

TABLE VII
DIPOLE MOMENTS PER MONOMER UNIT

ρ	μ	ρ	μ
Distyrene		1,2-Diphenylethane	
19.9	2.17	19.8	2.16
22.8	2.16	23.2	2.16
25.6	2.16	26.0	2.13
28.6	2.05		
Diphenylmethane		Tetralin	
19.8	2.17	19.3	2.21
22.7	2.16	22.3	2.22
25.8	2.16	25.2	2.20
28.8	2.15	28.3	2.20
1,1-Diphenylethane		Amylnaphthalene	
19.9	2.16	23.0	2.13
22.8	2.16	25.9	2.12
25.9	2.13	29.0	2.11
28.8	2.13		

In order to give some information on the influence of plasticizer on polar properties, in the last column of Table VI are given values of the static dielectric constants at 60° for 25% plasticizer. These are values obtained by interpolation on an ϵ_0 - ρ plot, for which the ϵ_0 values were obtained by the Cole extrapolation. It will be noted that ϵ_0 is larger for the polar plasticizers than for the hydrocarbons, which average to $\epsilon_0 = 8.3$. Diphenoxyethane comes somewhat higher, due to the polarity of the oxygens, and the esters are still higher. Dibenzyl sebacate is low, because the molecule contains a lot of non-polar methylenes, and dibenzyl ketone is highest. A very definite parallelism between the static dielectric constant at a given temperature and composition, and the relative dipole content of the plasticizer molecule is thus observed.

Summary

1. Data at 40 and 60°, at 60, 600 and 6000 cycles are given for polyvinyl chloride plasticized with 8 to 30% by weight of the following compounds: tetralin, diphenylmethane, diphenylmethylmethane, dibenzyl, amylnaphthalene, distyrene, di- α -methylstyrene, diphenoxyethane, dibenzyl ketone, dibenzyl maleate, dibenzyl succinate, dibenzyl phthalate, dibenzyl sebacate and dioctyl phthalate.

2. Plasticization is essentially a separation of chain molecules by the plasticizer molecules, accompanied by a rapid decrease in microscopic and macroscopic coefficients of friction.

3. A simple empirical relationship connecting loss factor and plasticizer concentration is given. Very roughly, the viscosity varies inversely as the third or fourth power of the relative concentration, depending on the temperature.

4. The concentration at which a given plasticizer produces a given internal viscosity, as measured by a characteristic electrical response, depends on the size and shape of the plasticizer molecule. A long cylindrical molecule is more effective in reducing viscosity than a spherical molecule of the same molecular weight.

5. Plasticizers of about the same size and shape are about equally effective as plasticizers, regardless of their chemical structure. For polyvinyl chloride, however, a polar or polarizable group must be present in the plasticizer in order for it to interact with the polymer.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, NEW YORK STATE COLLEGE FOR TEACHERS, AND COLUMBIA UNIVERSITY]

A Study of the Reaction of Ferric Ion with Orthophosphate in Acid Solution with Thiocyanate as an Indicator for Ferric Ions

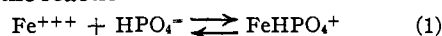
BY OSCAR E. LANFORD AND SAMUEL J. KIEHL

Introduction

It is well known that the addition of orthophosphoric acid to an acid solution of a ferric salt produces an extensive decrease in the activity of the ferric ions. This property probably constitutes the fundamental principle in the effectiveness of the Zimmerman-Reinhardt "Preventive Solution."^{1,2} Beyond this, however, little is known

concerning the reaction of ferric ions with phosphate. Therefore, to ascertain its nature and to discover, if possible, the type and formula of the complex formed, the present investigation was undertaken.

By the method used we were able not only to establish the reaction



but also to determine the dissociation constant of FeHPO_4^+ , the ferric phosphate complex formed. The method suggested by the recent

(1) Zimmerman and Reinhardt, *Ber.*, **14**, 775 (1881); *Chem. Ztg.*, **13**, 323 (1889).

(2) H. A. Fales and F. Kenny, "Inorganic Quantitative Analysis," The Century Company, New York, N. Y., 1939, p. 426.

work of Bent and French³ by means of which this information was obtained, is based upon the use of thiocyanate ion as an indicator for ferric ion. Moreover, these authors have demonstrated that the red color produced on the addition of sodium thiocyanate to a solution of a ferric salt is due to the formation of the ion FeCNS^{++} . In addition they determined its dissociation constant.

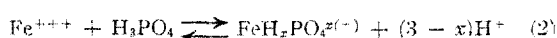
Further, the FeCNS^{++} ion itself has certain properties which make it well suited as an indicator for ferric ion in certain cases: *viz.*, it is relatively highly dissociated (its dissociation constant is of about the same magnitude as the first dissociation constant of phosphoric acid); and its color is so intense that one may accurately ascertain its concentration colorimetrically when relatively small quantities are present. Thus, with a visual spectrophotometer the concentration of ferric thiocyanate, even if the amount is considerably less than 5×10^{-5} m./l., may be established with an accuracy better than 1%.

The Ratio of Iron and Phosphorus in the Complex.—The ratio of iron to phosphorus in the ferric phosphate complex was determined by the method of continuous variations, proposed and published by Job in 1928.^{4,5} Accordingly, solutions of ferric nitrate and phosphoric acid were mixed in varying ratios so that the sum of the moles of ferric nitrate and phosphoric acid was constant throughout the series of solutions. The final volume of the solutions was also constant. The ferric ion concentration in each of these solutions was determined colorimetrically by use of sodium thiocyanate with the photometer described below. Inasmuch as the ferric phosphate complex itself is colorless its presence offers no difficulties in the use of the colorimetric method. The experimental and other related data are given in Table II.

Now, to find the ratio of iron to phosphorus the difference between the ferric ion concentration so found and that found by the same method for a corresponding solution from which the phosphoric acid had been omitted, designated $[\text{Fe}^{+++}]_0$, was plotted (Fig. 1) against the ratio $M_{\text{H}_3\text{PO}_4}/(M_{\text{H}_3\text{PO}_4} + M_{\text{Fe}(\text{NO}_3)_3})$ designated R , in Table II. For, it is evident, under the restrictions of the method, that the value of $[\text{Fe}^{+++}]_0$, the amount engaged in the complex, is dependent upon the ferric nitrate

present as well as upon the phosphoric acid, and that it will be a maximum if the ratio is the same as that in the complex but smaller with either a predominance of ferric nitrate or phosphoric acid. This difference thus becomes a maximum at the value of R which is equal to the ratio of moles of phosphorus to the sum of the moles of phosphorus plus the moles of iron in the complex. Experimentally the maximum was found at a value of 0.5 for R , which denotes that the ratio of iron to phosphorus in the complex is unity.

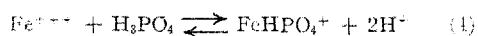
The Ionic State of the Phosphate which Forms the Complex.—By studying the effect of variations in concentration of acid upon the equilibrium between ferric ions, phosphoric acid and the ferric phosphate complex, the phosphate ion which forms the complex with iron was shown to be HPO_4^{--} . The data are presented in Table III. The method involved the reaction



which one may express by the equation

$$\log Kc - \log \frac{M_{\text{FeH}_x\text{PO}_4^{x(-)}}}{(M_{\text{Fe}^{+++}})(M_{\text{H}_3\text{PO}_4})} = (3-x) \log (M_{\text{H}^+}) \quad (3)$$

In this equation Kc refers to the equilibrium constant for reaction (2) in terms of molarities. To determine x , the value which determines the charge on the ferric phosphate complex, the variable term on the left (eq. 3) was plotted against the term on the right (Fig. 2) for a series of the above solutions, whose ionic strength was kept constant to obviate effects due to variations in activity coefficients which would ensue with different concentrations of acid. The slope of this curve equals the quantity $(3-x)$ in reaction (2) and equation (3). The value of $(3-x)$ the slope so found was 2, which indicates that the reaction is



and the formula of the ferric phosphate complex FeHPO_4^+ .

The Dissociation Constant of the Ferric Phosphate Complex.—The dissociation constant of this complex was derived from data obtained by colorimetric determination of ferric ion concentrations in solutions containing known quantities of total ferric nitrate and total phosphoric acid. The data are presented in Table IV. To each solution 0.1000 m./l. of nitric acid was added to reduce the correction for hydrolysis. The ionic strength was adjusted to 0.665 by sodium nitrate in each case.

(3) H. E. Bent and C. L. French, *THIS JOURNAL*, **63**, 568 (1941).

(4) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

(5) W. C. Veborough and Gerald R. Cooper, *THIS JOURNAL*, **63**, 437 (1941).

From the data so obtained the dissociation constant of the complex was evaluated.

Experimental

All reagents used in these experiments were of the highest purity obtainable. Wherever necessary, salts were recrystallized. Ferric nitrate solutions were standardized by the Zimmerman-Reinhardt method² as well as by use of the Jones reductor,⁸ after the volatilization of the nitric acid which they contained. Sodium thiocyanate solutions were prepared by carefully weighing recrystallized sodium thiocyanate which had been dried for eighteen hours at 160°. As an added precaution the concentration of the solution was determined argentometrically with eosin as an adsorption indicator.⁷ The silver nitrate solution was standardized against pure sodium chloride with fluorescein as an indicator.⁷ The results obtained by the titrations confirmed the purity of the sodium thiocyanate used.

Nitric, phosphoric and hydrochloric acids were standardized acidimetrically against a sodium hydroxide solution, free from carbonate, which had been previously standardized with potassium acid phthalate supplied by the U. S. Bureau of Standards.

For the colorimetric determination of ferric thiocyanate a Pulfrich photometer was employed. All extinction coefficients given in this paper refer to the use of an S55 ($\lambda = 550 \text{ m}\mu$) filter. This filter was selected because it was the most suitable for the concentration range encountered in these experiments. The nitric acid concentration was 0.1000 *M* in most solutions upon which the photometer was used; under these conditions the ferric nitrate solutions are completely colorless before the addition of thiocyanate. Thereby the absorption by the products of the hydrolysis of the ferric nitrate was reduced to a point where it need not be considered. However, as an added precaution, all solutions were observed in the photometer against a blank which contained all the constituents in the unknown except the sodium thiocyanate.

A calibration curve relating $M_{\text{FeCNS}^{++}}$ and the extinction coefficient was prepared by use of solutions containing known total ferric nitrate and sodium thiocyanate. These data are presented in Table I. The $M_{\text{FeCNS}^{++}}$ in these solutions was calculated by use of the value³ 0.033 for its dissociation constant at the same ionic strength. By employing the hydrolytic constant suggested by Bent and French,³ which is based on the data of Lamb and Jacques⁸ and on the data of Bray and Hershey,⁹ these calculations are corrected for the hydrolysis of ferric ion.

All values for extinction coefficients given in this paper are, respectively, the mean obtained from at least two series of solutions with approximately twenty readings for each solution. In general, the precision is 5 parts per thousand or better.

In the course of their experimentation Bent and French³ observed a fading of color due to changing of the ferric thiocyanate complex, on standing. During the progress of this work, in addition, preliminary evidence has been

obtained which suggests this fading to be due to an oxidation-reduction reaction involving, in our work, nitric acid and thiocyanate. However, since in our experiments the thiocyanate ion concentration was always much larger than the ferric thiocyanate concentration (approximately 10 times as large), the slow oxidation of thiocyanate did not produce noticeable fading within the first few minutes. Wherefore the sodium thiocyanate was always added last and the extinction coefficient determined immediately. Usually the readings were completed in less than ten minutes after mixing. Consequently, in no cases was a trend in the individual reading of the extinction coefficient observed and we believe no error was introduced from this source.

All pH determinations were made with a Beckmann glass electrode and assembly, which was calibrated against 0.05 *M* potassium acid phthalate.

All measurements were made at a temperature of 30 \pm 1°.

Discussion and Explanation of Experimental Data

Because of its importance to our investigation and because a prodigious amount of work was required in very carefully acquiring the experimental data and making the calculations for the construction of a calibration curve which establishes the relation between the extinction coefficient and the molar concentration of FeCNS^{++} , the results are given in Table I. The $M_{\text{FeCNS}^{++}}$, Column (c), was determined as described above. When these data are plotted on a large scale, it is found that the result is not exactly a straight line. But although the departure from linearity is not great, nevertheless, it has been taken into consideration in the use of the data.

TABLE I
DATA FOR RELATION BETWEEN EXTINCTION COEFFICIENT AND $M_{\text{FeCNS}^{++}}$ AT A WAVE LENGTH OF 550 $\text{m}\mu$

All solutions contain 0.1000 *M* nitric acid and are brought to an ionic strength of 0.665 by the addition of sodium nitrate. $M_{\text{FeCNS}^{++}}$ calculated by using the value 0.033 for its dissociation constant.³

Total $\text{Fe}(\text{NO}_3)_3$ m./l. $\times 10^3$ (a)	Total NaCNS, m./l. $\times 10^3$ (b)	Calcd. $M_{\text{FeCNS}^{++}}$ $\times 10^3$ (c)	ϵ^a (d)
4.075	4.075	0.408	1.62
3.668	3.668	.336	1.34
3.260	3.260	.373	1.10
2.853	2.853	.210	0.87
2.445	2.445	.158	.66
2.037	2.037	.114	.50
1.630	1.630	.074	.32
1.223	1.223	.040	.195
0.815	0.815	.019	.092
0.815	4.075	.090	.39

^a $\epsilon = \log(I_0/I)/s$ where I_0 and I refer to the intensities of the incident and transmitted light and s = thickness of the cell in cm.

(6) H. A. Fales and F. Kenny, ref. 2, p. 415.

(7) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1938, p. 453.

(8) A. B. Lamb and A. G. Jacques, *THIS JOURNAL*, **60**, 1215 (1938).

(9) W. C. Bray and A. V. Hershey, *ibid.*, **56**, 1889 (1934).

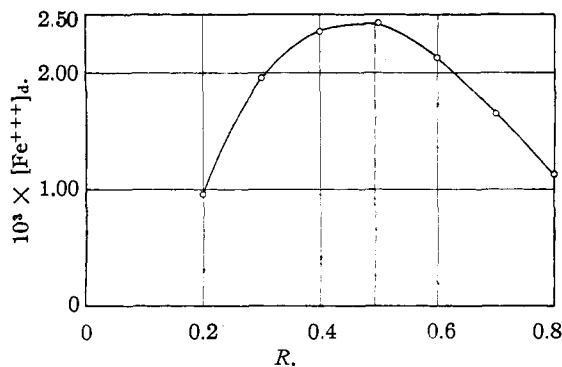


Fig. 1.

Table II contains the data from which the ratio of iron to phosphorus in the complex was obtained. In Columns (a) and (b), respectively, are the volumes of ferric nitrate and phosphoric acid solution of the indicated concentration respectively; Column (c) the value of R ; column (d) the extinction coefficient of the solution; and column (e) $M_{\text{FeCNS}^{++}}$ for the corresponding value of ϵ . Knowing the total sodium thiocyanate present one may calculate the values for $M_{\text{Fe}^{+++}}$, which are listed in Column (f). In Column (g) are tabulated $M_{\text{Fe}^{+++}}$ present in solutions containing the same total iron and sodium thiocyanate with the phosphoric acid omitted. The data in (f) and (g) are experimental. In Column (h) the differences between (f) and (g) are tabulated. In Fig. 1 these differences are plotted against the ratio, R , described above. The maximum in this curve which occurs at $R = 0.5$ indicates that the complex contains iron and phosphorus in the ratio 1:1. Inasmuch as the ionic strength of all the above solutions was constant, activity coefficients need not be considered.

From the data presented in Table III, the effect of variations in nitric acid on ferric ion concentration in the presence of phosphoric acid was

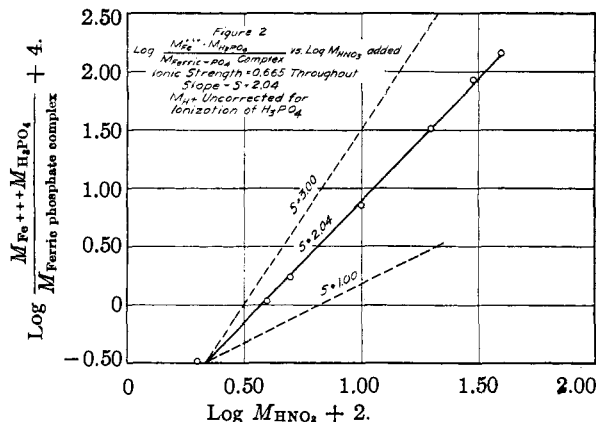


Fig. 2.

determined. In each of the experiments here listed the sum of the ferric nitrate concentration plus the phosphoric acid concentration was constant as well as the total sodium thiocyanate concentration and ionic strength. Column (a) gives molarity of added nitric acid, (b) molarity of FeCNS^{++} in the solution at equilibrium, (c) molarity of Fe^{+++} ($M_{\text{CNS}^-} = \text{total NaCNS} - M_{\text{FeCNS}^{++}}$). Column (d) is the molarity of the ferric phosphate complex. These values are obtained by subtracting from total iron the sum of $M_{\text{FeCNS}^{++}}$ plus $M_{\text{Fe}^{+++}}$ plus $M_{\text{FeOH}^{++}}$; the latter quantity was calculated by use of hydrolytic constant, 10^{-3} (see above). The molarity of free phosphoric acid is obtained by subtracting from total phosphoric acid concentration the molar concentration of the ferric phosphate complex. These values are shown in Column (e). Finally the molarity of molecular phosphoric acid is shown in Column (f). This last column is based on the value 3.02×10^{-2} for the first dissociation constant of phosphoric acid at an ionic strength of 0.665. A search of the literature failed to reveal data on the first dissociation constant of

TABLE II

DETERMINATION OF THE RATIO OF IRON TO PHOSPHORUS IN THE FERRIC PHOSPHATE COMPLEX

All solutions were 0.1000 M with respect to nitric acid and were adjusted to an ionic strength = 0.665 by the addition of sodium nitrate; all solutions contained sodium thiocyanate of molarity 4.075×10^{-3} , the total vol. in each case 100 cc.

$\text{Fe}(\text{NO}_3)_3$, cc., $m = 4.075 \times 10^{-2}$ (a)	H_3PO_4 , cc., $m = 0.05631$ (b)	$\frac{M_{\text{H}_3\text{PO}_4}}{M_{\text{H}_3\text{PO}_4} + M_{\text{Fe}(\text{NO}_3)_3}} = R$ (c)	ϵ (d)	$M_{\text{FeCNS}^{++}} \times 10^3$ (e)	$M_{\text{Fe}^{+++}} \times 10^3$ (f)	$M_{\text{Fe}^{+++}} \times 10^3$ for same amount $\text{Fe}(\text{NO}_3)_3$ in presence of NaCNS omitting H_3PO_4 (g)	$[\text{Fe}^{+++}]_d \times 10^3$ (g) - (f) (h)
16.00	2.90	0.2	1.75	0.446	4.36	5.32	0.96
14.00	4.34	.3	1.33	.330	2.91	4.87	1.96
12.00	5.80	.4	0.97	.234	2.01	4.36	2.35
10.00	7.24	.5	.654	.152	1.28	3.70	2.42
8.00	8.70	.6	.469	.107	0.890	3.02	2.13
6.00	10.14	.7	.314	.067	.553	2.21	1.66
4.00	11.60	.8	1.211	.045	.36	1.49	1.13

TABLE III

EFFECT OF VARIATIONS IN M_{H^+} ON $M_{Fe^{+++}}$ IN SOLUTIONS OF FERRIC NITRATE CONTAINING PHOSPHORIC ACID WITH THIOCYANATE AS THE INDICATOR FOR FERRIC ION CONCENTRATION

Total phosphoric acid = $5.631 \times 10^{-3} M$ throughout. Total ferric nitrate = total sodium thiocyanate = $4.075 \times 10^{-3} M$ throughout. Ionic strength constant at 0.665. Acidity varied as indicated by use of nitric acid.

M_{HNO_3} (a)	$M_{FeCNS^{++}} \times 10^3$ (b)	$M_{Fe^{+++}} \times 10^3$ (c)	M_{Fe-PO_4} cpx. $\times 10^3$ (d)	$M_{H_3PO_4}$ not in complex $\times 10^3$ (e)	$M_{molecular}$ $H_3PO_4 \times 10^3$ (f) ^a
0.0200	0.022	0.179	3.865	1.776	0.710
.0400	.041	.335	3.691	1.940	1.109
.0500	.0569	.467	3.542	2.089	1.307
.1000	.120	1.00	2.945	2.69	2.07
.2000	.222	1.903	1.941	3.69	3.34
.3000	.294	2.567	1.205	4.426	4.03
.4000	.326	2.865	0.877	4.754	4.42

^a K_{1c} for $H_3PO_4 = 3.02 \times 10^{-3}$.

TABLE IV

DETERMINATION OF THE DISSOCIATION CONSTANT OF $FeHPO_4^+$

All solutions contain total ferric nitrate = $4.075 \times 10^{-3} M$; total sodium thiocyanate = $4.075 \times 10^{-3} M$; nitric acid = $0.1000 M$.

Total H_3PO_4 added $M \times 10^3$ (a)	$M_{FeCNS^{++}} \times 10^3$ (b)	$M_{Fe^{+++}} \times 10^3$ (c)	$M_{FeHPO_4^+} \times 10^{3a}$ (d)	$M_{H_3PO_4}$ remaining at equilib- rium $\times 10^3$ (e)	$M_{molecular}$ H_3PO_4 at equilib- rium $\times 10^{3b}$ (f)	$M_{FeHPO_4^+} (M_{H^+})^2$ $\times 10^3$ (g)
2.86	0.222	1.90	1.93	0.93	0.72	11.0
3.14	.204	1.74	2.11	1.03	.80	13.2
3.38	.193	1.64	2.23	1.15	.90	14.8
3.72	.178	1.51	2.37	1.34	1.04	17.3
4.29	.160	1.35	2.55	1.74	1.35	20.8
4.57	.150	1.26	2.67	1.88	1.47	23.7
5.14	.133	1.11	2.82	2.33	1.81	28.2
5.63	.120	1.00	2.95	2.68	2.10	33.4
6.76	.098	0.82	3.15	3.60	2.81	44.3
7.88	.083	.68	3.30	4.58	3.58	56.1
9.01	.072	.59	3.40	5.61	4.38	67.0
10.14	.062	.51	3.50	6.64	5.18	80.8

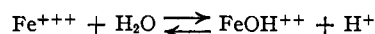
^a Corrected for hydrolysis. ^b Based on K_{1c} for $H_3PO_4 = 3.02 \times 10^{-2}$ at $\mu = 0.665$.

phosphoric acid at an ionic strength as high as 0.665. We have therefore evaluated this constant by measuring the hydrogen ion activity of solutions of potassium dihydrogen phosphate and hydrochloric acid to which potassium nitrate had been added to produce the desired ionic strength. The final value obtained was: K_{1c} for $H_3PO_4 = 3.02 \times 10^{-2}$, with $\mu = 0.665$ at 30° .

This value involves the use of cells with liquid junctions both in our measurements of a_{H^+} and in the use of activity coefficients of individual ions which are necessary in the calculation of K_{1c} . The activity coefficients of H^+ used are those of Scatchard,¹⁰ which are based upon the assumption of equal activity coefficients for K^+ and Cl^- . Therefore the above value for K_{1c} for phosphoric acid is not thermodynamically exact, but we believe however that it may be used here without introducing any serious error into our calculations.

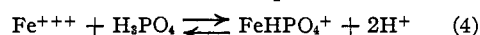
(10) George Scatchard, THIS JOURNAL, 47, 696 (1925).

Observations were also made on the effect of variations in nitric acid concentration at constant ionic strength and in the absence of phosphoric acid, upon the color of the solutions produced by ferric thiocyanate. In such cases, however, our experiments disclosed that within the acidity range here encountered, the variations of $M_{FeCNS^{++}}$ produced by changes in M_{H^+} were explainable by the hydrolytic reaction



by using the equilibrium constant, 10^{-3} , for it.^{3,8,9} The data thus acquired are tabulated in Table III.

These data were employed in Fig. 2 in accordance with the reaction and equation already discussed. The slope of the curve found graphically is 2.04. The reaction in question is, therefore



and the formula of the ferric phosphate complex is $FeHPO_4^+$.

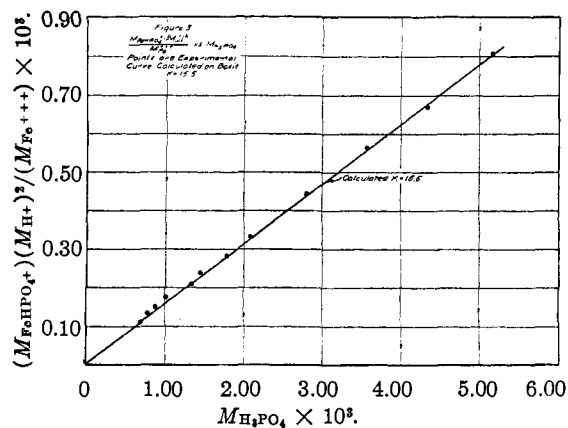


Fig. 3.

In Table IV the data used in evaluating the dissociation constant of the complex FeHPO_4^+ are listed. All these solutions contain a total ferric nitrate and a total thiocyanate concentration of 4.07×10^{-3} m./l. each, respectively, as well as nitric acid to make its concentration 0.1000 M . The ionic strength is kept constant at 0.665 by the addition of sodium nitrate. Column (a) contains the molarity of phosphoric acid (b) the $M_{\text{FeCNS}^{++}}$ determined colorimetrically. Columns (c), (d), (e), (f) are obtained precisely as in Table III. In the evaluation of the ratio $(M_{\text{FeHPO}_4^+})(M_{\text{H}^+})^2 / (M_{\text{Fe}^{+++}})$ in Column (g), the hydrogen ion produced in reaction (4) was considered. The slope of this curve, which equals the equilibrium constant, for reaction (4) above

$$K_c = \frac{(M_{\text{FeHPO}_4^+})(M_{\text{H}^+})^2}{(M_{\text{Fe}^{+++}})(M_{\text{H}_3\text{PO}_4})} \quad (5)$$

is found by plotting the above ratio against the $M_{\text{H}_3\text{PO}_4}$ (Fig. 3). Furthermore, in order to obtain the most probable result for the value of the slope from our data, the method of least squares

was used. The final value so obtained was 15.50 ± 0.28 . By dividing eq. (6)

$$(K_{1c}K_{2c})_{\text{H}_3\text{PO}_4} = \frac{(M_{\text{H}^+})^2(M_{\text{HPO}_4^-})}{(M_{\text{H}_2\text{PO}_4^-})} \quad (6)$$

by eq. (5) one obtains

$$\frac{(M_{\text{Fe}^{+++}})(M_{\text{HPO}_4^-})}{(M_{\text{FeHPO}_4^+})} = \frac{(K_{1c}K_{2c})_{\text{H}_3\text{PO}_4}}{15.5}$$

and by using our value of K_{1c} for phosphoric acid equal to 3.02×10^{-2} and the value of K_{2c} for phosphoric acid equal to 2.28×10^{-7} at an ionic strength of 0.665, which was calculated from the data of Cohn,¹¹ the stoichiometric dissociation constant of the ferric phosphate complex 4.44×10^{-10} , at an ionic strength of 0.665, is obtained.

By use of the method described in the foregoing paragraphs studies of other equilibria involving ferric ion are now in progress.

Summary

1. A study of the reaction between ferric ion and orthophosphoric acid in acid solution has been made and the formula of the complex, FeHPO_4^+ , established. Its dissociation constant, 4.44×10^{-10} , has been evaluated at an ionic strength of 0.665 and 30° .

2. The adaptability, reliability and applicability of ferric thiocyanate as a ferric ion indicator has been studied and its advantages discussed. Data relating $M_{\text{FeCNS}^{++}}$ and the extinction coefficient at a wave length of $550 \text{ m}\mu$ have been presented. The first dissociation constant of orthophosphoric acid at an ionic strength of 0.665 and 30° has been determined by use of cells with liquid junction.

ALBANY, N. Y.
NEW YORK, N. Y.

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(11) E. J. Cohn, *THIS JOURNAL*, **49**, 173 (1927).