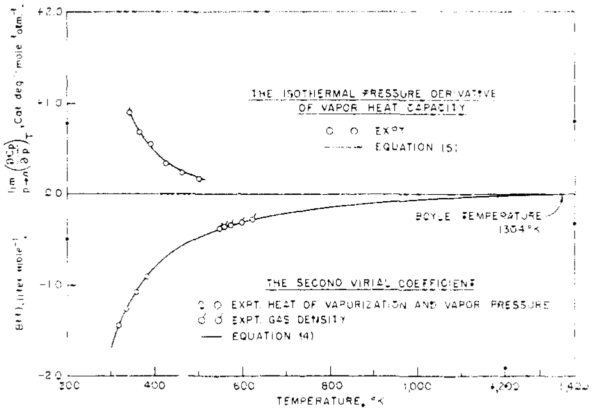

Fig. 6.—The second virial coefficient and the zero pressure limit of the isothermal pressure derivative of the vapor heat capacity of fluorobenzene.

lication.[21] A tabulation of the second virial coefficient function $F(\tau,t)$ that was used in determining the parameters has been given by Rowlinson[22] for the ranges $0.3 < \tau < 400$ and $0 < t < 1.5$; and a tabulation of the heat capacity function $\partial^2 F(\tau,t)/\partial T^2$ was given in ref. 21 for the ranges $0.5 < \tau < 3$ and $0 < t < 1.6$.[23] The observed values of the second virial coefficient that were used in determining the parameters are given in column 2 of Table IX. Between the temperatures 318.39 and 382.37°K., the observed values of $B(T)$ were determined from the Clapeyron equation and experimental vapor pressure and heat of vaporization data.[2] The observed values of $B(T)$ in the temperature range 548.26 to 623.30°K. are from Table VII. The observed values of $\lim_{p\to 0} (\partial C_p/\partial p)_T$, given in column 2 of Table X, were evaluated graphically from the molal heat capacity data of fluorobenzene given in Table X of reference 2.

TABLE X

A COMPARISON OF THE OBSERVED AND CALCULATED VALUES OF THE ISOTHERMAL PRESSURE DERIVATIVE OF VAPOR HEAT CAPACITY OF FLUOROBENZENE

T, °K.(Thermo.)	$\lim_{p\to 0} (\partial C_p/\partial p)_T$, cal. deg.⁻¹ mole⁻¹ atm.⁻¹ Obsd.[a]	Calcd. eq. 5[b]
343.19	0.90	0.92
364.20	.69	.69
389.21	.52	.51
426.23	.34	.34
463.25	.24	.24
500.27	.18	.18
513.40	..	.16
543.60	..	.13
604.00	..	.09
634.20	..	.08

[a] Evaluated, graphically, from the experimental values of the molal vapor heat capacity of fluorobenzene given in Table X of ref. 2. [b] The numerical values of the parameters used in equation 5 are: b_0 = 0.1995 liter mole^{-1}, θ = 302°K. and t = 0.9.

The method described above for treating the three parameters b_0, θ and t appears to be justified by the agreement between observed and calculated values of $B(T)$ and $\lim_{p\to 0} (\partial C_p/\partial p)_T$ for fluorobenzene. The calculated values for $\lim_{p\to 0} (\partial C_p/\partial p)_T$ which are shown in column 3 of Table X agree with the observed values within the experimental accuracy. Likewise, the calculated values for $B(T)$ listed in column 3 of Table IX agree with the observed values within the experimental accuracy over a temperature range in excess of 300°. The calculated values for $B(T)$ are shown in Fig. 6 up to the Boyle temperature 1304°K.

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[21] D. R. Douslin and G. Waddington, *J. Chem. Phys.*, **23**, 2453 (1955).

[22] J. S. Rowlinson, *Trans. Faraday Soc.*, **54**, 974 (1949).

[23] The tabulated values for the heat capacity function were calculated from the $Pj^{(2)}$ functions appearing in the report "The Virial Equation of State," by R. B. Bird and E. L. Spotz, University of Wisconsin CM-599 (1950).

[CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Heat, Free Energy and Entropy of the Ferrate(VI) Ion

BY ROBERT H. WOOD[1]

RECEIVED JULY 26, 1957

The heat of the reaction of aqueous K_2FeO_4 with perchloric acid (0.5 mole per kg. of water) to give O_2 and Fe^{+3} has been measured at 25°. From this datum the heat of formation of $FeO_4^=$(aq.) ($\Delta H_f^0 = -115 \pm 1$ kcal./mole) has been calculated. The entropy of $FeO_4^=$(aq.) has been estimated as 9 ± 4 e.u. From these values the free energy of formation of $FeO_4^=$(aq.) has been calculated; it is $\Delta F_f^0 = -77 \pm 2$ kcal./mole. The standard electromotive force of the half reaction $Fe(OH)_3 + 5OH^- \rightarrow FeO_4^= + 4H_2O + 3e^-$ has been estimated as $E^0 = -0.72 \pm 0.03$ volt. It has been verified that the ferrate ion at pH 10 is a dinegative species which decomposes only slowly. A method of analysis for aqueous K_2FeO_4 has been developed in which ferric hydroxide is removed by filtration and the total iron present is measured. This analysis has been shown to be accurate to better than ±1% by comparison with the volume of oxygen liberated on acidifying an aqueous K_2FeO_4 solution. The absorption spectrum of K_2FeO_4 has been measured.

Introduction

Although good methods for preparing and analyzing K_2FeO_4 have been described recently,[2a-4] no measurements of the thermodynamic constants of the aqueous ferrate(VI) ion have appeared in the

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[1] Abstracted in part from thesis, Robert H. Wood, University of California Radiation Laboratory unclassified document, UCRL-3751, 1957. The present address of the author is The University of Delaware, Newark, Delaware.

[2] (a) G. W. Thompson, L. T. Ockerman and J. M. Schreyer, THIS JOURNAL, **73**, 1379 (1951); (b) Von R. Scholder, H. V. Bunsen, F. Kindervater and W. Zeiss, *Z. anorg. allgem. Chem.*, **282**, 268 (1955).

[3] J. M. Schreyer, G. W. Thompson and L. T. Ockerman, *Anal. Chem.*, **22**, 691 (1950).

[4] J. M. Schreyer, G. W. Thompson and L. T. Ockerman, *ibid.*, **22**, 1426 (1950).

literature. In this investigation the heat of the reaction of aqueous K_2FeO_4 with 0.5*m* perchloric acid was measured. From this measurement the heat of formation of the ferrate ion was calculated. By estimating the entropy, the free energy of the ferrate ion can be calculated.

Preparation of K_2FeO_4.—The samples of K_2FeO_4 were prepared by the method of Thompson, Ockerman and Schreyer.[2a] One precaution should be noted in connection with the preparation. Aqueous K_2FeO_4 reacts quite readily with ethanol so that the K_2FeO_4 is destroyed if it is not thoroughly dried before being washed with ethanol. Analysis of the first sample by the methods of Schreyer, Thompson and Ockerman[3] gave for the total iron method 94.9 ± 0.4% K_2FeO_4 and 1.0% Fe(III) as Fe_2O_3; for the chromite method 94.3 ± 0.2% K_2FeO_4. The inaccuracy in the total iron method was due to an irreproducible blank. To reduce this error in the second sample, a Jones reductor was used instead of a $SnCl_2$ solution to reduce the Fe^{+3}. The second sample was found to contain 97.1 ± 0.1% K_2FeO_4 and 2.5% Fe^{+++} as Fe_2O_3.

Analysis of K_2FeO_4 Solutions.—After filtering out the $Fe(OH)_3$, the solutions of K_2FeO_4 in 10^{-4} *M*[5] NaOH used in the calorimetry were analyzed for total iron by: (1) adding acid to reduce the ferrate, (2) reducing the resulting Fe^{+3} with a Jones reductor and (3) titrating with Ce(IV) solution (ferrous *o*-phenanthroline sulfate as indicator).

This total iron method was confirmed by comparison with the oxidizing power of the solutions, as measured by the volume of oxygen liberated by 100 ml. of a solution on addition of 4 ml. of concentrated H_2SO_4 and $^1/_2$ g. of MnO_2. The MnO_2 was added because a small amount of H_2O_2 was formed under the conditions of the experiment. The MnO_2 decomposed the H_2O_2 and formed Mn^{++}, which was measured, and a suitable correction was applied to the gas volume. The K_2FeO_4 and sulfuric acid solutions were placed in a vacuum line and the pressure was lowered to remove dissolved gas. The solutions were then mixed and the resulting oxygen 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 I gives the results of these experiments.

TABLE I

VOLUME OF O_2 LIBERATED BY K_2FeO_4(aq)

Run no.	Total iron present, moles × 10^3	Equiv. of O_2, × 10^3	Correction for Mn^{++}	$\frac{\text{Equiv. } O_2}{\text{Fe}}$
1	1.729	5.188	−0.008	3.00
2	1.831	5.488	−0.03	2.98

I am indebted to Professor William L. 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 $FeO_4^{=}$ just after filtration. This experiment shows that under these conditions the total-iron method of analysis is accurate to 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,[6] who find a broad maximum at 5000 Å. and two minima, one at 3900 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 ± 0.01 mm. and the wave length 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 of solutions of K_2FeO_4 in 4 *m* NaOH were measured with a Beckman Model DU spectrophotometer at 5050, 5500, 6750, 3900 and 3800 Å. From these and the absolute extinction coefficient at 5050 Å. we have calculated the absolute extinction coefficients at several wave lengths. The molar extinctions and the slit widths used are given in Table II. For purposes of comparison the values from Kaufman and Schreyer are also given.[6] Their values were expected to be slightly higher because of the presence of about 15% $Fe(OH)_3$ in their solutions.

TABLE II

K_2FeO_4 SPECTRA

Wave length, Å.	Slit width, mm.	Extinction coefficient, l. /mole cm. Measured	Extinction coefficient, l. /mole cm. Kaufman and Schreyer
3800	0.10	341 ± 9	
3900	.10	318 ± 9	360
5050	.02	1070 ± 30	1130
5500	.02	967 ± 30	
6750	.04	211 ± 6	230

Heat of Formation of $FeO^{=}$.—The heat of formation of $FeO_4^{=}$ 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 *p*H at which the solutions were most stable. Solutions of K_2FeO_4 in strong alkali (3 *M* or above), although fairly stable,[7] were rejected because of formation of $Fe(OH)_3$ in the reaction with 0.5 *m* $HClO_4$. Our experience shows that aqueous K_2FeO_4 has another region of stability around *p*H 10 to 11. For instance: (a) Dilute solutions of K_2FeO_4 in 10^{-4} *M* NaOH show a relatively slow decomposition (see Fig. 1). (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 Ockerman[8] on the stability of

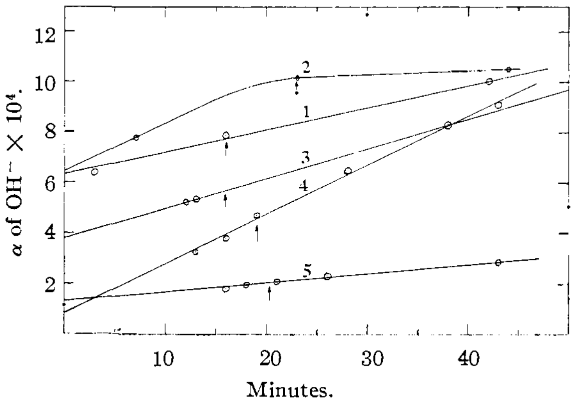

Fig. 1.—Activity of OH^- × 10^4 (or more precisely 10^{pH-10}) plotted against time elapsed since the ferric hydroxide was filtered out. The numbers indicate which run is being plotted (see Table III). The arrows indicate the time at which the R_2FeO_4 container in the calorimeter was broken in order to measure the heat of reaction.

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[5] *m* is used to denote moles per kg. of water and *M* is used to denote moles per liter of solution.

[6] Z. G. Kaufman and J. M. Schreyer, *Chem. Anal.*, **45**, 1312 (1951).

[7] R. H. Wood, University of California Radiation Laboratory Report UCRL-3751.

[8] J. M. Schreyer and L. T. Ockerman, *Anal. Chem.*, **23**, 1312 (1951).

TABLE III

HEAT OF REACTION OF K_2FeO_4

Results of 5 runs. Q_0 is the heat measured by the calorimeter; Q' is a correction, calculated from Fig. 2, from the heat of neutralization of the OH^- in the K_2FeO_4 solution; Q'' is the correction from Fig. 2 for the decomposition of the K_2FeO_4.

Run no.	K_2FeO_4 sample no.	Q_0, cal.	Q', cal.	Q'', cal.	Q_1, cal.	K_2FeO_4, mole × 10^3	ΔH_1, kcal./mole	$\Delta H'$, kcal. mole	ΔH_2, kcal. mole
1	1	64.7	−0.4	+0.1	64.4	0.947	−68.1	−0.1	−68.2
2	1	63.6	− .4	+ .3	63.5	.884	−71.8	− .1	−71.9
3	1	42.3	− .2	+ .1	42.2	.604	−69.8	− .7	−70.5
4	2	36.9	− .1	+ .3	37.1	.542	−68.5	− .8	−69.3
5	2	16.6	− .1	+ .1	16.6	.239	−69.5	−3.3	−72.8
								Av.	−70.4

aqueous K_2FeO_4 are consistent with these observations, and in addition show that the solutions are relatively unstable below *p*H 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 *p*H 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 *p*H meter with a blue glass electrode was used for this measurement. The electrode was standardized with Beckman *p*H 10 buffer. Figure 1 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.[9a,b] All runs were made at 25 ± 0.5°. 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 sodium hydroxide solution, which had been freshly standardized with potassium acid phthalate.

The main reaction in the calorimeter is given by

$$nK_2FeO_4\cdot 2.78H_2O + 0.500HClO_4\cdot 55.6H_2O \longrightarrow 2nKClO_4\cdot nFe(ClO_4)_3\cdot {}^3/_4nO_2\cdot(0.500 - 5n)HClO_4\cdot\left(55.6 + 2.78 + \frac{5n}{2}\right)H_2O \quad (1)$$

where *N* is the number of moles of K_2FeO_4 reacting. In addition there is a side reaction of OH^- in the K_2FeO_4 with $HClO_4$.

Hydrolysis of the K_2FeO_4 is shown to be negligible by the fact that Runs 4 and 5 (Fig. 1), 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 1×10^{-4} *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 presence of some sodium hydroxide in this sample.

Formation of hydrogen peroxide was shown to be unimportant by tests for hydrogen peroxide with Ti(IV) solution. In no case could the error due to hydrogen peroxide formation be greater than 0.5%. The oxygen 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 oxygen 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 ferric hydroxide is doubtful. A yellow color was barely visible in a 15-cm. column of the reaction products. For comparison purposes freshly precipitated ferric hydroxide was used. A solution containing 2×10^{-6} mole per liter of ferric hydroxide showed the same barely detectable yellow color. This would correspond to the presence of about 0.2% of ferric hydroxide.

Table III gives the results of five different calorimetric runs.

In calculating Q'' it is assumed that each mole of $FeO_4^=$ decomposing produces two moles of OH^-. It would be possible for the decomposition of the $FeO_4^=$ to produce either oxygen or hydrogen peroxide. In a separate experiment it was shown that 2×10^{-4} *M* $FeO_4^=$ reacts rapidly with 4×10^{-4} *M* hydrogen peroxide (half life = 20 sec.). Thus the decomposition of the aqueous K_2FeO_4 is given by

$$2FeO_4^= + 5H_2O \longrightarrow 2Fe(OH)_3 + 4OH^- + 3/2O_2 \quad (2)$$

The heat of reaction 1 is represented by Q_1, which is the sum of Q_0, Q' and Q''. The corresponding enthalpy per mole of iron for reaction 1 is given by ΔH_1. The correction to reduce reaction 1 to standard conditions, *i.e.*

$$K_2FeO_4 + 5HClO_4 \longrightarrow 2KClO_4 + Fe(ClO_4)_3 + 3/4O_2(aq.) + 5/2H_2O \quad (3)$$

is represented by $\Delta H'$. The net reaction is

$$FeO_4^=(aq.) + H^+(aq.) \longrightarrow Fe^{+3}(aq.) + 3/4O_2(aq.) + 5/2H_2O \quad (4)$$

This correction is the sum of the corrections for (a) the heat of reaction of the 50 ml. of water in the K_2FeO_4 solution with the 1 liter of $HClO_4$ solution, (b) the heat of dilution of the K_2FeO_4 solution, (c) the heat of dilution of the $HClO_4$ used up in the reaction, (d) the relative partial molal heat content of the $KClO_4$ formed, (e) the relative partial molal heat content of the H_2O formed, and (f) the relative partial molal heat content of the $Fe(ClO_4)_3$ formed. Bureau of Standards values have been used in this calculation whenever available and unless a reference is given Bureau of Standards values may be assumed.[10] The quantity $\Delta H'$ was calculated as follows.

(a) The correction for the heat of reaction of 50 ml. of H_2O with 1 liter of 0.500 *m* $HClO_4$ (ΔH

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(9) (a) H. W. Zimmerman and W. M. Latimer, THIS JOURNAL, **61**, 1550 (1939); (b) B. J. Fontana, "The Chemistry and Metallurgy of Miscellaneous Materials," National Nuclear Energy Series IV, 19B, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 321.

(10) National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1952.

= 1.0 ± 0.1 cal.) was measured with the calorimeter.

(b) The heat of dilution of K_2FeO_4 was assumed to be equal to the heat of dilution of K_2SO_4.

(c) The heat of dilution of $HClO_4$ is known.

(d) The relative partial molal heat content of $KClO_4$ in 0.5 *m* $HClO_4$ was estimated from a measurement of the reaction

$$0.005KClO_4 \cdot 2.78H_2O + 0.500HClO_4 \cdot 55.6H_2O \longrightarrow 0.005KClO_4 \cdot 0.500HClO_4 \cdot 58.4H_2O. \quad \Delta H = -1.3 \text{ cal.} \quad (5)$$

This value was combined with the heat of dilution of $KClO_4$ together with the heat of the reaction of 50 ml. of H_2O with 1 liter of 0.500 *m* $HClO_4$ ($\Delta H = +1.0$ cal., see above) to get a value for the relative partial molal heat content of infinitely dilute $KClO_4$ in 0.5 *m* $HClO_4$, $\bar{L}_2 = -1.1$ kcal./mole.

(e) The relative partial molal heat content of the water formed was negligible.

(f) No value for the relative partial molal heat content of $Fe(ClO_4)_3$ in 0.5 *m* $HClO_4$ has been reported. We have estimated it by using Fontana's value ($\Delta H = 9.53 \pm 0.04$ kcal./mole)[9b] for the reaction in 0.5 *m* $HClO_4$

$$Fe^{++} + H^+ \longrightarrow Fe^{+++} + 1/2H_2 \quad (6)$$

together with an estimation of the relative partial molal heat of dilution of $Fe(ClO_4)_2$.

This estimate was made by a comparison of other 2-1 electrolytes. Harned and Owen[11] give the relative partial molal heats of dilution of the chlorides, bromides and nitrates of magnesium, calcium, strontium and barium. In this comparison the nitrates, except magnesium nitrate, were not used since they show considerable ion pairing.[12] A reasonable extrapolation of the relative partial molal heats of dilution curves to an ionic strength of 0.5 ($m = 0.167$) gives values from 0 to +700 cal. Since the size of the cation does not seem to make much difference and since the bromides have lower values, I have estimated $\bar{L}_2$ for $Fe(ClO_4)_2$ as 0 ± 500 cal. A combination of this value, Fontana's value for reaction 6, and the National Bureau of Standards values at infinite dilution gives the relative partial molal heat content of infinitely dilute $Fe(ClO_4)_3$ in 0.5 *m* $HClO_4$, $\bar{L}_2 = -0.2 \pm 0.5$ kcal./mole.

The weighted average of the five runs for ΔH_2 (eq. 4) is −70.4 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 $FeO_4^{=}$ as $\Delta H_f^0 = -115 \pm 1$ 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_2O	−68.32 kcal./mole

Entropy and Free Energy of $FeO_4^{=}$.—The entropy of the aqueous $FeO_4^{=}$ 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.[13] Helferich 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.[14] For this reason I have estimated the entropy of $FeO_4^{=}$ aqueous as 9 ± 4 e.u.

Entropies of $MO_4^{=}$(aq) (from NBS)

Ion	S^0, e.u.
$SO_4^{=}$	4.1
$SeO_4^{=}$	5.7
$CrO_4^{=}$	9.2

From this estimate of the entropy, National Bureau of Standards values ($S^0_{Fe} = 6.5$ e.u., $S^0_{O_2} = 49.0$ e.u.), and the measured heat of formation (ΔH_f^0 $FeO_4^{=} = -115 \pm 1$ kcal./mole), I calculate for the free energy of formation $\Delta F_f^0 = -77 \pm 2$ kcal./mole.

The corresponding standard electromotive force for the half reaction

$$Fe^{+++} + 4H_2O \longrightarrow FeO_4^{=} + 8H^+ + 3e^-$$

is $E^0 = -2.20 \pm 0.03$ v.[15] Latimer's estimate of the entropy of ferric hydroxide[13] gives a standard electromotive force $E^0 = -0.72 \pm 0.03$ v. for the half reaction

$$Fe(OH)_3 + 5OH^+ \longrightarrow FeO_4^{=} + 4H_2O + 3e^-$$

There is no value in the literature for this standard electromotive force except for the very rough estimate, $E_B > -0.9$, made by Latimer on the basis of chemical evidence.[13]

Acknowledgments.—I am indebted to Prof. Wendell M. Latimer for his suggestion of this research project. Unfortunately, Prof. Latimer did not live to see its completion. I wish also to express my appreciation to Professor Richard E. Powell and to Professor Robert E. Connick for their many helpful suggestions in connection with this work.

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[11] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 541.

[12] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[13] W. M. Latimer, "Oxidation Potentials," Prentice-Hall Book Co., New York, N. Y., 1953.

[14] Von B. Helferich and K. Lang, *Z. anorg. allgem. Chem.*, **263**, 169 (1950).

[15] In this paper Latimer's sign convention (strong oxidizing agents have a negative sign) is used.