 10) the ferrate was immediately reduced by the I^- . However, the method used above for the analysis of the excess I_2 was not reproducible under these conditions.



In the next series of experiments 5 ml of 0.015 M $\text{FeO}_4^{=}$ solution was added to excess As(III) in 10 to 20 ml of 1 to 11 M NaOH. The remaining As(III) was titrated with standard ceric ion after addition of 100 ml of H_2O and 100 ml of 6 N H_2SO_4 . Osmate was used to catalyze the reaction of the ceric ion with As(III). This is one of the methods that Thompson, Ockerman, and Schreyer³ use for the analysis of K_2FeO_4 solid. In all the analyses, successive portions of the same $\text{FeO}_4^{=}$ solution showed lower analyses owing to the slow decomposition of the $\text{FeO}_4^{=}$ in the 10 M NaOH solutions. For this reason the results were hard to interpret. No difference in result was noticed when the concentration of NaOH was changed from 1 to 11 M. There was also no noticeable difference between analyses in which the rate of stirring was varied. The first portions of filtered $\text{FeO}_4^{=}$ solution gave results between 101% and 99% of the oxidizing power calculated on the basis of the total iron analysis. When samples of $\text{FeO}_4^{=}$ that had not been filtered were analyzed the results were 0.9% to 1.6% high. This result could be due to the oxidation of As(III) by dissolved O_2 , produced by previous decomposition of the $\text{FeO}_4^{=}$. It could also be due to slight decomposition of the $\text{FeO}_4^{=}$ when it comes in contact with the sintered-glass surface of the filter.



In this experiment the analysis recommended by Schreyer, Thompson, and Ockerman⁴ for solutions of K_2FeO_4 was used. In this method the $\text{FeO}_4^{=}$ is added to alkaline Cr(III). The resulting solution is acidified and titrated with standard Fe^{++} solution. The analyses of three aliquots gave 97.7% of the oxidizing power expected from the total iron analysis. The reason for the discrepancy is unknown.

Volume of O₂

In this experiment the volume of O₂ liberated by 100 ml of a solution on addition of 4 ml of concentrated H₂SO₄ and 1/2 g of MnO₂ was used as a measure of the oxidizing power of the solution. The MnO₂ was added because a small amount of H₂O₂ was formed under the conditions of the experiment. The MnO₂ decomposed the H₂O₂ and formed Mn⁺⁺, which was measured, and a suitable correction was applied to the gas volume. The K₂FeO₄ and H₂SO₄ solutions were placed in a vacuum line and the pressure was lowered to remove dissolved gas. The solutions were then mixed and the resulting O₂ was pumped off by a Toepler pump through three liquid nitrogen traps and into a bulb where the pressure was measured with a mercury manometer. Table II gives the results of these experiments.

Table II

Volume of O ₂ liberated by K ₂ FeO ₄ (aq)				
Run No.	Total iron present (moles x 10 ³)	Equiv of O ₂ (x 10 ³)	Correction for Mn ⁺⁺	Equiv O ₂ Fe
1	1.729	5.188	-0.008	3.00
2	1.831	5.488	-0.03	2.98

I am indebted to Dr. William J. Jolly for his suggestion of this method of analysis and for the use of his vacuum line in carrying out the analyses.

Because of the possible decomposition of these solutions while in contact with the sintered-glass filter and because of the slow decomposition of these solutions while standing, the total-iron method can only be relied upon to give the concentration of FeO₄⁼ just after filtration. This experiment shows that under these conditions the total-iron method of analysis is accurate to better than 1%.

Spectra of K_2FeO_4 Solutions

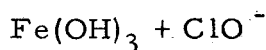
The absorption spectrum of K_2FeO_4 in 4 m NaOH (free from $Fe(OH)_3$) was taken with a Cary Model 11 recording spectrophotometer. The results confirm those of Kaufman and Schreyer,⁵ who find a broad maximum at 5000 Å and two minima, one at 3900 Å and one at 6750 Å. As a refinement on their measurements of the extinction coefficients, the optical density of a solution of K_2FeO_4 in 10^{-4} M NaOH was measured as a function of time and extrapolated to the time of filtering the solution. Measurements were made with a Beckman Model DU spectrophotometer. The extrapolated optical density was 0.259 and the rate of decomposition was 0.1% per minute. The cell length was $1.00 \pm .01$ mm and the wavelength was 5050 Å. Analyses of aliquots of the solution for total iron gave 2.435 mmoles per liter and 2.429 mmoles per liter. This corresponds to a molar extinction coefficient of 1070 ± 30 .

The relative extinction coefficients at 5050, 5500, 6750, 3900, and 3800 Å were measured on solutions of K_2FeO_4 in 4 m NaOH with a Beckman model DU spectrophotometer. From these and the absolute extinction coefficient at 5050 Å we have calculated the absolute extinction coefficients at several wavelengths. The molar extinction coefficients and the slit widths used are given in Table III. For purposes of comparison the values from Kaufman and Schreyer are also given.⁵ Their values were expected to be slightly higher because of the presence of about 15% $Fe(OH)_3$ in their solutions.

Table III

K_2FeO_4 spectra			
Wavelength Å	Slit width (mm)	Extinction coefficient (liters/mole cm)	
		Measured	Kaufman and Schreyer
3800	0.10	341 ± 9	
3900	0.10	318 ± 9	360
5050	0.02	1070 ± 30	1130
5500	0.02	967 ± 30	
6750	0.04	211 ± 6	230

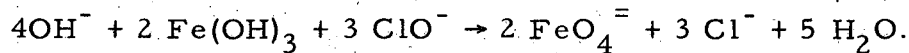
Equilibrium Measurements



The known potential of the ClO^- , Cl^- system and the estimated values of the $\text{FeO}_4^{=}$, Fe(OH)_3 couple indicated that a measurable equilibrium could be established between the two systems. In order to study the equilibrium between Fe(OH)_3 and ClO^- , the concentration of $\text{FeO}_4^{=}$ in various mixtures of Fe(OH)_3 , ClO^- , Cl^- and NaOH was measured with a Beckman DU spectrophotometer after centrifugation to settle the Fe(OH)_3 . The stock 12.5 m NaOH solution was standardized by measuring its specific gravity (sp. gr. = 1.39 at 25°C). The ClO^- solutions were prepared by dissolving Cl_2 in NaOH . These solutions were standardized by adding H_3PO_4 to make the solution acid, and 1 g KI . The solutions were then titrated with standard $\text{S}_2\text{O}_3^{=}$ solutions. The concentration of ClO^- at the end of the reaction was measured by adding 15 cc of 6 N H_2SO_4 , 10 cc of conc. H_3PO_4 , and 3 g of KI to 10 ml of the solution + 100 ml of water. The solution was then titrated with standard thiosulfate. The H_3PO_4 was added to make the oxidation of the KI by the Fe^{+++} negligible. NaClO_3 was added at the end point of one of these titrations to see if ClO_3^- interferes with the titration. The rate of oxidation of the I^- was negligible.

The concentration of $\text{FeO}_4^{=}$ increased to a maximum and then decreased. The decrease is probably due to the decomposition of the ClO^- . Table IV gives the concentrations of NaOH , ClO^- , and Cl^- at the beginning of the experiment. The maximum concentration of $\text{FeO}_4^{=}$ and the number of days elapsed before this concentration was reached are also given. When possible the concentration of Fe(OH)_3 has been estimated and included in Table IV.

From the tabulated data we can now proceed to show that the reaction of Fe(OH)_3 with ClO^- never comes close to an equilibrium value. The above concentrations give an equilibrium constant $K = 10^{-11}$ for the reaction



From the heat data we know that the equilibrium constant should be $K = 10^{18 \pm 3}$.

Table IV

Fe(OH) ₃ + ClO ⁻ Reaction						
	NaOH conc. (<u>m</u>)	ClO ⁻ conc. at start (<u>M</u>)	ClO ⁻ conc. at finish (<u>M</u>)	Cl ⁻ conc. at start (<u>M</u>)	Fe(OH) ₃ conc. (<u>M</u>)	FeO ₄ ⁼ conc. (<u>M</u> × 10 ⁴) Days
1	0.8	0.03		0.03		0
2	3.1	0.08		0.08		4.1 8
3	6	0.16		0.16		5.5 4
4	6.6	0.03	0.02	1.1	0.005	6.7 6
5	6.6	0.03	0.01	0.03	0.025	12 3
6	6.6	0.03		0.03	0.005	8.5 6
7	6.6	0.006		0.006	0.005	1 3

FeO₄⁼ + Cl⁻

In this experiment a solution which was 5.2 m in NaOH, 10⁻³ M in K₂FeO₄, and 0.1 M in Cl⁻ was analyzed for ClO⁻ after standing for 4 days. The results showed that the concentration of ClO⁻ was less than 2 × 10⁻⁷ M. The method of analysis for ClO⁻ was similar to that by Drogst and Mellon⁶ except that H₃PO₄ was added to decrease the oxidation of the o-tolidine by Fe⁺⁺⁺. The procedure is as follows: 10 ml of 6 N H₂SO₄ and then 1 ml of concentrated H₃PO₄ are added to 10 ml of the solution to be analyzed. The solution is cooled to room temperature and 1 ml of o-tolidine solution (0.5 g of o-tolidine in 150 ml of 0.2 N HCl) is added. The color produced in 10 minutes is compared to that of standard solutions. In a blank experiment the 10⁻³ M Fe⁺⁺⁺ (present after the addition of the acid to the K₂FeO₄) produced a color at a rate corresponding to the production of 10⁻⁸ mole per liter of ClO⁻ per minute.

The analysis of the FeO₄⁼, Cl⁻ solution produced a color corresponding to 10⁻⁷ M ClO⁻ after 10 minutes. The side reaction with Fe⁺⁺⁺ and o-tolidine probably contributed most of this color. The only conclusion is that the ClO⁻ concentration is not appreciably greater than 1 × 10⁻⁷ M, and may be much less.

Using -0.71 volt for the potential of the $\text{FeO}_4^{=}$, Fe(OH)_3 couple, one calculates an equilibrium concentration of ClO^- equal to 10^{-11} M.
 $\text{Fe(OH)}_3 + \text{BrO}^-$

Since BrO^- generally acts as a faster oxidizing agent than ClO^- , it was thought that the BrO^- , Br^- couple might establish a measurable equilibrium with the $\text{FeO}_4^{=}$, Fe(OH)_3 system where the ClO^- , Cl^- couple had failed.

In these experiments Fe(OH)_3 was added to a solution containing known concentrations of NaOH , BrO^- , and Br^- . The concentration of $\text{FeO}_4^{=}$ was measured from time to time in the following manner. The Fe(OH)_3 was removed from the sample by centrifugation. The optical density of the solution at 5500 A was measured with a Beckman model DU spectrophotometer. A correction, which never amounted to more than 10%, was applied for the absorption of the BrO^- at this wavelength.

Table V gives data on the spectra of BrO^- in concentrated NaOH which were used to calculate the correction for the adsorption of the BrO^- . The extinction coefficient as measured by a Beckman DU spectrophotometer is given by ϵ , and the wavelength by λ . For the data at 5050 A the slit width was 0.02 mm. For the data at 3800 A the slit width was 0.10 mm.

Table V

Spectra of BrO^-					
λ o A	Optical density	Cell length (cm)	Conc. of NaOH (<u>M</u>)	Conc. of BrO^- (<u>m</u>)	$\left(\frac{\epsilon}{\text{liters}} \right)$ (mole cm)
5500	0.12	1.000	6	1.45	0.08
	0.089	10.00	5.3	0.29	0.032
	0.03	10.00	5.3	0.072	0.04
3800	1.435	2.00	4.4	0.0118	60.8
	0.758	10.00	4.4	0.00118	65.2
	1.435	10.00	4.4	0.00239	60.0

Both the solutions used to determine the spectra of BrO^- and the solutions used in the ferrate experiments were analyzed for BrO^- by a method similar to the one used by Scholder and Kraus.⁷ The only difference is that I have used H_3PO_4 to adjust the acidity of the system instead of NaHCO_3 . The method is as follows: excess As(III) in NaHCO_3 is added to an appropriate volume of the solution to be analyzed. After addition of one drop of a 1% solution of phenolphthalein, concentrated H_3PO_4 is added dropwise until the phenolphthalein is colorless. The solution is then titrated with a standard I_3^- solution with starch as the indicator. A blank run in which As(III) solution was added to 5 m NaOH was unaffected by the presence of a large excess of BrO_3^- . Duplicate titrations agreed to within 1%.

The BrO^- solution in 30% NaOH was prepared by the method of Scholder and Kraus. The calculated concentration of BrO^- in this solution is 1.6 moles/liter. This calculation was made with the assumption that (a) no Br_2 was lost by evaporation while it was being added to the NaOH, and (b) no BrO_3^- was formed. Titration of the solution gave 1.45 moles/liter for the concentration of BrO^- . This represents a loss of almost 10% of the BrO^- , which is reasonable in view of the fact that Scholder and Kraus found from 3% to 6% of the Br_2 added was converted to BrO_3^- .

The 30% NaOH used in making up the solutions was prepared by weighing out Reagent Grade NaOH and adding it to a known volume of water.

In all the experiments the concentration of the $\text{FeO}_4^{=}$ increased fairly rapidly to a maximum and then slowly decreased. The slow decrease is probably due to the slow decomposition of the BrO^- . Table VI gives the results of the experiments. The columns headed Br^- (start) and BrO^- (start) give the concentrations of Br^- and BrO^- at the start of the experiment. The concentration of $\text{FeO}_4^{=}$ is the maximum value. The column BrO^- (finish) represents the concentration of BrO^- at the time the $\text{FeO}_4^{=}$ reached its maximum. The column marked 90% time is the time it took for the $\text{FeO}_4^{=}$ to reach 90% of its maximum value.

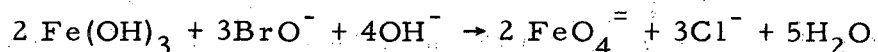
Table VI

BrO ⁻ + Fe(OH) ₃ reaction							
Expt. No.	NaOH conc. (M)	BrO ⁻ conc. (start) (M)	BrO ⁻ conc. (finish) (M)	Br ⁻ conc. (start) (M)	Fe(OH) ₃ conc. (M)	FeO ₄ ⁼ conc. (M x 10 ⁴)	90% time (hr)
1a	5.45	0.435	0.306	0.48		16	17
1b	5.45	0.203	0.113	0.63		9.9	192
2	5.00	0.063	0.054	0.08		3.1	75
3a	4.06	0.136	0.097	0.168	0.001	2.13	57
3b	4.06		0.075	0.73	0.001	1.5	see text
6	3.00	0.137	0.128	0.17	0.001	0.45	< 15

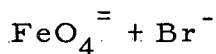
In Experiments 1b and 3b K₂FeO₄ and NaBr respectively were added to the solutions after the concentration of FeO₄⁼ had reached its maximum value. In Experiment 1b the concentration of FeO₄⁼ just after addition of the K₂FeO₄ was 7.7 x 10⁻³ M. From this point the concentration of FeO₄⁼ decreased fairly rapidly to a concentration of 9.9 x 10⁻⁴ M and then gradually decreased at the same rate as it had before the K₂FeO₄ was added.

From each of these experiments an apparent equilibrium constant for the reaction of Fe(OH)₃ with BrO⁻ could be calculated. However, there are two lines of evidence that indicate that this is a steady state rather than an equilibrium and that the computed equilibrium constant is not meaningful.

The first evidence is drawn from Experiment 3b, where the concentration of Br⁻ was increased to 0.73 M. There was no noticeable change in either the concentration of FeO₄⁼ or in the rate of decrease of the concentration of FeO₄⁼. This result shows that the system is not in equilibrium, since under equilibrium conditions the concentration of FeO₄⁼ would have been decreased tenfold by the additional Br⁻. The other evidence is based on the heat data, which show that the equilibrium constant for the reaction



should be $K = 10^{5 \pm 3}$. The highest value of the equilibrium constant calculated from these hypobromite experiments is $K = 10^{-11}$.



The reaction of $\text{FeO}_4^{=}$ with Br^- in 3.3 m and 4.4 m NaOH was studied in these experiments. Table VII gives the concentrations of the various species. The concentrations of Br^- and NaOH were determined by the amount of NaBr and 30% NaOH added to the solutions. The concentrations of $\text{FeO}_4^{=}$ and BrO^- were determined by measuring the optical density of the solution at 6750 and 3800 Å (Fe(OH)_3 was previously removed by centrifugation).

Table VII

$\text{FeO}_4^{=} + \text{Br}^-$ reaction					
Expt. No.	NaOH conc. (m)	$\text{FeO}_4^{=}$ conc. ($\text{M} \times 10^{-3}$)	Br^- conc. (M)	BrO^- conc. (M)	Calc. BrO^- conc. (M)
1	4.4	9.5	0.035	$< 10^{-3}$	$10^{-6 \pm 3}$
2	3.3	5.5	0.022	$< 10^{-3}$	$10^{-9 \pm 3}$

The calculated concentrations of BrO^- are the concentrations expected on the basis of the heat data if the system is in equilibrium.

The following equations were used to determine the concentrations of $\text{FeO}_4^{=}$ and BrO^- :

$$\text{O.D.}_{6750} = \left(C_{\text{FeO}_4^{=}} \right) \left(\epsilon_1 \right) L,$$

$$\text{O.D.}_{3800} = \left(C_{\text{FeO}_4^{=}} \right) \left(\epsilon_2 \right) L + \left(C_{\text{BrO}^-} \right) \left(\epsilon_3 \right) L,$$

where O.D.₆₇₅₀ and O.D.₃₈₀₀ are the optical densities at 6750 and 3800 Å respectively. The cell length is denoted by L, and the concentrations of $\text{FeO}_4^{=}$ and BrO^- are denoted by $C_{\text{FeO}_4^{=}}$ and C_{BrO^-} respectively. The molar extinction coefficients⁴ of $\text{FeO}_4^{=}$ at 6750 Å, $\text{FeO}_4^{=}$ at 3800 Å, and BrO^- at 3800 Å are given by ϵ_1 , ϵ_2 , and ϵ_3 . In these equations the absorption of the BrO^- at 6750 Å is

assumed to be negligible. The absorption spectrum of BrO^- as recorded by a Cary Model 11 spectrophotometer shows that this is a valid assumption.

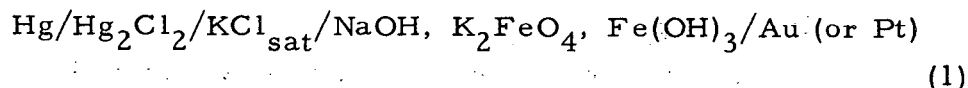
In both experiments the concentration of BrO^- was below the limit where confidence may be placed in the method of analysis. Unfortunately this limit (namely 10^{-3} M) is rather high because of the possibility of interference by colloidal $\text{Fe}(\text{OH})_3$. The column in Table VII headed Calculated BrO^- gives the concentration of BrO^- in equilibrium with the $\text{FeO}_4^{=}$, $\text{Fe}(\text{OH})_3^{=}$ couple. This calculation is based on the standard potential ($E^0 = 0.71 \pm .03$) for the $\text{FeO}_4^{=}$, $\text{Fe}(\text{OH})_3$ couple, as estimated from the calorimetric data.

$\text{Fe}(\text{OH})_3 + \text{MnO}_4^-$

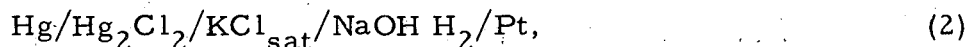
When $\text{Fe}(\text{OH})_3$ was added to an alkaline MnO_4^- solution (0.06 M in MnO_4^- and 10 m in NaOH) it catalyzed the reduction of the MnO_4^- by water; the solution turned green within 5 minutes. Spectroscopic examination of the reaction products showed that the concentration of $\text{FeO}_4^{=}$ was less than 10^{-3} M. Because of this reaction with water, the attempt to measure the equilibrium between the MnO_4^- , $\text{MnO}_4^{=}$ couple and the $\text{FeO}_4^{=}$, $\text{Fe}(\text{OH})_3$ couple was abandoned.

Electrode Measurements

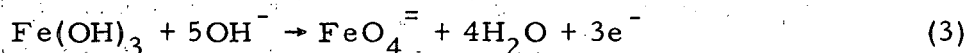
The potentials of the cells;



and



have been measured. From these data the standard potential E° of the half reaction



has been calculated.

A Beckman Model G pH meter which had been calibrated with a Rubicon potentiometer was used to measure the voltages. The accuracy of the instrument was ± 2 mv. A Beckman saturated KCl calomel electrode was used in all the experiments. An asbestos fiber sealed in glass formed the liquid junction. Four gold electrodes were used. Electrodes No. 1 and No. 2 were of unknown origin. Number 3 and No. 4 were made from pure sheet gold and then etched with aqua regia until the crystal structure was plainly visible. The platinum electrode was made of bright platinum sheet. The hydrogen electrodes were made by plating platinum black on bright platinum electrodes. The plating solution was a 3% solution of chloroplatinic acid. The plating was stopped as soon as the electrodes became noticeably darker. Ordinary tank hydrogen was used to saturate the electrodes. The hydrogen was first bubbled through a solution of NaOH of the same concentration as that being measured. All measurements were at $21^\circ\text{C} \pm 2^\circ$. The temperatures of the calomel electrode and of the solution were measured and a correction was applied to the measurements for the temperature coefficient of both the calomel and the $\text{FeO}_4^{=2}, \text{Fe(OH)}_3$ electrode. The correction was estimated from the temperature coefficient of the saturated calomel electrode $+ 0.76 \text{ mv}/^\circ\text{C}$ and the temperature coefficient of the $\text{FeO}_4^{=2}, \text{Fe(OH)}_3$ couple as calculated from the equations

$$\frac{\partial E}{\partial T} = \frac{\partial E^0}{\partial T} - \frac{2.3R}{nF} \log \frac{(a_{\text{FeO}_4^{=}})}{(a_{\text{OH}^-})^5}$$

and

$$\frac{\partial E^0}{\partial T} = \frac{\Delta S^0}{n \times 23,060} ,$$

where $2.3R/nF = 0.0007$ volt, $n = 3$ electrons, and ΔS^0 is the entropy change for the $\text{Fe}(\text{OH})_3, \text{FeO}_4^{=}$ half reaction. These equations assume that the temperature coefficient of the activity is negligible. In no case was the temperature correction over 4 mv. The NaOH solutions were prepared from Reagent Grade NaOH. The concentration of the NaOH was determined by titration with HCl. The HCl was standardized with both potassium hydrogen phthalate and AgNO_3 .

The concentration of $\text{FeO}_4^{=}$ (moles/liter) was determined by use of a Cary Model 11 spectrophotometer at a wavelength of either 505 m μ or 675 m μ .

In preliminary measurements of cell No. 1 it was found that dilute NaOH was unsuitable. For instance, at a concentration of $\text{NaOH} = 5 \times 10^{-4} \text{ M}$ and with the concentration of $\text{FeO}_4^{=} = 2 \times 10^{-3}$, a steady voltage of $0.49 \pm .02$ volt was reached after 10 minutes. From these data the calculated standard potential of Half Reaction (3) is 0.2 volt more positive than the value predicted from the heat-of-formation data.

In Fig. 1 the voltage of cell No. 1 vs the logarithm of the concentration of ferrate has been plotted for experiments in which concentration of NaOH was 2.57, 5.31, and 10.89 m. The experiments at 2.57 m are too irreproducible to be of any value. A straight line with the theoretical slope of 19.4 mv was fitted to the gold-electrode data for 5.31 and 10.89 m NaOH.

The measurements in 5.3 m NaOH at concentrations of $\text{FeO}_4^{=}$ below 10^{-3} m have not been used because in this region the slope of the curve of $-\log \text{conc}_{\text{FeO}_4^{=}}$ vs potential is much larger than the theoretical slope. Moreover, the potentials are very unstable.

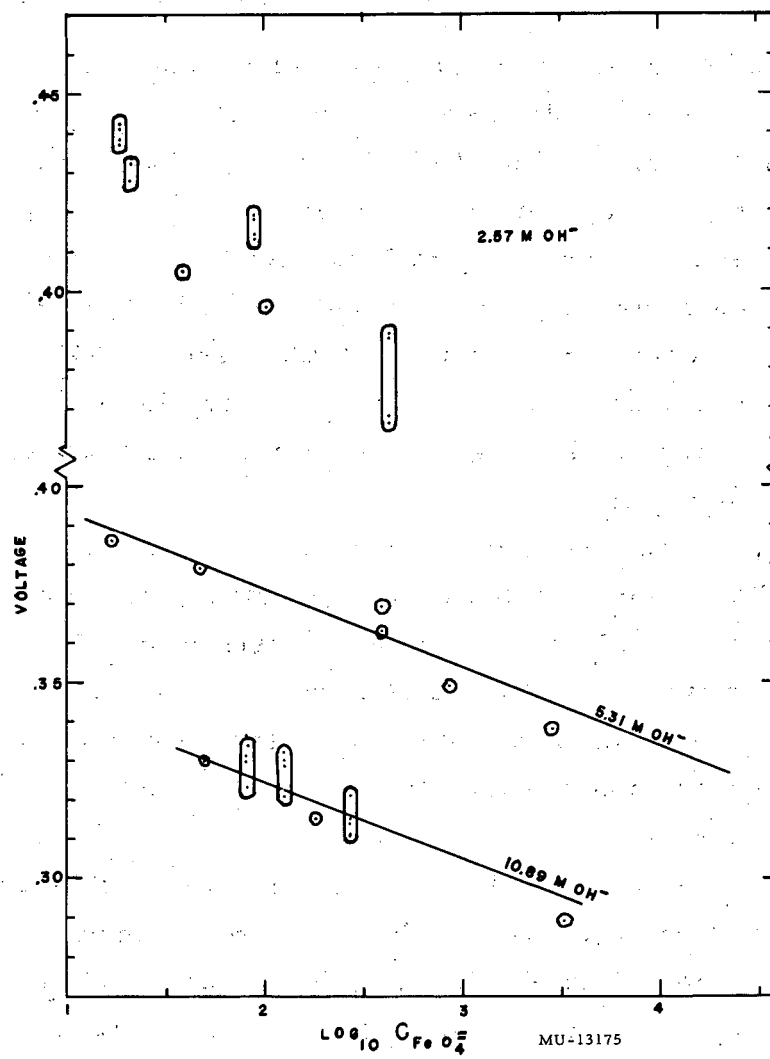


Fig. 1. Voltage of cell No. 1 plotted against the minus logarithm of the concentration of $\text{FeO}_4^{=}$ for 2.57 m, 5.31 m, and 10.89 m NaOH solutions.

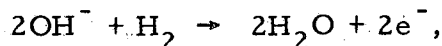
In all cases the platinum electrode was much slower than the gold electrode in reaching equilibrium. In many cases it was also sensitive to mechanical shock. When the platinum electrode did reach a steady state the voltage tended to be higher and more unstable than the voltage on the gold electrodes. For these reasons the data taken with the platinum electrode were discarded.

Cell No. 2 was measured in 5.31 and 10.89 m NaOH. The voltages were -1.107 and -1.137, respectively. In both cases three different platinum black electrodes were used, and the results differed by 1 mv or less. The final value of the potential was established within 10 to 30 min.

The E° for Half Reaction (3) was calculated from the equation

$$E^{\circ} = 0.824 + E_2 - E_1 - \frac{RT}{3F} \ln \frac{C_{OH^-}^2}{C_{FeO_4^{2-}} P_{H_2}} \frac{\gamma_{NaOH}^4}{\gamma_{Na_2FeO_4}^3 \gamma_{H_2O}^4}$$

In this equation 0.824 is the potential at 21°C of the half reaction



and E_1 and E_2 are the voltages for cells No. 1 and No. 2 respectively. The activity coefficient of Na_2CrO_4 at the same ionic strength was used as an estimate of the activity coefficient of Na_2FeO_4 . The activity coefficients of NaOH, Na_2CrO_4 , and H_2O were taken from Robinson and Stokes.⁸ The pressure of hydrogen was calculated by subtracting the vapor pressure of the solution from the barometric reading.

In 5.31 and 10.89 m NaOH the calculated E° 's for Half Reaction (3) were -0.768 and -0.807 volt, respectively. These values differ considerably from each other and from the value $E^{\circ} = -0.71 \pm .03$ volt estimated from the heat-of-formation data. Because of this serious inconsistency, the electrode data are not reliable enough so that any weight can be attached to them.

Rate of Decomposition of K_2FeO_4 in Concentrated NaOH

In the course of the electrode measurements described above, the concentration of $FeO_4^{=}$ in solutions of concentrated NaOH was measured as a function of time. From these data the rate of decomposition of $FeO_4^{=}$ at $21^\circ C$ in the various solutions has been calculated. These calculations are for the rate of decomposition of K_2FeO_4 dissolved in Reagent Grade NaOH and in the presence of gold, platinum, and glass surfaces. Table VIII gives the concentrations of K_2FeO_4 , the time elapsed between the two measurements, and the corresponding rate of decomposition. The rate of decomposition of the $FeO_4^{=}$ in 5.31 m NaOH is independent of the concentration of $FeO_4^{=}$ as long as the concentration of $FeO_4^{=}$ is between 2.6×10^{-3} and 2×10^{-5} M. In the 2.57 m NaOH solution the rate of decomposition can be described by the expression

$$-\frac{d C_{FeO_4^{=}}}{dt} = 2.0 \times 10^{-3} C_{FeO_4^{=}},$$

where $C_{FeO_4^{=}}$ denotes the concentration of $FeO_4^{=}$ and t is the time in minutes. The first-order decomposition is what would normally be expected. In the more alkaline medium the first-order rate constant seems to be strongly repressed. The small residual zero-order decomposition actually observed is probably to be ascribed to catalysis by either the metal or glass surface.

Table VIII

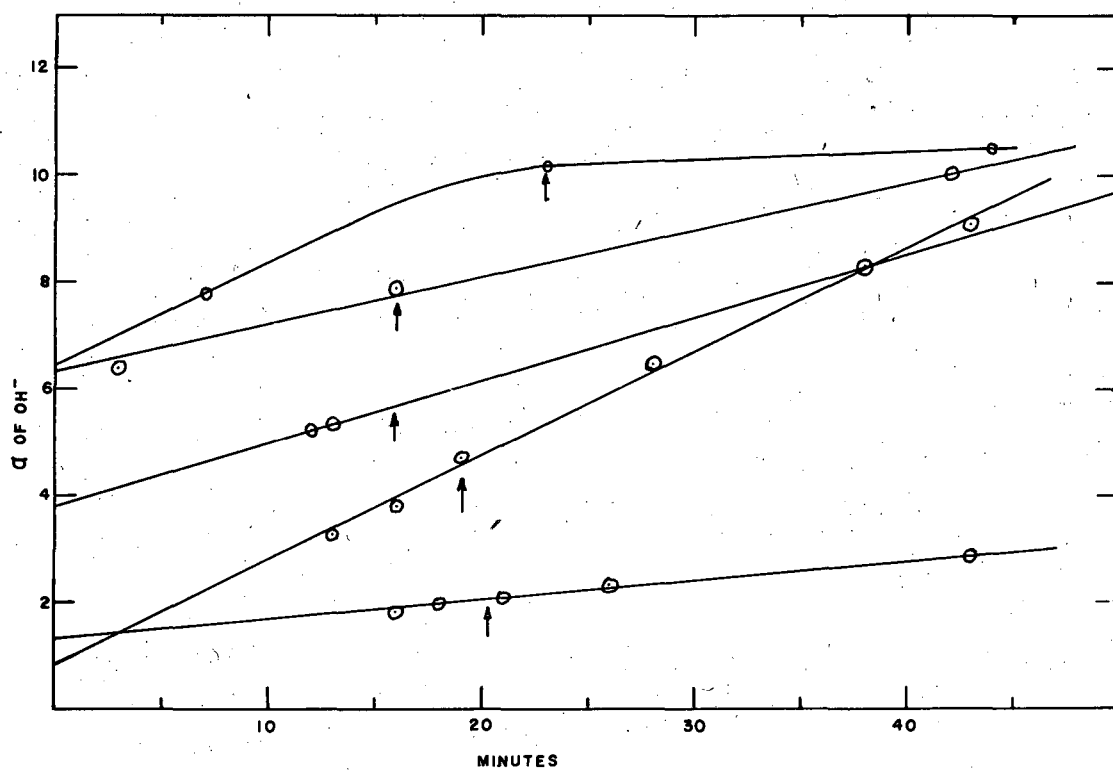
Rate of decomposition of $\text{FeO}_4^{=}$ in NaOH					
NaOH conc. (<u>m</u>)	$\text{FeO}_4^{=}$ conc., start (<u>M</u>)	$\text{FeO}_4^{=}$ conc., end (<u>M</u>)	Time (min)	Rate of decomposition (moles/liter min)	Rate $\frac{\text{Rate}}{C_{\text{FeO}_4^{=}}}$ ($\times 10^3$)
5.31	3.5×10^{-5}	1.8×10^{-5}	19	0.9×10^{-6}	
	4.7×10^{-4}	3.9×10^{-4}	21	4×10^{-6}	
	3.9×10^{-4}	3.5×10^{-4}	29	1.4×10^{-6}	
	2.66×10^{-3}	2.61×10^{-3}	46	1×10^{-6}	
	2.1×10^{-2}	2.1×10^{-2}	30	$< 3 \times 10^{-5}$	
2.57	2.51×10^{-3}	2.33×10^{-3}	36	5.0×10^{-6}	2.1
	1.23×10^{-2}	1.11×10^{-2}	41	2.9×10^{-5}	2.5
	2.58×10^{-2}	0.97×10^{-2}	450	3.58×10^{-5}	2.0
	2.87×10^{-2}	2.58×10^{-2}	66	4.4×10^{-5}	1.6
	5.31×10^{-2}	4.89×10^{-2}	48	1.0×10^{-4}	2.0
0.9	10^{-3}	0	8	10^{-4}	

Heat of Formation of $\text{FeO}_4^{=}$

The heat of formation of $\text{FeO}_4^{=}$ was determined by measuring the heat of the reaction of aqueous K_2FeO_4 with 0.5 m HClO_4 . In order to minimize the correction to the calorimetric measurements for the decomposition of the aqueous K_2FeO_4 solution it was desirable to work at the pH at which the solutions were most stable. Solutions of K_2FeO_4 in strong alkali (3 M or above), although fairly stable, were rejected because of formation of $\text{Fe}(\text{OH})_3$ in the reaction with 0.5 m HClO_4 . Our experience shows that aqueous K_2FeO_4 has another region of stability around pH 10 to 11. For instance:

(a) Dilute solutions of K_2FeO_4 in 10^{-4} M NaOH show a relatively slow decomposition. (See Fig. 2). (b) In 10^{-3} M NaOH , K_2FeO_4 is about 50% decomposed in 90 minutes. (c) In 10^{-2} M NaOH , K_2FeO_4 is completely decomposed in 3 minutes. The data of Schreyer and Ockerman⁹ on the stability of aqueous K_2FeO_4 are consistent with these observations, and in addition show that the solutions are relatively unstable below pH 10.

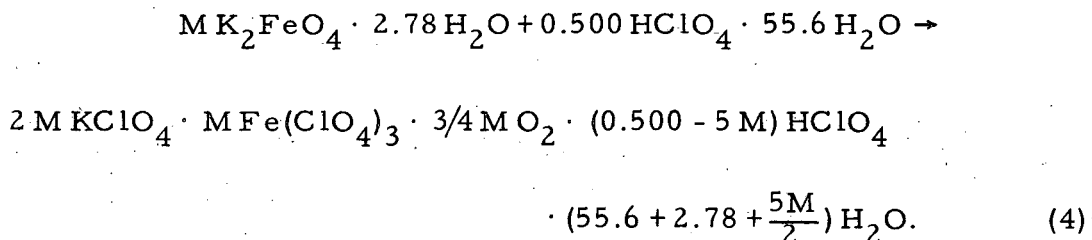
The procedure in each calorimetric run was as follows: K_2FeO_4 was dissolved in 10^{-4} M NaOH and filtered through a fine sintered-glass filter. Three aliquots of the solution were set aside for analysis. The pH of one of these samples was measured at various times during the run to give the concentration of hydroxide ion as a function of time. A Beckman Model G pH meter with a blue glass electrode was used for this measurement. The electrode was standardized with Beckman pH 10 buffer. Figure 2 gives the activity of OH^- vs time after filtration, for the various runs. The arrows indicate the time at which the heat was measured. Fifty ml of the solution was pipetted into a glass bulb and placed in the calorimeter with 1 liter of 0.500 m HClO_4 . As soon as the temperature drift was constant the bulb was broken and the heat produced was measured. The calorimeter has been described previously.^{10, 11} All runs were made at $25 \pm 0.5^\circ\text{C}$. The 0.500 m HClO_4 solution was prepared by diluting G. F. Smith double vacuum-distilled HClO_4 (Pb free). The concentrated reagent was standardized with NaOH solution, which had been freshly standardized with potassium acid phthalate.



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Fig. 2. Activity of $\text{OH}^- \times 10^4$ plotted against time elapsed since $\text{Fe}(\text{OH})_3$ was filtered out.

The main reaction in the calorimeter is given by

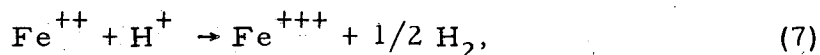


Hydrolysis of the K_2FeO_4 is shown to be negligible by the fact that Runs 4 and 5 (Fig. 2), where the second sample of K_2FeO_4 was used, extrapolate back to about 10^{-4} M OH^- , which is the original concentration of hydroxide ion in the solutions. A variation of $1 \times 10^{-4} \text{ M OH}^-$ would amount to only 1% hydrolysis in Run No. 4 and 2% hydrolysis in Run No. 5. The runs in which the first K_2FeO_4 sample was used probably show larger initial concentrations of OH^- because of the larger amount of $\text{Fe}(\text{OH})_3$ impurity in these samples. This impurity catalyzes the decomposition of the $\text{FeO}_4^{=}$ until it is removed by the filtration. Catalysis of the decomposition of $\text{FeO}_4^{=}$ by $\text{Fe}(\text{OH})_3$ has been reported by Schreyer and Ockerman⁹ and confirmed by my observation that solutions that have been filtered take much longer to decompose.

Formation of H_2O_2 was shown to be unimportant by tests for H_2O_2 with Ti(IV) solution. In no case could the error due to H_2O_2 formation be greater than 0.5%. The O_2 produced in the reaction is written as aqueous, since in a trial run in which the bulb was broken in a beaker of 0.5 m HClO_4 no O_2 bubbles were observed. This was expected, because the concentration of oxygen was only about one-half the solubility at one atmosphere pressure.

As the reaction products were clear and almost colorless, the presence of appreciable $\text{Fe}(\text{OH})_3$ is doubtful. A yellow color was barely visible in a 15-cm column of the reaction products. For comparison purposes freshly precipitated $\text{Fe}(\text{OH})_3$ was used. A solution containing 2×10^{-6} mole per liter of $\text{Fe}(\text{OH})_3$ showed the same barely detectable yellow color. This would correspond to the presence of about 0.2% of $\text{Fe}(\text{OH})_3$.

Fontana's value ($\Delta H = 9.53 \pm .04$ kcal/mole)¹¹ for the reaction in 0.5 m HClO₄,



together with an estimation of the relative partial molal heat of dilution of Fe(ClO₄)₂. This estimate was made by plotting the heats of dilution of other 2-1 electrolytes against the crystal volume. In Fig. 3 the partial molal heats of dilution ($\bar{L}_2$) of the chlorides, bromides, and nitrates of calcium, magnesium, strontium, and barium are plotted vs the crystal volume. The data at (moles per kg of water)^{1/2} = 0.1, 0.2, and 0.3 are taken from Harned and Owen.¹³ The data at $\underline{m}^{1/2} = 0.4$ are calculated from National Bureau of Standards values.¹² The crystal volume is obtained by dividing the molecular weight by the density of the unhydrated crystal. The estimated crystal volume of Fe(ClO₄)₂ is 87 ± 5 . For a 2-1 electrolyte at 0.167 m the ionic strength is 0.5 and $\underline{m}^{1/2} = 0.408$. From Fig. 3 we can see that for a crystal volume of 87 ± 5 cm³/mole the relative partial molal heat content at $\underline{m}^{1/2} = 0.408$ will be -1.5 ± 0.5 kcal/mole. A combination of this value, Fontana's value of $\Delta H = 9.53 \pm 0.04$ kcal/mole for Reaction (7), and the National Bureau of Standards values at infinite dilution gives the relative partial molal heat content of infinitely dilute Fe(ClO₄)₃ in 0.5 m HClO₄, $\bar{L}_2 = -1.7 \pm 0.5$ kcal/mole.

The weighted average of the five runs for ΔH_2 (Eq. 5) is -68.9 kcal/mole. Runs 3 and 4 were weighted by a factor of two in taking the average value of ΔH_2 because the estimated probable error was one-half that of the other runs. From this value for ΔH_2 , and from the Bureau of Standards values at infinite dilution for the heats of formation of the reactants and products of Reaction (5), we have calculated the heat of formation of FeO₄⁼ as $\Delta H_f^0 = -116 \pm 1$ kcal/mole. (The Bureau of Standards values are

H ⁺	0.00	kcal/mole
ClO ₄ ⁻	-31.41	kcal/mole
Fe ⁺⁺⁺	-11.4	kcal/mole
O ₂ (aq)	-3.8	kcal/mole
H ₂ O	-68.32	kcal/mole.)

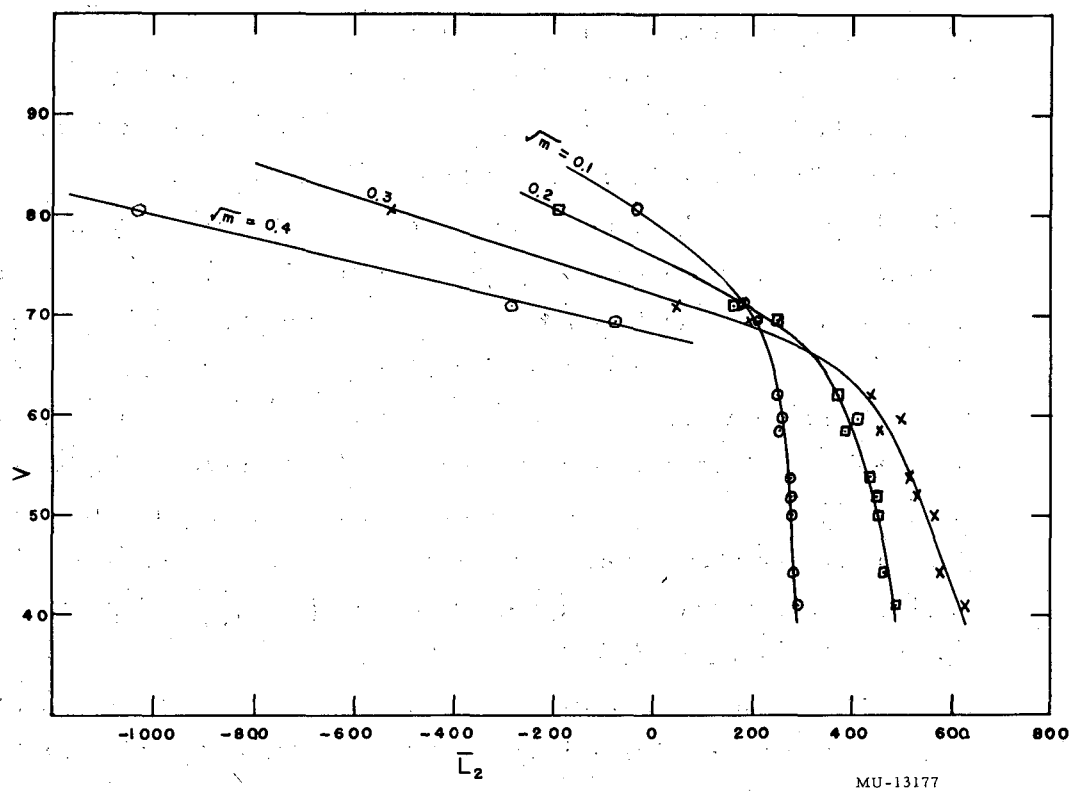


Fig. 3. Relative partial molal heat contents of 2-1 electrolytes at various concentrations vs the crystal volume of the electrolyte.

ENTROPY AND FREE ENERGY OF FeO_4^-

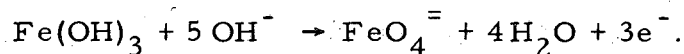
The entropy of the aqueous FeO_4^- ion can be estimated by comparison with the entropies of similar ions. Entropies of some ions with the formula MO_4^- are given below. The data are taken from Latimer.¹⁴ Helfferich and Lang report from x-ray studies that there is no more than 1% difference in size between K_2CrO_4 and K_2FeO_4 .¹⁵ For this reason I have estimated the entropy of FeO_4^- aqueous as 9 ± 4 eu.

Entropies of MO_4^- (aq) (from NBS)

Ion	S°
SO_4^-	4.1 eu
SeO_4^-	5.7 eu
CrO_4^-	9.2 eu

From this estimate of the entropy National Bureau of Standards values ($S^\circ_{\text{Fe}} = 6.5$ eu, $S^\circ_{\text{O}_2} = 49.0$ eu), and the measured heat of formation ($\Delta H^\circ_f \text{FeO}_4^- = -116 \pm 1$ kcal/mole), I calculate for the free energy of formation $\Delta F^\circ_f = -78.1 \pm 2$ kcal/mole.

Using Latimer's estimate of the entropy of Fe(OH)_3 ¹⁶ I calculate the standard potential ($E^\circ = 0.71 \pm .03$ volts) for the half reaction



There is no value in the literature for this potential except the very rough estimate, $E_B > -0.9$, made by Latimer on the basis of chemical evidence.¹⁶

CONCLUSIONS

1. Some fairly pure samples of K_2FeO_4 have been prepared.

2. Methods of analysis of K_2FeO_4 solutions in 10^{-4} M NaOH involving alkaline I^- , As(III), and Cr(III) as the reducing agent have been investigated. A method of analysis that is accurate to better than 1% and that consists of measuring the total iron content (after $Fe(OH)_3$ has been removed by filtration) has been developed. This method has been confirmed by measurements of the volume of O_2 liberated when K_2FeO_4 solutions are acidified.

3. The molar extinction coefficients of aqueous K_2FeO_4 at various wavelengths have been measured. The extinction coefficients in liters/mole cm are

at 3800 A, $\epsilon = 341 \pm 9$;

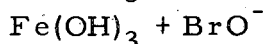
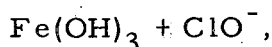
at 3900 A, $\epsilon = 318 \pm 9$;

at 5050 A, $\epsilon = 1070 \pm 30$;

at 5500 A, $\epsilon = 967 \pm 30$;

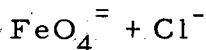
at 6750 A, $\epsilon = 211 \pm 6$.

4. Studies of the reactions

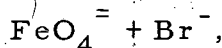


show that these systems are quite far from equilibrium even though steady states are set up.

5. In a study of the reactions



and



no ClO^- or BrO^- could be detected.

6. The decomposition of alkaline MnO_4^- solutions is catalyzed by $Fe(OH)_3$.

7. The electrode system K_2FeO_4 , NaOH, $Fe(OH)_3$ /gold or Pt is irreversible.

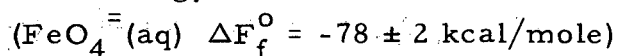
8. The rate of decomposition of K_2FeO_4 in concentrated NaOH has been measured at $21^\circ C$. In 2.57 M NaOH the rate of decomposition is first order. The rate constant k is 2.0×10^{-3} per min in the concentration range 5×10^{-2} to 1×10^{-3} mole/liter. In

5.31 m NaOH the rate of decomposition was 10^{-6} mole/liter min in the concentration range 2.6×10^{-3} to 1.8×10^{-5} mole/liter. The decomposition in 0.9 m NaOH is quite rapid.

9. The heat of the reaction of aqueous K_2FeO_4 with 0.5 m $HClO_4$ to give $O_2 + Fe^{+++}$ was measured. From this measurement the heat of formation of $FeO_4^{=}$ (aq) ($\Delta H_f^\circ = -116 \pm 1$ kcal/mole) has been calculated.

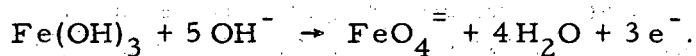
10. The entropy of the $FeO_4^{=}$ (aq) ion has been estimated; $S^\circ = 9 \pm 4$ eu.

11. From the estimated entropy and the measured heat of formation the free energy of formation of



has been calculated.

12. Using Latimer's estimate of the entropy of $Fe(OH)_3$ ($S^\circ = 23$ eu),¹⁶ we have calculated the standard potential ($E^\circ = -0.71 \pm 0.03$ volts) for the half reaction



THE HEAT, FREE ENERGY, AND ENTROPY OF THE
FERRATE(VI) AND SELENIDE IONS

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Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

April 9, 1957

PART II: THE SELENIDE ION

ABSTRACT

Three methods for the analysis of alkaline solutions of H_2Se have been developed. These methods involve (a) weighing the selenium as the metal, (b) precipitating Ag_2Se , and (c) reduction of I_2 to I^- by the $\text{Se}^{=}$.

The hydrolysis constant of H_2Se has been calculated from the following measurements: (a) The titration curve of H_2Se with KOH , (b) the change in pH on addition of H_2Se to 0.2 M KOH at 0.5°C , and (c) the solubility of Na_2Se as a function of the concentration of OH^- . The results are (a) for 0.5°C and an ionic strength of 0.2, $K_{\text{H}}^{0.2} = 1.1 \pm 0.4$, and (b) for 22°C and an ionic strength of 4.2, $K_{\text{H}}^{4.2} = 0.25 \pm 0.09$. By estimating the activity coefficients of the various ions and the temperature coefficient of K_2 , I have calculated the second ionization constant of H_2Se (for 22°C and zero ionic strength $K_2^0 = 10^{-15.0 \pm 0.6}$). Because of the unexpectedly small second ionization constant of H_2Se , the heat of neutralization of H_2Se was not measured.

INTRODUCTION

The value of $\bar{S}_{\text{Se}}^0$ found in the National Bureau of Standards tables is 20 eu.¹² This appears to be considerably too positive for a monatomic, dinegative ion.¹⁷ The value is based on Fabre's data on the heat of neutralization of H_2Se ¹⁸ and on Latimer's estimate of the second ionization constant of H_2Se ($K_2 = 10^{-14}$).¹⁴ Latimer's estimate was based on studies by J. J. Lingane and L. W. Niedrach, who measured the polarographic waves of H_2Se at various values of pH.¹⁹ Their data indicate, for H_2Se , $K_2 \leq 10^{-14}$. There is considerable discrepancy between this value and the value that H. Hagiwara reported ($K_2 = 10^{-11}$) from a titration curve of H_2Se with NaOH using a glass electrode.²⁰

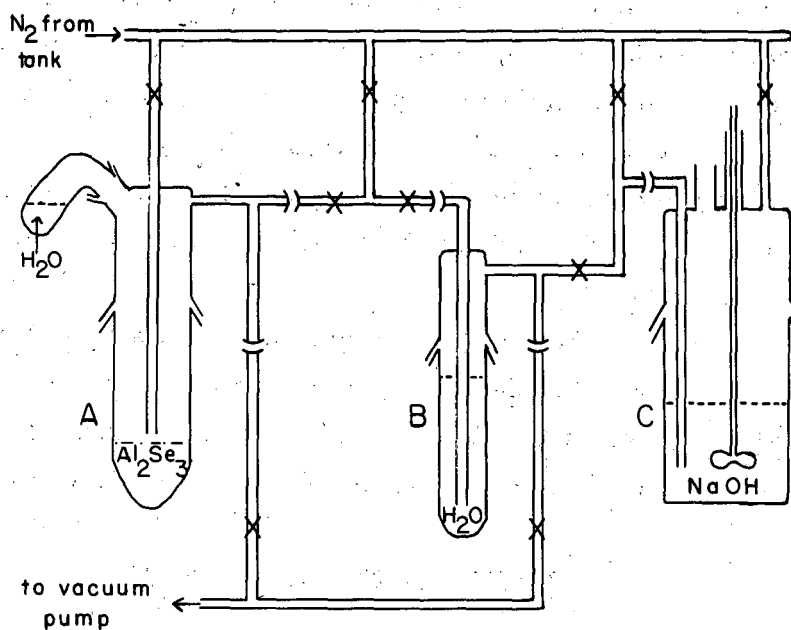
The intention of this investigation was to calculate the entropy of the aqueous selenide ion from a measurement of the second ionization constant of H_2Se and a remeasurement of the heat of neutralization of H_2Se by use of modern calorimetric techniques.

EXPERIMENTAL PROCEDURE

Preparation of H_2Se

The H_2Se used in these experiments was prepared by adding water to Al_2Se_3 . The Al_2Se_3 was prepared by the method of G. R. Waitkins and R. Shutt.²¹ In this preparation a mixture of powdered selenium and aluminum is ignited with magnesium ribbon. The selenium used was Fisher certified reagent grade. The manufacturer's analysis gave the sulfur content as 0.05%.

The apparatus for preparing the H_2Se is shown in Fig. 4. The generator was swept with N_2 to remove O_2 before the water and Al_2Se_3 were combined. To generate the last part of the H_2Se the system was warmed to 60° or 70°C . After being washed with water the H_2Se was ready for use.



- A = H_2Se generator
- B = H_2Se washer
- C = reaction flask
- ⇌ = ground glass joint
- ⇒ = ball joint
- X = stopcock

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Fig. 4. Apparatus for generating H_2Se .

Analysis of ($\text{HSe}^- + \text{Se}^-$)

Three methods for the analysis of solutions of HSe^- and Se^- were developed. The procedure for the first method is as follows: The solution to be analyzed is allowed to stand in air until all the Se is oxidized to either Se metal or $\text{SeO}_3^{=}$. Concentrated HNO_3 is added to oxidize all the selenium to selenite. The solution is neutralized with NH_4OH and then made just acid with HCl . Excess hydrazine sulfate is added and, after all of the selenium has precipitated, the solution is heated at 50° to 60° for 10 hours to convert the red amorphous selenium to the grey form. The solution is filtered with a weighed, medium sintered-glass filter, washed with H_2O , and then with ethyl alcohol. The selenium and filter are weighed after drying at 110°C for 1 to 2 hours. Loss of H_2Se during the air oxidation should be negligible, since in all cases there was no odor of H_2Se detectable above the solution. The method of analyzing the $\text{SeO}_3^{=}$ is substantially the same as that given by Treadwell and Hall.²² Both $\text{SeO}_4^{=}$ and $\text{SeO}_3^{=}$ are reduced to Se by this method. Table X gives the results of several trial analyses in which pure selenium was used as the starting material. The final volume is the volume of the solution from which the selenium is precipitated. The results show that the analysis is accurate to 0.2% if the final volume is kept at about 50 ml per gram of selenium.

Table X

Selenium Analysis No. 1			
No.	Wt of Se Taken (g)	Final vol (ml)	% Recovered
1	0.8745	50	99.9
2	0.8004	50	100.05
3	0.9019	50	100.25
4	1.1553	200	99.8
5	0.8178	400	99.1

The second method of analysis consists of adding a measured volume of the selenide solution to a solution of I_3^- in acetic acid and potassium iodide. The selenium is oxidized to the metal by the I_3^- . The excess I_3^- is titrated with $S_2O_3^{2-}$, with starch as the indicator. The acid is added to reduce the possibility of reaction of the I_3^- with alkaline Se^{2-} to produce SeO_3^{2-} instead of selenium metal. In the third method of analysis a known volume of solution is added to excess $AgNO_3$ in an acetic acid solution. The excess Ag^+ is titrated with standard $KSCN$, with a silver electrode as an end-point indicator. The acetic acid is used to reduce the formation of Ag_2O and its subsequent coprecipitation. Both these methods of analysis were used by McAmis and Felsing for the analysis of H_2Se solutions.²³ McAmis and Felsing weighed the Ag_2Se precipitate, whereas I have titrated the excess Ag^+ . Their results agreed to within 0.2% when aqueous H_2Se was being analyzed. Table XI gives the results of several experiments in which the second and third analyses were checked against each other.

Table XI

Analysis of ($HSe^- + Se^{2-}$). (NaOH conc. = 0.6 m.)				
2N Acetic acid (ml)	H_2O (ml)	0.02035N IO_3^- (ml)	0.02000N $AgNO_3$ (ml)	Selenium (mole $\times 10^3$)
10	0		15.01	0.1096
5	5		15.01	0.1099
5	5		15.01	0.1096
10	5	15.01		0.1093
5	5	15.01		0.1096

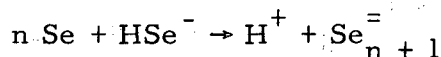
In the I_2 method a known volume of standard KIO_3 solution was added to 3 grams of KI and varying amounts of 2 N CH_3COOH and water. A pipette with a stopcock attached to two side arms was used to transfer the selenium solutions. The solution was drawn up past the stopcock into one arm of the pipette. After the tip of the pipette was

wiped off, the solution in the lower part of the pipette was drained; the other side arm let in air. The pipette was rinsed by first drawing up and returning some of the solution into which it had been drained, and then drawing up distilled water and adding this to the reactants. The volume of the pipette was found by calibration with mercury to be 2.158 ml. A similar pipette with a volume of 6.079 ml was also constructed for use where the concentration of selenium was small. In the silver titration a known volume of standard AgNO_3 was used instead of the IO_3^- and I_2 . The Ag^+ titrations at first gave results that were about 1% high. It was found that, after standing for 1 or 2 days, the solution contained more Ag^+ . This effect is undoubtedly due to some coprecipitation of Ag_2O . No further Ag^+ was formed after another week of standing. The final results show that the two methods agree to within 0.2%. When the I_2 titration was checked in 1 M KOH solution it was found that a sevenfold excess of I_2 gave results that were 7 to 12% high. A solution of H_2Se in 3.7 M NaOH , when titrated by use of I_2 , gave answers that increased severalfold as the concentration of I_2 was increased and the concentration of acetic acid was decreased. However, the Ag^+ titrations gave reproducible values, which were about 20% lower than the lowest value obtained with an I_2 titration. The variation of the I_2 results is undoubtedly due to the oxidation of $\text{Se}^{=}$ to $\text{SeO}_3^{=}$ by the I_2 .

Titration Curve

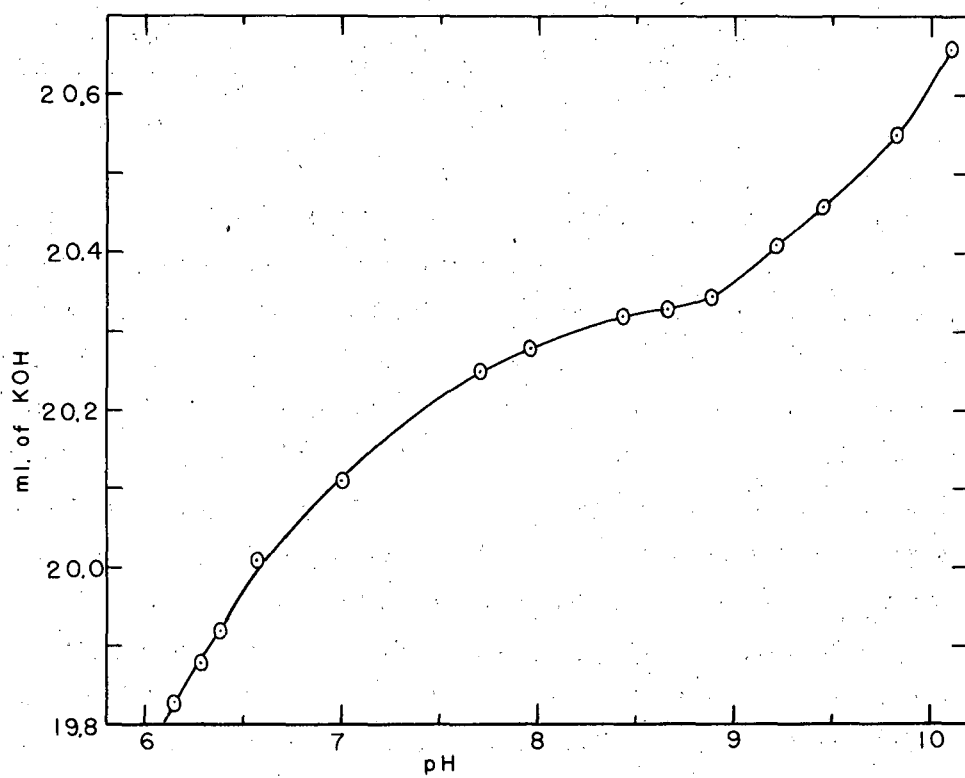
In this experiment the titration of H_2Se with 0.141 M KOH was followed with a Beckman blue glass electrode and a Model G pH meter. The electrodes were standardized in Beckman pH 4 buffer. Hydrogen selenide was added to 50.0 ml of H_2O , and this was titrated with the 0.141 N KOH. The titration curve is given in Fig. 5. The lower portion of the titration curve is somewhat uncertain, because solution of H_2Se from the gas phase caused the pH to drift slowly. Some selenium (formed by oxidation of H_2Se by traces of O_2) was present in the titration mixture. This selenium was present as a grey metallic selenium until a pH of about 8 was reached. At this point a red solution of polyselenide was gradually formed as the pH was increased. The solution is much more buffered than expected. This is probably owing to the presence of 1% or 2% $\text{CO}_3^{=}$.

From Fig. 5, the first ionization constant of H_2Se ($K_2 = 2.3 \times 10^{-3}$),^{23, 24} and the equations by Ricci for the titration of a diprotic acid with a strong base,²⁵ the following calculations were made. (a) From the lower portion of the curve I calculated the total concentration of selenium as 0.0408 M. From the points at pH 10.10, 9.82, 9.45, and 9.21, I calculate for $K_2^{0.04}$ the values 1.3×10^{-12} , 1.6×10^{-12} , 2.2×10^{-12} and 2.4×10^{-12} . That the reaction



is occurring in the pH region is indicated by the visual observation that the selenium is dissolving, and confirmed by the fact that there is a discontinuity in the titration curve at pH 8.9, with the curve rising sharply from this point. Because the formation of any polyselenide increases the calculated values of K_2 , the above calculations represent a lower limit to the second ionization constant of H_2Se .

The formation of polyselenide is quite likely responsible for the value $K_2 = 10^{-11}$ reported by H. Hagisawa from a titration curve.

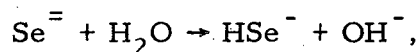


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Fig. 5. Titration of H₂Se with 0.141 M KOH.

Glass Electrode Measurements

In this experiment I measured the change in the pH of KOH solutions after adding H_2Se . From these data I have calculated the hydrolysis constant ($K_H^{0.2}$) for the selenide ion at an ionic strength of 0.20. The equations are



$$K_H^{0.20} = \frac{C_{\text{HSe}^{-}} C_{\text{OH}^{-}}}{C_{\text{Se}^{2-}}} = K_H^0 \frac{\gamma_{\text{Na}_2\text{Se}}^3}{\gamma_{\text{NaHSe}}^2 \gamma_{\text{NaOH}}^2}$$

The pH was measured with a Beckman Model GS pH meter (which can be read to 0.002 pH) and a Beckman blue glass electrode with sat KCl calomel reference electrode. The KOH solution was standardized with HCl that had previously been standardized against both AgNO_3 and potassium hydrogen phthalate. To remove the CO_3^{2-} from the solution some $\text{Ba}(\text{OH})_2$ was added. All the experiments were carried out at $0.5^\circ \pm 0.5^\circ\text{C}$. After the measurements of the hydrolysis constant the glass electrode was checked by measuring the pH change on adding standard HCl to the KOH solution. The data are given in Table XII. In the calibration run the measured pH change is slightly lower than the calculated change. The pH changes measured in the H_2Se experiments have been adjusted for this effect. The adjusted changes in pH are given in the column labeled "Calculated ΔpH ." The reasonableness of this assumption is indicated by the observation that in the calibration of the glass electrode at higher concentrations of KOH, the measured pH change is increasingly smaller than the calculated pH change. The concentration of selenium was measured by precipitating and weighing the selenium as the metal (see section on analysis for details).

The calculations were made as follows: From the pH change the change in the concentration of KOH was calculated, on the assumption that the activity coefficients of H^+ and OH^- remain constant. This assumption is based on the fact that the ionic strength varies

Table XII

Glass electrode experiments

$\mu = 0.21 \pm .01$

Experiment No.	KOH at start (mole $\times 10^3$)	Δ pH measured	Δ pH calc	KOH final (mole $\times 10^3$)	H ₂ Se added (mole $\times 10^3$)	HSe ⁻ calc (mole $\times 10^3$)	Se ⁼ calc (mole $\times 10^3$)	Volume (ml)	K _H ^{0.21}
1	4.26	0.416	0.439 ± 0.01	1.55 ± 0.05	2.52	2.33 ± 0.05	0.19 ± 0.05	20.4	1.0 $\pm$ 0.3
2	6.50	0.314	0.331 ± 0.1	3.03	3.22	2.97	0.25	32.4	1.3 $\pm$ 0.5
Calibration	6.52	0.296	0.313	3.46	-----				
Weighted average 1.1 $\pm$ 0.4									

very little during the addition of the H_2Se . From the change in concentration of the KOH, the moles of H^+ neutralized can be calculated. From this and the total concentration of selenium the concentrations of HSe^- and $\text{Se}^{=}$ were calculated. When attempts were made to use higher concentrations of KOH a white precipitate of BaSe was formed (KOH containing no Ba did not give the precipitate). Because the glass electrode does not work nearly so well in more alkaline solutions, no measurements were made at higher concentrations of OH^- .

Solubility of Na_2Se

In this experiment the solubility of Na_2Se at 22°C has been measured as a function of the concentration of OH^- . From these data the solubility product of Na_2Se and the hydrolysis constant of $\text{Se}^{=}$ have been calculated.

Hydrogen selenide was added to various mixtures of 3.72 m NaOH and 4.32 m $\text{CH}_3\text{COO Na}$ until a precipitate of Na_2Se was obtained. The concentration of selenium was determined by the Ag_2Se method. The solution was sucked up through a medium sintered-glass filter and into the pipette. In all cases the solutions were checked at least a week after being titrated to see if any Ag_2O had dissolved. The silver ion formed in this period was never more than 1% of the total. When an estimate of the Na_2Se formed was needed, the solution was stirred rapidly and an unfiltered aliquot taken out and analyzed for selenium. The difference between this analysis and the analysis of the filtered solution gives the amount of Na_2Se precipitated. The pH measurements were made by withdrawing a sample of the solution and placing it in a beaker with a Beckman blue glass and reference electrodes. The electrodes were standardized before and after being used with Beckman pH 10 buffer. The cell was constantly swept with N_2 . The pH was measured with a Beckman Model G pH meter. The NaOH solution was analyzed for OH^- and $\text{CO}_3^{=}$ by titrating with standard HCl to the phenolphthalein and the bromcresol-green end points. The NaAc was analyzed by drying aliquots of the solution to constant weight at 140°C .

Table XIII

Solubility of K_2Se vs. C_{OH^-}

Experiment No.	NaOH conc. at start (m)	Na^+ conc. at start (m)	Na_2Se conc. (m)	pH	Na^+ conc., final (m)	$(HSe^- + Se^{2-})$ conc. (m)	$(Na^+)^2 (HSe^- + Se^{2-})$ conc. (m)	OH^- conc., final (m)
1	3.72	3.72	$.02 \pm .01$	-	3.68	.00524	.0709	3.67
2	1.40	4.13	$.01 \pm .005$	-	4.11	.00283	.0473	1.37
3	0.370	4.31	.004	-	4.30	.00396	.0732	0.369
4	0.130	4.31	$.05 \pm .01$	12.46 ± 0.10	4.21	.01538	0.272	$0.022 \pm .006$
5	0.095	4.31	$.02 \pm .01$	11.47 ± 0.05	4.27	.0590	1.07	$0.008 \pm .002$

The data are given in Table XIII. The calculation of the final concentration of OH^- was made in one of two ways. In Experiments 1, 2, and 3, where the concentration of NaOH was fairly high, the concentration of NaOH was calculated by the formula

$$C_{\text{OH}^-} \text{ final} = C_{\text{OH}^-} \text{ start} - C_{(\text{HSe}^- + \text{Se}^{2-})} - 2C_{\text{Na}_2\text{Se}} - C_{\text{Se}^{2-}},$$

where C_{OH^-} indicates the concentration of the hydroxide ion etc. The $C_{\text{Se}^{2-}}$ has been calculated by first assuming that it is zero and then calculating the solubility product of Na_2Se . From the solubility product, the concentration of Se^{2-} is calculated and the correction is applied iteratively. In Experiments 4 and 5, where the concentration of OH^- is quite low, the glass electrode measurements were used for the calculation of the concentration of OH^- . The correction for the effect of Na^+ on the electrodes (0.07 to 0.10 pH) was taken from a graph published by Beckman Instruments, Inc. The activity coefficient of NaOH in this solution was assumed to be the same as that of NaOH at the same ionic strength. The activity coefficient of NaOH was taken from Robinson and Stokes.⁸ The activity of the water in this solution was assumed to be the same as in 4.2 m NaOH; i. e., 0.85. The results of the calculations are given in Table XIII. In Experiment No. 1 (in 3.72 m NaOH) the analysis was about 1.4 times as high as the value expected on the basis of the other data. This is probably due either to some coprecipitation of Ag_2O with the Ag_2Se or to the formation of Se_2^{2-} . This latter explanation is made more probable by the fact that the solution was noticeably yellow, whereas in the other experiments the yellow color, if present, was much lower in intensity. This experiment was discarded in calculating K_{sp} and K_{H} .

The dependence of the solubility is given by the following equations:

$$K_{\text{sp}} = C_{\text{Na}^+}^2 \cdot C_{\text{Se}^{2-}}, \quad (8)$$

$$K_{\text{H}} = \frac{C_{\text{HSe}^-} \cdot C_{\text{OH}^-}}{C_{\text{Se}^{2-}}}, \quad (9)$$

or

$$(C_{Se^{=}} + C_{HSe^{-}}) = \frac{K_{sp}}{C_{Na^{+}}^2} \left(1 + \frac{K_H}{C_{OH^{-}}}\right), \quad (10)$$

or

$$1 = \frac{K_{sp}}{(C_{Na^{+}})^2 (C_{Se^{=}} + C_{HSe^{-}})} + \frac{K_{sp} K_H}{(C_{Na^{+}})^2 (C_{Se^{=}} + C_{HSe^{-}}) (C_{OH^{-}})} \quad (11)$$

In these equations we assume that if the ionic strength is constant the activity coefficients are also constant. Figure 6 is a plot of

$$1/(C_{Na^{+}})^2 (C_{HSe^{-}} + C_{Se^{=}}) \text{ vs } 1/(C_{Na^{+}})^2 (C_{Se^{=}} + C_{HSe^{-}}) (C_{OH^{-}}).$$

The intercepts of a straight line drawn through these points should give $(1/K_{sp} K_H)$ and $(1/K_{sp})$ respectively. The two straight lines in Fig. 6 are my estimates of the limits of accuracy with which the points determine a straight line. From these lines I calculate $K_{sp}^{4.2} = 0.040 \pm .002$ and $K_H^{4.2} = 0.25 \pm 0.09$. The ionic strength of the solutions is 4.2 ± 0.1 .

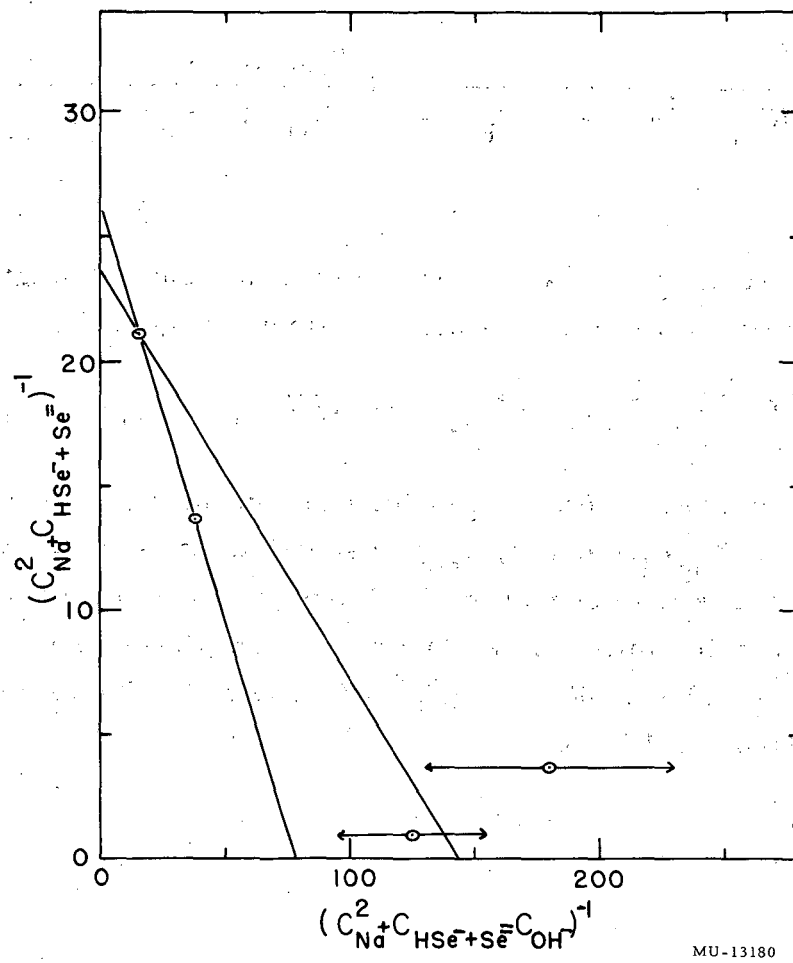


Fig. 6. Plot of data on Na_2Se solubility as a function of hydroxide concentration.

INTERPRETATION AND DISCUSSION

The experiments described above have measured

(a) $K_H^{0.2} = 1.1 \pm 0.4$ at 0.5°C and an ionic strength of 0.2, and

(b) $K_H^{4.2} = 0.25 \pm 0.09$ at 22°C and an ionic strength of 4.2. To calculate the second ionization constant of H_2Se , I have used the equations

$$K_H^0 = K_H^\mu \frac{\gamma_{\text{NaHSe}}^2 \gamma_{\text{NaOH}}^2}{\gamma_{\text{Na}_2\text{Se}}^3},$$

$$K_2^0 = \frac{K_w^0}{K_H^0},$$

and

$$\frac{d\Delta F^0}{dt} = -\Delta S^0,$$

where K_H^0 is the hydrolysis constant, in terms of activities; K_H^μ is the hydrolysis constant at an ionic strength of μ ; γ is the mean activity coefficient of the electrolyte at this ionic strength; K_2^0 is the second ionization constant of H_2Se ; K_w^0 is the ionization constant of H_2O , ΔF^0 is the change in free energy; and ΔS^0 is the change in entropy.

In making this calculation I have made the following assumptions:

(a) The activity coefficients of NaHSe and Na_2Se in these solutions are the same as those of NaOH and Na_2SO_4 respectively, at the ionic strength of the solutions, (b) Latimer's estimate of the entropies of HSe^- and Se^{2-} , namely, 22 and 0 eu respectively,¹⁴ are correct. These calculations give, from the measurements at 0.5°C , $K_2^0 = 10^{-14.5 \pm 0.4}$ at 22°C , where the limits of error come from the limits of error of the original measurement and my estimate of the reliability of the above assumptions. The measurement at 22°C gives $K_2^0 = 10^{-15.9 \pm 0.8}$. If both measurements are taken into account with their estimated limits of error, the best value is probably $K = 10^{-15.0 \pm 0.6}$.

Table XIV gives the pKs (where $\text{pK} = -\log K$) of several of the acids analogous to H_2Se .

Table XIV

Acid constants of H ₂ A				
Compound	pK ₁	pK ₂	pK ₂ -pK ₁	References
H ₂ O	15.7			
H ₂ S	7.0	12.9	5.9	26, 27
H ₂ Se	3.6	15	11.4	24
H ₂ Te	2.6	11	8.4	24, 19

Assuming a simple electrostatic model, one obtains the equations

$$pK_1 = \frac{C z_1 z_2}{r} = \frac{C}{r},$$

$$pK_2 = \frac{C z_1 z_2}{r} = \frac{2C}{r} \quad \text{and} \quad pK_2 - pK_1 = \frac{C}{r},$$

where C is a constant, z_1 and z_2 are the charges on the ions, and r is the distance between the atoms. On the basis of this model one would expect that pK_1 , pK_2 , and $pK_2 - pK_1$ would increase from the heavier members of the series to the lighter members. This does not occur. The discrepancy is shown most distinctly by $pK_2 - pK_1$, where the value is lower for H₂S than for either H₂Te or H₂Se. Therefore on the basis of this model one would conclude that the value of K_2 for H₂S is anomalous. The assignment of partially covalent character to the bonds does nothing to help resolve this anomaly.

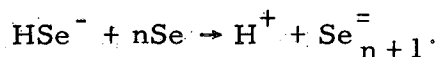
HEAT OF FORMATION OF Se^-

In order to get an appreciable fraction of the selenium as Se^- , the concentration of OH^- must be 2 to 4 m. Even in solutions so concentrated in OH^- , my measurements of the hydrolysis constant do not give the ratio of Se^- to HSe^- very accurately. For this reason, and also because of the difficulty of interpreting measurements at a high ionic strength, the measurement of the heat of formation of Se^- was abandoned. For the same reason Fabre's measurements of the heat of neutralization of H_2Se ¹⁸ cannot be used to calculate an accurate value for the heat of formation of Se^- : his measurements were at 0.25 M NaOH or lower, at which concentrations the ratio of Se^- to HSe^- is low.

CONCLUSIONS

Three methods for the analysis of alkaline H_2Se solutions have been developed. These involve (a) The air oxidation of the selenium to the metal and SeO_3^- , oxidation of all the selenium to SeO_3^- with HNO_3 , reduction of the SeO_3^- with hydrazine sulfate, and weighing the selenium as the metal; (b) the oxidation of Se^- with a solution of I_3^- in acetic acid with subsequent titration of the excess I_3^- with $\text{S}_2\text{O}_3^{2-}$; (c) precipitation of Ag_2Se by a solution of AgNO_3 in acetic acid, with subsequent titration of the excess silver with thiocyanate.

The second ionization constant of H_2Se has been determined by three separate methods. The methods and results are as follows. (a) The titration of H_2Se with KOH was followed with a glass electrode. The results indicated $K_2 = 2 \times 10^{-12}$. A visual observation that selenium was dissolving to form polyselenide and the fact that there is a discontinuity in the titration curve show that this result is due to the reaction



(b) On adding H_2Se to a 0.20 M KOH solution at 0.5°C the change in concentration of OH^- was measured with a glass electrode and the concentration of selenium was determined by analysis of the solution.

These data give, for the hydrolysis constant at 0.5°C , $K_2^{0.2} = 1.1 \pm 0.4$.

(c) The solubility of Na_2Se in solutions 4.2 m in Na^+ has been measured at 22°C as a function of the concentration of OH^- . These data give, for the solubility product of Na_2Se in terms of concentrations, $K_{\text{sp}}^{4.2} = 0.040 \pm .002$, and for the hydrolysis constant at 22°C in terms of the concentrations $K_{\text{H}}^{4.2} = 0.25 \pm 0.09$.

From the results of Methods (b) and (c) I estimate for the second ionization constant of H_2Se , $K_2^0 = 10^{-15.0 \pm 0.6}$ at 22°C .

Because of the unexpectedly small second ionization constant for H_2Se , the calorimetric determination of the heat of formation of $\text{Se}^{=}$ was impracticable.

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