

# POTENTIOMETRIC STUDIES IN THE FORMATION AND STABILITY OF COLLOIDAL SOLUTIONS.

## Part I. Ferric Oxide Sols.

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### 1. Introduction.

THE hydrogen ion concentration at which the precipitation of ferric oxide takes place from ferric salt solutions is a factor of considerable significance. The literature reveals the scanty data<sup>1</sup> and the non-reproducible nature of the results so far obtained. Britton<sup>2</sup> has titrated acidified solutions of ferric chloride against sodium hydroxide using oxygen electrode. He states that coagulation of ferric oxide sets in at pH 6.6. A correct knowledge of the pH changes during titrations of ferric salt solutions is necessary for a clear understanding of (a) the range of stability of ferric oxide sols, and (b) the composition of the ferric oxide at the equivalence point. Results of pH determinations of purified ferric oxide sols have been, until recently, rather uncertain. Earlier workers<sup>3</sup> conclude from their measurements using the hydrogen electrode that the pH of ferric oxide sols was practically the same as that of water, and did not suffer change by coagulation. Mukherjee and his co-workers<sup>4</sup> have experienced difficulties in the measurement of the pH of ferric oxide sols. Roy Chowdury in another paper<sup>5</sup> reports the pH of ferric oxide sols to be 6.0 by employing the indicator method. Mukherjee and his co-workers<sup>6</sup> have taken the pH of the liquid obtained by coagulating the sol by potassium sulphate to be the hydrogen ion concentration of the original sol. In a later part of their paper, however, they state that the 'liquid obtained by coagulation has a different hydrogen ion concentration from that of the intermicellary liquid'.<sup>7</sup>

<sup>1</sup> Vide Britton, *Hydrogen Ions*, 1932 Edition, p. 325.

<sup>2</sup> *J. C. S.*, 1925, **127**, 2148.

<sup>3</sup> Browne, *J. Amer. Chem. Soc.*, 1923, **45**, 297; Pauli and Matula, *Koll. Zeits.*, 1917, **21**, 49.

<sup>4</sup> *J. Ind. Chem. Soc.*, 1931, **8**, 373.

<sup>5</sup> *J. Ind. Chem. Soc.*, 1934, **11**, 13.

<sup>6</sup> *Loc. cit.*

<sup>7</sup> *Loc. cit.*, p. 384.

W. L. McClatchie<sup>8</sup> has shown by a comparative study of different electrodes, that glass and quinhydrone electrodes give correct and reproducible potentials with ferric oxide sols. He points out that the results obtained by earlier workers are unreliable. McClatchie states that the pH of ferric oxide sols lies in the range 4.05–4.43 depending upon the concentration of the sol and the extent of dialysis of the hot liquid.

In view of the importance of hydrogen ion concentration in colloid chemical analysis<sup>9</sup> and the elucidation of the nature of reaction at interfaces, a systematic investigation of the formation and stability of ferric oxide sols has been undertaken in our laboratory. The present paper deals with potentiometric titrations of ferric salt solutions against alkali using the quinhydrone electrode, the object of the work being to elucidate (a) the existence or otherwise of basic salts of definite chemical composition, (b) the pH range of stability of ferric oxide sols, (c) the influence of the time of contact of the ferric salt solution with alkali on the pH developed, and (d) the effect of neutral salts on the course of the titration. The pH of dialysed ferric oxide sols, and the influence of dilution and neutral salt solutions on their pH have also been investigated.

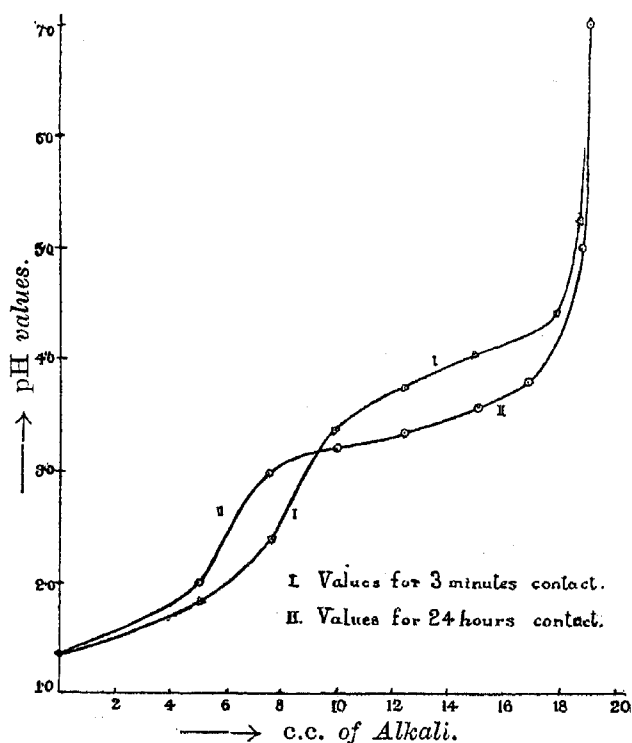


FIG. 1. Titration of acidified Ferric Chloride vs. NaOH (Table IV).

## 2. Experimental Details.

Two sets of ferric chloride solutions were prepared: (a) unacidified solutions, which are unstable on long standing, (b) acidified solutions containing known quantities of hydrochloric acid. The potentiometric titrations were carried out in steamed Jena bottles which contained known volumes of the solution saturated with quinhydrone. A bright gold electrode was used. The potential was measured against a saturated calomel electrode. A U-tube containing a jelly of agar in saturated KCl served as the salt bridge. A Tinsley's potentiometer

<sup>8</sup> *J. Phys. Chem.*, 1932, **36**, 2087.

<sup>9</sup> Cf. Mukherjee, *Koll. Zeits.*, 1933, **63**, 43.

reading to a millivolt was used for the measurements. The ferric chloride solutions were made up in carbonate-free distilled water. Carbonate-free alkali of known strength was run in from an automatic microburette. Potential measurements were carried 3 minutes after the addition of alkali. For studying the effect of time of contact with alkali on the potential, the solutions were mixed in stoppered Jena bottles and kept for 24 hours and the potential measured again.

The values are recorded in Tables I to V. Fig. 1 represents a typical curve obtained in all these cases. The following points were observed. During the initial stages of the titration corresponding to pH range 1.06—3.20, the pH steadily increases with time reaching a constant value within 24 hours, while in the second stage of the titration corresponding to the pH range 3.2—4.5, the pH decreases with time of contact reaching a steady value within the same period. For intermediate ranges of pH in the neighbourhood of 3.20, the value remains steady with time.

TABLE I.

*Titration of unacidified ferric chloride solution vs. NaOH.*

Strength of NaOH = 0.0756N.

Strength of FeCl<sub>3</sub> soln. = 0.074 M.

Vol. of NaOH	E.M.F. in millivolts	pH	Remarks	Vol. of NaOH	E.M.F. in millivolts	pH	Remarks
0.0 c.c.	387	1.06	Clear soln.	20.0 c.c.	229	3.81	Opalescent soln.
4.0 "	370	1.38	"	22.0 "	222	3.93	" "
8.0 "	339	1.91	"	24.0 "	213	4.08	" "
10.0 "	310	2.64	Slightly red coloured soln.	26.0 "	197	4.36	" "
12.0 "	272	3.07	" "	26.5 "	192	4.47	Practically opaque.
14.0 "	250	3.46	Opalescent soln.	27.0 "	182	4.62	Partial coagulation.
16.0 "	242	3.59	Increasingly opalescent soln.	27.5 "	160	5.00	" "
18.0 "	235	3.71	" "	28.0 "	60	6.00	Coagulation complete.

Vol. of FeCl<sub>3</sub> soln. = 10 c.c. of stock soln. + 10 c.c. of water.

End point (corresponding to second inflexion in potential) = 27.75 c.c. of alkali.

Ratio of  $\frac{\text{Moles of FeCl}_3}{\text{Moles of NaOH}}$  at end point = 1 : 2.81.

TABLE II.

Titration of unacidified FeCl<sub>3</sub> solution in presence of N. KCl.

Strength of NaOH and FeCl<sub>3</sub> (same as in Table I).

Vol. of NaOH	E.M.F. in millivolts	pH	Remarks	Vol. of NaOH	E.M.F. in millivolts	pH	Remarks
0.0 c.c.	389	1.07	Clear soln.	15.0 c.c.	241	3.60	Increasingly opalescent
4.0 "	370	1.38	"	17.0 "	233	3.74	" "
6.0 "	350	1.73	"	20.0 "	222	3.93	" "
8.0 "	338	1.91	"	22.0 "	215	4.05	Practically opaque
9.0 "	321	2.22	Slightly red	24.0 "	207	4.21	" "
10.0 "	292	2.72	"	25.0 "	199	4.33	" "
11.0 "	268	3.14	Becomes opalescent	26.0 "	193	4.44	Partial coagulation
12.0 "	255	3.36	"	27.0 "	177	4.71	" "
13.0 "	246	3.51	"	27.5 "	162	4.97	" "
14.0 "	245	3.53	"	28.0 "	114	5.79	Coagulation complete
				28.5 "	40	7.07	"

Vol. of FeCl<sub>3</sub> soln. = 10 c.c. of stock soln. + 10 c.c. of N. KCl.

End point = 27.75 c.c.

$$\text{Ratio of } \frac{\text{Moles of FeCl}_3}{\text{NaOH}} \text{ at end point} = 1:2.81.$$

Whether the ferric chloride solution is initially acidified or unacidified one can notice two inflexions. The first inflexion is not very sharp and occurs roughly during the pH range 2.0–3.0. It is difficult to assign any stoichiometric ratio between the ferric chloride and the added alkali (corresponding to this inflexion) because the inflexion is not very sharp. Britton<sup>10</sup> has, however, formulated the existence of basic complexes of the type Fe(OH)<sub>0.74</sub> Cl<sub>2.26</sub>.

The first inflexion represents the stage at which the free acid formed by hydrolysis is neutralised. The pH range 3.20–4.46 represents the range of stability of colloidal ferric oxide. The solution is found to become increasingly opalescent during this range and finally becomes opaque before coagulation. Partial coagulation sets in at pH 4.46 beyond which there is a sharp rise in pH followed by complete coagulation at

<sup>10</sup> *Loc. cit.*

TABLE III.

*Titration of unacidified ferric chloride in presence of 0.57 N. K<sub>2</sub>SO<sub>4</sub>.*  
Strength of NaOH and FeCl<sub>3</sub> (same as in Table I).

Vol. of NaOH	E.M.F. in milli-volts	pH	Remarks	Vol. of NaOH	E.M.F. in milli-volts	pH	Remarks
0.0 c.c.	362	1.52	Clear solution	20.0 c.c.	219	3.98	Increasing amounts coagulated
4.0 "	344	1.83	"	22.0 "	211	4.13	" "
8.0 "	315	2.33	Red and colloidal	24.0 "	198	4.35	" "
10.0 "	286	2.83	" "	26.0 "	172	4.79	" "
11.0 "	268	3.14	" "	27.0 "	117	5.74	Coagulation complete
12.0 "	256	3.35	Partial coagulation	27.5 "	73	6.50	"
14.0 "	240	3.62	" "	28.0 "	27	7.29	"
16.0 "	232	3.76	Increasing amounts coagulated				
18.5 "	225	3.88	" "				

Vol. of FeCl<sub>3</sub> soln. = 10 c.c. of stock soln. + 10 c.c. of 0.57 N. K<sub>2</sub>SO<sub>4</sub>.  
End point of titration (inflexion in potential) = 27.0 c.c.  
Molar ratio at end point = 1 : 2.72.

TABLE IV.

*Titration of acidified ferric chloride solution, showing the effect of time of contact with alkali.*

Strength of FeCl<sub>3</sub> soln. = 0.049 M.  
Strength of soln. with respect to HCl = 0.0052 N.  
Strength of NaOH = 0.075 N.

Vol. of NaOH	E.M.F. after 3 min.	pH	Remarks	Vol. of NaOH	E.M.F. after 24 hrs.	pH	Remarks
0.0 c.c.	373	1.33	Clear solution	0.0 c.c.	373	1.33	Clear solution
5.0 "	343	1.85	"	5.0 "	335	1.98	"
7.5 "	314	2.35	Colloidal and opalescent	7.5 "	276	3.00	Colloidal and opalescent
10.0 "	254	3.38	"	10.0 "	264	3.21	"
12.5 "	231	3.78	Increasing opalescence	12.5 "	255	3.36	"
15.0 "	217	4.02	"	15.0 "	244	3.55	Increasingly opalescent
17.0 "	204	4.24	"	17.0 "	230	3.79	"
18.0 "	193	4.43	Coagulation sets in	18.0 "	210	4.14	Coagulation sets in
19.0 "	147	5.22	Coagulation complete	19.0 "	160	5.00	Coagulation complete
19.5 "	20	7.41	" "	19.5 "	30	7.40	"

Vol. of FeCl<sub>3</sub> soln. = 10 c.c. of stock solution + 10 c.c. of water.  
End point (corresponding to inflexion in potential) = 19.25 c.c. in both cases.  
Molar ratio at end point = 1 : 2.85.

TABLE V.

*Titration of acidified ferric chloride solution in presence of neutral salts, showing also the effect of time of contact with alkali.*

Strengths of solutions (same as in Table IV).

Volume of alkali	In presence of 0.57N. K <sub>2</sub> SO <sub>4</sub> 3 minutes		In presence of 0.57N. K <sub>2</sub> SO <sub>4</sub> 24 hours		In presence of N. KCl 3 minutes		In presence of N. BaCl <sub>2</sub> 3 minutes		In presence of N. KNO <sub>3</sub> 3 minutes	
	E.M.F.	pH	E.M.F.	pH	E.M.F.	pH	E.M.F.	pH	E.M.F.	pH
0.0 c.c.	342	1.86	342	1.86	372	1.33	372	1.33	369	1.40
5.0 "	307	2.47	303	2.53	338	1.83	336	1.84	340	1.83
7.5 "	294	2.69	270	3.10	288	2.79	284	2.79	313	2.36
10.0 "	232	3.76	254	3.36	236	3.69	232	3.70	250	3.49
12.5 "	216	4.03	240	3.62	218	4.00	218	4.00	218	4.00
15.0 "	200	4.31	224	3.90	205	4.22	203	4.22	208	4.17
17.0 "	182	4.60	200	4.31	191	4.48	190	4.48	194	4.41
18.0 "	155	5.09	153	5.12	176	4.72	174	4.72	183	4.60
19.0 "	20	7.41	50	6.70	123	5.62	122	5.62	132	5.48
19.5 "	..	..	..	..	22	7.38	..	..	33	7.19
Vol. of FeCl <sub>3</sub>	10 c.c. of stock soln. + 10 c.c. of 0.57 N. K <sub>2</sub> SO <sub>4</sub>		10 c.c. of stock soln. + 10 c.c. of K <sub>2</sub> SO <sub>4</sub>		10 c.c. of stock soln. + 10 c.c. of N. KCl		10 c.c. of stock soln. + 10 c.c. of N. BaCl <sub>2</sub>		10 c.c. of stock soln. + 10 c.c. of N. KNO <sub>3</sub>	
End point	18.5 c.c.		18.3 c.c.		19.0 c.c.		19.0 c.c.		19.1 c.c.	
Molar ratio at end point	1 : 2.72		1 : 2.69		1 : 2.80		1 : 2.80		1 : 2.82	

pH 6. The molar ratio between sodium hydroxide and ferric chloride has been calculated corresponding to the end point of the titration as indicated by the second inflexion in potential. No stoichiometric ratio is found to exist; the concentration of the reacting substances and the ion environment determine this value. Tables I-V show that the ratio decreases in the order water > NO<sub>3</sub>' > Cl' > SO<sub>4</sub>'. The end point of the titration is not affected by the time of contact of the ferric chloride with alkali. Experiments have also been conducted to find out if cations (Ba<sup>++</sup>, Mg<sup>++</sup>) have any influence on the end point of the titration. The

results show that the end point is affected by the presence of the chlorides of the cations to the same extent as an equivalent amount of KCl.

### 3. Experiments with Ferric Oxide Sols.

A ferric oxide sol was prepared and dialysed according to the method of McClatchie.<sup>11</sup> The sol was used for the experiments after it had 'aged' for a month. The pH of the sol and its variation with dilution have been tabulated below:—

TABLE VI.

*Effect of dilution on the pH of ferric oxide sols.*

Original sol contains 2.5 gr. of Fe<sub>2</sub>O<sub>3</sub> in 100 c.c.

Dilution ..	Original Sol	2	4	8	10	20	
pH ..	5.37	5.13	4.93	4.89	4.89	4.89	

The changes in pH when ferric oxide sols are mixed up with neutral salt solutions, have been investigated as these data can be correlated with the titration values of ferric salts (in presence of neutral salts). It also enables one to form a picture of the disposition of ions in the interfacial layer. Previous workers have assumed that the pH of ferric oxide sols remains constant when coagulated by neutral salt solutions.<sup>12</sup> Table VII, however, shows that there are appreciable changes in pH on coagulation.

TABLE VII.

*pH of mixtures of ferric oxide sols and neutral salt solutions.*

	Mixture used	pH (after 24 hours)	Remarks
(a)	Original sol .. .. .	4.89	
(b)	10 c.c. sol + 10 c.c. of N/5 K <sub>2</sub> SO <sub>4</sub>	7.93	Complete coagulation.
(c)	10 c.c. of sol + 0.1 c.c. of N/5 K <sub>2</sub> SO <sub>4</sub>	8.10	„
(d)	10 c.c. of sol + 10 c.c. of N. KCl ..	7.50	„
(e)	10 c.c. of sol + 10 c.c. of N. KNO <sub>3</sub> ..	7.25	„

### 4. Discussion of Results.

The first inflexion in potential which occurs in the pH range 2.0–3.0 corresponds to the neutralisation of the free acid formed by hydrolysis:

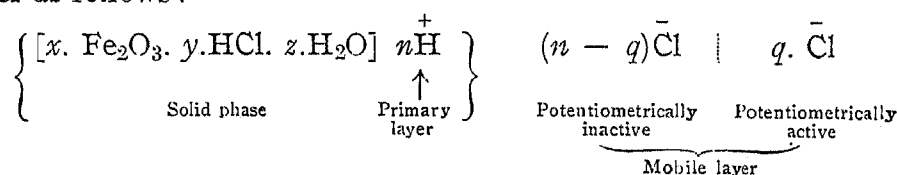
<sup>11</sup> *Loc. cit.*

<sup>12</sup> Weiser, *J. Phys. Chem.*, 1931, **34**, 1.

During this period, particles of ferric oxide of amicronic size are being formed. This is indicated by the fact that the solution remains perfectly clear and the intensity of the Tyndall cone is very slight.

In the second part of the titration, there is the neutralisation of the hydrogen ions from the micelle by the hydroxyl ions of the added alkali. This corresponds to the pH range 3.45—4.45. A similar variation in pH has been observed in the potentiometric titration of stearic acid sols against sodium hydroxide.<sup>13</sup>

If one assumes the formation of definite basic salts during the course of the titration, the pH and Cl<sup>-</sup> ion concentration of the solution ought to remain constant over a certain range where the basic salt is stable. This is, however, contrary to the observations recorded in this paper. Weiser, Pauli and others<sup>14</sup> have shown that the micelles contain varying amounts of HCl. The structure of colloidal ferric oxide is represented by Weiser as follows:—



Weiser has shown that the chlorine ions in the mobile layer are not all potentiometrically active. From the inflexion in potential corresponding to the end point of the titration, one notices that the molar ratio varies between the limits 2.69—2.85, depending upon the anion environment in which the titration is carried out; the ratio being least in presence of potassium sulphate and greatest in the absence of any salt. These results also run parallel with the changes observed in the sol during the titration. An aqueous solution of ferric chloride in the absence of a neutral salt is not coagulated until the end point of the titration is reached. If the titration is carried in presence of KCl, partial coagulation sets in before the end point is reached. In presence of K<sub>2</sub>SO<sub>4</sub>, the coagulation sets in at a much earlier stage. This shows that the positively charged sol gets coagulated by the anions of the salt. The lower molar ratio in presence of neutral salts also shows that a certain amount of alkali is liberated during the coagulation of the sol by neutral salt.

The structure formulated by Weiser<sup>15</sup> for ferric oxide sols has to be modified in view of the experimental evidence obtained in this paper. In

<sup>13</sup> M. P. V. Iyer, *J. Mys. University*, July 1932, 6.

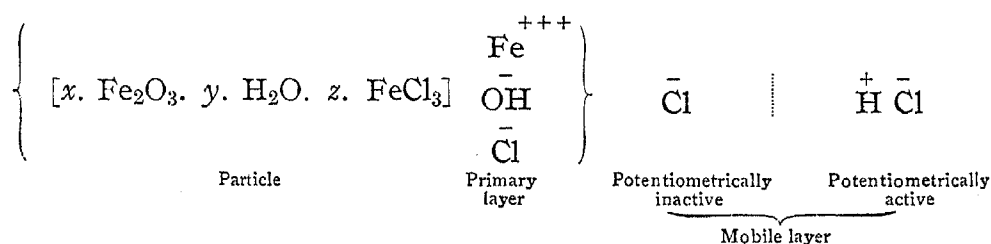
<sup>14</sup> *Loc. cit.*

<sup>15</sup> *Loc. cit.*



deciding about the correct structure of the interfacial layer, one has to take into consideration the following facts: (a) The pH of the sol is of the order 4.05–4.45 as shown by McClatchie and confirmed by the present author; (b) the chlorine ion concentration of the sols is of the order  $0.70 \times 10^{-3}$  to  $2.93 \times 10^{-3}$ ; Weiser has shown that this depends on the method of preparation of the sol and the extent of dialysis; and (c) the liberation of alkali when ferric oxide sols are treated with neutral salt solutions.

The structure of the colloidal ferric oxide may therefore be represented as follows:—



According to this scheme the micelle may be supposed to have in the primary layer  $\text{Fe}^{+++}$ ,  $\text{OH}^-$  and  $\text{Cl}^-$  ions. The cations are largely in excess over the anions. The anions are mainly  $\text{OH}^-$ . It would be unreasonable, however, to assume that the primary layer is entirely free of chloride ions. With the progress of dialysis of the sol, both the hydrogen and chlorine ion concentrations fall off. The fall in concentration of H ion may not be exactly equivalent to the fall in concentration of the  $\text{Cl}^-$  ion. (This is a point which deserves careful investigation and is now being studied by the author.) The liberation of alkali by neutral salts is due to the replacement of the hydroxyl ions in the primary layer by the anions of the salt. Such replacement in the primary layer has been noticed previously.<sup>16</sup>

When barium chloride is the neutral salt employed the same values are obtained as with potassium chloride of equivalent concentration, thus showing that the cation of the neutral salt has no detectable influence on the end point of the titration. Considerations based on the 'chemical theory', *i.e.*, the formation of basic salts of definite chemical composition cannot possibly explain these observations since one would expect for these complexes a constancy in composition, pH and solubility.

*Effect of time of contact (with alkali) on the fluctuations in pH.*

In the initial stages of the titration, till pH 3.2 is reached, (point X on curve. Fig. 1) the ferric oxide formed is first of all in a molecularly dispersed condition; and in course of time forms micelles. A phase

<sup>16</sup> M. P. V. Iyer, *J. Ind. Chem. Soc.*, 1931, 8, 613.

separation takes place in the system at this stage. This region corresponds to an increase in the total area of the particle-liquid interface. The micelles, at the moment of their formation, adsorb primarily on their surface their constituent ions (*i.e.*,  $\text{Fe}^{+++}$  and  $\text{OH}^-$ ). This is followed by the reaction between the hydrogen ions in the intermicellary liquid and the hydroxyl ions in the primary layer. A reaction between the ion in the intermicellary liquid and an ion in the primary adsorbed layer is generally recognised to be slow. Thus the intermicellary liquid becomes less acidic with time and reaches an equilibrium value in about 24 hours. Corresponding to pH 3.2, the acidity of the intermicellary liquid does not alter with time of contact with alkali. The Tyndall effect is noticed in solutions above pH 3.2.

In the second stage of the titration corresponding to pH 3.20–4.45, the particles of the ferric oxide grow in size with time. The state of coalescence is governed by pH of the intermicellary liquid. Aggregation of the micelles results in a decrease of the free surface. This brings about a desorption of the ferric and hydroxyl ions from the primary layer. Since the number of ferric ions is far in excess over the hydroxyl ions (the surface being positively charged), the ferric ions released into the intermicellary liquid reacts with water to form fresh micelles of ferric oxide liberating at the same time hydrogen ions. This explains why at this stage the intermicellary liquid becomes more acidic with time.

*Variation in pH of ferric oxide sols on dilution.*

As indicated in the introductory part there have been differences of opinion regarding the pH of ferric oxide sols. The results obtained in this paper (Table VI) confirm those of McClatchie and indicate also the influence of dilution on pH. On diluting the sol the acidity increases and reaches a limiting value when the original sol (containing 2.5 gr. of  $\text{Fe}_2\text{O}_3$  in 100 c.c.) is diluted 8 times. Dilution of a sol brings into operation phenomena which work in opposite directions: (1) A decrease in acidity due to mere dilution, (2) An increase of the ratio between the liquid to solid phase brings out a desorption from the micelles of ferric ions as well as  $\text{OH}^-$  ions (the latter being correspondingly fewer in number). The reaction of ferric ions with water (indicated above) results in the production of fresh micelles of ferric oxide and an increase in hydrogen ion concentration. This hydrolysis is progressive and is essentially governed by the pH of the intermicellary liquid. Since the second factor counterbalances the first in the initial stages of the dilution, the acidity of the sol first increases on dilution and reaches a limiting value at a stage where the two factors just counterbalance.

*Variation in pH of ferric oxide sols treated with neutral salt solutions.*

When ferric oxide sol is treated with neutral salt solutions, the pH increases, the magnitude of the increase following the usual series  $\text{SO}_4'' > \text{Cl}' > \text{NO}_3'$ . These anions slowly replace the hydroxyl ions in the primary layer. The hydroxyl ions so liberated neutralise the hydrogen ions in the mobile layer. If the hydroxyl ions are in sufficient excess, the pH of the liquid after coagulation is of the order 7.5–8.0. Attention has already been drawn to the relation between the alkali liberated by neutral salts and the lower stoichiometric ratio at the end point of the titrations in presence of these salts. The ratio varies from 1 : 2.69 to 1 : 2.85 depending upon the nature of the neutral salt; the order being  $\text{SO}_4'' < \text{Cl}' < \text{NO}_3' < \text{water}$ . Thus  $\text{SO}_4''$  is most efficient in the replacement of hydroxyl ions from the primary layer; so is the amount of alkali required to react with ferric salts in presence of  $\text{SO}_4''$  a minimum.

*5. Summary and Conclusion.*

1. Potentiometric titrations of acidified and unacidified ferric chloride solutions have been conducted against carbonate-free sodium hydroxide, with and without the addition of neutral salts.
2. The titration curves show that the range of stability of ferric oxide sols is between the pH limits 3.20–4.45, the precipitation of ferric oxide commences in the neighbourhood of pH 4.5, and is complete at pH 6.0.
3. The composition of the precipitate of ferric oxide is found to vary with the neutral salt added. The molar ratio between ferric chloride and sodium hydroxide varies between the limits 1 : 2.69 to 1 : 2.85, the theoretical ratio being 1 : 3.0. The molar ratio at the end point follows the series  $\text{SO}_4'' < \text{Cl}' < \text{NO}_3' < \text{water}$ .
4. The different stages in the formation of micelles of ferric oxide and their subsequent coagulation have been elucidated.
5. The variations in pH of ferric oxide sols with dilution have been studied, and the results support the view proposed by the author that there is an equilibrium between the ions in the micelle and those in the intermicellary liquid.
6. An explanation has been offered for the development of alkalinity on addition of neutral salts to ferric oxide sols. The liberation of  $\text{OH}^-$  ions on addition of salts has been correlated with the lower molar ratio obtained in the titrations of ferric chloride against alkali.

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