

## Ferric-phosphoric Acid System

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Spectrophotometric, *pH*-titration, and paper electrophoresis studies of the ferric-phosphate system indicate presence of the unique complex of the composition  $\text{FeHPO}_4^+$  below *pH* 2. The thermodynamic stability constants of  $\text{FeHPO}_4^+$ , determined from *pH*-titration and spectrophotometric studies, are  $4.2 \times 10^{10}$  and  $7.04 \times 10^{10}$ , respectively, at 25°. The  $\Delta F$ ,  $\Delta H$ , and  $\Delta S$  values of the system,  $\text{Fe}^{3+} + \text{HPO}_4^{2-} \rightleftharpoons \text{FeHPO}_4^+$  determined from spectrophotometric measurements at 25°, are respectively  $-14.85$  kcal./mole,  $-3.77$  kcal./mole, and 37 e. u.

Phosphate ions have a marked tendency to form complexes with trivalent metals. Although there is plenty of evidences of the ferric-phosphate complexes in the literature, only a few attempts, however, have been made to calculate their stability constants and thermodynamic properties. Recently, Faucherre and Msika<sup>2</sup> have studied the nature of the complex polarographically and also by potentiometry. They have also made a critical review of the earlier works.

Most of the evidence available, however, is based on studies where either  $\text{NO}_3^-$ ,  $\text{Cl}^-$  or  $\text{CNS}^-$  ions are also present. In such cases, complications due to co-ordination of these ions in the complexes are likely to arise and the lack of agreement in the reports may be due to this. Consequently, a study of the ferric-phosphate system in absence of interfering ions seems desirable.

The investigation has been carried out at low *pH*s (below *pH* 2) to avoid hydrolysis of  $\text{Fe}(\text{ClO}_4)_3$  and formation of other complicated species [there is, of course, some evidence<sup>3</sup> that  $\text{Fe}(\text{ClO}_4)_3$  is also associated, but it is very little].

Attempts have been made to determine the nature of the complex by spectrophotometric method, *pH*-titration, and by electrophoretic method. Stability constants have been determined by spectrophotometry and *pH*-titration.

### EXPERIMENTAL

Ferric perchlorate was prepared in the same way as described by Nanda *et al.*<sup>4</sup>.

Iron content of the solution was estimated iodometrically as well as with a standard dichromate solution. The total acid was estimated volumetrically by a standardised  $\text{NaOH}$  solution, using phenolphthalein as indicator. Phosphoric acid ( $\text{H}_3\text{PO}_4$ ), prepared from G. R. (E. Merck)  $\text{H}_3\text{PO}_4$  by dilution, was standardised against a standard  $\text{NaOH}$  solution,

1. Abstracted from a part of the D. Phil. thesis by S. C. Lahiri, University of Calcutta, 1964.
2. *Bull. Soc. Chim.*, 1962, 1824.
3. Sutton, *Nature*, 1952, 169, 71; Sykes, *J. Chem. Soc.*, 1959, 2473.
4. *This Journal*, 1957, 34, 577.

using bromocresol green as indicator.  $\text{NaClO}_4$  was prepared by neutralising  $\text{HClO}_4$  (E.P.-E. Merck) with  $\text{Na}_2\text{CO}_3$  (E.P., E, Merck). It was purified by recrystallising the crystallised product and estimated gravimetrically. The solutions were prepared in double distilled water and all other chemicals were of reagent grade.

UV spectra of  $\text{Fe}(\text{ClO}_4)_3$  ( $2.708 \times 10^{-4}M$ ) at different  $p\text{H}$ s (0.54-2.32) were studied, exhibiting sharp absorption maxima at  $240 m\mu$  at  $p\text{H}$  below 1.8; above this  $p\text{H}$  the peak gradually disappeared. The UV spectra of  $M/100\text{-H}_3\text{PO}_4$  showed no appreciable absorption. The UV spectra of a mixture  $\text{Fe}(\text{ClO}_4)_3$  and  $\text{H}_3\text{PO}_4$  in the ratio 1 : 1 and an excess of phosphoric acid were studied. The absorption peak was shifted to  $255 m\mu$ , indicating formation of a complex of  $\text{Fe}(\text{ClO}_4)_3$  and  $\text{H}_3\text{PO}_4$ .

For absorption measurements, a Beckman model D. U. spectrophotometer in a room, thermostated at  $25^\circ (\pm 0.5^\circ)$ , was used\*. The  $p\text{H}$  measurements were made with a Cambridge bench type battery-operated  $p\text{H}$ -meter with an accuracy of  $\pm 0.02$  units. The glass electrode was checked with phthalate, phosphate, and borax buffers.

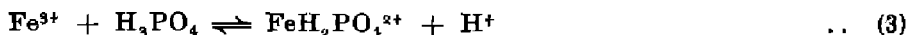
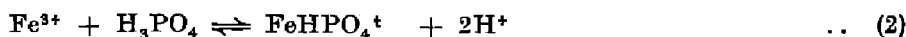
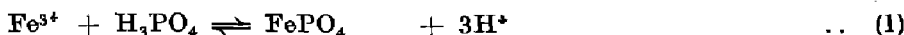
#### *Determination of the Composition of the Complex*

*Spectrophotometric Method.*—The molecular composition of the complex was determined by Job's method<sup>5</sup> of continued variations. The  $p\text{H}$  of the solutions for each set was kept constant. The optical densities of the mixtures as well as the blank solutions were measured at 270, 280, 290, and  $300 m\mu$ . The values of  $\bar{D}$ , the difference between the observed optical density of the mixture and the corresponding blank, were plotted against the ratio of

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{3+}] + [\text{H}_3\text{PO}_4]}$$

at three different  $p\text{H}$ s, viz.,  $1.88 \pm 0.03$ ,  $1.60 \pm 0.02$ , and  $1.33 \pm 0.02$ , at four different wave lengths, viz., 270, 280, 290, and  $300 m\mu$ , with solutions having three different total molarities ( $5.416 \times 10^{-4}$ ,  $8.124 \times 10^{-4}$ , and  $10.832 \times 10^{-4}$ ). The plots at particular  $p\text{H}$  and molarity are shown in Fig. 1. The occurrence of the maximum of  $\bar{D}$  is in every case at the composition ratio of 0.5 indicates that under the experimental conditions (below  $p\text{H}$  2.0)  $\text{Fe}^{3+}$  and  $\text{H}_3\text{PO}_4$  combine to form a 1:1 complex.

*pH-titration Method.*—Since formation of the complex is in the ratio of 1:1 of  $\text{Fe}(\text{ClO}_4)_3$  to  $\text{H}_3\text{PO}_4$ , the species may be one of the following:



To decide which of these shows the true picture,  $p\text{H}$ s of solutions of ferric-perchlorate with different amounts of phosphoric acid were measured and analysed in the same way as done by Salmon<sup>6</sup>. The concentration of  $\text{H}^+$  ions, liberated in the reaction between  $\text{Fe}^{3+}$

5. *Ann. Chim.*, 1928, 9, 113.

6. *J. Chem. Soc.*, 1952, 2316; 1953, 2644; 1957, 959, 3239.

\*Experiments were performed at other temperatures as well.

ions and  $\text{H}_3\text{PO}_4$ , were calculated from the difference in the  $p\text{H}$  values and the activity coefficient of  $\text{H}^+$  ion from the empirical relationship suggested by Davies<sup>7</sup>.

$$-\log f_i = 0.5Z_i^2 \left\{ \frac{\mu^{\frac{1}{2}}}{1+\mu^{\frac{1}{2}}} - 0.2\mu \right\} \quad \dots \quad (4)$$

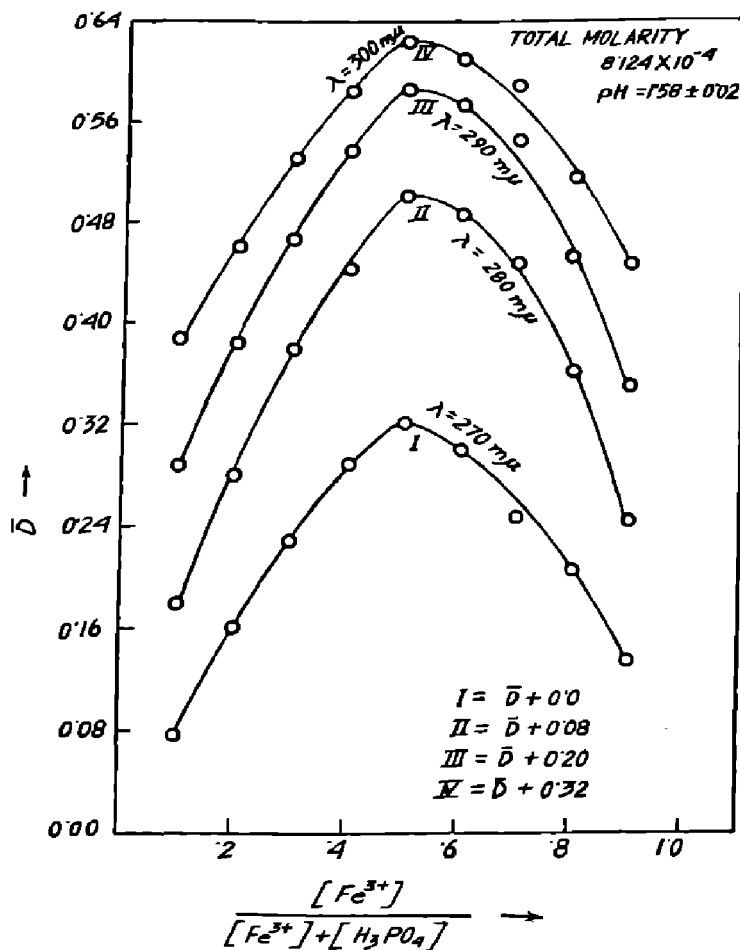


FIG. 1

*Paper Electrophoresis Method.*—The paper electrophoresis experiments of  $\text{Fe}(\text{ClO}_4)_3$  were carried out in solutions of  $\text{HClO}_4$  and  $\text{H}_3\text{PO}_4$  of different  $p\text{H}$ s and also in phosphate buffer at different  $p\text{H}$ s.

With  $\text{Fe}(\text{ClO}_4)_3$  in  $\text{HClO}_4$  and  $\text{H}_3\text{PO}_4$  below  $p\text{H}$  2, only one band moved towards the cathode. The movement of  $\text{Fe}^{3+}$  ion in  $\text{H}_3\text{PO}_4$  was always found to be lower than that in  $\text{HClO}_4$ , indicating complex formation between  $\text{Fe}^{3+}$  ion and  $\text{H}_3\text{PO}_4$ . Again, since the movement was always towards the cathode below  $p\text{H}$  2, the complex must be cationic in character. Around  $p\text{H}$  2.3 and above and in excess of phosphate ion, the spot appeared to

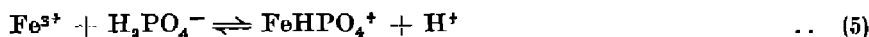
The results of  $p\text{H}$  measurements show that nearly two  $\text{H}^+$  ions are liberated per  $\text{Fe}$  atom at a mole ratio 1:1 of  $\text{Fe}(\text{ClO}_4)_3$  to  $\text{H}_3\text{PO}_4$  in accordance to equation (2). Thus it may be concluded that at  $p\text{H}$  below 2,  $\text{FeHPO}_4^+$  is the species formed.

move towards the anode, indicating a negatively charged species. This may be  $\text{Fe}(\text{HPO}_4)_2^-$ , observed by Banerjee<sup>8</sup> and Faucherre and Msika<sup>2</sup> and also by Salmon *et al.*<sup>6</sup>. Electrophoretic measurements were not carried out beyond *pH* 2.8 because  $\text{Fe}^{3+}$  ion was hydrolysed and adsorbed by the paper.

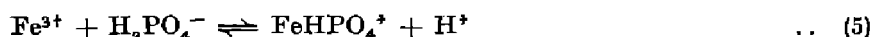
The three methods, outlined above, showed absence of complexes like  $[\text{Fe}(\text{H}_2\text{PO}_4)_4]^-$ , observed by Atma Ram *et al.*<sup>9</sup>. *pH*-titration studies indicate the species  $\text{FeHPO}_4^+$  and not the complexes like  $\text{FeH}_2\text{PO}_4^{2+}$ , as suggested by Jensen<sup>10</sup>.

Job's curves and electrophoretic measurements rule out the possibility of —ve charged and neutral species at *pH* below 2.

According to Faucherre and Msika<sup>2</sup>  $\text{Fe}(\text{HPO}_4)_2^-$  should be the predominating species in acidic solution and probably  $\text{FeHPO}_4^+$  is formed only in solutions, poor in  $\text{H}_3\text{PO}_4$ , according to the scheme:



The *pH*-titration studies in the present investigation show that the liberation of  $\text{H}^+$  ions at *pH* below 2 is intermediate between 1 and 2 according to the reactions:



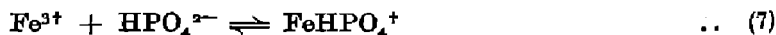
since the amount of  $\text{H}_3\text{PO}_4$  present as  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  is dependent on *pH*.

The *pH*-titration experiments also show that concentration of  $\text{FeHPO}_4^+$  formed is relatively small at low *pH* and gradually increases with increasing *pH* in accordance with the above equations. At *pH* above 2.1,  $\text{H}_2\text{PO}_4^-$  predominates and in presence of excess  $\text{H}_3\text{PO}_4$ , the negatively charged complex, as observed from electrophoretic measurements, may be due to reactions (5) and (6), suggested by Faucherre and Msika<sup>2</sup>. This is also in accord with the observations of Banerjee<sup>8</sup> and Salmon *et al.*<sup>6</sup>.

Thus, at *pH*s below 2, the complex may be regarded as  $\text{FeHPO}_4^+$ . This is in agreement with the observations of Lanford and Kiehl<sup>11</sup>, Banerjee<sup>8</sup>, Salmon<sup>6</sup> *et al.*, D' Amore<sup>12</sup>, and Faucherre and Msika<sup>2</sup>.

#### Determination of the Stability Constant of $\text{FeHPO}_4^+$

By *pH*-titration.—The equilibrium constant *K* of the reaction:



can be written as

$$K = \frac{a_{\text{FeHPO}_4^+}}{a_{\text{Fe}^{3+}} \times a_{\text{HPO}_4^{2-}}} = \frac{C_{\text{FeHPO}_4^+} \times f_{\pm}}{C_{\text{Fe}^{3+}} \times f_{3+} \times C_{\text{HPO}_4^{2-}} \times f_{2-}} \quad \dots (8)$$

8. *This Journal*, 1950, 27, 417.

9. *J. Sci. Ind. Res.*, 1954, 13B, 217; 1956, 15B, 78.

10. *Z. anorg. Chem.*, 1922, 125, 28.

11. *J. Amer. Chem. Soc.*, 1942, 64, 291.

12. D' Amore, *Atti della Soc. Pelor*, 1956, 5, 95.

In order to avoid dilution effect, solutions were prepared in volumetric flasks with the same amount of  $\text{Fe}(\text{ClO}_4)_3$  solutions and different amounts of  $\text{H}_3\text{PO}_4$  and made to the mark. The  $p\text{H}$ -readings of the solutions were taken.

The  $p\text{H}$  of the blank solution was obtained by adding to the  $p\text{H}$  of solutions containing  $\text{Fe}(\text{ClO}_4)_3$  alone the contribution of  $a_{\text{H}^+}$  (from the equation :

$$p\text{H} = pK + \lg \frac{a_{\text{H}_2\text{PO}_4^-}}{a_{\text{H}_3\text{PO}_4}}$$

and total phosphoric acid, where  $a_{\text{H}_2\text{PO}_4^-} = a_{\text{H}^+}$ ) that would have liberated due to the addition of  $\text{H}_3\text{PO}_4$  alone without interaction with  $\text{Fe}^{3+}$  ion by the process of successive approximation.  $a_{\text{FeHPO}_4^+}$  was obtained from the difference of  $a_{\text{H}^+}$  values of the experimental and blank solutions divided by  $(2r+1)/(r+1)$  similar to  $\text{FeHPO}_4$  complex<sup>13</sup>. To calculate  $r = \frac{a_{\text{H}_3\text{PO}_4}}{a_{\text{H}_2\text{PO}_4^-}}$ , average  $p\text{H}$  of the experimental solution and that of the blank calculated, is taken.

Knowing  $a_{\text{FeHPO}_4^+}$ ,  $C_{\text{FeHPO}_4^+}$  and  $C_{\text{Fe}^{3+}}$  can be calculated.  $a_{\text{HPO}_4^{2-}}$  can be known in the same way as in our previous communication<sup>13</sup>.

Thus from the knowledge of the  $p\text{H}$ , total  $\text{H}_3\text{PO}_4$ ,  $\text{FeHPO}_4^+$ ,  $a_{\text{HPO}_4^{2-}}$  and values of  $f_1$  and  $f_{3+}$ , calculated from the empirical relationship suggested by Davies<sup>7</sup>, the thermodynamic stability constant was calculated.

The average thermodynamic value obtained is  $4.2 \times 10^{10}$  at  $25^\circ$ , which we consider as an approximate value in view of the error in  $p\text{H}$  measurements. The results are recorded in Table I.

TABLE I  
Temp.  $\approx 25^\circ$ .

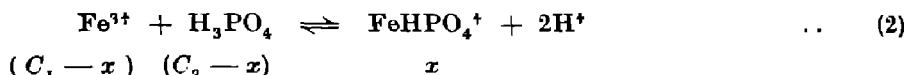
Concentration ( $M \times 10^2$ ) of		pH of the			Ionic strength.	Thermodynamic $K \times 10^{-10}$ .
$\text{Fe}(\text{ClO}_4)_3$ .	$\text{H}_3\text{PO}_4$ .	Mixture.	Soln. containing $\text{Fe}(\text{ClO}_4)_3$ alone.	Blank (calc.).		
1.0	1.000	1.38	1.53	1.51	0.1	4.5
1.0	0.765	1.40	1.53	1.51	0.1	3.9
1.0	0.574	1.42	1.53	1.51	0.1	1.4
1.0	1.000	1.41	1.60	1.56	0.1	6.8
1.0	0.800	1.44	1.60	1.57	0.1	4.2
1.0	1.000	1.32	1.45	1.43	0.1	5.0
1.0	0.800	1.33	1.45	1.43	0.1	6.5
1.0	0.600	1.36	1.45	1.44	0.1	5.6
2.0	2.000	1.14	1.28	1.26	0.2	3.1
2.0	1.530	1.17	1.28	1.26	0.2	1.6

Average  $K = 4.2 \times 10^{10}$

*By Spectrophotometry.*—To calculate the stability constant of the complex by spectrophotometric method, a series of solutions containing  $\text{Fe}(\text{ClO}_4)_3$  and  $\text{H}_3\text{PO}_4$  at different concentrations and the corresponding blank solutions containing  $\text{Fe}(\text{ClO}_4)_3$  were prepared and optical densities were taken at  $25^\circ$ . This was done at different  $p\text{H}$ s and ionic strengths.

For a particular set at constant pH and ionic strength, the optical density values were taken at different temperatures, namely 25°, 35°, 42°, and 50°.

Since the extinction coefficient,  $\epsilon$ , of  $\text{FeHPO}_4^+$  could not be determined directly, an indirect method was applied to calculate the equilibrium constant. The equilibrium between  $\text{Fe}^{3+}$  ion and  $\text{H}_3\text{PO}_4$  can be written as



Let  $C_1$  and  $C_2$  be the concentration of ferric perchlorate and phosphoric acid, respectively, and  $x$  be the concentration of  $\text{FeHPO}_4^+$  formed, the equilibrium constant can be written as

$$K' = \frac{a_{\text{FeHPO}_4^+} \cdot (a_{\text{H}^+})^2}{a_{\text{Fe}^{3+}} \cdot a_{\text{H}_3\text{PO}_4}} = \frac{C_{\text{FeHPO}_4^+} \cdot (C_{\text{H}^+})^2}{C_{\text{Fe}^{3+}} \cdot C_{\text{H}_3\text{PO}_4}} \times \frac{f_+ \times f_+^2}{f_+^2} \quad \dots (9)$$

(since  $\text{H}_3\text{PO}_4$  is uncharged). At constant pH,

$$K'' = \frac{K'}{(a_{\text{H}^+})^2} = \frac{C_{\text{FeHPO}_4^+}}{C_{\text{Fe}^{3+}} \times C_{\text{H}_3\text{PO}_4}} \times \frac{f_+}{f_{3+}}$$

or

$$K'' = \frac{x}{(C_1 - x)(C_2 - x)} \cdot \frac{f_+}{f_{3+}} \quad \dots (10)$$

If  $d_1$  be the absorbance of  $\text{Fe}(\text{ClO}_4)_3$  with no  $\text{H}_3\text{PO}_4$  in it,  $d_2$ , the absorbance of a solution containing  $\text{H}_3\text{PO}_4$ , and  $\epsilon_1$  and  $\epsilon_2$  be the extinction coefficients of  $\text{Fe}(\text{ClO}_4)_3$  and  $\text{FeHPO}_4^+$  species, respectively, we have

$$d_1 = \epsilon_1 C_1 l \quad (l = \text{length of the cell}) \quad \dots (11)$$

$$d_2 = \epsilon_1 (C_1 - x) l + \epsilon_2 x l \quad \dots (12)$$

Thus,

$$d_2 - d_1 = \epsilon_2 x l - \epsilon_1 x l = x (\epsilon_2 - \epsilon_1) l$$

or

$$x = \frac{d_2 - d_1}{(\epsilon_2 - \epsilon_1) l} \quad \dots (13)$$

Substituting the value of  $x$  in (10), we have

$$\frac{C_1}{d_2 - d_1} = \frac{1}{(\epsilon_2 - \epsilon_1) l} + \frac{1}{(\epsilon_2 - \epsilon_1) l (C_2 - x)} \cdot \frac{1}{K''} \left( \frac{f_+}{f_{3+}} \right) \quad \dots (14)$$

At constant ionic strength, the ratio of  $f_+ / f_{3+}$  can be regarded as fixed.

Thus, if  $C_1 / (d_2 - d_1)$  is plotted against  $1 / (C_2 - x)$ , the intercept will provide  $1 / (\epsilon_2 - \epsilon_1) l$  and the slope,  $1 / (\epsilon_2 - \epsilon_1) l K''$ , from which the stability constant can be calculated. Since the value of  $x$  is unknown, a series of approximation is done (two to three approximations are sufficient) for obtaining the value of the association constant.

In the first rough plots, the points lie scattered and a mean straight line is drawn, but with two or three approximations, the points lie fairly well on a straight line. The process

was repeated with solutions of different  $pH$ s, each having a constant value of  $pH$  ( $\pm 0.02$ ) till constant values of the intercept and the slope were obtained. The final plot of  $C_1/(d_2-d_1)$  vs.  $1/(C_2-x)$  at a particular  $pH$  and ionic strength is shown in Fig. 2.

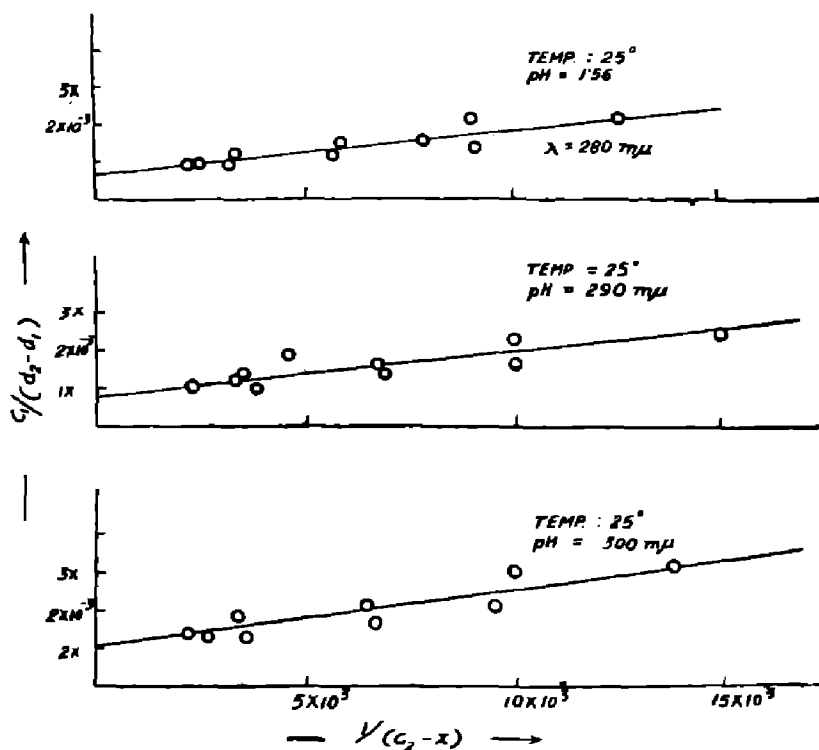


FIG. 2

The optical density measurements were carried out at three different wave lengths, namely, 280, 290, and 300  $m\mu$ . From each of the sets, the association constants were calculated and averaged to provide the association constant for a particular  $pH$  and temperature. The values of  $K''$  are recorded in Table II.

TABLE II

Temp. = 25°

$pH$ .	Ionic strength.	$K'' \times 10^{-3}$ at			Average $K'' \times 10^{-3}$ .	*Factor $\bar{n} \times 10^{-6}$ .	$K \times 10^{-10}$ .
		280 $m\mu$ .	290 $m\mu$ .	300 $m\mu$ .			
1.20	1.700	1.43	1.62	1.59	1.55	9.240	11.50
1.38	0.870	2.80	3.07	2.85	2.90	4.410	21.90
1.56	0.040	5.42	6.60	6.60	6.20	2.040	5.79
1.76	0.037	18.10	20.0	20.00	19.00	0.932	7.46
1.80	0.026	22.00	28.00	31.00	27.00	0.850	7.66

\*Calculated on the basis of Davies' equation.

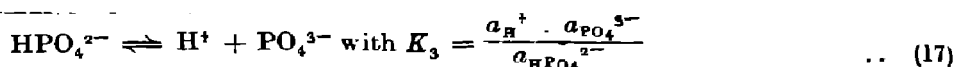
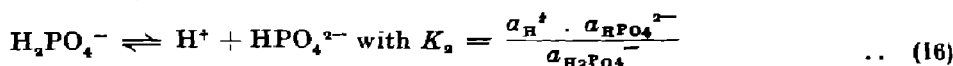
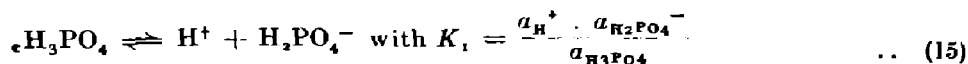
Now, if the equilibrium of  $\text{FeHPO}_4^+$  is written as



$$\text{the constant } K \quad \left( K = \frac{a_{\text{FeHPO}_4^+} \cdot f_{\pm}}{a_{\text{Fe}^{3+}} \cdot f_{3+} \cdot a_{\text{HPO}_4^{2-}} \cdot f_{2-}} \right)$$

can be had from  $K'$  at any known  $p\text{H}$ .

To obtain the value of  $K$ , we have to consider the phosphoric acid equilibria, which can be written as



Now, at equilibrium in presence of  $\text{Fe}^{3+}$  ions,

$$[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] + [\text{FeHPO}_4^+] = [\text{total phosphoric acid}] \quad \dots (18)$$

$$\text{or } [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = [\text{total free phosphate ion}]$$

$$\text{or } \frac{a_{\text{H}^+}^2 \times a_{\text{HPO}_4^{2-}}}{K_1 K_2} + \frac{a_{\text{H}^+} \times a_{\text{HPO}_4^{2-}}}{K_2 f_{-}} + \frac{a_{\text{HPO}_4^{2-}}}{f_{2-}} + \frac{a_{\text{HPO}_4^{2-}} \cdot K_3}{f_{3-} \cdot a_{\text{H}^+}} = [\text{total free phosphate ion}]$$

$$\text{or } a_{\text{HPO}_4^{2-}} \left[ \frac{a_{\text{H}^+}^2}{K_1 K_2} + \frac{a_{\text{H}^+}}{K_2 f_{-}} + \frac{1}{f_{2-}} + \frac{K_3}{f_{3-} \cdot a_{\text{H}^+}} \right] = [\text{total free phosphate ion}]$$

Under our experimental conditions,

$$a_{\text{HPO}_4^{2-}} = \frac{[\text{Total free phosphate ion}]}{\frac{(a_{\text{H}^+})^2}{K_1 K_2} + \frac{a_{\text{H}^+}}{K_2 f_{-}}} \quad \dots (19)$$

Thus, factor  $\bar{n}$

$$= \frac{[\text{Total free phosphate ion}]}{a_{\text{HPO}_4^{2-}}} = \frac{(a_{\text{H}^+})^2}{K_1 K_2} + \frac{a_{\text{H}^+}}{K_2 f_{-}} \quad \dots (20)$$

$\bar{n}$  is dependent on  $p\text{H}$ , which can be determined by knowing  $pK$ ,  $f_{-}$  and thermodynamic values of  $K_1$  and  $K_2$  respectively (thermodynamic  $pK_1 = 2.1$  and  $pK_2 = 7.2$ ).

The multiplication of  $K'$  with  $\bar{n} \times f_{\pm}/f_{3+}$ , provides the value of thermodynamic  $K$ . These are shown in Table I.

The agreement of the thermodynamic values obtained at low ionic strengths are very good. On the basis of the Davies equation<sup>7</sup>, the values are:  $5.79 \times 10^{10}$  ( $4.39 \times 10^{10}$ ) at an ionic strength 0.04 and  $p\text{H}$  1.56;  $7.46 \times 10^{10}$  ( $4.18 \times 10^{10}$ ) at an ionic strength; 0.037 and  $p\text{H}$  1.76;  $7.86 \times 10^{10}$  ( $5.97 \times 10^{10}$ ) at an ionic strength 0.026 and  $p\text{H}$  1.80.



The values at high ionic strengths are:  $1.15 \times 10^{11}$  ( $1.36 \times 10^{11}$ ) at an ionic strength 1.70 and  $pH$  1.20 and  $2.19 \times 10^{11}$  ( $1.90 \times 10^{11}$ ) at an ionic strength 0.87 and  $pH$  1.38. The values in parenthesis are obtained by using the Debye-Hückel equation with  $a = 9\text{Å}$  (value for  $\text{Fe}^{3+}$  ion)<sup>14</sup>.

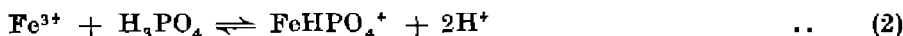
At higher ionic strengths, values obtained are a little too high. This may be due to the fact that determination of activity coefficients from the Debye-Hückel equation and the Davies equation does not yield quite accurate values. Considering the limitations, the agreement of the thermodynamic values at these high ionic strengths may be taken to be good.

The average thermodynamic value obtained is  $7.04 \times 10^{10}$  at  $25^\circ$  (considering the values obtained by using the Davies equation at low ionic strengths).

Lanford and Kiehl<sup>11</sup> recorded a value  $4.44 \times 10^{10}$  for  $K$  of  $\text{FeHPO}_4^+$  at  $30^\circ$  and at an ionic strength 0.665. In view of the fact that these authors used ferric-nitrate and also because of the uncertainties involved in the activity corrections, their value may be considered to be in agreement with the present one.

#### *Determination of Thermodynamic Properties from Spectrophotometric Measurements*

The dissociation constant  $K''$  was determined at an ionic strength of 0.037 and  $pH$  1.76 at  $25^\circ$ ,  $35^\circ$ ,  $42^\circ$  and  $50^\circ$  (Table III). Considering the  $pH$ ,  $K_1$ ,  $K_2$ , and  $\Delta H$  to be unaffected in the temperature range studied, the values of  $\log K''$  were plotted against  $1/T$ . The slope of the plot provides the value  $-\Delta H/2.303R$  from which  $\Delta H$  can be calculated. Thus for the reaction



$\Delta H$  is  $-4.85$  k cal. Combining this with the  $\Delta H$ 's<sup>15</sup> for



we have for  $\text{Fe}^{3+} + \text{HPO}_4^{2-} \rightleftharpoons \text{FeHPO}_4^+$ ,  $\Delta H = -3.77$  kcal. Using the expression  $\Delta F = \Delta H - T\Delta S$  ( $\Delta F$  being equal to  $-RT \ln K$ ),  $\Delta S$  has been calculated. The average value of  $\Delta S$  is 37 e.u. The value of  $\Delta F$  at  $25^\circ$  is  $-14.85$  kcal. The thermodynamic values are also recorded in Table IV.

TABLE III

$pH = 1.76$ . Ionic strength = 0.037.

Temp.	$K'' \times 10^{-4}$ at		Average $K'' \times 10^{-4}$
	290 m $\mu$ .	300 m $\mu$ .	
$25^\circ$	2.00	2.00	2.00
$35^\circ$	1.45	1.42	1.43
$42^\circ$	1.33	1.25	1.29
$50^\circ$	1.06	1.04	1.05

14. Kolthoff and Elving, "Treatise on Analytical Chemistry", Vol I, Part I, Interscience Encyclopedia Inc. N.Y., p. 243.

TABLE IV



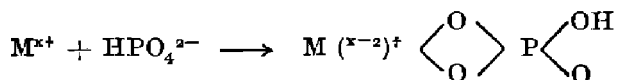
$\Delta F$ (kcal./mole).	$\Delta H$ (kcal./mole)	$\Delta S$ (e.u.)
-14.85	-3.77	+ 37

## DISCUSSION

The thermodynamic data show that in the case of ferric complex, the reaction is exothermic and both  $\Delta H$  and  $\Delta S$  favour complex formation, whereas in the case of ferrous complex, the reaction is endothermic, heat change is unfavourable, and the entropy change is favourable for the formation of complex.

Entropy change in complex formation is due to decrease in the number of ions, partial neutralisation of electric charge, and displacement of water from the hydration sphere. In terms of 'iceberg' concept of Frank and Evans<sup>6</sup>, the removal of ions from solutions, as in the process of complex formation between two charged complex ions, will lead to the breakdown of the 'icebergs' and a resulting entropy change will favour complex formation. This is found in the case of  $\text{FeHPO}_4^+$  and  $\text{FeHPO}_4$ . In the case of  $\text{FeHPO}_4$ , entropy change would, however, be expected to be more favourable compared to  $\text{FeHPO}_4^+$  which has got a residual charge of unity. Our results also indicate the same.

The difference of entropy in the formation of  $\text{FeHPO}_4^+$  and  $\text{FeHPO}_4$ <sup>13</sup> may be attributed to the difference in hydrational entropies of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{FeHPO}_4^+$ , and  $\text{FeHPO}_4$  respectively.  $\text{HPO}_4^{2-}$  may be regarded as a bidentate group. The formation of four-membered rings<sup>17</sup> is possible in the case of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions having the following structures:



The optimum radius of metal ions for chelate ring formation is about 0.7 Å. Since  $\text{Fe}^{2+}$  ion have much greater ionic radius<sup>8</sup> (0.76 Å) than  $\text{Fe}^{3+}$  ion<sup>8</sup> (0.64 Å), the ring is likely to be strained due to greater ionic radius. Thus,  $\text{FeHPO}_4$  is much less stable compared to  $\text{FeHPO}_4^+$ .

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