

3. The purification of the solvents was described.

4. The experimental methods were described and unusual features in the results were discussed.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## THE CONSTITUTION OF FERRIC OXIDE HYDROSOL FROM MEASUREMENTS OF THE CHLORINE- AND HYDROGEN-ION ACTIVITIES

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In the course of a study of the heat of coagulation of ferric oxide hydrosol with electrolytes<sup>2</sup> it was found impossible to give a quantitative interpretation of the results with sols of low purity because of lack of knowledge of the nature and distribution of the electrolytes in these sols. This investigation was carried out with the purpose of supplying these data through a study of the chloride- and hydrogen-ion activities of the sols<sup>3</sup> and of solutions of ferric chloride.

The sol is regarded as an aqueous solution of ferric chloride and hydrochloric acid in hydrolytic equilibrium in which are dispersed particles of hydrous ferric oxide which adsorb varying amounts of ferric chloride, hydrogen chloride, ferric and hydrogen ions. The activity coefficient for chloride ion was first determined in ferric chloride solutions of various concentrations in which hydrolysis was minimized by keeping the solution acid with nitric or sulfuric acid. From similar measurements on ferric chloride solutions which contained no added acid and had been allowed to come to hydrolytic equilibrium it was possible to deduce the amount of ferric chloride and of hydrochloric acid in these solutions. Assuming then that the dispersion medium of a ferric oxide sol<sup>4</sup> has the same constitution as a ferric chloride solution of the same content of chloride ion, it was possible to arrive at the constitution of the hydrosols from measurements of their chloride-ion activities.

Further light on the constitution of the sols was obtained by means of measurements of the hydrogen-ion activities. For this purpose a special

<sup>1</sup> National Research Fellow in Chemistry.

<sup>2</sup> Browne and Mathews, *THIS JOURNAL*, **43**, 2336 (1921).

<sup>3</sup> Pauli and Matula, *Kolloid-Z.*, **21**, 49 (1917), made such measurements with one sol of high purity and lower concentration.

<sup>4</sup> HCl and FeCl<sub>3</sub> were the only electrolytes in the sols.

technique was developed for employing the hydrogen electrode in the presence of small amounts of ferric ion.

The ferric oxide in these sols is generally considered to be highly hydrous,<sup>5</sup> that is, to carry a large amount of adsorbed water. It might be expected that this would introduce an important error in these measurements by making the volume of water acting as solvent for the electrolytes in the sol less to a great and unknown extent than the total volume of water in the sol. That this is not the case is shown by measurements of the depression of the freezing point of the sol caused by the addition of a given amount of dextrose.

### Preparation of Hydrosols

Graham's method of preparation of ferric oxide sol by addition of ammonium carbonate to ferric chloride solution has the disadvantage of leaving ammonium chloride in the sol as a by-product. The sols were, therefore, prepared by Neidle's method;<sup>6</sup> 200 g. of ferrous chloride was dissolved in a liter of water and 3% hydrogen peroxide solution added slowly and with constant stirring until no test for ferrous ion was obtained on spotting out with potassium ferricyanide. As any excess of hydrogen peroxide is decomposed rapidly in the presence of the ferric chloride formed during the reaction, the sol contains only ferric oxide, ferric chloride, and the hydrochloric acid formed by hydrolysis from the ferric chloride. Twelve liters of the sol was prepared in this way and dialyzed in the manner already described,<sup>3</sup> samples being withdrawn from time to time as the preparation attained different purities. The sols were analyzed for iron by dissolving them in hydrochloric acid and titrating by the Rheinhardt-Zimmermann method and for chlorine by solution in nitric acid and precipitating as silver chloride.

This method of preparation of ferric oxide sol is a "condensation method." Experiments were also carried out with a sol prepared by a "dispersion method" as follows. Ferric oxide was precipitated from ferric chloride solution with a slight excess of ammonium hydroxide. The precipitate was washed thoroughly by decantation, and the centrifuge used to hasten the settling until, on further washing, the precipitate began to be peptized again in considerable quantity.<sup>7</sup> A fairly thick mud was then prepared from the precipitate, stirred vigorously, and analyzed for iron and chlorine. The ratio, equiv. Fe/equiv. Cl, was found to be 73.6. Various amounts of this mud were then weighed into liter measuring flasks, 100 cc. of *N* ferric chloride solution was added to each, and the mixture made up to the mark with water. The flasks were allowed to stand with occasional shaking until the ferric oxide was completely peptized, yielding clear, red-brown sols in appearance exactly like those made by the Neidle method. In the case of the sol of highest purity<sup>8</sup> made by this method, 10.3, this required a month and a half. The purities of the sols were checked by analysis.

### Measurements of Chloride-Ion Activities

The chloride-ion activities were measured at 25° by means of the calomel electrode, using a *N* potassium chloride calomel electrode as reference

<sup>5</sup> See (a) Bancroft, *J. Phys. Chem.*, **19**, 232 (1915); and (b) Weiser, *ibid.*, **24**, 277 (1920).

<sup>6</sup> Neidle, *THIS JOURNAL*, **39**, 2334 (1917).

<sup>7</sup> Compare Bradfield, *ibid.*, **44**, 965 (1922).

<sup>8</sup> The purity of the sol is defined as the ratio, equiv. Fe/equiv. Cl.

electrode and a saturated potassium chloride salt bridge. The temperature was maintained constant by means of an oil thermostat. The mercury was purified by repeatedly passing it through a column of mercurous nitrate solution, acid with nitric acid. The calomel was made by dissolving this mercury in redistilled nitric acid, precipitating with redistilled hydrochloric acid, washing the salt thoroughly, and filtering and drying it. The potassium chloride was precipitated from saturated solution by hydrogen chloride and heated in platinum vessels almost to fusion. For the salt bridges a c. p. potassium chloride from stock was employed. Cells were always allowed to stand in the thermostat for several hours before measurements were made in order to insure equilibrium. For all measurements, 2 cells were prepared from the solution under examination and connected through a single salt bridge with 2 reference electrodes in order to obtain check readings. Fresh reference electrodes were frequently prepared and checked against the ones previously in use. The potential measurements were made with a high grade commercial potentiometer capable of reading to 0.01 mv. and a high sensitivity galvanometer, the whole electrical system being protected by an equipotential shield.<sup>9</sup>

The chloride-ion activities,  $a_{\text{Cl}}$ , were computed from the potential readings,  $E_{\text{Cl}}$ , by the equation,  $E_{\text{Cl}} = 0.0126 + 0.0591 \log a_{\text{Cl}}$ . The potentials were recorded to 0.1 mv., but no greater accuracy than 1 mv. can be claimed in view of the uncertainties regarding the boundary potential between the cell containing the colloid and the salt bridge. This gives an accuracy of about 3% in the figures for  $a_{\text{Cl}}$ .

All of the ferric chloride solutions were prepared by diluting a stock *N* solution of ferric chloride, with or without the addition of acid.

The results of the measurements with ferric chloride solutions and the ferric oxide sols are given in Tables II-V.

### Measurements of Hydrogen-Ion Activities

With sols having a purity greater than about 14, in which the ferric-ion concentration is very small indeed, the measurement of the hydrogen-ion activity presented no difficulty. An electrode of the Hildebrand type was employed. The *N* potassium chloride calomel cell was again used as reference electrode with the saturated potassium chloride salt bridge. The measurements were made at 25°. In these sols the electrode behaved normally, coming up to a definite potential after 10 or 15 minutes and then remaining constant.

With sols having a purity less than 14 the usual method of employing the hydrogen electrode cannot be used because of the presence of ferric ion. The difficulty was overcome by adopting a modification of a

<sup>9</sup> White, THIS JOURNAL, 36, 2011 (1914).

method suggested by Dr. John Arthur Wilson.<sup>10</sup> A dozen electrodes of the Hildebrand type were prepared in which the electrode surface consisted of about 0.5 cm. of No. 25 B. and S. gage platinum wire, projecting through the end of the inner glass tube. The electrodes were platinized by electrolyzing a platinum chloride solution, and were then made cathode in dil. sulfuric acid. Immediately before use they were washed thoroughly in distilled water.

Fig. 1 shows the apparatus employed.

R is the calomel reference electrode, S the salt bridge, and C the cell containing the sol or solution under examination. C is closed by a rubber stopper provided with an outlet tube for hydrogen and a hole for the hydrogen electrode  $E_1$ . The liquid in C is first saturated with hydrogen by bubbling the gas through it for 5 or 10 minutes. One of the electrodes prepared as described above is then inserted as shown in the figure so that the platinum wire fails to touch the liquid in C. Hydrogen is then passed

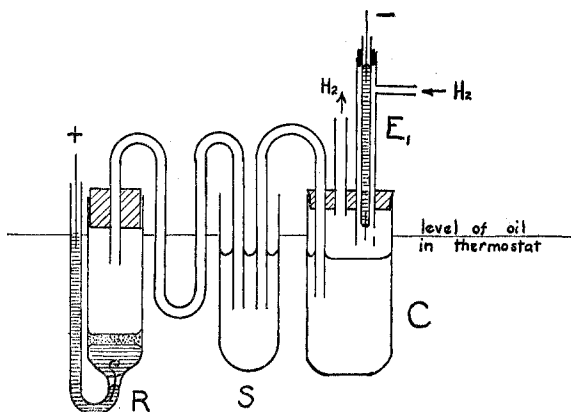


Fig. 1.—Apparatus used for the determination of hydrogen-ion activities.

through it for 5 minutes in order to saturate the electrode and the film of water adhering to it. The potentiometer is set as near the final potential as possible to estimate, the electrode is then quickly thrust into the liquid in C and the potentiometer swung rapidly to zero deflection of the galvanometer. The potential of the hydrogen electrode in equilibrium with hydrogen ion of the concentration existing in the liquid in C is registered by the electrode immediately and remains constant for several seconds, depending upon the ferric-ion concentration of the solution, after which it falls off rapidly. As soon as the reading has been taken, the electrode  $E_1$  is removed and a second one employed in the same manner. The first 3 or 4 electrodes serve to fix the approximate value of the potential for the preliminary setting of the potentiometer, after which the final value can be obtained with the remaining electrodes.

The data of Table I serve to show how the method works out. The figures give the e.m.f. observed immediately after submerging fresh electrodes in solutions having the composition indicated at the top of the columns. In the 0.0485 *N* solution of hydrochloric acid the e.m.f. was 0.3660

<sup>10</sup> Private communication.

v. at once and remained constant. In the solution of 0.0485 *N* hydrochloric acid and 0.0205 *N* ferric chloride the potential was 0.366 v. at the start, but after the first few seconds began to fall off rapidly. With the solution containing 0.0515 *N* ferric chloride the potential began to fall so rapidly that it was possible to demonstrate merely that it was greater than 0.35 v. The last column gives the observations made on a sol of low purity, 3.92, in which it will be shown later the concentration of ferric ion was 0.044 *N*. It was possible to measure the potential in this case within about 0.5 mv.

TABLE I  
USE OF HYDROGEN ELECTRODE IN PRESENCE OF FERRIC CHLORIDE

	Solution of: 0.0485 <i>N</i> HCl	0.0485 <i>N</i> HCl	0.0485 <i>N</i> HCl	Fe <sub>2</sub> O <sub>3</sub> sol
	V.	0.0205 <i>N</i> FeCl <sub>3</sub>	0.0515 <i>N</i> FeCl <sub>3</sub>	Purity 3.92
E.m.f. immediately after submerging electrode in solution	0.3660	0.366	0.35+	0.34+
	0.3660	0.366	0.35+	0.36+
	0.3660	0.366	0.35+	0.39-
	0.3660	0.366	....	0.385+
	0.3660	0.366	....	0.387-
	0.3660	0.366	....	0.386+
	....	...	....	0.3865
....	...	....	0.3865	

The hydrogen-ion activities,  $a_{\text{H}}$ , were computed from the potential measurements,  $E_{\text{H}}$ , by means of the equation,  $E_{\text{H}} = 0.283 + 0.0591 \log(1/a_{\text{H}})$ . The results of the measurements in ferric oxide sols are given in Table VI.

### Discussion and Results

Since we have assumed that the dispersion medium of a ferric oxide sol is a solution of ferric chloride in equilibrium with its products of hydrolysis it is first necessary to determine the composition of dil. ferric chloride solutions. Such solutions hydrolyze more or less to form hydrochloric acid and ferric oxide, the latter separating as a solid phase which settles or remains colloiddally dispersed depending upon conditions. The concentrations of hydrochloric acid and ferric chloride were computed from the chloride-ion activities,  $a_{\text{Cl}}$ , and the activity coefficients for hydrochloric acid and ferric chloride on the basis of the following equations,

$$\begin{cases} C_{\text{HCl}} + C_{\text{FeCl}_3} = N_{\text{FeCl}_3} \\ [\alpha_{\text{Cl}}]_{\text{HCl}} \cdot C_{\text{HCl}} + [\alpha_{\text{Cl}}]_{\text{FeCl}_3} \cdot C_{\text{FeCl}_3} = a_{\text{Cl}} \end{cases}$$

in which  $N_{\text{FeCl}_3}$  represents the nominal concentration of the solution, which is equal to the total amount of iron or of chlorine present, determined analytically,  $C_{\text{HCl}}$  and  $C_{\text{FeCl}_3}$  the concentration of hydrochloric acid and of ferric chloride actually present,  $a_{\text{Cl}}$  the activity of chloride ions in the solution as measured by the calomel electrode, and  $[\alpha_{\text{Cl}}]_{\text{HCl}}$  and  $[\alpha_{\text{Cl}}]_{\text{FeCl}_3}$  the activity coefficients for chloride ion in hydrochloric acid or ferric chloride solutions of concentration  $N_{\text{FeCl}_3}$ .

$[\alpha_{\text{Cl}}]_{\text{HCl}}$  was obtained from the data of Lewis and Randall<sup>11</sup> and  $[\alpha_{\text{Cl}}]_{\text{FeCl}_3}$  was obtained from the measurements of  $a_{\text{Cl}}$  in ferric chloride solutions in which hydrolysis was prevented by making the solution 0.05 *N* with respect to nitric acid or 0.075 *N* with respect to sulfuric acid. These data are recorded in Table II. In Table III are the data for solutions

TABLE II  
CHLORIDE-ION ACTIVITIES IN UNHYDROLYZED FERRIC CHLORIDE SOLUTIONS

$C_{\text{FeCl}_3}$ G. equiv./l.	$a_{\text{Cl}}$ in FeCl <sub>3</sub> solutions containing		$[\alpha_{\text{Cl}}]_{\text{FeCl}_3}$
	0.05 <i>N</i> HNO <sub>3</sub>	0.075 <i>N</i> H <sub>2</sub> SO <sub>4</sub>	
0.250	0.045	0.045	0.18
0.125	0.029	0.028	0.23
0.0625	0.0180	0.0175	0.28
0.0313	0.0100	0.0105	0.34
0.0157	0.0065	0.0067	0.42
0.0078	0.0039	0.0033	0.46
0.0039	0.0021	0.0025	0.59

TABLE III  
CHLORIDE-ION ACTIVITIES IN FERRIC CHLORIDE SOLUTIONS IN HYDROLYTIC EQUILIBRIUM

$N_{\text{FeCl}_3}$ G. equiv./l.	$a_{\text{Cl}}$ G. equiv./l.	$[\alpha_{\text{Cl}}]_{\text{HCl}}$	$[\alpha_{\text{Cl}}]_{\text{FeCl}_3}$	$C_{\text{HCl}}$ G. equiv./l.	$C_{\text{FeCl}_3}$ G. equiv./l.
0.257	0.084	0.77	0.18	0.0640	0.193
0.129	0.054	0.80	0.23	0.0427	0.0863
0.0643	0.028	0.85	0.28	0.0178	0.0465
0.0322	0.016	0.88	0.34	0.0094	0.0228
0.0161	0.010	0.90	0.42	0.0067	0.0094
0.0080	0.006	0.93	0.46	0.0050	0.0030
0.0040	0.004	0.96	0.59	0.0040	0.0000

of ferric chloride containing no added acid. Fig. 2 shows the variation of  $C_{\text{HCl}}$  and of  $C_{\text{FeCl}_3}$  with  $a_{\text{Cl}}$ .

The ferric oxide present in the hydrolyzed solutions adsorbs a certain amount of ferric chloride, but for present purposes this can be neglected as it will not affect the results by more than 1 or 2%.

<sup>11</sup> Lewis and Randall, *THIS JOURNAL*, **43**, 1112 (1921); see p. 1117. It will be noted that the activity coefficient of HCl in the solutions containing both HCl and FeCl<sub>3</sub> is assumed to have the same value as it does in a solution of pure HCl having an equivalent concentration equal to the total electrolyte content of the mixture. Lewis and Randall (pp. 1134, 1140) find that this assumption, which has been made by a number of investigators, is not accurate and show that the activity coefficient for any electrolyte in a mixture of strong electrolytes depends upon the "ionic strength" of the solution. Since the adoption of this principle would have made the calculations more involved without altering the results beyond the limits of the experimental errors, the older point of view was adopted. For example, in the solution, Table III, having the total electrolyte concentration,  $N_{\text{FeCl}_3} = 0.257$ , the value of  $[\alpha_{\text{Cl}}]_{\text{HCl}}$  was taken as 0.77 and  $C_{\text{HCl}}$  and  $C_{\text{FeCl}_3}$  were calculated to be, respectively, 0.0640 and 0.193. Such a solution would have an "ionic strength" of 0.449, and the corresponding value of  $[\alpha_{\text{Cl}}]_{\text{HCl}}$  is 0.76 instead of 0.77. This change in  $[\alpha_{\text{Cl}}]_{\text{HCl}}$  would alter the value of  $C_{\text{FeCl}_3}$  only from 0.193 to 0.192.

Tables IV and V give the results of the measurements of chloride-ion activities in ferric oxide sols of different purities and concentrations. Sol

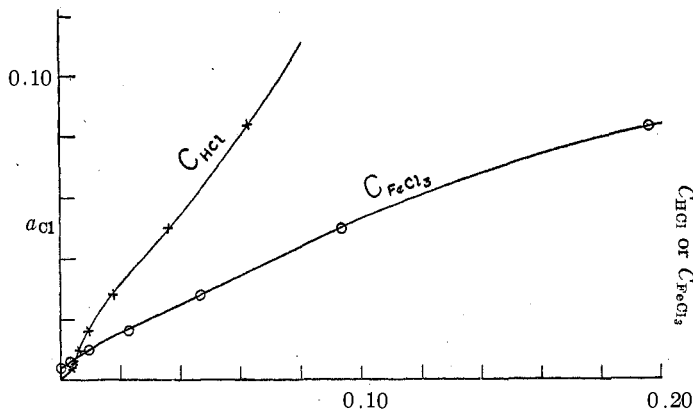


Fig. 2.—The concentrations of hydrochloric acid and ferric chloride in ferric chloride solutions having chloride-ion activities up to 0.1 g. equiv. per liter.

25 was prepared by Neidle's method, and Sol 24 by peptization of ferric oxide in ferric chloride. It will be seen that the two methods approach the equilibrium condition of the sol from opposite sides, the first from

TABLE IV  
CONSTITUTION OF FERRIC OXIDE SOL 25 FROM CHLORIDE-ION ACTIVITIES

Purity	$C_{Fe}$ (analyt.) G. eq./l.	$C_{Cl}$ (analyt.) G. eq./l.	$a_{Cl}$ G. eq./l.	$\alpha_{Cl}$	$C_{HCl}$ G. eq./l.	$C_{FeCl_3}$ G. eq./l.	$A_{Cl}$ G. eq./l.	$C_{Fe_2O_3}$ G. eq./l.	$\frac{A_{Cl}}{C_{Fe_2O_3}}$
1.55	0.374	0.241	0.070	0.29	0.052	0.144	0.045	0.185	0.24
	0.187	0.120	0.041	0.34	0.029	0.073	0.018	0.096	0.19
	0.094	0.060	0.025	0.41	0.015	0.040	0.005	0.049	0.10
	0.047	0.030	0.014	0.47	0.008	0.018	0.004	0.025	0.16
	0.023	0.015	0.010	0.67	0.006	0.009	0.000	0.014	0.00
3.92	0.656	0.167	0.045	0.28	0.032	0.082	0.053	0.521	0.10
	0.328	0.084	0.027	0.32	0.016	0.044	0.024	0.260	0.09
	0.164	0.042	0.017	0.41	0.010	0.024	0.008	0.132	0.06
	0.082	0.021	0.012	0.57	0.007	0.014	0.000	0.068	0.00
	0.041	0.010	0.006	0.65	0.005	0.004	0.001	0.036	0.03
8.40	0.020	0.005	0.003	0.6	0.004	0.000	0.001	0.019	0.05
	0.547	0.065	0.020	0.31	0.011	0.030	0.024	0.493	0.04
	0.274	0.033	0.011	0.33	0.007	0.012	0.014	0.248	0.06
	0.137	0.016	0.006	0.37	0.005	0.003	0.008	0.126	0.06
	0.068	0.008	0.003	0.38	0.004	0.000	0.004	0.064	0.06
14.6	0.034	0.004	0.002	0.50	0.002	0.000	0.002	0.032	0.06
	0.539	0.0389	0.0056	0.14	0.005	0.003	0.031	0.505	0.06
	0.270	0.0195	0.0033	0.17	0.004	0.000	0.016	0.254	0.06
	0.135	0.0097	0.0020	0.21	0.002	0.000	0.007	0.128	0.05
	0.068	0.0049	0.0015	0.31	0.0015	0.000	0.003	0.065	0.05
	0.034	0.0024	0.0010	0.42	0.001	0.000	0.001	0.033	0.03

TABLE IV (Continued)

Purity	$C_{Fe}$ (analyt.) G. eq./l.	$C_{Cl}$ (analyt.) G. eq./l.	$a_{Cl}$ G. eq./l.	$\alpha_{Cl}$	$C_{HCl}$ G. eq./l.	$C_{FeCl_2}$ G. eq./l.	$A_{Cl}$ G. eq./l.	$C_{Fe_2O_3}$ G. eq./l.	$\frac{A_{Cl}}{C_{Fe_2O_3}}$
17.5	0.463	0.0264	0.0033	0.13	0.004	0.000	0.022	0.441	0.05
	0.232	0.0132	0.0020	0.15	0.002	0.000	0.011	0.221	0.05
	0.116	0.0066	0.0016	0.24	0.0016	0.000	0.005	0.111	0.05
	0.058	0.0033	0.0010	0.30	0.001	0.000	0.002	0.056	0.04
	0.029	0.0017	0.0008	0.47	0.0008	0.000	0.001	0.028	0.04
22.0	0.454	0.0206	0.0025	0.12	0.0025	0.000	0.018	0.436	0.04
	0.227	0.0103	0.0018	0.17	0.0018	0.000	0.008	0.219	0.04
	0.114	0.0051	0.0012	0.24	0.0012	0.000	0.004	0.110	0.04
	0.057	0.0026	0.0008	0.31	0.0008	0.000	0.002	0.055	0.04
30.4	0.936	0.0308	0.0045	0.15	0.005	0.001	0.024	0.911	0.03
	0.468	0.0154	0.0020	0.13	0.002	0.000	0.013	0.455	0.03
	0.234	0.0077	0.0013	0.17	0.0013	0.000	0.006	0.228	0.03
	0.117	0.0038	0.0010	0.26	0.001	0.000	0.003	0.114	0.03
47.5	0.058	0.0019	0.0006	0.32	0.0006	0.000	0.001	0.057	0.02
	0.630	0.0133	0.0028	0.21	0.0028	0.000	0.010	0.620	0.016
	0.315	0.0067	0.0013	0.19	0.0013	0.000	0.005	0.310	0.016
	0.158	0.0034	0.0007	0.21	0.0007	0.000	0.003	0.155	0.019

TABLE V

## CONSTITUTION OF FERRIC OXIDE SOL 24 FROM CHLORIDE-ION ACTIVITIES

Purity	$C_{Fe}$ (analyt.) G. eq./l.	$C_{Cl}$ (analyt.) G. eq./l.	$a_{Cl}$ G. eq./l.	$\alpha_{Cl}$	$C_{HCl}$ G. eq./l.	$C_{FeCl_2}$ G. eq./l.	$A_{Cl}$ G. eq./l.	$C_{Fe_2O_3}$ G. eq./l.	$\frac{A_{Cl}}{C_{Fe_2O_3}}$
1.49	0.152	0.1020	0.031	0.30	0.020	0.052	0.030	0.070	0.43
	0.076	0.0510	0.018	0.35	0.010	0.027	0.014	0.035	0.40
	0.038	0.0255	0.015	0.59	0.009	0.020	0.000	0.018	0.00
	0.019	0.0128	0.008	0.63	0.005	0.007	0.001	0.011	0.09
3.93	0.203	0.0505	0.020	0.39	0.011	0.030	0.008	0.165	0.05
	0.101	0.0258	0.013	0.50	0.008	0.016	0.002	0.083	0.02
	0.052	0.0129	0.007	0.58	0.005	0.006	0.002	0.044	0.04
7.08	0.764	0.1078	0.025	0.23	0.019	0.040	0.049	0.673	0.07
	0.382	0.0539	0.018	0.33	0.010	0.026	0.018	0.338	0.05
	0.191	0.0270	0.011	0.41	0.007	0.012	0.008	0.171	0.05
10.3	0.096	0.0135	0.006	0.48	0.005	0.004	0.005	0.087	0.06
	1.154	0.1116	0.027	0.24	0.016	0.045	0.051	1.058	0.05
	0.577	0.0558	0.016	0.29	0.009	0.022	0.025	0.530	0.05
	0.289	0.0279	0.010	0.36	0.006	0.009	0.013	0.268	0.05
	0.145	0.0140	0.006	0.43	0.005	0.003	0.006	0.136	0.04

molecular dispersion and the second from coarse suspension. The close agreement between the results with the 2 sols is strong evidence in favor of the view that ferric oxide sols represent a true equilibrium condition and the properties are fixed when the variables, pressure, temperature, concentration and purity, are fixed. Further evidence in this connection will be brought up later.

The first column gives the purity of the sol, equal to  $C_{Fe}/C_{Cl}$ , the next two give, respectively, the total concentrations of iron,  $C_{Fe}$ , and of chlorine,



$C_{Cl}$ , determined analytically. The fourth column gives the chloride-ion activity as determined by the calomel electrode and the fifth the activity coefficient, equal to  $a_{Cl}/C_{Cl}$ . The sixth and seventh columns give, respectively, the concentrations of hydrochloric acid and of ferric chloride in the dispersion medium as read off from the curve, Fig. 2. It will be seen that the sum of  $C_{HCl}$  and  $C_{FeCl_3}$  is always less than the total chlorine concentration of the sol,  $C_{Cl}$ : The difference represents the chlorine, in the form of hydrochloric acid or of ferric chloride, adsorbed by the ferric oxide disperse phase and is given in the eighth column under  $A_{Cl}$ . The ninth column gives the concentration of ferric oxide computed as follows:  $C_{Fe} - (C_{FeCl_3} + a_{Cl})$ . This computation involves a slight uncertainty which may be neglected at present in that  $a_{Cl}$  may represent hydrochloric acid in part. The last column gives the ratio,  $a_{Cl}/C_{Fe_2O_3}$ .

It will be seen at once that the activity coefficients,  $\alpha_{Cl}$ , are in general low, particularly for sols of high purity. In Fig. 3 is shown the variation

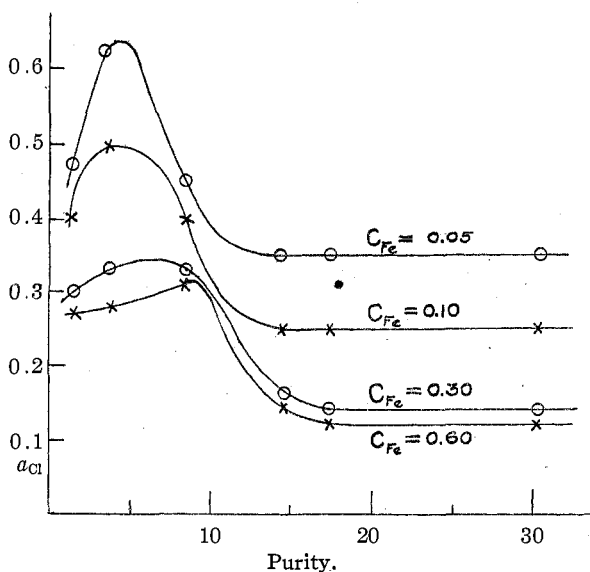


Fig. 3.—The variation of the activity coefficient for chloride ion with the purity of the sol for sols having the total iron concentrations of 0.6, 0.3, 0.1 and 0.05 g. equiv. per liter, respectively.

of  $\alpha_{Cl}$  with the purity for sols having respectively the concentrations of total iron of 0.60, 0.30, 0.10, and 0.05. The region of low purity with relatively high values for  $\alpha_{Cl}$  is that in which the dispersion medium is rich in hydrochloric acid and ferric chloride. The sudden drop in  $\alpha_{Cl}$  in the neighborhood of Purity 10 is due to rapid withdrawal of these electrolytes from the aqueous phase. From a purity of about 10–14 on, the dispersion

medium is practically free from hydrogen ion or ferric ion, as indicated by the hydrogen-electrode measurements, Table VI; hence, in these sols the only positively charged ions are the colloidal particles themselves, and the aqueous phase contains only chloride ions in amount equivalent to the number of faradays of positive electricity on the colloid particles.

That only a fraction of the chlorine in ferric oxide sols of high purity is ionizable has been observed previously by Malfitano,<sup>12</sup> by Duclaux,<sup>13</sup> and by Pauli and Matula.<sup>3</sup> The latter as well as Neidle<sup>6</sup> noted that ferric ion is absent from the filtrate after coagulation of such sols with sulfates, and Pauli and Matula found that hydrogen ion is also absent. These writers look upon the colloid as a "compound in variable proportions" of ferric oxide, ferric chloride, and water, or as a mixture of basic ferric chlorides, in either case ionizing to give a complex colloidal cation and chloride ions. The writer prefers to follow Bancroft<sup>5a</sup> in looking upon the system as composed of particles of ferric oxide suspended in the aqueous phase, adsorbing water and more or less of any ions present depending upon their nature and concentration. Hydrogen ion and ferric ion are very much more strongly adsorbed than chloride ion, in consequence of which the particles are positively charged. With sols of a purity greater than 14 and a concentration of iron of 0.5 or less, the hydrogen ion and ferric ion are completely adsorbed leaving only chloride ion in the aqueous phase. This condition is attained for lower  $C_{Fe}$  at lower purities and for higher  $C_{Fe}$  at somewhat higher purity. When the purity is less than the value at which the adsorption of hydrogen ion is nearly complete,  $\alpha_{Cl}$  is relatively high because of the high dissociation of hydrochloric acid, but when the purity reaches the value at which adsorption of hydrogen ion and ferric ion is complete,  $\alpha_{Cl}$  falls to a minimum and remains constant on further increase in purity.

At any given purity  $\alpha_{Cl}$  increases as  $C_{Fe}$  decreases, at first slowly and then more rapidly. For sols above the purity at which adsorption of hydrogen ion and ferric ion is complete,  $\alpha_{Cl}$  is a measure of the charge on the particles of disperse phase; hence, at given purity the ratio of charge to mass of disperse phase increases with dilution parallel with  $\alpha_{Cl}$ . Since the stability of a colloid is linked up with the size of the charge per unit of mass and a certain minimum charge is necessary for stability, it would be expected that for a sol of any given concentration there would be a maximum purity at which it would be stable and that this maximum purity would increase with the dilution of the sol at first slowly, then more rapidly. That such is the case has already been shown by Duclaux<sup>13</sup> and by Neidle.<sup>14</sup>

The hydrogen-ion activities,  $a_H$ , given in Table VI, check the values of

<sup>12</sup> Malfitano, *Z. physik. Chem.*, **68**, 232 (1909).

<sup>13</sup> Duclaux, *J. chim. phys.*, **5**, 29 (1907); **7**, 405 (1909).

<sup>14</sup> Ref. 6, Fig. 3.

$C_{\text{HCl}}$  deduced from the chloride-ion activities (for convenience recorded again in the last column of Table VI) in the region of purity under 10, that is, in the region in which the aqueous phase is rich in ferric chloride and hydrochloric acid. At higher purities  $a_{\text{H}}$  falls very rapidly to the order of  $10^{-7}$ , that is, to the value in pure water. The values of  $C_{\text{HCl}}$  still indicate a low concentration of hydrochloric acid in the dispersion medium of these sols since they are based on the measurements of  $a_{\text{Cl}}$  and the chlor-

TABLE VI  
 HYDROGEN-ION ACTIVITIES IN FERRIC OXIDE SOLS

Purity	$C_{\text{Fe}}$ G. eq./l.	$a_{\text{H}}$ G. eq./l.	$C_{\text{HCl}}$ G. eq./l.
3.92	0.656	0.040	0.032
..	0.164	0.017	0.010
..	0.082	0.009	0.007
8.40	0.547	0.010	0.011
..	0.274	0.007	0.007
10.5	1.154	0.015	0.016
14.6	0.539	$6.4 \cdot 10^{-6}^a$	0.005
17.5	0.463	$0.9 \cdot 10^{-7}^a$	0.004
22.0	0.454	$1.1 \cdot 10^{-7}^a$	0.0025
30.4	0.936	$2.7 \cdot 10^{-7}^a$	0.005
47.5	0.630	$0.9 \cdot 10^{-7}^a$	0.0028

<sup>a</sup> The constancy of the potential of the hydrogen electrode indicates that the sol is practically free from ferric ion.

ide ion is not as strongly adsorbed as the hydrogen ion. In other words, the hydrogen ion of this hydrochloric acid is completely adsorbed by the disperse phase.

At the higher purities the potential of the hydrogen electrode remains constant indicating that the aqueous phase is practically free from ferric

TABLE VII  
 COMPOSITION OF DIALYZATE

Original Sol			Sol after dialysis			Dialyzate		
Purity	$C_{\text{Fe}}$ G. eq./l.	$C_{\text{Cl}}$ G. eq./l.	Purity	$C_{\text{Fe}}$ G. eq./l.	$C_{\text{Cl}}$ G. eq./l.	$C_{\text{Fe}}$ (qual.)	$C_{\text{Cl}}$ G. eq./l.	$a_{\text{H}}$ G. eq./l.
1.55	1.50	0.966	5.41	0.785	0.145	large amt.	0.087	....
3.92	0.656	0.167	7.62	0.602	0.079	large amt.	0.033	....
8.40	0.547	0.065	...	0.526	....	small amt.	0.0115	0.010
14.6	0.539	0.0389	15.4	0.653	0.0424	faint trace	0.0027	0.0020
17.5	0.463	0.0264	18.8	0.438	0.0234	absent	0.0014	0.0010
22.0	0.454	0.0206	22.3	0.445	0.0200	absent	0.0007	0.0003
30.4	0.936	0.0308	30.7	0.873	0.0284	absent.	0.0012	....

ion. This would, of course, necessarily be the case because ferric chloride hydrolyzes completely in solutions whose value for  $a_{\text{H}}$  is less than about  $10^{-2}$  or  $10^{-3}$ . The values for  $C_{\text{FeCl}_3}$  in Table IV agree excellently with this conclusion, showing the complete absence of ferric chloride from the dispersion medium at purities above about 14. On dialysis of these sols the

dialyzate contains only hydrochloric acid, and is free from ferric ion, as shown in Table VII.

The values for  $C_{\text{FeCl}_3}$  agree very closely with observations of Neidle<sup>15</sup> which have been transcribed in Table VIII. He coagulated ferric oxide

TABLE VIII  
PURITY ABOVE WHICH FERRIC OXIDE SOLS GIVE NO TEST FOR FERRIC ION IN FILTRATE  
AFTER COAGULATION WITH POTASSIUM SULFATE  
(Taken from Neidle)

$C_{\text{Fe}}$ G. eq./l.	Purity	$C_{\text{Fe}}$ G. eq./l.	Purity
0.0311	3.86	0.124	14.7
0.0621	7.32	0.186	14.7

sols of various purities and concentrations with potassium sulfate and tested the filtrate for ferric ion with potassium thiocyanate. Above a certain purity, which depends on  $C_{\text{Fe}}$ , the filtrate contains no ferric ion. When these values are compared with the corresponding ones in Table IV it is found that they mark the borderline at which  $C_{\text{FeCl}_3}$  falls to zero.

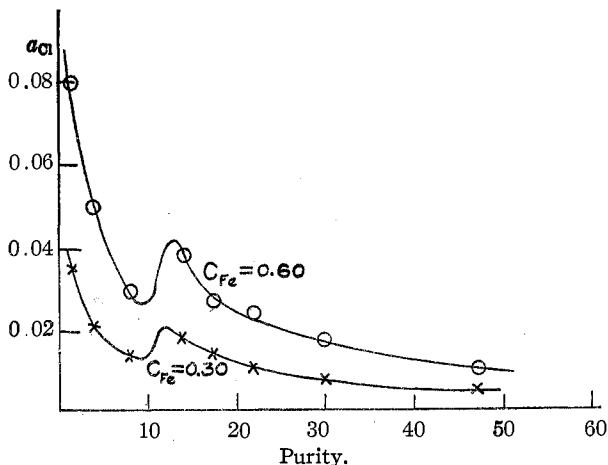


Fig. 4.—The relation between the total amount of chlorine (in the form of ferric chloride or hydrochloric acid) adsorbed by the ferric oxide in ferric oxide sols of varying purity and having the total iron concentration of 0.6 and 0.3 g. equiv. per liter, respectively, and the purity of the sol.

The adsorbed chlorine,  $a_{\text{Cl}}$  of Table IV, varies with the purity of the sol between much narrower limits than  $C_{\text{HCl}}$  or  $C_{\text{FeCl}_3}$ . At the lower purities it amounts to only a fraction of the total chlorine in the sol, while at the higher purities it constitutes nearly all of the chlorine present. Fig. 4 shows the variation of  $a_{\text{Cl}}$  with purity for sols of  $C_{\text{Fe}}$  0.60 and 0.30.

<sup>15</sup> Ref. 6, p. 2344.

The sharp inflexion of the curves between Purities 8 and 14 is to be noted especially. This is undoubtedly to be linked with the fact that ferric ion and hydrogen ion disappear from the aqueous phase in this region.

The data of Table VII were obtained as a check on some of the observations discussed above. Samples of sols of various purities were placed in collodion sacks and suspended in beakers of distilled water, the whole then covered with a bell jar and allowed to stand for 2 weeks. The first 3 columns give the analysis of the sols before dialysis, the next 3 the analyses at the end of 2 weeks, and the last 3 give the results of a qualitative test for ferric ion in the dialyzate by means of potassium thiocyanate, the analysis of the dialyzate for chlorine, and a test for  $a_{\text{H}}$  by the indicator comparison method. As has been mentioned already, the dialyzate gives a test for ferric ion only with those sols which according to Table IV contain ferric chloride in the dispersion medium; with the sols of higher purity only hydrochloric acid passes through the membrane. At the higher purities the concentration of chlorine in the dialyzate at equilibrium is very much less than the  $C_{\text{Cl}}$  in the sol and considerably less than  $a_{\text{Cl}}$  or  $C_{\text{HCl}}$  indicated in Table IV. At the same time, the  $a_{\text{H}}$  in the dialyzate is much greater than  $a_{\text{H}}$  in the sol as given in Table VI. These facts are in line with the conclusions reached already that at the higher purities the hydrogen ion and ferric ion are completely adsorbed by the ferric oxide, the chloride ion only partly adsorbed. The chloride ion tends to pass through the membrane until the  $a_{\text{Cl}}$  on both sides is the same, but each chloride ion passing through the membrane must be accompanied by a hydrogen ion. The latter can be obtained only by withdrawal of some of the adsorbed hydrochloric acid or ferric chloride which is opposed by the strong forces of adsorption. (Any ferric chloride released is immediately hydrolyzed in a solution of such low  $a_{\text{H}}$ .) For this reason equilibrium across the membrane ensues when the  $a_{\text{Cl}}$  is much greater inside than outside, and the  $a_{\text{H}}$  is much greater outside than inside.

Purification of ferric oxide by dialysis proceeds rapidly at purities below about 14 and very slowly after a purity of about 20 has been reached. The reason for this is obvious after inspecting Table VII. From the fact that dialysis goes on much more rapidly at higher temperatures<sup>16</sup> we may infer that the adsorption by ferric oxide decreases with rise in temperature. This is also indicated by the fact that the heat of adsorption is positive as will be shown in the paper following.

Although ferric oxide is highly hydrous, the adsorption of part of the water present by the ferric oxide does not measurably decrease the amount of water in the system acting as solvent for other substances present in solution, or in other words, all the water in the sol acts as solvent for any soluble substance present in the sol. Since the deductions made above

<sup>16</sup> Neidle, *THIS JOURNAL*, 39, 71 (1917).

from the measurements of  $a_{Cl}$  in the sols involve this assumption, it was necessary to obtain evidence to support it. This was done by a study of the effect of dextrose on the freezing point of the sol.

It was found that on freezing ferric oxide sol in a bath slightly below  $0^\circ$  and then bringing it back to room temperature its properties remained unchanged. It was also found that saturating the sol with dextrose produced no observable alteration in its properties. The "molecular weight" of the dextrose used was determined by measuring the depression of the freezing point of pure water in the Beckmann apparatus under the same experimental conditions used with the sol and found to be  $176(C_6H_{12}O_6 = 180)$ . The depression of the freezing point of a measured volume of sol caused by the addition of a given weight of dextrose was measured and the weight of water in the sol acting as solvent computed by means of the equation,  $W = 1860 m/dM$ , where  $W$  is the mass of water in the sol acting as solvent,  $m$  the mass of dextrose taken,  $d$  the freezing-point depression, and  $M$  the "molecular weight" of the dextrose, in this case 176. A sol of high purity, 30.4, and high concentration,  $C_{Fe} = 1.88$ , was taken for the experiment because the ferric oxide is more hydrous in sols of higher purity.

Freezing point of water. . . . .	4.607°	Freezing point of sol. . . . .	4.605°
Volume of sol taken. .60.0 cc. =	62.4 g.	Freezing point after addition.	4.167°
Mass of dextrose taken. . . . .	2.432 g.	Freezing-point depression. . . . .	0.438°
		Water present as solvent. . . . .	58.7 g.

Since the 62.4 g. of sol contain 3.0 g. of ferric oxide, the total water present in the sol is 59.4 g. of which 58.7 g. acts as solvent for the dextrose, leaving 0.7 g. of water combined with the ferric oxide in such a way as to be withdrawn from the solvent water. This is negligible for present purposes.

### Summary

1. By means of the calomel electrode, measurements have been made of the chloride-ion activity in solutions of ferric chloride and in ferric oxide hydrosols of various concentrations and widely varying purity.

2. A method is described for using the hydrogen electrode in the presence of dil. ferric chloride solution and has been applied to the measurement of the hydrogen-ion activity in ferric oxide sol.

3. Ferric oxide sols having a total iron concentration of about 0.5 g. equiv. per liter and a purity less than 14 contain ferric chloride and hydrochloric acid in the aqueous phase and the dispersed ferric oxide carries considerable amounts of adsorbed ferric chloride and hydrochloric acid. The adsorption of ferric ion and hydrogen ion is greater than that of chloride ion, giving the dispersed phase a positive charge. At higher purities the adsorption of ferric ion and hydrogen ion is complete and the aqueous phase contains only chloride ion the "anions" for which are the dispersed particles.

4. At lower concentration of total iron, ferric ion and hydrogen ion disappear from the aqueous phase at somewhat lower purity and at higher concentrations at higher purity.

5. Tables are given showing the concentrations of chloride ion and its distribution between ferric chloride and hydrochloric acid in sols of widely varying purity and concentration, as well as the total chloride compounds adsorbed by the ferric oxide.

6. It is shown by the effect of dextrose on the freezing point of ferric oxide sol that practically all the water present in the sol acts as solvent for substances dissolved in the sol.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## THE HEAT OF COAGULATION OF FERRIC OXIDE HYDROSOL WITH SODIUM SULFATE

BY FREDERICK L. BROWNE<sup>1</sup>

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During an earlier study<sup>2</sup> it was found that when ferric oxide hydrosol is mixed with sodium sulfate solution there is a considerable absorption of heat if the purity<sup>3</sup> of the sol is less than 6; above this there is an evolution of heat, reaching a maximum at a purity between 8 and 12, after which it falls off rapidly, approaching zero at the higher purities. It was concluded that these heat effects are due entirely to the interaction between the sodium sulfate and the electrolytes in the sol and not to any energy change accompanying the change in dispersity of the ferric oxide, but since at the time the exact nature and amounts of the electrolytes present in sols of different purity were not known, it was not possible to show quantitatively that the reaction between the electrolytes in question and the sodium sulfate would account for the observed results.

Since that time the constitution of ferric oxide sol made by Neidle's method<sup>4</sup> of oxidizing ferrous chloride with hydrogen peroxide has been worked out<sup>5</sup> for the range of purity and concentration suitable for the coagulation experiments. The present paper is concerned with the more detailed study of the heat effects accompanying the coagulation of ferric oxide sols with sodium sulfate, particularly at the lower purities, with a view to discovering their cause more exactly.

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<sup>2</sup> Browne and Mathews, *THIS JOURNAL*, **43**, 2336 (1921).

<sup>3</sup> The purity of the sol is defined as the ratio  $\frac{\text{g. equiv. Fe}}{\text{g. equiv. Cl}}$ .

<sup>4</sup> Neidle, *ibid.*, **39**, 2334 (1917).

<sup>5</sup> Browne, *ibid.*, **45** (1923).