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THERMODYNAMICS OF THE PARTITION OF OXINE
AND ITS NI(II) AND FE(III) CHELATES

by

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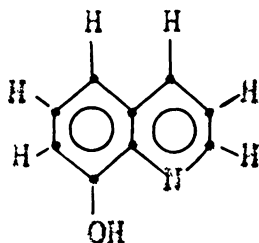
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I. INTRODUCTION

8-Hydroxyquinoline^a --to be known as oxine in this work--is of particular interest among chelating agents because it reacts with most metals to form chelates--to be known as oxinates in this work--that are insoluble in water but soluble in organic solvents. Several investigations have been made of the ionization constants of oxine, the partition coefficient of oxine between aqueous buffers and organic solvents, the formation constant of the oxinates and the partition of the oxinates between aqueous buffers and chloroform. Since the determinations were done in a variety of media, it is difficult to compare the values. Little data have been reported for the above equilibrium constants of oxine and the oxinates as a function of temperature.

a



The present work reports the thermodynamic quantities ΔG° , ΔS° , and ΔH for the ionization of oxine, the partition of oxine between aqueous buffers and several organic solvents; specifically, benzene, toluene, nitrobenzene, and chloroform, and for the partition of nickel (II) oxinate and iron (III) oxinate between aqueous buffers and chloroform.

The determination of equilibrium constants such as stability constants and partition coefficients has been a productive approach to the understanding of chelates and the relationships which govern their formation and structure. The thermodynamic quantities ΔG° , ΔS° , and ΔH may be calculated by determining the equilibrium constants for the pertinent reactions at several temperatures. These quantities can give insight into the structure of the chelate and the nature of the solvent-chelate interaction.

It was also of interest to determine whether the McDevit and Long theory for nonelectrolytes in aqueous salt solutions could be applied.

II. REVIEW OF THE LITERATURE

Oxine has been used for the analytical determination of many metals, since it forms chelates which are slightly soluble in water. The analytical methods have been extensively covered in the monograph of Berg (5) and by Hollingshead (37).

In general, the structure of a chelate has been found to depend upon the coordination number of the metal ion, the size and number of the rings the organic anion may form, and the arrangement of the rings with respect to one another (59). The stability of a chelate has been found to increase with an increase in the number of rings (12). Calvin and Bailes (12) have shown an increase in the stability constant with an increase in the base strength of the organic anion.

Inner-complexes (non-ionic chelates) have a low water solubility and high solubility in organic solvents provided the complex is relatively free of groups that can be hydrated. Aqueous solubility of a chelate cannot be used as a criterion for stability as the chelate can have an intrinsic solubility. The intrinsic solubility is the equilibrium concentration

in solution of that metal-containing species present in the crystal.

For a non-ionic solute that exists in the same molecular form in the two phases, the equilibrium constant for the extraction equilibrium has been shown to be approximately equal to the ratio between the solubilities of the solute in the two phases (50). Kolthoff and Sandell (46) and Irving and Williams (42) have derived theoretical relationships to interpret the course of chelate extraction. The solvent extraction of a neutral chelate has been found to depend upon the hydrogen ion concentration of the aqueous layer, the stability of the chelate, and the concentration of the organic chelating agent. A comprehensive review of solvent extraction of metal chelates can be found in the book by Morrison and Freiser (65).

Oxine has been shown to form intermediate charged complexes of the form MeOx_n^{n-1} (78). In the determination of the stability constants of metal oxinates it is necessary to incorporate the equilibrium constants for these charged complexes. Many of the original determinations of the stability

constants of metal oxinates did not take into account the possibility of these intermediate complexes (49). Recently Nasanen and co-workers (67,68,69,70), Fresco and Freiser (30,31), and Irving and co-workers (41,43) have determined the stability constants for many metal oxinates taking into account these intermediate complexes.

The relative stabilities of the divalent metal oxinates have been found to be $Cu > Ni > Co > Zn > Pb > Cd > Mn > Mg$ (44), while Irving and Williams (43) found the following order which also applied to several other chelating agents; specifically, quinaldinic acid, salicylaldehyde, anthranilic acid, dithizone, and cupferron, $Cu > Ni > Co > Fe > Mn$. Irving and Williams (43) have correlated the regularity of this stability sequence with the monotonic decrease in the ionic radii and the monotonic increase in the second ionization potential in passing from manganese to copper.

Charles (14) and Charles and Langer (15) have shown that the temperature range of volatilization and the heat of precipitation of the divalent metal oxinates--copper, nickel, cobalt, zinc, lead, manganese,

and strontium--are functions of the metal ion electronegativity.

The crystal structures of the copper, nickel, cobalt, zinc, and lead oxinates were shown by x-ray diffraction to be isomorphous dihydrates (60,61). The metal atom and bonded ligand atom lie in a plane, with the two water molecules above and below the plane at the corners of a distorted octahedron. In a thermogravimetric analysis of several metal oxinates Borrel and Paris (7) found all the oxinates to have definite stoichiometry except titanium and zirconium. Copper (II) salts upon reaction with oxine in both methanol and water solutions were found to exist in two forms: $\text{Cu}(\text{C}_9\text{H}_6\text{NO})\text{X}$, where X is chloride or bromide, and $\text{Cu}(\text{C}_9\text{H}_6\text{NO})_2$ (25). Cadmium (81) and strontium (23) formed compounds of the form $\text{MOx}_2 \cdot 2\text{HOx}$.

Dyrssen studied the extraction of strontium into chloroform, using oxine (23). He found that strontium oxinate was extracted into chloroform as $\text{SrOx}_2 \cdot 2\text{HOx}$, as shown by the fact that the solubility in the organic phase was found to be proportional to the square of the concentration of oxine in the organic phase. Thus, a high concentration of organic reagent favors the

extraction of strontium into the organic layer. Hellwege and Schweitzer (81) found this to be true of the cadmium system also.

Few systems have been investigated thoroughly, but recently Freiser and co-workers (10,47,84) have reported a comprehensive study of the extraction of divalent metals into acetylacetonate with acetylacetonate as the chelating agent. Stary (83) in a systematic study of the solvent extraction of 32 metal oxinates into chloroform solution reports the stability of the metal oxinates decreases with an increase in ionic radius. Hellwege and Schweitzer (81) have done the only thermodynamic study of the partition of a metal oxinate. They have studied the extraction of cadmium oxinate into chloroform as a function of temperature.

The logarithm of the partition coefficient of oxine between aqueous buffers and chloroform has been reported for a variety of solutions and temperatures. The following systems are at 0.1M ionic strength for the chloroform extraction: at 18°C. Lacroix (49) found $\log P$ to be 2.9, at 25°C. Dyrssen (23) and Fresco and Freiser (31) found $\log P$ to be 2.66, while Hellwege and Schweitzer (81) gave the following equation to represent

their data for the chloroform system as a function of temperature:

$$\log P = 1.35 + 370 T^{-1}$$

with a value of $\log P$ being 2.6 at 25°C. Since the actual data were good to only ± 0.1 pH units, the equation gives more significant figures for the logarithm of the partition coefficient than is warranted.

At a very low ionic strength Moeller and Pundsack (64) found $\log P$ to be 2.56 at 25°C. Spindler (77) calculated $\log P$ to be 2.80 at 25°C. from the solubility of oxine in chloroform (431 g. per liter or 2.97M) and in water saturated with chloroform (0.681 g. per liter or 4.75×10^{-3} M). Berges (77) found $\log P$ to be 2.85 at 20°C. from the solubility of oxine in chloroform (2.55M) and the solubility in water (3.56×10^{-3} M).

Dyrssen (24) found a small dependence of the distribution constant of oxine on the concentration of oxine in chloroform. These data show an increase of 0.03 in $\log P$ for every 0.1M increase in oxine concentration. Dyrssen (23) found that oxine

perchlorate may exist in organic solvents and found the log P to be -0.96 at 25°C. from 0.1M perchlorate solution.

Umland and Puchelt (87) found the log P to be 2.60 at 25°C. at about 0.1M ionic strength for the extraction of oxine into benzene.

Zharovskii and Chernov (89) found the solubilities of oxine in chloroform, ethylene chloride, benzene, and carbon tetrachloride. They also determined the distribution coefficient of oxine between an aqueous solution and these organic solvents. The extraction was found to decrease in the order chloroform > ethylene chloride > benzene > toluene > carbon tetrachloride. The values for the partition coefficients in these experiments are an order of magnitude low. Zharovskii and Chernov found that the extraction of the iron derivative of oxine by these solvents paralleled the extraction of oxine.

The determination of the dissociation constants of oxine has been done in a variety of ways, with many different values. Table 1 gives the pK_1' and pK_2' (the negative logarithms of the dissociation constants in salt media), the method, the temperature, and the investigators.

TABLE 1

Literature Review of the Dissociation
Constants of Oxine

pK_1'	pK_2'	Method	Reference
4.5	9.7	Calorimetric at 18°C. No data.	45
4.8	10.36	Salt hydrolysis and partition measurements.	28
	10.38	Solubility of oxine in an alkaline buffer, 25°C.	85
	10.37	Spectrophotometric at room temperature.	85
5.23	9.70	Potentiometric titration at 20°C. and 0.1M ionic strength.	49
$5.000 \pm$ 0.006	$9.658 \pm$ 0.006	Potentiometric titration in 0.1M NaClO ₄ at 25°C.	23
5.33	9.60	Derived from scandium oxinate partition at 25°C. and approximately 0.1M ionic strength.	37
	$\log K =$ $7.30 +$ $710T^{-1}$	Partition measurements in 0.1M NaClO ₄ from 15° to 50°C.	81

TABLE 1 (Continued)

pK_1°	pK_2°	Method	Reference
5.011		pH measurement when the ionic species were approximately stoichiometric at 20°C.	66
	9.305	Same method as above, but at 25°C.	66
4.910	9.814	Spectrophotometric at 25°C.	66
5.00 ± 0.10	9.85 ± 0.05	Spectrophotometric and solubility measurements at 20°C.	40

III. EXPERIMENTAL

A. Chemicals

All the inorganic chemicals used in these experiments were of reagent grade quality, except the potassium acid phthalate, which was of primary standard quality. Sodium chloride, potassium chloride, and potassium nitrate were recrystallized from twice distilled water and were dried in an oven at 120-130°C. for 24 hours. Sodium acetate, potassium acetate, sodium dihydrogen phosphate, and potassium dihydrogen phosphate were dried in an oven at 120-130°C. for 24 hours and were used without further purification. Sodium perchlorate was used as received.

Oxine was purified by two methods; specifically, recrystallization and steam distillation.

(a) Recrystallization. Oxine (Fisher Scientific Company) was dissolved in boiling ethanol, and twice distilled water was added to the boiling solution until the first signs of crystallization. Several drops of ethanol were added to redissolve the oxine and the solution was allowed to cool overnight. The crystals formed were collected on a suction filter and washed three times with twice distilled water. The white

crystals were dried overnight in a vacuum desiccator over calcium chloride and showed a melting point of 73.8-74.8°C. [72-74°C. (22)].

(b) Steam distillation. A 3 g. sample of oxine in 350 ml. of once distilled water was placed into a 500 ml. side arm distillation flask. A 250 ml. side arm distillation flask was attached to the side arm of the larger flask as a receiving vessel. A stream of cool water was sprayed on the receiving flask to cool the distillate. The first 75 ml. of distillate was discarded and a 200 ml. middle cut was collected. The crystals from the distillation were collected on a suction filter and washed three times with twice distilled water. The white crystals were dried overnight in a vacuum desiccator over calcium chloride and showed a melting point of 73.8-74.8°C. The oxine was stored at 13 mm. Hg. in a vacuum desiccator covered with tape to prevent light from entering.

Since the analytical method for this work was to be spectrophotometry, the oxine was used from the steam distillation rather than from the recrystallization from alcohol. It was felt that

adsorbed alcohol might cause inconsistent spectrophotometric readings.

The purity of the oxine was established by bromination of a 25.00 ml. aliquot portion of a standard oxine-hydrochloric acid solution, which was placed in an iodine flask and diluted with twice distilled water to 75 ml. (88). Potassium bromide (0.5 g.) was added and the solution stirred magnetically and cooled in an ice-water mixture. Twenty-five ml. of concentrated hydrochloric acid and 35 ml. of sodium acetate were added and the flask immediately stoppered. A 25% potassium iodide solution was placed in the neck of the iodine flask. The oxine solution was stirred and cooled to insure a negative pressure allowing the potassium iodide solution to enter the flask. The solution was titrated rapidly to a starch endpoint with standard sodium thiosulfate solution. The error in the titrated value and in the amount of oxine placed in the standard solution was two parts per thousand.

Thiophene free benzene (Baker reagent, b.p. 80.1°C.) was distilled through a Vigreux column. The middle cut used showed a boiling point of 78.6°C./714 mm. Hg. (86).

Toluene (Baker reagent) was used as received. It showed a boiling point of 109°C./713 mm. Hg. (86).

Chloroform (Baker reagent, b.p. 61.6°C.) was purified by washing with twice distilled water (31). A 300 ml. aliquot portion of chloroform was extracted with three 75 ml. samples of twice distilled water.

Nitrobenzene [m.p. 5.7°C.; $n_{24.5}$ 1.5501 (86)] (Fisher Scientific Company) was used as received, because attempts to purify it by distillation resulted in substantial decomposition. The liquid had a slight yellow color, which showed a refractive index at 24.5°C. of 1.5507 and a melting point of 5.6-5.7°C.

1. Preparation of Standard Solutions.

Ferric Chloride. Concentrated hydrochloric acid was added to 1.0428 g. of ferrous ammonium sulfate hexahydrate in 20 ml. of twice distilled water to make the solution acidic. Hydrogen peroxide (10 ml. of 30% solution) was added to oxidize the ferrous ion to ferric ion. Warming the solution destroyed the excess hydrogen peroxide. Ferric hydroxide was precipitated by the addition of filtered concentrated ammonium hydroxide to the cool solution. The mother liquor was decanted and the precipitate washed three times with 10 ml.

portions of hot water. The precipitate was dissolved in concentrated hydrochloric acid and diluted with twice distilled water to 1.000 liter of solution. The method of Gran (33) was used to determine the hydrogen ion concentration of the standard iron solution.

Nickelous Chloride. Twice distilled water was added to 0.3065 g. of nickelous chloride hexahydrate (Baker reagent, freshly opened jar) to give 1.000 liter of solution.

2. Preparation of Nickel Oxinate (88).

A 100 ml. aqueous solution of nickelous chloride hexahydrate (2 g.), ammonium chloride (2 g.), phenolphthalein (20 drops of a 1% alcoholic-water solution), and enough 6M ammonium hydroxide (filtered) to turn the solution blue, was heated to 70-80°C. A yellow-green precipitate formed upon addition of a 5% oxine in 2N acetic acid solution. The precipitate was digested for one half-hour on a steam bath and then the hot solution was filtered through a glass filter crucible (fine pore). The precipitate was washed three times with a 1% ammonium hydroxide solution and dried for one and one-half hours at 120°C. and then for 14 hours at 230°C. (7).

B. Apparatus

Tumbler. A glass and stainless steel aquarium (29" x 12" x 17" inside dimensions) was insulated with alternate layers of asbestos sheeting and aluminum foil. The entire aquarium was then encased in masonite.

The temperature of the water in the tumbler was held to $\pm 0.1^\circ\text{C}$. of the experimental temperature with a Fisher unitized control box consisting of 500 watt heater, stirring motor, and mercury temperature sensor.

The tumbling device was made from one-half inch (inside diameter) copper tubing (K gage) fitted with a four inch V-pulley, which was secured to a 26 sprocket bicycle pulley. The copper tubing revolved in shoulders made from teflon and graphite.^a The teflon shoulders were embedded in wooden blocks for support. The wooden blocks were secured to bakelite boards attached to the sides of the aquarium by six inch "C" clamps. A Dayton gear-box motor (one-half horsepower, 1500 r.p.m. Westinghouse motor adapted to 89 r.p.m.) was fitted with a three inch V-pulley attached to a ten sprocket bicycle pulley and connected to the larger

^aThe teflon shoulders used in the tumbler were courtesy of Miss Rose Shaly, Chemical and Power Products, Inc., New York 4, New York.

pulley by a bicycle chain. The apparatus rotated at the rate of 36 r.p.m. The tumbling vessels, 100 ml. volumetric flasks with screw caps, were secured to the copper tubing with clamps and entirely immersed in the bath.

pH meters. The Beckman Model G pH meter and the Radiometer pHM4 meter, fitted with general purpose glass electrodes, were used to determine the pH in these experiments.

Spectrophotometer. All spectrophotometric measurements were made using a Beckman DU spectrophotometer, equipped with a Beckman Dual Thermospacer Set. Water from a Fisher Unitized constant temperature bath was pumped through the thermospacers and held the temperature constant to $\pm 0.1^{\circ}\text{C}$. of the experimental temperature.

C. The Extinction Coefficients
of H_2Ox^+ and Ox^-

A series of oxine in hydrochloric acid and oxine in sodium hydroxide solutions was prepared from aliquot portions taken from three stock oxine in hydrochloric acid and oxine in sodium hydroxide solutions. Each concentration of oxine over the range of investigation was reproduced from each of the three stock solutions in order to insure the reproducibility of the absorbance reading.

The solutions were prepared by placing an aliquot portion of the desired stock solution into a 100 ml. volumetric flask and diluting with 0.6M hydrochloric acid or 0.1M sodium hydroxide for the determination of the absorbance of H_2Ox^+ and Ox^- , respectively. A sample of the solution was placed in a quartz cell, which had been rinsed three times with the solution, and the absorbance readings for the solution taken at 358 m μ for the H_2Ox^+ and at 355 m μ for the Ox^- at 25.0°, 35.0°, and 45.0°C. The data were analyzed by a Beer's law graph of absorbance versus concentration and the extinction coefficient determined from the slope of the resulting line.

D. The Extinction Coefficients of Ferric and
Nickelous Oxinates

A series of ammonium hydroxide-ammonium chloride solutions varying in metal ion concentration was prepared and extracted with an oxine-chloroform solution in order to determine the applicability of Beer's law to the study of the oxinates. The solutions were prepared by placing an aliquot portion of the standard metal ion solution into a screw top flask and diluting the solution with an ammonium hydroxide-ammonium chloride buffer. The extraction of iron (III) and nickel (II) oxinates into chloroform is essentially complete at a pH of eight (62). A 25.00 ml. solution of 0.05M oxine in chloroform was added to the aqueous solution and the two phases tumbled at 25.0°C. for one-half hour and one hour for iron and nickel, respectively. After tumbling, the two phases were separated and a sample of the chloroform layer placed in a quartz cell, which had been rinsed three times with the solution. The absorbance readings were made in the spectrophotometer at 25.0°, 35.0°, and 45.0°C. at 470 m μ and 395 m μ for iron oxinate and nickel oxinate, respectively. The data were analyzed by a Beer's law

graph of absorbance versus concentration and the extinction coefficient determined from the slope of the resulting line.

E. The Measurement of the pH as a
Function of Temperature

The operational definition of pH is

$$\text{pH} = \text{pH}_s + \frac{F(E - E_s)}{2.303 RT}$$

where:

pH = the pH of the unknown liquid

pH_s = the stated pH of the reference buffer

E = the difference in potential between the reference electrode and glass electrode in the unknown liquid

E_s = the difference in potential between the reference electrode and the glass electrode in the reference buffer.

The pertinent equations for the temperatures of interest are:

$$\text{pH} = \text{pH}_s + \frac{E - E_s}{0.0592} \quad \text{at } 25.0^\circ\text{C.}$$

$$\text{pH} = \text{pH}_s + \frac{E - E_s}{0.0611} \quad \text{at } 35.0^\circ\text{C.}$$

$$\text{pH} = \text{pH}_s + \frac{E - E_s}{0.0631} \quad \text{at } 45^\circ\text{C.}$$

To determine the pH at temperatures other than at 25.0°C., the temperature compensator was kept at the 25°C. setting and the pH meter used essentially as a millivolt meter to measure $E - E_s$. The meter was standardized at the given temperature using 0.05M potassium acid phthalate as a standard, since the pH of 0.05M potassium acid phthalate is accurately known as a function of temperature.

In order to calculate the pH at 35.0° and 45.0°C. from the experimental quantities, the following equations were used,

$$\text{pH} = \text{pH}_s + \frac{0.0592 (\text{pH}_n - \text{pH}_s)}{0.0611} \quad \text{at } 35.0^\circ\text{C.}$$

$$\text{pH} = \text{pH}_s + \frac{0.0592 (\text{pH}_n - \text{pH}_s)}{0.0631} \quad \text{at } 45.0^\circ\text{C.}$$

since $0.0592 (\text{pH}_n - \text{pH}_s) = E - E_s$. pH_n is the nominal pH of the unknown liquid at the experimental temperature.

The pH meters were tested with two known buffer solutions in order to see if the above equations could

be applied. The results of these experiments showed that the above equations could be applied.

F. Determination of pK_1' and pK_2' of Oxine

The two dissociation constants of oxine were determined by two essentially independent methods; specifically, spectrophotometry and pH titration.

(a) Spectrophotometric. A series of oxine solutions in varying acetic acid-acetate buffers was prepared in order to measure the first dissociation constant of oxine. Each solution was prepared in a volumetric flask from a standard oxine-hydrochloric acid solution, standard sodium acetate solution, and sodium chloride solution at room temperature. Each solution was diluted with twice distilled water to give the desired concentration at the experimental temperature.

After equilibration for one hour in the temperature bath, a sample was placed in the spectrophotometer. The sample was allowed to come to thermal equilibrium (one-half hour) and the H_2Ox^+ concentration determined at 358 m μ .

From the pK_a of acetic acid (57) and the acetic acid-acetate ratio, the pH of the solution was calculated.

In order to determine the effect of oxine on the pK_a of acetic acid, several solutions of known acetic acid-acetate ratios were prepared in sodium chloride medium with and without oxine. The pH of the solutions was measured with the Beckman General Purpose electrode and the Beckman Model G pH meter. The values for the pK_a of acetic acid found in these experiments agreed with one another and with the value of MacInnes, Belcher, and Shedlovsky (57).

A series of oxine solutions in varying carbonate-bicarbonate buffer ratio was prepared in order to determine the second dissociation constant of oxine. Each solution was prepared in a volumetric flask from a standard oxine-sodium carbonate solution, standard sodium bicarbonate solution, and sodium chloride solution at room temperature under nitrogen. The solution was diluted with twice distilled water (boiled to eliminate carbon dioxide) to give the desired concentration at the experimental temperature.

After equilibration for one hour in the temperature bath a sample was placed in the spectrophotometer. Again

the sample was allowed to come to thermal equilibrium (one-half hour) and the Ox^- concentration determined at 355 mu. The pH of the solution was measured with the Beckman Model G pH meter using the Beckman General Purpose electrode versus a standard borate solution.

(b) Potentiometric. A standard oxine-hydrochloric acid solution was diluted with sodium chloride solution to make 100.00 ml. of 0.1M ionic strength. In a constant temperature bath the solution was titrated with standard sodium hydroxide from a microburet. The solution was maintained at 0.1M ionic strength. The solution was stirred and the pH determined with a Radiometer pH4 meter with a General Purpose electrode.

The dissociation constants were determined analytically by the method of Gage (32).

1

G. The Determination of pK_1 of Oxine as
a Function of the Ionic Strength

A series of oxine solutions varying in acetic acid-acetate buffer ratio and varying in ionic strength from 0.1M to 1.5M was prepared in order to determine

the first dissociation constant of oxine as a function of the ionic strength. Each solution was prepared from a standard oxine-acid solution, standard acetate solution, and a background salt. Aside from the hydrogen ion and the acetate ion, the solutions were prepared so as to have only one cation and one anion as the supporting electrolyte. For example, in a solution prepared from oxine-hydrochloric acid and sodium acetate, sodium chloride would be used as the background salt. For a solution prepared from oxine-hydrochloric acid and potassium acetate, potassium chloride would be used as the background salt. Each solution was diluted with twice distilled water to give the desired concentration at 25.0°C.

After equilibration for one hour in the temperature bath a sample was placed in the spectrophotometer. The sample was allowed to come to thermal equilibrium for one-half hour and the H_2Ox^+ concentration determined at 358 m μ . The pH of the solution was measured with the Beckman Model G pH meter using the Beckman General Purpose electrode versus a standard potassium acid phthalate solution.

H. Procedure for Oxine and Chelate Distribution Measurements

The procedure for the oxine and chelate distribution measurement will be described in three parts; specifically, preparation, tumbling, and analysis of the solutions.

(a) Preparation. The aqueous phase was prepared by addition from a buret of the required number of moles of each standard solution of salt at room temperature and diluting with twice distilled water to give the desired concentration at the experimental temperature. A 25.00 ml. aliquot portion of the solution was pipetted into a screw top 100 ml. flask, which was painted black to prevent decomposition of the chelate by light. The organic phase was prepared by weighing the required amount of oxine into a volumetric flask and diluting with the organic solvent, which was saturated with the aqueous solution, at the experimental temperature. The organic solution was pipetted into the flask containing the aqueous sample using the same pipette. Volume change of each phase upon transfer to the tumbling vessel was limited by having the pipette at the experimental temperature.

(b) Tumbling.

Oxine. A tumbling time of three hours was found to give good equilibrium values for the distribution coefficient in all of the solvents.

Ferric Oxinate. A tumbling time of one hour was found to give reproducible results.

Nickel Oxinate. A tumbling time of greater than three and one-half hours but less than four hours was necessary to achieve reproducibility in the nickel oxinate system. At times less than three and one-half hours the absorbance of the organic phase changed as a function of time indicating non-equilibrium. After four hours scum formation at the organic-aqueous interface caused inconsistent absorbance readings.

(c) Analysis. After tumbling under water the flasks were transferred to another constant temperature bath. Exerting a positive air pressure as the pipette passed through the organic phase (top layer), an aliquot portion of the aqueous phase was placed into a dry glass holder^a 2-1/2" deep, 2-1/4" in diameter at the top, and 1-1/4" in diameter at the bottom. The pH of the

^aCourtesy of Dr. J. W. Murray.

solution at the experimental temperature was measured using a Beckman General Purpose glass electrode with shielded leads. It was found convenient to transfer the solutions to six inch test tubes when the organic layer was heavier (chloroform) than the aqueous layer.

In the distribution of oxine experiments a 15.00 ml. aliquot portion of the aqueous phase was transferred to a 25.00 ml. volumetric flask, diluted to the mark with one molar hydrochloric acid, and the absorbance measured at 353 m μ .

Aqueous solutions saturated with nitrobenzene showed significant absorption at the wavelength used for the determination of H_2Ox^+ . This complication was eliminated by back extraction according to the following procedure: after dilution of the aqueous phase to 25.00 ml. with hydrochloric acid, the solution was extracted three times with ten ml. portions of benzene to remove the nitrobenzene. Oxine was not extracted, since it was in the form of the H_2Ox^+ ion, and the absorbance of the aqueous phase measured.

In the chelate systems the absorbance measurement was done on the organic phase at 470 m μ and 395 m μ

for ferric oxinate and nickel oxinate in chloroform,
respectively.

IV. DATA AND RESULTS

A. The Extinction Coefficients

of H_2Ox^+ and Ox^-

The applicability of the spectrophotometric method for the pertinent systems was confirmed by tests of Beer's law for the absorbing species and their extinction coefficients over the concentration range of interest. A series of solutions was prepared containing $0.6 - 5.0 \times 10^{-4}$ M oxine in 0.6M hydrochloric acid solution and in 0.1M sodium hydroxide solution to determine the extinction coefficient of H_2Ox^+ and Ox^- , respectively. The results of these experiments gave a value for the extinction coefficient of $1.70 \pm 0.02 \times 10^3$ for the H_2Ox^+ ion and $2.89 \pm 0.04 \times 10^3$ for the Ox^- at 25.0°, 35.0°, and 45.0°C. as shown in Figure 1 and Tables 2 and 3. Nasanen, Lumme, and Mukula (66) report a value for the extinction coefficient of H_2Ox^+ of $1.66 \pm 0.03 \times 10^3$ and a value of $2.83 \pm 0.04 \times 10^3$ for the Ox^- .

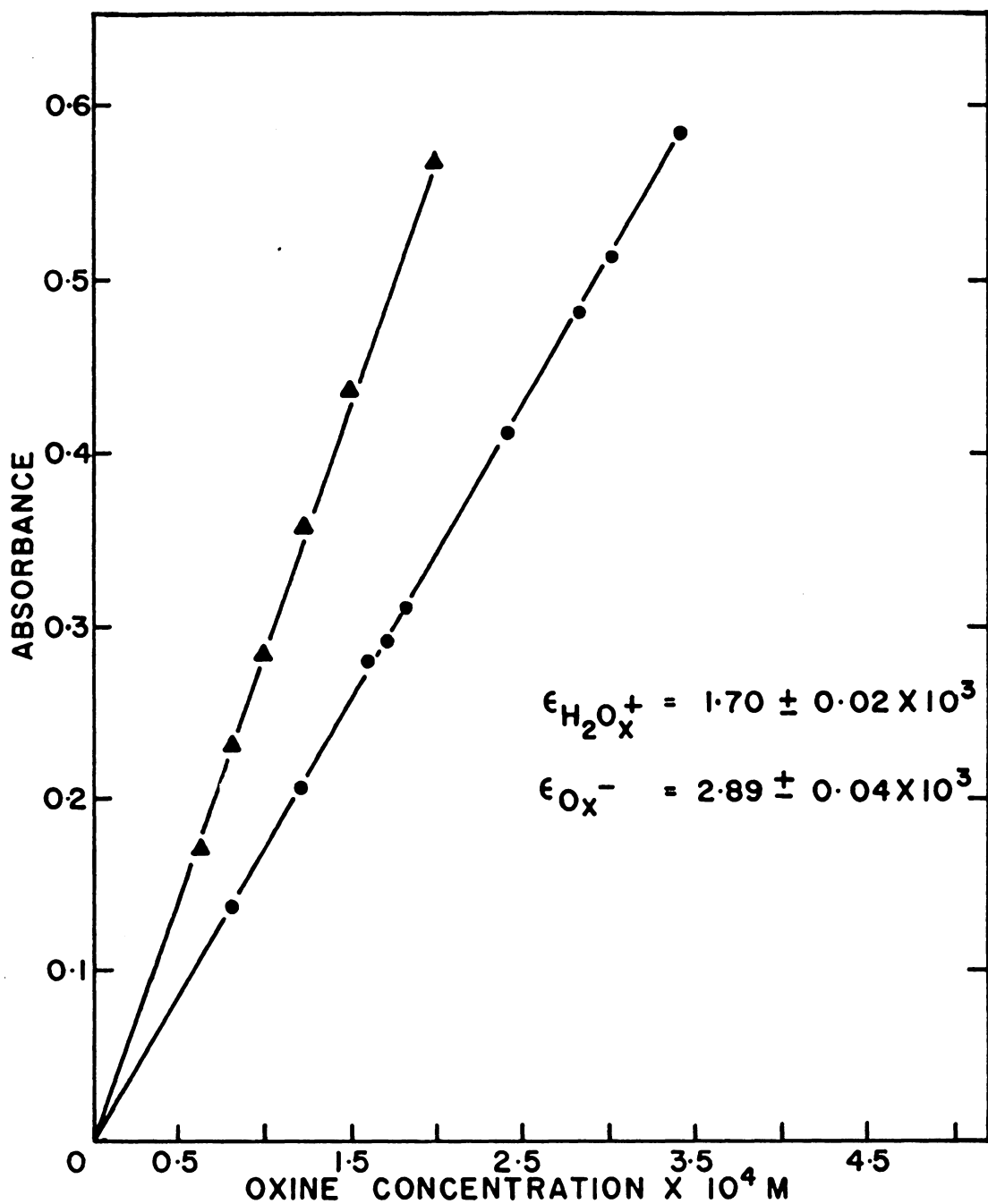


Figure 1. Extinction Coefficient of H_2Ox^+ (\bullet , 358 m μ) and Ox^- (\blacktriangle , 355 m μ)

TABLE 2

Extinction Coefficient of H_2Ox^+ at 358 $\text{m}\mu$ ^a

	Absorbance	$[\text{H}_2\text{Ox}^+] \times 10^4 \text{M}$	$\epsilon \times 10^{-3}$ liter/mole cm.
1)	0.137	0.810	1.72
2)	0.149	0.856	1.74
3)	0.206	1.22	1.69
4)	0.293	1.71	1.70
5)	0.310	1.82	1.70
6)	0.410	2.43	1.69
7)	0.434	2.57	1.69
8)	0.534	3.42	1.71
9)	0.823	4.86	<u>1.69</u>
			$1.70 \pm 0.02 \times 10^3$

^aSlit width 1.15 mm.

TABLE 3

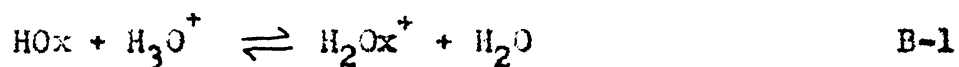
Extinction Coefficient of Ox^- at 355 μ ^a

	Absorbance	$[\text{Ox}^-] \times 10^4 \text{M}$	$\epsilon \times 10^{-3}$ liter/mole cm.
1)	0.171	0.602	2.86
2)	0.234	0.802	2.92
3)	0.289	1.00	2.88
4)	0.361	1.25	2.88
5)	0.437	1.50	2.91
6)	0.569	2.01	2.84
			<u>2.89 \pm 0.04 $\times 10^3$</u>

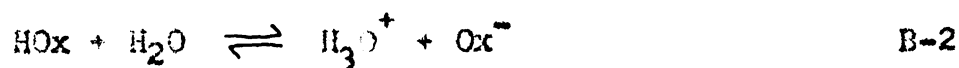
^a Slit width 0.15 mm.

B. The Spectrophotometric Determination of
 pK_1' and pK_2' of Oxine as a function of
Temperature

In aqueous solutions oxine reacts as follows:



and



The law of mass action gives

$$\frac{[\text{H}^+][\text{HOx}]}{[\text{H}_2\text{Ox}^+]} = K_1 \quad \text{B-3}$$

and

$$\frac{[\text{H}^+][\text{Ox}^-]}{[\text{HOx}]} = K_2 \quad \text{B-4}$$

where the symbols in brackets denote concentration in moles per liter. K_1 and K_2 are concentration dissociation constants of the acids H_2Ox^+ and HOx . Since the hydrogen ion concentration was measured with a pH meter, the "mixed" constants:

$$\frac{(H^+) [HOx]}{[H_2Ox^+]} = K_1' \quad B-5$$

and

$$\frac{(H^+) [Ox^-]}{[HOx]} = K_2' \quad B-6$$

are needed. The negative logarithm of equations B-5 and B-6 give

$$pK_1' = pH - \log \frac{[HOx]}{[H_2Ox^+]} \quad B-7$$

and

$$pK_2' = pH - \log \frac{[Ox^-]}{[HOx]} \quad B-8$$

respectively.

Six solutions of oxine in acetic acid-acetate buffers (varying in buffer ratio from 1.21 to 1 acetate-acetic acid to 1.28 to 1 acetic acid-acetate) were prepared with added sodium chloride to maintain the desired ionic strength. The pH of the solutions was calculated using the following values for the pK_a of acetic acid: 4.640 at 25.0°, 4.635 at 35.0° and 45.0°C. (57). The H_2Ox^+ ion concentration was found spectrophotometrically and the HOx concentration by

difference. The average value for pK_1' was 5.103 ± 0.008 at 25.0° , 4.960 ± 0.008 at 35.0° , and 4.840 ± 0.017 at $45.0^\circ C$. as shown in Table 4. Values and methods of determination of pK_1' are shown in Table 1.

The determination of the pK_2' of oxine proved difficult. Repetitive determinations of the ionization constant gave different results. Eight solutions of oxine in carbonate-bicarbonate buffers (varying in buffer ratio from 1.555 to 1 carbonate-bicarbonate to 1.909 to 1 bicarbonate-carbonate) were found to give consistent values of pK_2' of 9.76 at $25.0^\circ C$. These solutions were prepared with sodium chloride to maintain the desired ionic strength. At the higher temperatures it proved more difficult to obtain consistent results. Only two buffer ratios gave consistent results (1.909 to 1 and 1.272 to 1 bicarbonate-carbonate) with values of 9.65 at $35.0^\circ C$. and 9.48 at $45.0^\circ C$. for the pK_2' as shown in Table 5.

The values for pK_2' compare favorably with those of Hellwege and Schweitzer's (81) values done in sodium perchlorate medium and calculated from the distribution

TABLE 4
 pK_1' of Oxine^a

T °C.	[H ₂ Ox ⁺] x10 ⁴	[HOAc] x10 ²	[OAc ⁻] x10 ²	pH calc.	pK_1'
25.0	2.09	1.743	1.437	4.556	5.103
	2.04	1.743	1.596	4.602	5.106
	1.99	1.743	1.755	4.643	5.106
	1.94	1.743	1.914	4.681	5.095
	1.90	1.743	2.073	4.715	5.101
	1.87	1.743	2.232	4.747	<u>5.111</u>
				Av.	5.103 ± 0.008
35.0	1.93			4.551	4.960
	1.86			4.597	4.952
	1.81			4.638	4.953
	1.78			4.676	4.969
	1.72			4.710	4.965
	1.67			4.742	<u>4.960</u>
				Av.	4.960 ± 0.008
45.0	1.80			4.551	4.857
	1.71			4.597	4.840
	1.66			4.638	4.849
	1.59			4.676	4.842
	1.54			4.710	4.841
	1.45			4.742	<u>4.811</u>
				Av.	4.840 ± 0.017

^aSodium chloride was added to the acetic acid-acetate buffer in order to maintain the ionic strength at 0.1M.

^bTotal oxine concentration is $2.662 \times 10^{-4}M$.

TABLE 5

pK_2' of Oxine^a

Spectrophotometric Determination

T °C.	[Ox ⁻]x10 ⁵ M	pH	pK_2'	[CO ₃ ⁼]x10 ² M	[HCO ₃ ⁻]x10 ² M
25.0	0.701 ^b	9.77	9.76	1.782	3.399
	0.829 ^b	9.92	9.77	1.782	2.266
	2.00 ^c	10.07	9.76	2.115	2.266
	2.04 ^c	10.10	9.76	2.115	2.039
	2.10 ^c	10.15	9.77	2.115	1.812
	2.16 ^c	10.19	9.76	2.115	1.586
	2.23 ^c	10.24	<u>9.76</u>	2.115	1.360
		Av. 9.76			
35.0	8.22 ^b	9.82	9.67		
	7.46 ^b	9.67	<u>9.62</u>		
			Av. 9.65		
45.0	9.26 ^b	9.72	9.44		
	8.12 ^b	9.66	<u>9.52</u>		
			Av. 9.48		

^a Sodium chloride was added to the carbonate-bicarbonate buffer in order to maintain the ionic strength at 0.10M.

^bTotal oxine concentration is $1.759 \times 10^{-4}M$.

^cTotal oxine concentration is $3.713 \times 10^{-4}M$.

measurements of cadmium oxinate. They expressed their data for pK_2' by the following equation,

$$\log K = 7.30 + 710 T^{-1}$$

where T is the absolute temperature in degrees Kelvin. The values of pK_2' calculated from this equation are: 9.7 ± 0.1 at 25° , 9.6 ± 0.1 at 35° , and 9.5 ± 0.1 at 45°C . From the above equation it appears that the results might be reported to the second decimal place, but the pH was only determined to plus or minus one-tenth of a unit.

C. The Potentiometric Determination of pK_1' and pK_2' of Oxine

In order to check the dissociation constants of oxine found spectrophotometrically, it was desired to determine them by an independent method; specifically, pH titration.

Using the Gage method (32) of determining the ionization constant of a weak acid or base gave a convenient method to compute both the pK_1' and pK_2' from the same experiment.

In acid solution the mass balance equation can be written

$$[\text{Na}^+] + [\text{H}^+] + [\text{H}_2\text{Ox}^+] = [\text{Cl}^-] \quad \text{C-1}$$

and the experimental values are

$$\frac{C_B V_B}{V_T} + [\text{H}^+] + [\text{H}_2\text{Ox}^+] = \frac{C_A V_A}{V_T} \quad \text{C-2}$$

where

C_B = molar concentration of the base

V_B = volume of base

V_T = total volume of the solution

C_A = molar concentration of the strong acid

V_A = volume of the strong acid.

Rearranging C-2 yields

$$[\text{H}_2\text{Ox}^+] = \frac{C_A V_A}{V_T} - \frac{C_B V_B}{V_T} - [\text{H}^+] \quad \text{C-3}$$

The total oxine in the solution, C_{HOx} , is represented by

$$C_{\text{HOx}} = [\text{H}_2\text{Ox}^+] + [\text{HOx}] \quad \text{C-4}$$

therefore,

$$[\text{H}_2\text{Ox}^+] = C_{\text{HOx}} - [\text{HOx}] = x \quad \text{C-5}$$

and

$$C_{\text{HOx}} - x = [\text{HOx}] \quad \text{C-6}$$

Substituting the results of C-5 and C-6 into

$$K' = \frac{(\text{H}^+)[\text{HOx}]}{[\text{H}_2\text{Ox}^+]} \quad \text{C-7}$$

gives

$$K' = \frac{(\text{H}^+)[C_{\text{HOx}} - x]}{[x]} \quad \text{C-8}$$

The analysis is usually done graphically by plotting $x/(\text{H}^+)$ as the abscissa and x as the ordinate and drawing the best straight line, the slope of the line being K' . The slope of the line can also be determined analytically and this method was used in these experiments.

In a basic solution the mass balance equation can be written

$$[\text{Na}^+] = [\text{Ox}^-] + [\text{Cl}^-] + [\text{OH}^-] \quad \text{C-9}$$

and the experimental values are

$$\frac{C_B V_B}{V_T} = [\text{Ox}^-] + \frac{C_A V_A}{V_T} + [\text{OH}^-] . \quad \text{C-10}$$

Rearranging C-10 yields

$$[\text{Ox}^-] = \frac{C_B V_B}{V_T} - \frac{C_A V_A}{V_T} - [\text{OH}^-] . \quad \text{C-11}$$

The total oxine in the solution, C_{HOx} , is represented by

$$C_{\text{HOx}} = [\text{HOx}] + [\text{Ox}^-] \quad \text{C-12}$$

therefore,

$$[\text{Ox}^-] = C_{\text{HOx}} - [\text{HOx}] = y \quad \text{C-13}$$

and

$$[\text{HOx}] = C_{\text{HOx}} - y . \quad \text{C-14}$$

Substituting the results of C-13 and C-14 into

$$K' = \frac{(\text{H}^+)[\text{Ox}^-]}{[\text{HOx}]} \quad \text{C-15}$$

gives

$$K' = \frac{(H^+)[y]}{[C_{HOx} - y]}$$

C-16

The analysis is usually done graphically by plotting y as the ordinate and $y(H^+)$ as the abscissa and drawing the best straight line. The slope of the line is the reciprocal of the ionization constant. The slope of the line can also be determined analytically as was done in these experiments.

The pK_1' determined from the potentiometric titration of $1.975 \times 10^{-3} M$ oxine in hydrochloric acid at a constant ionic strength of $0.1M$ in sodium chloride medium was 5.11 at 25.0° , 4.92 at 35.0° , and 4.81 at $45.0^\circ C.$, in satisfactory agreement with the spectrophotometric determination.

The pK_2' was determined on the above solutions. The pK_2' at 25.0° and $45.0^\circ C.$ had values of 9.74 and 9.51, respectively, which are in good agreement with the spectrophotometric values. The value at $35.0^\circ C.$ for the pK_2' was 9.55, which was not in agreement with the spectrophotometric value of 9.65. The data and results of these experiments are shown in Table 6.

TABLE 6

The Potentiometric Determination of the Second Dissociation Constant of Oxine

			HCl 0.1618M (2.500 ml.)		NaOH 0.1917M		$C_{HOx} 1.975 \times 10^{-3}M$	
T °K.	Volume NaOH ml.	pH	1	2	3	1 - 2 - 3		pK_2'
			$\frac{C_B V_B}{V_T}$ $\times 10^3 M$	$\frac{C_{Cl} V_{Cl}}{V_T}$ $\times 10^3 M$	$[OH^-]^a$ $\times 10^5 M$	y $\times 10^3 M$	y (H ⁺) $\times 10^{13} M$	
298.2	2.300	9.063	4.31	3.95	1.92	0.34	2.92	9.75
	2.400	9.283	4.49	3.95	3.18	0.51	2.66	9.74
	2.500	9.460	4.67	3.95	4.78	0.68	2.36	9.74
	2.600	9.606	4.86	3.94	6.69	0.85	2.10	9.73
	2.702	9.746	5.04	3.94	9.27	1.01	1.81	<u>9.73</u>
							Av.	9.74
308.2	2.600	9.403	4.86	3.94	8.82	0.83	3.27	9.54
	2.805	9.686	5.23	3.94	16.9	1.13	2.32	9.56
	3.000	9.909	5.58	3.93	28.1	1.38	1.70	<u>9.54</u>
							Av.	9.55

TABLE 6 (Continued)

T °K.	Volume NaOH ml.	pH	1 $\frac{C_B V_B}{V_T}$ $\times 10^3 M$	2 $\frac{C_{Cl} V_{Cl}}{V_T}$ $\times 10^3 M$	3 [OH ⁻] ^a $\times 10^5 M$	1 - 2 - 3 y $\times 10^3 M$	y (H ⁺) $\times 10^{13} M$	pK ₂ '
318.2	2.400	9.004	4.49	3.95	6.85	0.48	4.71	9.50
	2.600	9.305	4.86	3.94	13.7	0.78	3.86	9.49
	2.800	9.505	5.22	3.94	23.7	0.95	2.72	9.53
	3.000	9.762	5.53	3.93	39.2	1.26	2.19	9.51
							Av.	9.51

^aThe [OH⁻] was calculated using the following values for K_w:
 1.659×10^{-14} [25.0°C.], 3.485×10^{-14} [35.0°C.], and 6.785×10^{-14}
[45.0°C.] (35).

D. Thermodynamics of the Oxine Dissociation

For an equilibrium reaction the free energy change may be found from the following relationship

$$\Delta G^{\circ} = - 2.303 R T \log K \quad D-1$$

where

ΔG° = the free energy change

R = the gas constant

T = the temperature in degrees Kelvin

K = the equilibrium constant of the reaction.

The free energy change is related to the other thermodynamic functions by the following relationship

$$\Delta G^{\circ} = \Delta H - T \Delta S^{\circ} . \quad D-2$$

If the values of K are known over a range of temperatures, the change in enthalpy, ΔH , and the change in entropy, ΔS° , can be calculated.

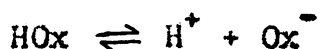
For the equilibrium reaction



the free energy change was found to be 7.0 ± 0.5 kcal/mole, the enthalpy change

5.7 ± 0.5 kcal/mole, and the entropy change -4 ± 3 cal/mole degree for the spectrophotometric determination of the first ionization constant at 25.0°C . The value for the thermodynamic constants determined by the potentiometric method for the first ionization constant gave a free energy change of 7.0 ± 0.5 kcal/mole, an enthalpy change of 6.6 ± 0.5 kcal/mole, and an entropy change of -1 ± 3 cal/mole degree at 25.0°C . The results of all the experiments are tabulated in Table 7.

For the equilibrium reaction



D-4

the free energy change was found to be 13.3 ± 0.5 kcal/mole, the enthalpy change 6.5 ± 0.5 kcal/mole, and the entropy change -22 ± 3 cal/mole degree at 25.0°C . Hellwege and Schweitzer (81) report a free energy change of 13 kcal/mole, an enthalpy change of 3 kcal/mole, and an entropy change of -34 cal/mole degree on data from the extraction of cadmium oxinate in sodium perchlorate medium at an ionic strength of 0.1M. The results of all the experiments are shown in Table 8.

TABLE 7

Thermodynamic Values of the First
Dissociation of Oxine

pK_1^i	ΔG° kcal/mole	ΔH kcal/mole	ΔS° cal/mole degree	T °K.
A. Spectrophotometric Determination				
5.103	6.96	5.7	-4	298.2
4.960	6.99	5.7	-4	308.2
4.840	7.05	<u>5.7</u>	<u>-4</u>	318.2
	Av.	5.7	-4	
B. Potentiometric Determination				
5.11	6.97	6.6	-1	298.2
4.92	6.94	6.5	-1	308.2
4.81	7.00	<u>6.6</u>	<u>-1</u>	318.2
	Av.	6.6	-1	

TABLE 8

Thermodynamic Values of the Second
Dissociation of Oxine

pK_2'	ΔG° kcal/mole	ΔH kcal/mole	ΔS° cal/mole degree	T °K.
A. Spectrophotometric Determination				
9.77	13.3	6.3	-23	298.2
9.65	13.6	6.4	-24	308.2
9.48	13.8	<u>6.3</u>	<u>-23</u>	318.2
		Av. 6.3	-23	
B. Potentiometric Determination				
9.74	13.3	6.8	-22	298.2
9.55	13.7	6.9	-22	308.2
9.51	13.8	<u>6.8</u>	<u>-22</u>	318.2
		Av. 6.8	-22	

E. The First Dissociation Constant of Oxine
as a Function of the Ionic Strength

The study of the partition of oxine between benzene-aqueous buffers as a function of salt concentration necessitated a knowledge of the first dissociation constant of oxine as a function of salt type and concentration. It has been customary to try to obtain the pK_1^O , the thermodynamic constant, by fitting the results of these equilibrium experiments to Debye-Huckel functions. The thermodynamic constant is defined as

$$K_1^O = \frac{f_{HOx}}{f_{H_2Ox^+}} K_1' \quad E-1$$

where f is the activity coefficient of the species.

The Debye-Huckel expression for the activity is

$$-\log f = \frac{A \sqrt{\mu}}{1 + B \sqrt{\mu}} \quad E-2$$

where A is a constant made up of the charge of the species, dielectric constant, and temperature; B is a function of the ion size.

The dissociation constant of oxine was studied as a function of ionic strength for the four salts sodium chloride, potassium chloride, potassium nitrate, and sodium perchlorate. The ionic strength varied from 0.1 to 1.5M for sodium chloride and potassium chloride solutions, and from 0.1 to 1.25M for potassium nitrate and sodium perchlorate solutions.

For potassium chloride the results fit a curve of pK_1' versus $\frac{0.509 \sqrt{\mu}}{1 + 0.972 \sqrt{\mu}}$ which gave a value of

4.92 for pK_1^0 , the thermodynamic dissociation constant, by the method of least squares, which is in agreement with the results of Nasanen, Lummo, and Mukula (66).

The sodium chloride data fit a curve of pK_1' versus $\frac{0.509 \sqrt{\mu}}{1 + 0.970 \sqrt{\mu}}$. The data for the potassium nitrate

and sodium perchlorate media did not fit such simple functions. The values for the pK_1' are shown as a function of ionic strength and salt in Table 9.

TABLE 9

The First Dissociation of Oxine as a Function
of the Ionic Strength

Salt	Ionic Strength						
	0.1	0.25	0.50	0.75	1.00	1.25	1.50
NaCl	5.10	5.03	5.08	5.10	5.13	5.14	5.18
KCl	5.06	5.10		5.19	5.19	5.20	5.25
KNO ₃	5.11	5.01	5.09	5.09	5.14	5.17	
NaClO ₄	5.03	5.02	5.13	5.18	5.23	5.26	

F. The Partition of Oxine Between Phosphoric
Acid Buffers and Benzene, Chloroform,
Toluene, and Nitrobenzene

The distribution of oxine between an organic
solvent and an aqueous solution is given by its
extraction coefficient:

$$D = \frac{[\text{HOx}]_o}{\sum [\text{HOx}]_w} \quad \text{F-1}$$

where

$$\sum [\text{HOx}]_w = [\text{HOx}]_w + [\text{H}_2\text{Ox}^+]_w + [\text{Ox}^-]_w \quad \text{F-2}$$

Designating the partition coefficient of
molecular oxine by

$$P = \frac{[\text{HOx}]_o}{[\text{HOx}]_w}, \quad \text{F-3}$$

it is found from equations B-5 and B-6

$$\frac{(\text{H}^+)[\text{HOx}]}{[\text{H}_2\text{Ox}^+]} = K_1' \quad \text{B-5}$$

and

$$\frac{(H^+)[Ox^-]}{[HOx]} = K_2' \quad B-6$$

that

$$P = D \frac{[K_1'(H^+) + (H^+)^2 + K_1' K_2']}{K_1'(H^+)} \quad F-4$$

In acid solution $K_1' K_2'$ is smaller than $K_1'(H^+) + (H^+)^2$; therefore, simplifying

$$P = \frac{D [K_1' + (H^+)]}{K_1'} \quad F-5$$

According to equation F-1 a plot of D versus pH should give a sigmoid shaped curve with an inflection point at D equal to one, where the organic phase and the aqueous phase have equal concentrations of oxine. This inflection point is defined as the pH of half extraction or $pH_{1/2}$. From equation F-4 there should be two sigmoid shaped curves for oxine, one at an acid pH and the other at a basic pH. The two sigmoid shaped curves are connected by a plateau region in which D equals P.

In order to get a profile of the sigmoid shaped curve and to check the possibility of the oxine forming polymolecular species in the organic phase, the distribution measurements were made at several pH values about the pH of half extraction. The organic phase contained $1 \times 10^{-4} M$ oxine and was extracted into phosphoric acid buffers using sodium chloride to maintain the ionic strength of 0.1M.

The distribution curves showed a displacement towards lower pH values as the temperature was increased, which means that the extraction is more efficient at the higher temperature though the partition coefficient decreases with an increase in temperature.

For the benzene system the pH of half extraction was found to decrease from 2.66 to 2.59 to 2.49 at 25.0°, 35.0°, and 45.0°C., respectively. The logarithm of the partition coefficient decreased at each temperature with values of 2.44, 2.37, and 2.35 at 25.0°, 35.0°, and 45.0°C., respectively. See Table 10.

Toluene exhibited a higher value for the pH of half extraction than benzene at each temperature with values of 2.78, 2.66, and 2.57 at 25.0°, 35.0°, and 45.0°C., respectively. The logarithm of the partition

TABLE 10

Distribution Data of Oxine Between Benzene
and Phosphoric Acid Buffers^a

T °C.	pH	D	%	pH _{1/2}	log P
25.0	2.89	1.7	62	2.66	2.44
	2.60	0.85	46		
	2.42	0.56	36		
	2.25	0.40	29		
	2.16	0.31	24		
35.0	2.99	2.5	71	2.59	2.37
	2.71	1.3	56		
	2.52	0.81	45		
	2.34	0.59	37		
	2.19	0.45	31		
45.0	2.99	3.2	76	2.49	2.35
	2.68	1.5	60		
	2.51	1.1	52		
	2.34	0.71	41		
	2.24	0.55	36		

^aSodium chloride was added to the phosphoric acid buffer in order to maintain the ionic strength at 0.10M.

coefficient decreased at each temperature with values of 2.33, 2.29, and 2.27 at 25.0°, 35.0°, and 45.0°C., respectively. See Table 11.

The pH of half extraction was found to be 2.40, 2.29, and 2.25 at 25.0°, 35.0°, and 45.0°C., respectively, for the chloroform system. The logarithm of the partition coefficient for this system was found to be 2.70, 2.67, and 2.59 at 25.0°, 35.0°, and 45.0°C., respectively. See Table 13.

The errors in each of the determinations is no greater than 0.02 units in the pH of half extraction or in the logarithm of the partition coefficient.

Because of the difficulty in the experimental determination, the values for the logarithm of the partition coefficient and the pH of half extraction for the nitrobenzene system were not considered to be as precise or accurate as the partition coefficient of the pH of half extraction values for the other systems. The tentative values for the pH of half extraction are 2.43, 2.31, and 2.25 at 25.0°, 35.0°, and 45.0°C., respectively. The values for the logarithm of the partition coefficient are 2.67, 2.65, and 2.59 at 25.0°, 35.0°, and 45.0°C., respectively. See Table 12.

TABLE 11

Distribution Data of Oxine Between Toluene
and Phosphoric Acid Buffers^a

T °C.	pH	D	%E	pH _{1/2}	log P
25.0	2.94	1.5	60	2.78	2.33
	2.67	0.72	42		
	2.47	0.48	32		
	2.33	0.36	26		
	2.20	0.30	23		
35.0	3.63	9.3	90	2.66	2.29
	3.19	3.4	77		
	2.97	1.9	66		
	2.62	0.92	48		
	2.44	0.60	38		
45.0	3.00	2.7	73	2.57	2.27
	2.69	1.5	60		
	2.49	0.78	44		
	2.33	0.59	37		
	2.24	0.41	29		

^aSodium chloride was added to the phosphoric acid buffer in order to maintain the ionic strength at 0.10M.

TABLE 12

Distribution Data of Oxine Between Nitrobenzene
and Phosphoric Acid Buffers^a

T °C.	pH	D.	%E	pH _{1/2}	log P
25.0	2.42	0.98	49	2.43	2.67
	2.30	0.72	42		
	2.29	0.71	41		
35.0	2.64	2.1	68	2.31	2.65
	2.46	1.4	59		
	2.29	0.95	49		
45.0	2.31	2.4	71	2.25	2.59
	2.20	2.3	70		
	2.10	2.2	69		

^aSodium chloride was added to the phosphoric acid buffer in order to maintain the ionic strength at 0.10M.

TABLE 13

Distribution Data of Oxine Between Chloroform
and Phosphoric Acid Buffers^a

T °C.	pH	D	%E	pH _{1/2}	log P
25.0	2.700	1.84	64.6	2.40	2.703
	2.468	1.20	54.6		
	2.320	0.861	46.3		
35.0	2.82	3.4	77	2.29	2.67
	2.74	2.8	74		
	2.39	1.3	56		
45.0	2.72	2.9	75	2.25	2.59
	2.53	1.9	66		
	2.38	1.3	57		

^aSodium chloride was added to the phosphoric acid buffer in order to maintain the ionic strength at 0.10M.

The results of all the distribution experiments are plotted in Figures 2, 3, and 4.

Umland and Puchelt (87) found the pH of half extraction to be 2.73 and the logarithm of the partition coefficient to be 2.60 at 25.0°C. for the benzene system. However, Umland and Puchelt report a negative logarithm of 5.33 for the first dissociation constant at approximately 0.1M ionic strength. Recalculating their data using the results for the first dissociation constant found in this work, the logarithm of the partition coefficient is within the experimental error of the results found in this work.

G. Thermodynamics of the Oxine Partition

In section D it was shown that the change in free energy for an equilibrium reaction could be found from the following equation

$$\Delta G^{\circ} = -2.303 R T \log K \quad D-1$$

and that the enthalpy and entropy changes could be found from the following equation

$$\Delta G^{\circ} = \Delta H - T \Delta S^{\circ} \quad D-2$$

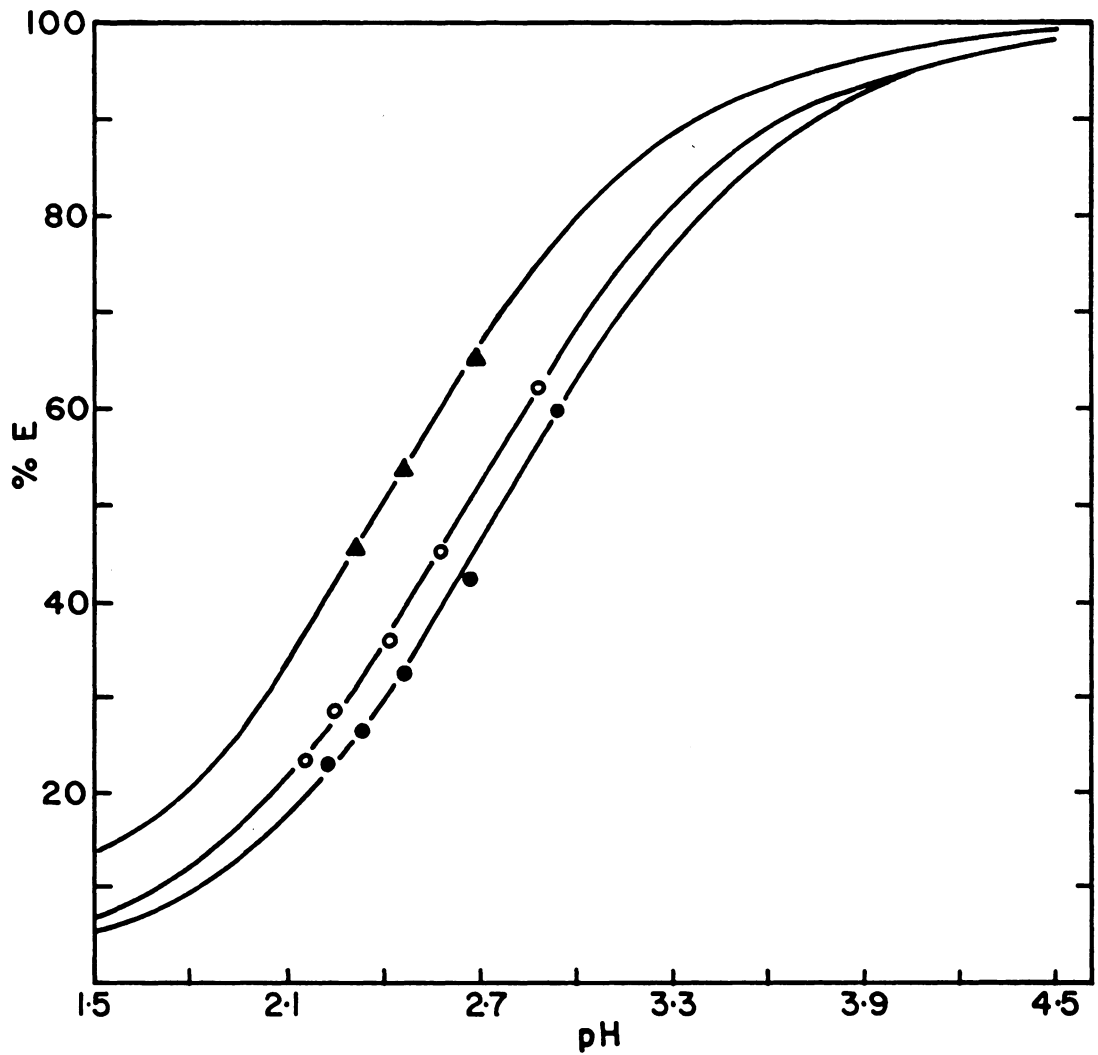


Figure 2. Percent Extraction of Oxine versus pH, 25.0°C. Benzene o, Toluene ●, Chloroform ▲.

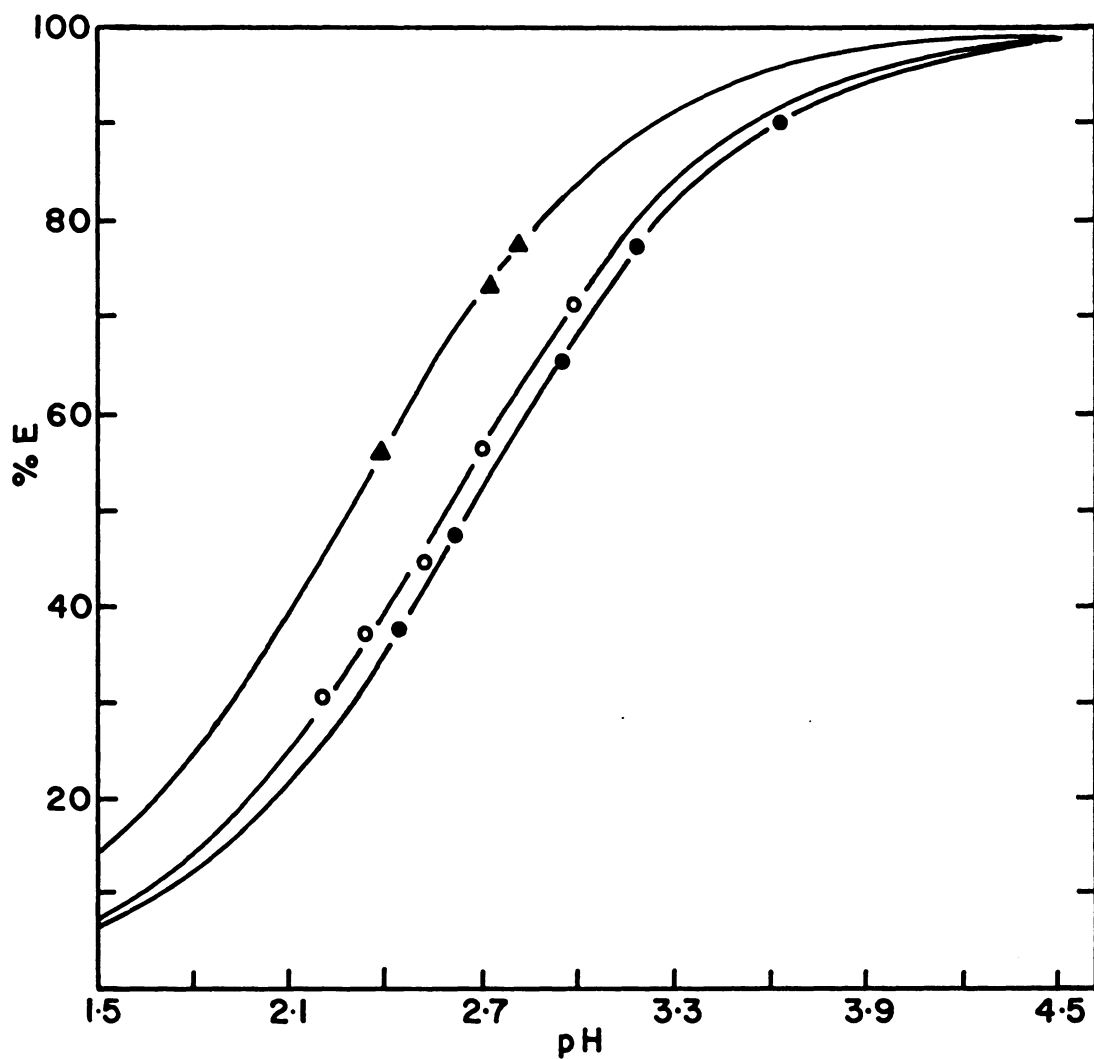


Figure 3. Percent Extraction of Oxine versus pH, 35.0°C. Benzene o, Toluene ●, Chloroform ▲.

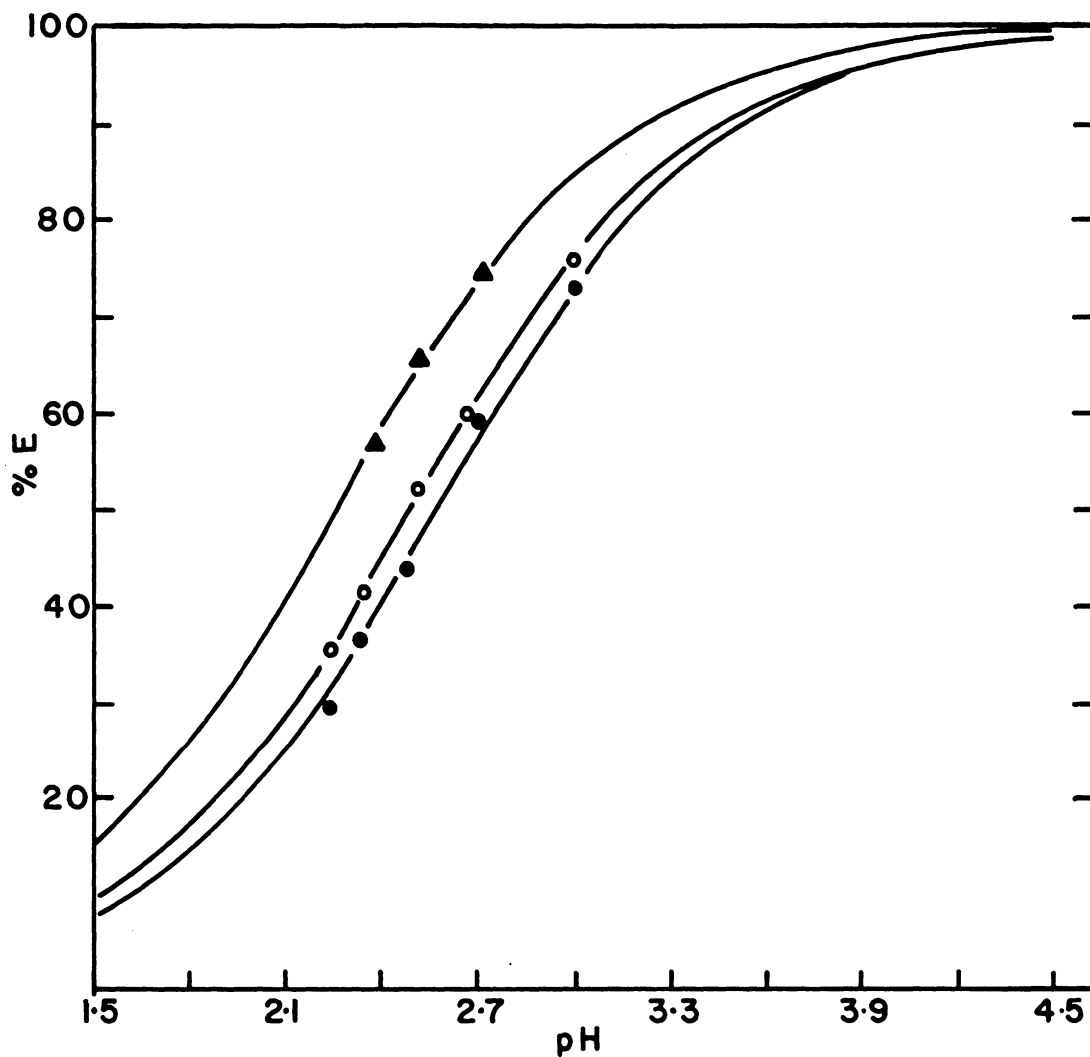
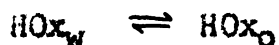


Figure 4. Percent Extraction of Oxine versus pH, 45.0°C. Benzene o, Toluene ●, Chloroform ▲.

For the equilibrium reaction



G-1

the partition coefficient, P , is the equilibrium constant for the reaction. Therefore, the K in equation D-1 may be replaced by P and the changes in the free energy, enthalpy, and entropy may be calculated, since the partition coefficient has been determined at several temperatures.

For the benzene system at 25.0°C. the free energy change was found to be -3.3 ± 0.5 kcal/mole, the enthalpy change -2.0 ± 0.5 kcal/mole, and the entropy change 4 ± 3 cal/mole degree.

The free energy change at 25.0°C. for the toluene system was found to be -3.2 ± 0.5 kcal/mole, the enthalpy change -1.3 ± 0.5 kcal/mole, and the entropy change 6 ± 3 cal/mole degree.

The free energy change at 25.0°C. for the nitrobenzene system was found to be 3.6 ± 0.5 kcal/mole, the enthalpy change -1.7 ± 0.5 kcal/mole, and the entropy change 7 ± 3 cal/mole degree.

The free energy change for benzene and its two derivatives is in the order: nitrobenzene > benzene > toluene, while the enthalpy change is in the order:

benzene > nitrobenzene > toluene. All the systems showed an entropy change of 6 ± 3 cal/mole degree.

For the chloroform system at 25.0°C. the free energy change was found to be -3.7 ± 0.5 kcal/mole, the enthalpy change -2.5 ± 0.5 kcal/mole, and the entropy change 4 ± 3 cal/mole degree.

The error of 0.5 kcal/mole given for the free energy change for all of these systems is probably a maximum error in these values. With an error in the equilibrium measurements no larger than ± 0.2 units, the free energy change may be in error by as little as ± 0.2 kcal/mole. The enthalpy and entropy changes may be in error by as much as the values given, which are probably the minimum errors.

Hellwege and Schweitzer (81) report a free energy change of -4 kcal/mole, an enthalpy change of -2 kcal/mole, and an entropy change of 6 cal/mole degree for the chloroform system at 0.1M ionic strength in sodium perchlorate medium. Their results are in agreement with the results reported here; however, they do not give the error in their values. From the manner the experiments were done the values should have

twice the error as those reported in this work. The results of all experiments are shown in Table 14.

H. The Partition Coefficient of the Benzene System as a Function of Concentration and Nature of 1-1 Electrolytes

The partition coefficient at infinite dilution may be defined as

$$P_a = \frac{C_{HOx_o} f_{HOx_o}}{C_{HOx_w} f_{HOx_w}} \quad H-1$$

where

C_{HOx_o} = concentration of oxine in the benzene phase

f_{HOx_o} = activity coefficient of oxine in the benzene phase

C_{HOx_w} = concentration of oxine in the aqueous phase

f_{HOx_w} = activity coefficient of oxine in the aqueous phase.

The activity coefficient of oxine in the organic phase is considered a constant and usually taken as

TABLE 14

Thermodynamic Data of the Partition of Oxine
Between Four Organic Solvents and
Phosphoric Acid Buffers

Solvent	ΔG° kcal/mole	ΔH kcal/mole	ΔS° cal/mole degree	T °K.	log P
Benzene	-3.33	-2.00	4.5	298.2	2.44
	-3.34	-1.97	4.4	303.2	2.37
	-3.42	-2.00	4.5	318.2	2.35
	Av.	-2.0	4.5		
Toluene	-3.18	-1.32	6.2	298.2	2.33
	-3.24	-1.32	6.2	303.2	2.29
	-3.30	-1.32	6.2	318.2	2.27
	Av.	-1.3	6.2		
Nitro- benzene	-3.64	-1.66	6.6	298.2	2.67
	-3.73	-1.68	6.7	303.2	2.65
	-3.77	-1.66	6.6	318.2	2.59
	Av.	-1.7	6.6		
Chloroform	-3.69	-2.53	3.8	298.2	2.70
	-3.77	-2.57	4.0	303.2	2.67
	-3.77	-2.53	3.8	318.2	2.59
	Av.	-2.5	3.9		

unity; therefore, the concentration of oxine and the activity of oxine are the same in the organic phase. This is not true for the aqueous phase. The logarithm of equation H-1 is

$$\begin{aligned} \log P_a &= \log f_{\text{HOx}_o} + \log C_{\text{HOx}_o} - \log f_{\text{HOx}_w} \\ &\quad - \log C_{\text{HOx}_w} \end{aligned} \quad \text{H-2}$$

In equation H-2 $\log f_{\text{HOx}_o}$ is not necessarily zero.

The concentration partition coefficient, P_c , may be substituted into equation H-2 for the oxine concentration in the organic phase and in the aqueous phase giving

$$\log P_a = \log P_c + \log f_{\text{HOx}_o} - \log f_{\text{HOx}_w} \quad \text{H-3}$$

Rearranging equation H-3 yields

$$\log P_c = \log P_a - \log f_{\text{HOx}_o} + \log f_{\text{HOx}_w} \quad \text{H-4}$$

Electrostatic theory (20) has yielded an equation of the form

$$\log f = k \mu \quad \text{H-5}$$

indicating that the logarithm of the activity coefficient of a nonelectrolyte should be proportional to the ionic strength. Therefore,

$$\log P_c = \log P_a - \log f_{HOx_0} + k \mu . \quad H-6$$

Equation H-6 predicts a straight line when the logarithm of the partition coefficient P_c is plotted against the ionic strength, μ .

As seen in Figures 5 and 6 a good straight line was found and the least squares slope of the line gave the following values for k_s : sodium chloride 0.118, potassium chloride 0.167, potassium nitrate 0.045, and sodium perchlorate 0.007. The values for the partition coefficient of oxine as a function of the ionic strength for the salts studied are shown in Table 15. The value of $\log P_a$ obtained from the graphs is 2.31 ± 0.04 .

I. The Extinction Coefficients of Ferric and Nickel Oxinates

The applicability of the spectrophotometric method for the pertinent systems was confirmed by tests of Beer's law for the absorbing species and

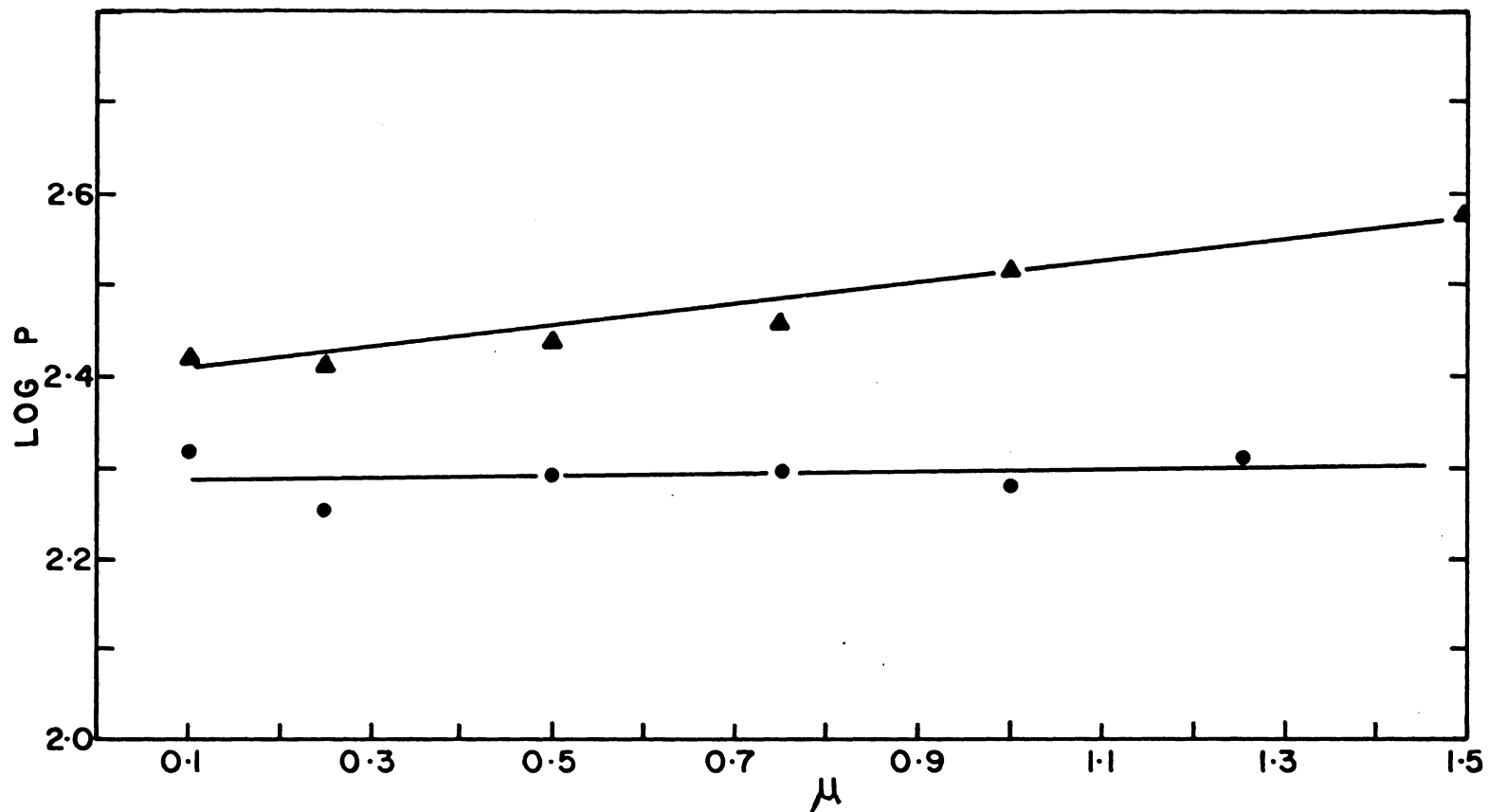


Figure 5. The Logarithm of the Partition Coefficient of Oxine in the Benzene-Water System versus the Ionic Strength in Sodium Chloride (▲) and Sodium Perchlorate (●) Media.

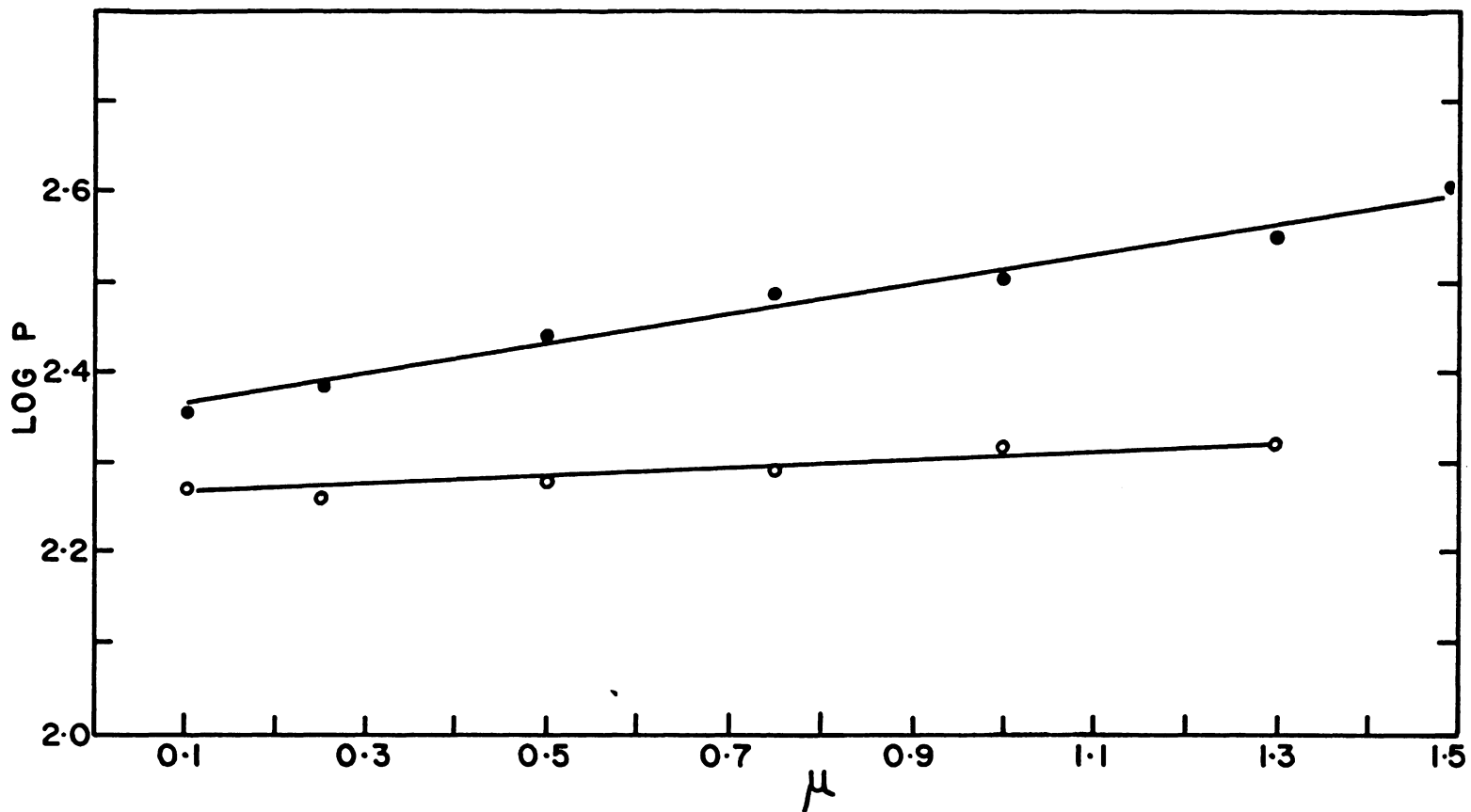


Figure 6. The Logarithm of the Partition Coefficient of Oxine in the Benzene-Water System versus the Ionic Strength in Potassium Chloride (●) and Potassium Nitrate (○) Media.

TABLE 15
 Logarithm of the Partition of Oxine Between Benzene
 and Aqueous Salt Solutions

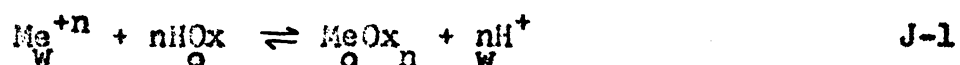
Salt	Ionic Strength							k_s
	0.1	0.25	0.50	0.75	1.00	1.25	1.50	
NaCl	4.42	2.41	2.44	2.46	2.52		2.58	0.118
KCl	2.36	2.39	2.44	2.49	2.51	2.55		0.167
KNO ₃	2.27	2.26	2.28	2.28	2.32	2.32	2.32	0.045
NaClO ₄	2.32	2.25	2.29	2.30	2.28	2.31		0.007

their extinction coefficients over the concentration range of interest. A series of solutions was prepared containing $3.3 \times 10^{-5} M$ to $8.3 \times 10^{-5} M$ iron and $0.05M$ oxine in chloroform. The results at $470 m \mu$ showed the extinction coefficient to be $6.30 \pm 0.10 \times 10^3$ at 25.0° , 35.0° , and $45.0^\circ C$.

The Beer's law determination of nickel oxinate in chloroform as a function of temperature proved to be more difficult because of the absorption of oxine at $395 m \mu$. A series of solutions was prepared containing $3.2 \times 10^{-5} M$ to $8.0 \times 10^{-5} M$ nickel and $0.05M$ oxine in chloroform. Plotting the results on a graph with the ordinate designating absorbance and the abscissa designating concentration gave a straight line intercepting the y axis indicating oxine absorption at this wavelength. A determination of the extinction coefficient of oxine at this wavelength was made and the results subtracted from the value found in the nickel oxinate determination. The extinction coefficient was found to be $4.20 \pm 0.10 \times 10^3$ at $395 m \mu$ at 25.0° , 35.0° , and $45.0^\circ C$.

J. The Partition of Ferric and Nickel Oxinates
Between Chloroform and Aqueous Solutions

For the equilibrium reaction of metal ion Me^{+n} reacting with reagent HOx to give the extractable compound $MeOx_n$ the following equation may be written:

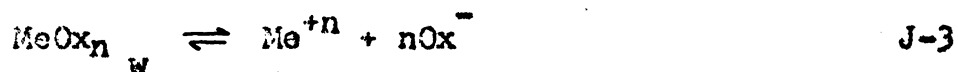


with the equilibrium constant K_e

$$K_e = \frac{[MeOx_n]_o [H^+]_w^n}{[Me^{+n}]_w [HOx]_o^n} \quad J-2$$

where o and w refer to the organic solvent and water phases, respectively.

Equation J-2 may be derived on the basis of the following considerations. In the aqueous phase an equilibrium exists among metal ions, ligand ions, and the dissolved metal chelate:



with equilibrium constant K_m

$$K_m = \frac{[Me^{+n}] [Ox^-]^n}{[MeOx_n]_w} \quad J-4$$

The metal chelate partitions between the aqueous and organic solvent phases:



with the equilibrium constant K_p

$$K_p = \frac{[MeOx_n]_o}{[MeOx_n]_w} \quad J-6$$

Dividing equation J-6 by equation J-4:

$$\frac{[MeOx_n]_o}{[Me^{+n}]_w} = \frac{K_p [Ox^-]^n}{K_m} \quad J-7$$

For the reagent HOx the second dissociation constant K_2' is

$$\frac{(H^+) [Ox^-]}{[HOx]} = K_2' \quad J-8$$

and

$$\frac{[\text{HOx}]_o}{[\text{HOx}]_w} = P \quad \text{J-9}$$

is the partition coefficient.

The substitution of equation J-9 into equation J-8 gives

$$[\text{Ox}^-] = \frac{K_2' [\text{HOx}]_o}{P (\text{H}^+)} \quad \text{J-10}$$

Substitution of equation J-10 into equation J-7 gives

$$\frac{[\text{MeOx}_n]_o}{[\text{Me}^{+n}]_w} = \frac{K_p K_2'^n [\text{HOx}]_o^n}{K_m P^n [\text{H}^+]_w^n} \quad \text{J-11}$$

By rearranging equation J-11 it is seen that K_e is made up of four other constants, K_p , K_2' , K_m , and P .

$$K_e = \frac{K_p K_2'^n}{K_m P^n} \quad \text{J-12}$$

therefore, if K_p , K_2' , K_m , and P are known, K_e can be calculated.

In these experiments K_e was determined, but K_p could not be obtained for the nickel oxinate as it would not dissolve in chloroform or benzene. The determination of K_m was not attempted in this work.

A series of aqueous solutions varying in hydrogen ion concentration was prepared containing $1.3 \times 10^{-4} M$ nickel chloride and enough sodium chloride to maintain the ionic strength at 0.1M. These solutions were extracted with a 0.05M oxine-chloroform solution letting the oxine serve as the buffering medium. Consistent results were obtained for $\log K_e$ at 25.0° and 35.0°C. with values for $\log K_e$ of -2.73 and -3.69, respectively; and inconsistent results were obtained at 45.0°C., as shown in Table 16. Stary (83) found a value for $\log K_e$ of -2.18 at 20°C. Extrapolating the results found at 25.0° and 35.0°C. a value of -2.25 for $\log K_e$ is found in fair agreement with the results of Stary.

Consistent results for $\log K_e$ were readily obtained at all three experimental temperatures for the ferric oxinate partition. The extraction was found to take place at a pH of 1.2 to 1.5. No supporting electrolyte such as sodium chloride was used, since the ionic strength of the buffer solutions

TABLE 16
 Partition Data of Nickel Oxinate Between
 Chloroform and Aqueous Solutions

$\mu = 0.10M$ $[NiOx_2]_o$ $\times 10^5 M$	$[Ni^{+2}]_w$ $\times 10^5 M$	D	pH	log K_e	T $^{\circ}C.$
8.62	4.28	2.01	2.937	-2.75	25.0
9.00	3.90	2.31	2.951	-2.72	
10.02	2.88	3.47	3.036	-2.75	
10.07	2.83	3.57	3.033	-2.72	
				Av. -2.73	
3.93	8.97	0.438	3.03	-3.67	35.0
3.76	9.14	0.411	3.02	-3.70	
3.83	9.07	0.422	3.03	-3.69	
4.36	8.54	0.511	3.07	-3.70	
4.38	8.52	0.514	3.07	-3.69	
				Av. -3.69	
5.05	7.85	0.643	3.12	-3.92	45.0
5.45	7.45	0.732	3.12	-3.66	
5.69	7.21	0.789	3.12	-3.63	
7.78	5.12	1.52	3.40	-3.96	
7.86	5.04	1.56	3.35	-3.84	
3.86	9.04	0.427	3.02	-3.67	
3.98	8.92	0.446	3.00	-3.61	
2.81	10.90	0.258	3.11	-4.09	
5.00	7.90	0.633	3.37	-4.27	

was 0.1M or slightly greater. The solutions were poorly buffered, but no difficulty was found in preparing solutions of reproducible pH. A 0.05M oxine-chloroform solution was placed in contact with an aqueous solution of ferric chloride and hydrochloric acid and the $\log K_e$ determined. The values of $\log K_e$ found were 3.97 ± 0.03 at 25.0°C ., 3.56 ± 0.03 at 35.0°C ., and 3.42 ± 0.03 at 45.0°C . Stary (83) reports a value for $\log K_e$ of 4.11 ± 0.02 at 20°C . An extrapolation of the values found at 25° , 35° , and 45°C . in this work give a value of $\log K_e$ of 4.11 for the ferric oxinate system in excellent agreement with Stary's results. See Table 17.

An attempt was made to determine $\log K_e$ as a function of temperature in the benzene system, but inconsistent results were obtained at 25.0° and 35.0°C . and the study was abandoned after many trials.

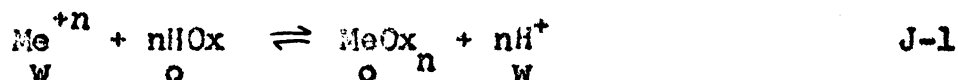
TABLE 17

Partition Data of Ferric Oxinate Between
Chloroform and Aqueous Solutions

$\mu = 0.1M$ $[FeOx_3]_o$ $\times 10^5M$	$[Fe^{+3}]_w$ $\times 10^5M$	D	pH	$\log K_e$	T °C.
4.85	1.80	2.69	1.270	3.985	25.0
4.84	1.81	2.67	1.270	3.985	
1.88	4.77	0.394	1.130	3.960	
4.54	2.11	2.15	1.267	3.957	
4.61	2.04	2.26	1.267	3.978	
				Av. 3.97 ± 0.02	
3.31	3.34	0.991	1.222	3.524	35.0
3.29	3.36	0.979	1.216	3.569	
3.28	3.37	0.973	1.219	3.557	
4.67	1.98	2.30	1.274	3.600	
4.51	2.04	2.26	1.282	3.544	
4.61	2.04	2.26	1.273	3.592	
				Av. 3.56 ± 0.03	
3.69	2.96	1.25	1.239	3.441	45.0
3.61	3.04	1.19	1.239	3.420	
3.62	3.03	1.19	1.239	3.420	
5.28	1.37	3.85	1.335	3.382	
				Av. 3.42 ± 0.03	

K. Thermodynamics of Iron and Nickel
Oxinate Partition

For the equilibrium reaction



the equilibrium constant, K_e , at 25.0°, 35.0°, and 45.0°C. can be substituted into the pertinent equations (D-1 and D-2) and the thermodynamic functions ΔG° , ΔS° , and ΔH determined.

For the ferric oxinate-chloroform system at 25.0°C. the free energy change was -5.4 ± 0.5 kcal/mole, the enthalpy change -12 ± 0.5 kcal/mole, and the entropy change -22 ± 10 cal/mole degree.

For the nickel oxinate-chloroform system at 25.0°C. the free energy change is tentatively given as 4.5 ± 0.5 kcal/mole, the enthalpy change as -41 ± 0.5 kcal/mole, and the entropy change of -148 ± 10 cal/mole degree. See Table 18.

TABLE 18

Thermodynamic Values of the Partition of Nickel
Oxinate and Ferric Oxinate Between
Chloroform and Aqueous Buffers

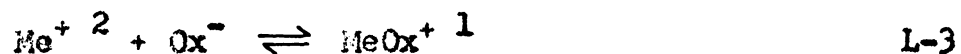
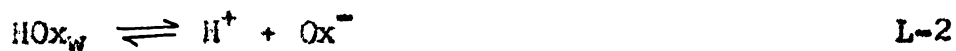
$\log K_e$	ΔG° kcal/mole	ΔH kcal/mole	ΔS° cal/mole degree	T °K.	
A. Nickel Oxinate					
-2.73	0.02	3.73	-40.4	-148	293.2
-3.69	0.02	5.21	<u>-40.4</u>	<u>-148</u>	303.2
		Av.	-40.4	-148	
B. Ferric Oxinate					
3.97	0.02	-5.42	-14.1	-29	293.2
3.56	0.03	-5.02	-13.9	-29	303.2
3.42	0.03	-4.93	<u>-14.2</u>	<u>-29</u>	313.2
		Av.	-14.1	-29	

L. Preliminary Kinetic Study of the Nickel
Oxinate Partition

It was of interest to examine the non-equilibrium extraction of a metal oxinate in order to establish the factors limiting the rate of extraction. Few studies have been reported in the literature on the rate of extraction of a chelate and none on the extraction of a metal oxinate.

Honaker and Freiser (38) found that the rate of extraction of zinc ion from an aqueous solution using an organic solution of dithizone was first order with respect to zinc, first order with respect to dithizone, and inverse first order with respect to hydrogen ion. From their data they formulated the rate-controlling step as consisting of the reaction of a dithizonate ion with a hydrated zinc ion in the aqueous phase.

The extraction process of a divalent metal oxinate probably involves the following steps:



The results of the preliminary runs on the extraction of nickel oxinate between aqueous buffer and benzene (0.05M oxine) showed that the extraction was half way to equilibrium within 15 minutes at a pH of 3.3. This indicates that steps L-1 through L-5 are very rapid. The results of the runs were not reproducible.

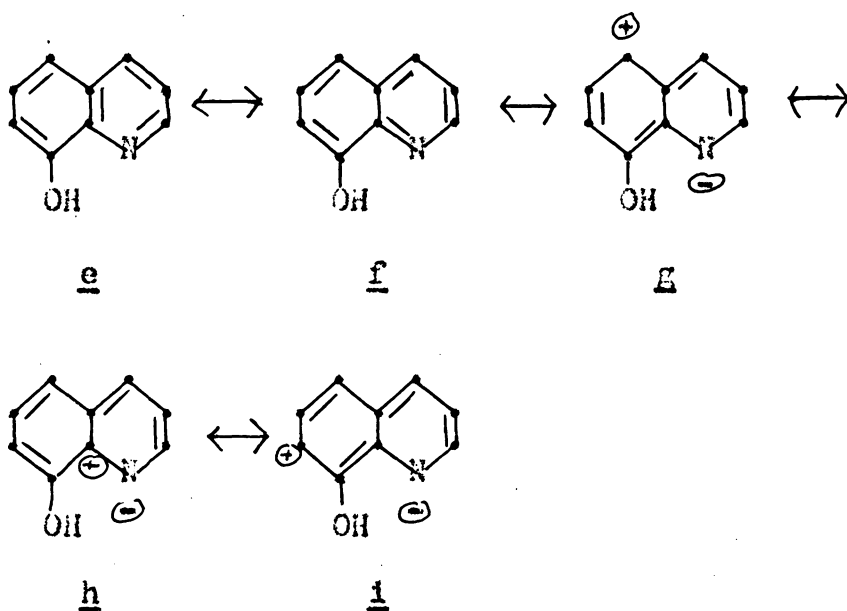
The irreproducibility of the data may be contributed by various factors in the experimental procedure; specifically, (1) the possibility that the extraction began with the introduction of the chelating agent in the organic phase to the metal ion in the aqueous phase; (2) the analytical method required the stopping of the tumbler in order to take a sample and the assumption that no extraction took

place when the vessels were not tumbling; (3) the rate of the extraction was too fast causing large differences in metal oxinate concentration in the organic phase on the different runs at the time intervals used for the measurement.

eight position, while quinoline has only a hydrogen atom. The question of foremost interest is what effect does the hydroxyl group have on the hydrogen-nitrogen bond in a? Would the quinolinium ion or the oxinium ion be the stronger acid in aqueous solution?

It can be shown that the hydroxyl group affects the nitrogen atom in several ways. It has been found that oxine is intramolecularly hydrogen bonded (56)--the hydroxyl group hydrogen atom bonding with the nitrogen atom as shown in (A-1b)--causing the electronegative nitrogen atom to appear less negative. The hydroxyl group exerts an inductive effect which acts in the same direction as the above effect. These effects result in a weaker bond between the nitrogen atom and the hydrogen ion from the aqueous solution. Conversely, in equation A-1 the nitrogen in species a should give up its hydrogen ion more easily than the nitrogen atom in the quinolinium ion--making the oxinium ion the stronger acid.

The third effect is a resonance effect. In A-3 the structures which contribute to the stability of the resonance hybrid are illustrated.

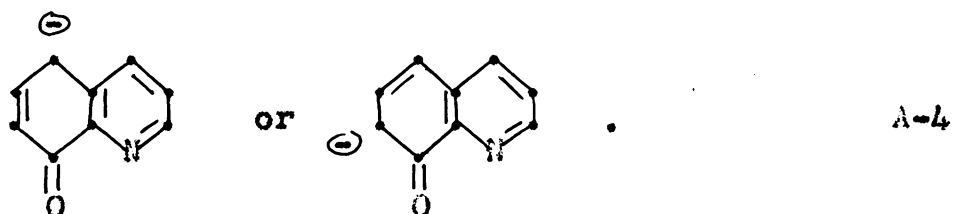


A-3

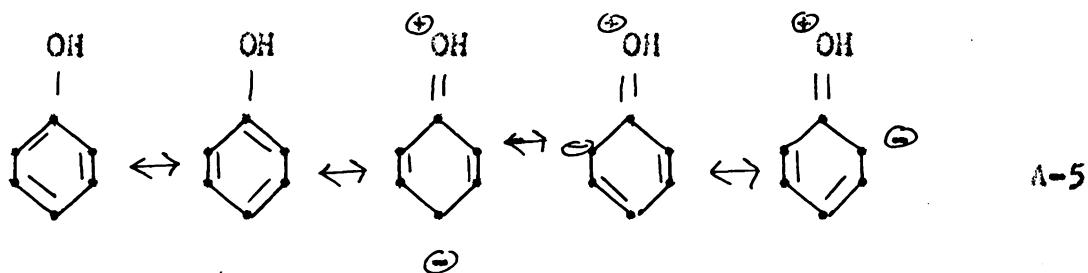
In structures g, h, and i there is an increase in the electron density on the electronegative nitrogen atom; therefore, the nitrogen atom can bond strongly with the hydrogen ion from the solution. Conversely, in equation A-1 the nitrogen atom in species a should give up its hydrogen ion less easily than the nitrogen atom in a quinolinium ion.

The pK_a of the quinolinium ion has been reported as 4.80 (76) at 25°C. and 4.94 (1) at 20°C., while the pK_a of oxine has a value of 4.91 at 25.0°C. From these data the resonance effect appears to be stronger than the field effect and the inductive effect causing the oxinium ion to be less acidic than the quinolinium ion.

It is seen from equation A-2 that the second dissociation involves the hydrogen on the hydroxyl group. Stone and Friedman (85) from spectrophotometric studies suggest that the Ox^- ion is in the keto form



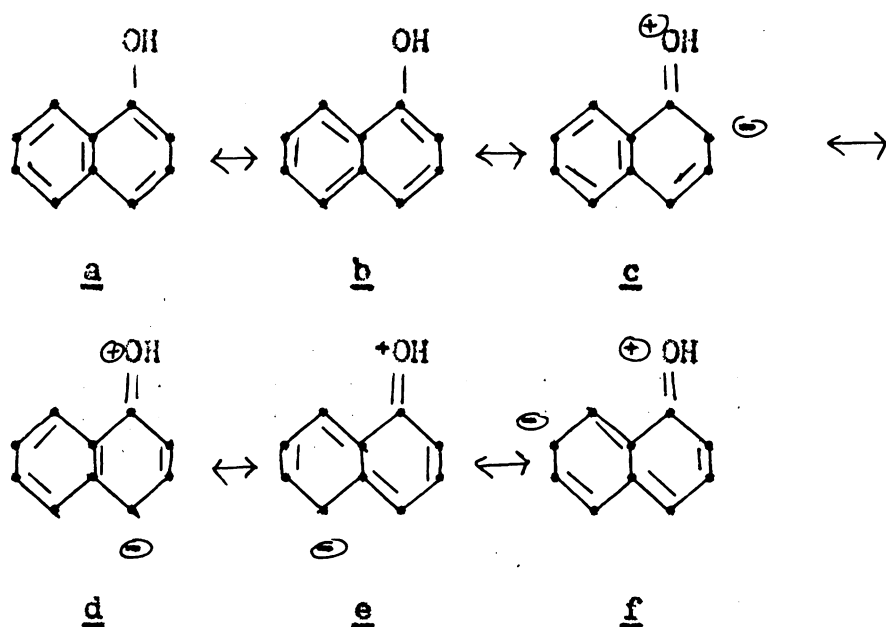
In order to account for the greater acidity of the hydroxyl hydrogen moiety in a phenolic compound than in an alcoholic compound, one possible explanation (27) has been that the phenolic hydroxyl group contributes to a resonance hybrid such as



in which the oxygen atom has a positive charge facilitating the release of the hydrogen ion, while in an alcoholic compound no appropriate structures can be found to contribute to a resonance hybrid.

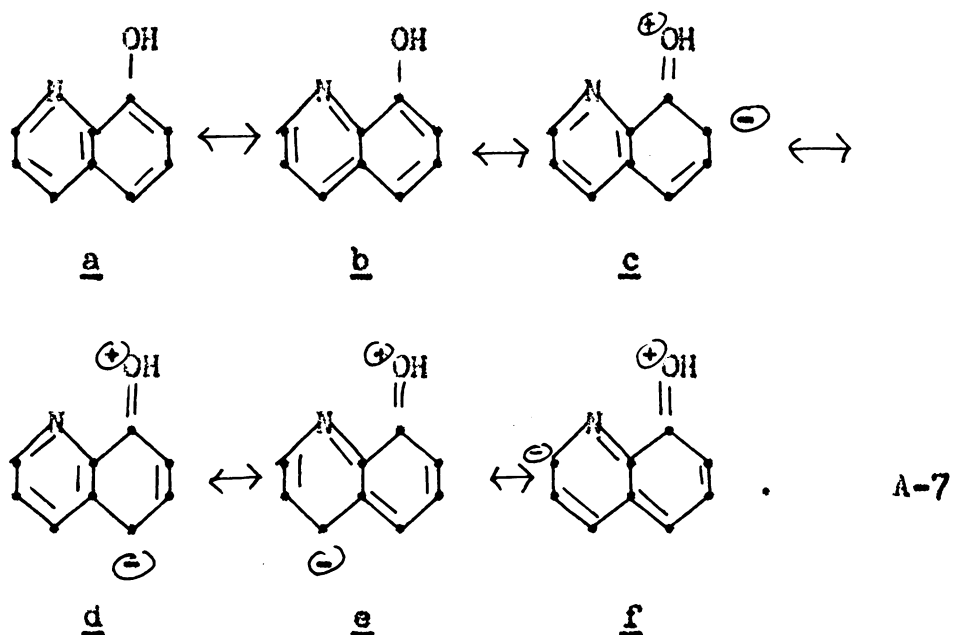
A correlation can be found among the pK_a 's of several phenolic compounds. For phenol, naphthol, and oxine the reported pK_a 's at 25°C. are 10.00 (6), 9.85 (80), and 9.81 (66), respectively. Phenol is the most basic and oxine the least basic of the three compounds. An explanation for this order is the number of hybrids that contribute to the stability of the resonance hybrid. From A-5 five structures contribute to the resonance hybrid of phenol.

For naphthol the following structures may contribute to the hybrid:



A-6

and in oxine the following structures



Comparing the number of structures that can contribute to the stability of the resonance hybrid in equations A-5, A-6, and A-7 oxine and naphthol have six structures each to five structures for phenol; therefore, this would account for the greater acidity of naphthol and oxine.

The slightly greater acidity of oxine can be accounted for by the greater stabilization of structures e and f in equation A-7 by the electronegative nitrogen atom, while structures e and f in equation A-6 do not have this stabilization.

B. Thermodynamics of Oxine Dissociation

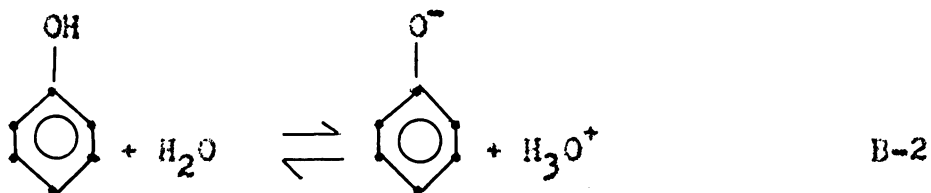
For the reaction



where B is a pyridine type base, Sacconi, Paoletti, and Ciampolini (76) found the change in entropy to be a positive value. They state that the positive entropy change shows that less order exists on the right hand side of the equation than on the left hand side. This phenomenon can be explained by the water molecules hydrating B and H⁺ being set "free" upon the formation of BH⁺. For quinoline these authors found an entropy change of 3.95 cal/mole degree and an enthalpy change of -5365 ± 15 cal/mole at 25.0°C.

For the first dissociation of oxine the entropy change was 4 cal/mole degree and an enthalpy change of -5.7 kcal/mole at 25.0°C. in agreement with the above results for a pyridine type base. From these data the hydrogen bonding of the hydroxyl group to the nitrogen atom does not have a large effect on the thermodynamic properties of oxine.

For the reaction



the thermodynamic constants have been calculated from the data of Binns (6). At 25°C. the entropy change was found to be -27 cal/mole degree and the enthalpy change 5.6 kcal/mole, in agreement with the results of Chen and Laidler (17) and Fernandez and Hepler (26).

The large negative entropy change shows that there is more order on the right side of equation B-2 than on the left hand side. This phenomenon may be explained by the difference in hydration of phenol and phenoxide ion. The phenoxide ion would be expected to be more hydrated than the phenol molecule. Therefore, on proceeding from the left hand side of the equation to the right hand side there is an increase in order accounting for the large negative entropy change.

For the second dissociation of oxine the entropy change found was -23 cal/mole degree and the enthalpy change 6.3 kcal/mole in close agreement with the thermodynamic properties of phenol.

C. Partition of Oxine

In the ideal case the partition of a compound between two solvents will be proportional to the solubility of the compound in each solvent. It is well known that polar compounds are soluble in polar solvents and nonpolar compounds are soluble in nonpolar solvents. The partition of a compound between two immiscible solvents necessarily means that one solvent is polar and the other nonpolar.

Polar solvents are highly oriented liquids due to the dipoles of the molecules interacting with one another. In order for a solute to be soluble in this liquid the solute must break the orientation of the solvent molecules. Also, a polar solute is highly oriented and in order to dissolve in a solvent energy must be supplied to break the forces between the molecules or ions. This energy can be gotten by solvation of the solute molecules or ions by the solvent.

The nonpolar solvent is not as highly oriented as the polar solvent and little energy is required to break the forces between the molecules. Should a polar solute be placed in a nonpolar solvent, the

solute would not dissolve because there is no solvation process to supply the energy required to overcome the solute-solute attractive forces.

In the ideal case the partition of a solute between two immiscible solvents can be formulated;



however, in one phase the solute may be polymeric



Another factor that can cause non-ideality is the reaction of the solute with the solvent(s).



In organic solution approximately $1 \times 10^{-4}M$ in oxine a two-fold change in the oxine concentration did not cause a change in the partition coefficient. Dyrssen (24) reported a small dependence of the distribution constant of oxine on the concentration of oxine in chloroform in solution 0.1M or greater.

In order to study the effect of the hydroxyl group on the distribution a comparison of oxine with quinoline can be made. Dyrssen and Antikainen (2)

report the partition of quinoline between chloroform and 3M aqueous sodium perchlorate and benzene and 3M aqueous sodium perchlorate solutions. Their values for the logarithm of the partition coefficient are 2.784 ± 0.020 and 2.146 ± 0.002 for the chloroform and benzene systems, respectively. In these experiments the initial quinoline concentration in the organic phase was 0.1M and 0.01M for chloroform and benzene, respectively.

The partition of the oxine or quinoline in chloroform is a non-ideal system of the second type-solvent-solute interaction, there is an acid-base reaction, since chloroform has an acidic hydrogen (39), which can react with the basic nitrogens of quinoline and oxine. The pK_a of the quinolinium ion has been reported as 4.80 (76) and the pK_a for oxine has been found to be 4.91 at 25.0°C. From these data quinoline is a stronger base and reacts more strongly with chloroform giving a more favorable partition. Overall, the acid-base reaction of oxine and quinoline with chloroform should enhance the value of the partition coefficient over that found in the benzene system because the energy supplied from the acid-base reaction can

assist in overcoming the hydration in the aqueous phase. Since benzene can be considered a neutral species, no chemical reaction between benzene and oxine or quinoline can occur. An explanation for the lower partition coefficient of quinoline than that of oxine in the benzene system is the neutrality (less hydration) of the oxine nitrogen due to the hydrogen bonding of the hydroxyl group, while the quinoline nitrogen can interact strongly with the aqueous phase.

In order to substantiate this line of thinking, the partition of several amines between chloroform-water and benzene-water systems can be compared. The value of the difference in the logarithm of the partition coefficient between the chloroform system and the benzene system is as follows: ammonia = 0.91 (71), methylamine = 0.39 (71), dimethylamine = 0.61 (71), trimethylamine = 0.67 (71), quinoline = 0.63 (71), and oxine = 0.26.

Results of the distribution experiments show that the partition coefficient for the benzene related solvents to decrease in the order nitrobenzene > benzene > toluene. This order can be accounted for by the electron-withdrawing group and electron-releasing

groups on the ring. The nitro group, which is an electron-withdrawing group, causes the pi electron cloud in the ring to be relatively more positive than the pi cloud in benzene. Since oxine has a high electron density in the nitrogen ring, there is less repulsion between the pi clouds of oxine and nitrobenzene. Conversely, the methyl group, which is an electron-releasing group, causes the pi cloud in the ring to be relatively more negative than the cloud in benzene; therefore, there is an increase in the repulsion between the two pi clouds.

From the works of Cheesman and Ladner (16) and Rollet, Elkain, Toledano, and Sing (74) the heat of mixing of the benzene-toluene system is a positive value, while from the results of Lutskii, Obukhova, and Petrentko (55) the heat of mixing of the benzene-nitrobenzene system is negative in accord with the order of oxine partition above.

D. Thermodynamics of Oxine Partition

Inspection of Table 14 shows that for the benzene, toluene, and nitrobenzene systems the ΔG° term is composed of approximately equal contributions from the ΔH term and from the $T\Delta S^\circ$ term. In the chloroform system the ΔG° term is composed mainly of the ΔH term rather than the $T\Delta S^\circ$ term as the ΔH term in this system may be considered a composite ΔH with a ΔH of extraction and a ΔH from the acid-base reaction.

The positive ΔS° term can be accounted for by the Frank and Ten (29) treatment of nonpolar solutes in water. In this treatment the non-interacting hydrocarbon molecules force the water to assume a quasi-crystalline structure lowering the entropy of solvation. Similarly, oxine causes the aqueous phase to be a more rigid structure than without oxine and upon extraction of the oxine the aqueous phase becomes less rigid and an increase in entropy is observed.

E. Salt Effects

The problem of explaining salt effects is essentially the problem of calculating ΔG , the non-ideal free energy for transferring a molecule of nonelectrolyte from pure water to the salt solution. Since at a given temperature the chemical potential of a nonelectrolyte is the same in all saturated solutions,

$$kT \ln f = \Delta G$$

E-1

where k is Boltzmann's constant, T is the absolute temperature in degrees Kelvin, and f is the activity coefficient.

The most widely known theories on salt effect are those of Debye and McAulay (20) and Debye (18) according to which f depends primarily upon ionic charge and radius, and the molar dielectric decrement of the neutral solute in water. The first theory predicts a linear limiting dependence of $\ln f$ on salt concentration and the latter a linear dependence of $1/G$ on salt concentration. These theories predict the general order of magnitude of the effects, but fail to

predict the marked specific effects of different salts, that is, salting-in and salting-out.

In order to account for the phenomenon of salting-in McDevit and Long (54) found it more feasible to relate the observed variation in the effects of different salts to other observable properties of the particular salt solution. They assumed that the only role of the nonpolar solute was to simply occupy volume and thus to modify the ion-water interactions in this simple fashion, they derived a limiting expression for the free energy of transfer of nonpolar solute from water to the salt solution and from this predicted values of k_s , the Setschenow constant, the limiting slope of $\log f$ versus salt concentration.

Employing a procedure similar to that used by Hildebrand and Scott (36) for determining the influence of volume changes on the free energy of mixing liquids, McDevit and Long showed that the excess work which must be done against ion-solvent forces to introduce a volume, V_1 , into the salt solution is proportional to the volume change ΔV^m which occurs on mixing (liquid) salt and water,

$$\frac{\lim_{\substack{c_s \rightarrow 0 \\ n_1 \rightarrow 0}} d \log f}{d c_s} = \frac{\bar{V}_1^0 (V_s - \bar{V}_s^0) k_s}{2.3 \beta_0 RT}$$

E-2

where c_s is the molar concentration of salt and n_1 the number of moles of neutral solute.

A physical interpretation of the above equation follows from the fact that the contraction in total volume, $V_s - \bar{V}_s^0$, which take place (generally) on mixing salt and water, can be interpreted as a compression of the solvent. This compression makes it more difficult to insert the volume, V_1 , of the neutral solute and results, experimentally, in salting-out.

The limiting law correctly predicts the high salting-out of sodium sulfate and sodium hydroxide and the low salting-out for lithium and hydrogen chlorides. For a solute such as benzene the above equation correctly predicts the salting-in for perchloric acid and tetramethylammonium bromide.

Deno and Spink (21) have extended the McDevit and Long equation to include solutes which specifically bond to the solvent,

$$RT \ln f = V \Delta P_e + \Delta F_H \quad E-3$$

where ΔP_e is the difference in internal pressures of two liquid phases, V is the molecular volume of the solute, and ΔF_H is the free energy change due to hydrogen bonding. They found the ΔF_H was characteristic of the type of functional group and exactly proportional to the number of such groups. Dono and Spink differentiated equation E-3 with respect to salt concentration,

$$RT (d \ln f / dc_s) = V (d \Delta P_e / dc_s) + d \Delta F_H / dc_s \quad E-4$$

This equation predicts that the Setschenow constant for a solute that is hydrogen bonded to solvent depends on the rate of change of ΔF_H with salt concentration, as well as the internal pressure changes.

McDevit and Long (54) estimated the \bar{V}_1^0 for benzene from the density of the liquid and the molecular weight. Since no density data are available for oxine, \bar{V}_1^0 could not be estimated directly. Comparing estimated \bar{V}_1^0 from compounds similar in structure, such as quinoline (118 ml./mole), 8-methylquinoline (133 ml./mole), chloronaphthalene (136 ml./mole), and naphthol (118 ml./mole), it would

be expected that 125 ± 10 ml./mole would approximate the \bar{V}_1^0 of oxine.

In general, k_s calculated from equation E-2 is approximately three times larger than the experimental value. Using the experimental k_s for the oxine system, \bar{V}_1^0 for oxine was calculated from equation E-2 and tripled to give an estimate of \bar{V}_1^0 . For the salts used in these experiments the \bar{V}_1^0 ranged from 129 ml./mole for potassium chloride to 15 ml./mole for the sodium perchlorate. The value of \bar{V}_1^0 from the potassium chloride is reasonable, but the value from the sodium perchlorate is not rational.

Inserting a value of 125 ml./mole for \bar{V}_1^0 of oxine into equation E-2 k_s values were obtained that did not reproduce the experimental order of potassium chloride > sodium chloride > potassium nitrate > sodium perchlorate nor the range in values of k_s . The markedly low value of 0.007 for k_s in the sodium perchlorate system was not approached.

Significantly, from the review of McDevit and Long (53), the works of Long and Bergen (52), Seno and Spink (21), and Saylor, Whitten, Claiborne, and Gross (79), only one solute, benzylamine, showed the

potassium chloride-sodium chloride inversion in k_s , while 60 other solutes, polar and nonpolar, gave the "normal" order in k_s of sodium chloride > potassium chloride.

Part A of Table 19 shows the values of \bar{V}_1^0 calculated from equation E-2 and the k_s/\bar{V}_1^0 from the experimental data. Part B of Table 19 is the data calculated from an estimated \bar{V}_1^0 of 125 ml./mole, while part C of the table shows the data for benzene a "typical" nonpolar solute.

For each of the salts the k_s/\bar{V}_1^0 calculated from \bar{V}_1^0 obtained from equation E-2 compares favorably with the values of k_s/\bar{V}_1^0 obtained from the estimated value of \bar{V}_1^0 obtained from the estimated value of \bar{V}_1^0 of 125 ml./mole.

According to Deno and Spink (21) a value of k_s/\bar{V}_1^0 of a solute within 50% of the k_s/\bar{V}_1^0 value of the benzene system shows no interaction of the solute with the solvent--no hydrogen bonding. Parts A and B of Table 19 show that k_s/\bar{V}_1^0 for oxine is within the 50% range for a noninteracting solute. However, should the value of k_s/\bar{V}_1^0 be evaluated from the experimental k_s and the estimated \bar{V}_1^0 of 125 ml./mole, except for

TABLE 19

Salt Effects on Oxine Using the McDevit and Long Equation

Salt	k_s exp't.	$(V_s - \bar{V}_s^0)$ ml./mole	$3 \bar{V}_i^0$ calc.	$\frac{k_s \text{ exp't.}}{3 \bar{V}_i^0 \text{ calc.} \times 10^3}$	$\frac{k_s \text{ exp't.}}{\bar{V}_i^0 = 125 \times 10^3}$
A. Oxine					
NaCl	0.118	18.5	75	1.5	0.9
KCl	0.167	10	129	1.3	1.3
KNO ₃	0.045	8.9 ^a	39	1.1	0.4
NaClO ₄	0.007	7.5	15	0.5	0.06
B. Oxine $\bar{V}_i^0 = 125$					
Salt	k_s calc.	$\frac{k_s \text{ calc.}}{3}$	$\frac{k_s \text{ calc.}}{3 \bar{V}_i^0 \times 10^3}$		
NaCl	0.600	0.200	1.6		
KCl	0.480	0.160	1.3		
KNO ₃	0.427	0.142	1.1		
NaClO ₄	0.360	0.120	1.0		

TABLE 19 (Continued)

Salt	k_g exp't.	k_g calc.	$\frac{k_g \text{ calc.}}{3}$	$\frac{k_g \text{ exp't.}}{\bar{V}_i^0}$
C. Benzene ^b $\bar{V}_i^0 = 89.4$				
NaCl	0.195			2.2
KCl	0.166			1.9
KNO ₃		0.304	0.101	(1.1) ^c
NaClO ₄	0.106			1.2

^aCalculated from the compression data of Branca and Carrelli (8).

^bData of McDevit and Long (54).

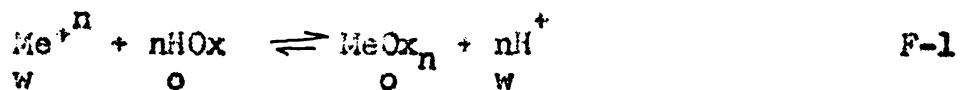
^cDerived from calculated results.

the potassium chloride system oxine would show a significant interaction with the solvent. From the data acquired throughout this work the latter hypothesis does not seem valid.

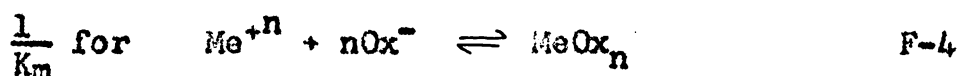
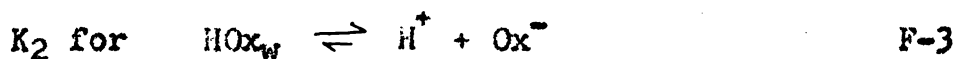
The compressibility, β_o , of the solvent, water, was taken as 45.6 bars^{-1} at 25°C . The contraction of the solvent in the potassium nitrate solution was estimated from the compressibility data of Branca and Carrelli (8).

F. Partition of Ni(II) and Fe(III) Oxinates

For the reaction



the equilibrium constant, K_o , was shown in equation J-12 on Data and Results to be made up of four other constants; namely, K_p , K_2' , K_m , and P . These constants came from the probable steps involved in the formation of the chelate and its subsequent extraction and are



In this work K_e for the Ni(II) and Fe(III) oxinate systems, P and K_2' were determined. Since the oxinates are quite insoluble in water, the formation constants are determined in dioxane-water solutions. From the work of Johnston and Freiser (44) the logarithm of the formation constant, $-\log K_m$, for Ni(II) oxinate in 50% dioxane-water and 0.3M sodium perchlorate salt medium at 25°C. is 21.38. Using these data, $\log K_p$ can be estimated as 0.82 for Ni(II) oxinate in the chloroform-water system. This means that Ni(II) oxinate is 6.5 times more soluble in chloroform than in water, while oxine is 500 times more soluble in chloroform than in water.

No data on the formation constant of Fe(III) oxinate could be found.

According to valence bond theory the orbital available for bonding by Ni^{+2} are dsp^2 --square planar

and $\text{Fe}^{+3} d^2 sp^3$ --octahedral. From the crystal structure study of nickel oxinate dihydrate (60,61) it is shown that the metal atom and bonded ligand atom lie in a plane, with the two water molecules above and below the plane at the corners of a distorted octahedron. Since there has been no study of it, ferric oxinate must be assumed to be octahedral. Borrel and Paris (7) have shown that ferric oxinate does not form a hydrate of known composition and that the water of hydration does not adhere tenaciously. The waters of hydration in the nickel compound adhere very tenaciously--the compound must be heated to 230°C . to eliminate the water of hydration. Though both oxinates are octahedral in structure, one encompasses water of hydration in its structure and the other does not. This could account for any differences in $\log K_p$ for these two oxinates.

G. Thermodynamics of Ni(II) and Fe(III)

Oxinate Partition

In section F of the Discussion the probable steps involved in the formation of the chelate and its subsequent extraction were outlined as steps F-1, F-2, F-3, F-4, and F-5. Each step is an equilibrium reaction and for steps F-1, F-2, and F-3 the thermodynamic data have been determined in this work. The formation constant of nickel oxinate has been determined at 20.0° and 25.0°C., but not under the same conditions. However, a rough estimate of the thermodynamic functions can be made and, therefore, an estimate of the thermodynamic values for step F-5 in the nickel system. No data could be found for the formation of ferric oxinate.

From the data of Johnston and Preiser (44) and Irving and Rossotti (41) the thermodynamic functions were calculated for the formation of nickel oxinate. These values are $\Delta G^\circ = -28.76$ kcal/mole, $\Delta H = 55.3$ kcal/mole, and $\Delta S^\circ = 282$ e.u. Using these data and the data for steps F-1, F-2, and F-3 the following values were found for step F-5: $\Delta G^\circ = -1.49$ kcal/mole, $\Delta H = -113$ kcal/mole, and $\Delta S^\circ = -376$ e.u.

ΔG° is the difference between a large negative ΔH and a large positive $T\Delta S^\circ$.

Analyzing the thermodynamic data for the overall reaction shows the main driving force for the extraction is the large negative ΔH in step F-5 and the positive ΔS° term in step F-4.

An estimate of step F-5 for the nickel oxinate system may be gotten from the distribution coefficient of copper oxinate between the chloroform-water system (31). The values for the thermodynamic functions are as follows: $\Delta G_{25^\circ\text{C}}^\circ = -4.75$ kcal/mole, $\Delta H = -1.3$ kcal/mole, and $\Delta S^\circ = 15$ e.u. Using these values the thermodynamic functions for step F-4 are as follows: $\Delta G_{25^\circ\text{C}}^\circ = -25.4$ kcal/mole, $\Delta H = -68$ kcal/mole, and $\Delta S^\circ = -94$ e.u. These values for the thermodynamic functions for steps F-4 and F-5 seem more reasonable than the values calculated from the formation constants in the different media.

Ferric Oxinate. The thermodynamic data for step F-1, the overall extraction process, shows a favorable ΔG° due to a negative ΔH term. Since no data could be found to estimate ΔH and ΔS° for steps F-4 and F-5, a complete analysis of the reaction cannot

be given. Steps F-2 and F-3 do not favor the overall process which means that the favorable steps must be F-4 and F-5.

VI. CONCLUSIONS

1. In the partition of oxine between chloroform and aqueous buffer the ΔH term is a composite ΔH made up of a ΔH of extraction and a ΔH from the acid-base reaction between chloroform and oxine.

2. The partition coefficient of oxine decreases in the order nitrobenzene > benzene > toluene because the pi cloud in nitrobenzene is relatively more positive than the pi cloud in benzene and the pi cloud in toluene is relatively more negative than the pi cloud in benzene because of the electron-withdrawing effect of the nitro group and the electron-releasing effect of the methyl group.

3. The Deno and Spink extension of the McDavit and Long equation adequately describes the effects of salts on oxine.

VII. SUMMARY

1. The extinction coefficients of H_2Ox^+ and Ox^- were found to be 1.70×10^3 and 2.89×10^3 , respectively.

2. The pK of H_2Ox^+ was found to be 5.103, 4.960, and 4.840 at 25.0°, 35.0°, and 45.0°C., respectively, at 0.1M ionic strength--sodium chloride medium.

3. The pK of HOx was found to be 9.76, 9.65, and 9.48 at 25.0°, 35.0°, and 45.0°C., respectively, at 0.1M ionic strength--sodium chloride medium.

4. The thermodynamic values of the first dissociation of oxine are $G_{25.0^\circ C.}^\circ = 6.96$ kcal/mole, $\Delta H = 5.7$ kcal/mole, and $\Delta S^\circ = -4$ e.u.

5. The thermodynamic values of the second dissociation of oxine are $\Delta G_{25.0^\circ C.}^\circ = 13.3$ kcal/mole, $\Delta H = 6.3$ kcal/mole, and $\Delta S^\circ = -23$ e.u.

6. The pK of H_2Ox^+ was determined as a function of ionic strength at 25.0°C. using four salts; specifically, sodium chloride, potassium chloride, potassium nitrate, and sodium perchlorate.

7. The distribution of oxine determined at 25.0°, 35.0°, and 45.0°C. in four systems; specifically, benzene-water, toluene-water, nitrobenzene-water, and

chloroform-water at 0.1M ionic strength-sodium chloride medium.

8. The logarithm of the partition coefficient of oxine is as follows: benzene 2.44 (25.0°C.), 2.37 (35.0°C.), 2.35 (45.0°C.); toluene 2.33 (25.0°C.), 2.29 (35.0°C.), 2.27 (45.0°C.); nitrobenzene 2.67 (25.0°C.), 2.65 (35.0°C.), 2.59 (45.0°C.); chloroform 2.703 (25.0°C.), 2.67 (35.0°C.), 2.59 (45.0°C.).

9. The following thermodynamic data for the partition have been found: benzene $\Delta G_{25.0^\circ\text{C.}}^\circ = -3.33$ kcal/mole, $\Delta H = -2.0$ kcal/mole, and $\Delta S^\circ = 4.5$ e.u.; toluene $\Delta G_{25.0^\circ\text{C.}}^\circ = -3.13$ kcal/mole, $\Delta H = -1.3$ kcal/mole, and $\Delta S^\circ = 6.2$ e.u.; nitrobenzene $\Delta G_{25.0^\circ\text{C.}}^\circ = -3.64$ kcal/mole, $\Delta H = -1.7$ kcal/mole, and $\Delta S^\circ = 6.6$ e.u.; chloroform $\Delta G_{25.0^\circ\text{C.}}^\circ = -3.69$ kcal/mole, $\Delta H = -2.5$ kcal/mole, and $\Delta S^\circ = 3.9$ e.u.

10. The logarithm of the partition coefficient of oxine in the benzene-water system was determined as a function of the ionic strength in four salts; specifically, sodium chloride, potassium chloride, potassium nitrate, and sodium perchlorate.

11. The logarithm of the partition coefficient of oxine in the benzene-water system at zero ionic strength was found to be 2.31.

12. The Setschenow constant, k_s , for oxine has the following values: NaCl = 0.113, KCl = 0.167, KNO_3 = 0.045, and NaClO_4 = 0.007.

13. The logarithm of the partition coefficient of nickel oxinate between chloroform-water was found to be -2.73 and -3.69 at 25.0° and 35.0°C., respectively. Due to inconsistent results the value at 45.0°C. was not found.

14. The logarithm of the partition coefficient of ferric oxinate between chloroform-water was found to be 3.97, 3.56, and 3.42 at 25.0°, 35.0°, and 45.0°C., respectively.

15. The following thermodynamic data have been found for the partition: nickel oxinate $\Delta G_{25.0^\circ\text{C.}}^\circ = 3.73$ kcal/mole, $\Delta H = -40.4$ kcal/mole, and $\Delta S^\circ = -148$ e.u.; ferric oxinate $\Delta G_{25.0^\circ\text{C.}}^\circ = -5.42$ kcal/mole, $\Delta H = -14.1$ kcal/mole, and $\Delta S^\circ = -29$ e.u.

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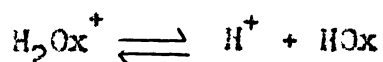
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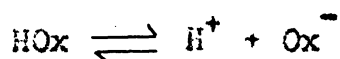
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ABSTRACT

The effects of temperature on the first and second acid dissociation constants of 8-hydroxyquinoline (oxine) have been measured and the following thermodynamic values assigned to solutions of 0.1M ionic strength. For the process,



at 25°C., $\text{pK}_1 = 5.103$, $\Delta H = 5.7$ kcal/mole, and $\Delta S^\circ = -4$ e.u. For the second acid dissociation constant,



at 25°C., $\text{pK}_2 = 9.76$, $\Delta H = 6.3$ kcal/mole, and $\Delta S^\circ = -23$ e.u. The values for the second dissociation constant agree with those previously published. The values for the first dissociation constant have not been previously determined but are consistent with the results expected for reactions of this charge and chemical type.

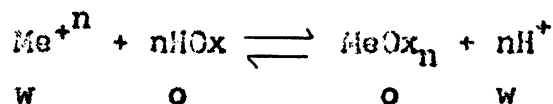
The partition of 8-hydroxyquinoline was determined as a function of temperature for the following systems; water-benzene, water-nitrobenzene, water-toluene, and

water-chloroform. The pertinent thermodynamic values for the partitions are as follows:

a. Water-benzene	log P = 2.44 ΔH = -2.0 kcal/mole ΔS° = 4.5 e.u.
b. Water-nitrobenzene	log P = 2.67 ΔH = -1.7 kcal/mole ΔS° = 6.6 e.u.
c. Water-toluene	log P = 2.33 ΔH = -1.3 kcal/mole ΔS° = 6.2 e.u.
d. Water-chloroform	log P = 2.703 ΔH = -2.5 kcal/mole ΔS° = 3.9 e.u.

The values obtained for the water-chloroform system agree well with the literature and serve as a check on the rest of the data.

The effect of temperature on the overall extraction constant of nickel oxinate and ferric oxinate was measured for the system water-chloroform. The thermodynamic values found for the process



are the following at 25°C. and an ionic strength of 0.1M:

- a. Nickel oxinate $\log K_e = -2.73$
 $\Delta H = -40.4$ kcal/mole
 $\Delta S^\circ = -148$ e.u.
- b. Ferric oxinate $\log K_e = 3.97$
 $\Delta H = -14.1$ kcal/mole
 $\Delta S^\circ = -29$ e.u.

The effect of ionic strength on the partition of 8-hydroxyquinoline between water and benzene was determined for four different uni-univalent salts: potassium chloride, sodium chloride, potassium nitrate, and sodium perchlorate. The "salting out" of oxine observed is typical of non-electrolytes.