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

[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[1]

Received October 13, 1922

During an earlier study[2] it was found that when ferric oxide hydrosol is mixed with sodium sulfate solution there is a considerable absorption of heat if the purity[3] 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[4] of oxidizing ferrous chloride with hydrogen peroxide has been worked out[5] 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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[1] National Research Fellow in Chemistry.

[2] Browne and Mathews, THIS JOURNAL, **43**, 2336 (1921).

[3] The purity of the sol is defined as the ratio $\frac{\text{g. equiv. Fe}}{\text{g. equiv. Cl}}$.

[4] Neidle, *ibid.*, **39**, 2334 (1917).

[5] Browne, *ibid.*, **45** (1923).

The ferric oxide sols used in the earlier experiments on heat of coagulation were prepared by Graham's method of adding ammonium carbonate to ferric chloride solution and dialyzing. This method leaves ammonium chloride in the sol as a by-product. Since by using Neidle's method[4] similar sols can be prepared containing only ferric chloride and the hydrochloric acid produced by its hydrolysis, the latter method was employed for the study of the constitution of ferric oxide sol. This made it necessary to repeat the determination of the heat of coagulation with sodium sulfate, using the sols prepared by this method. Experiments were also carried out with sols prepared by peptizing ferric oxide in ferric chloride, and with sols made by adding various amounts of hydrochloric acid to a sol of high purity. This last method was employed on the theory that it amounts to a reversal of the process of purification by dialysis.

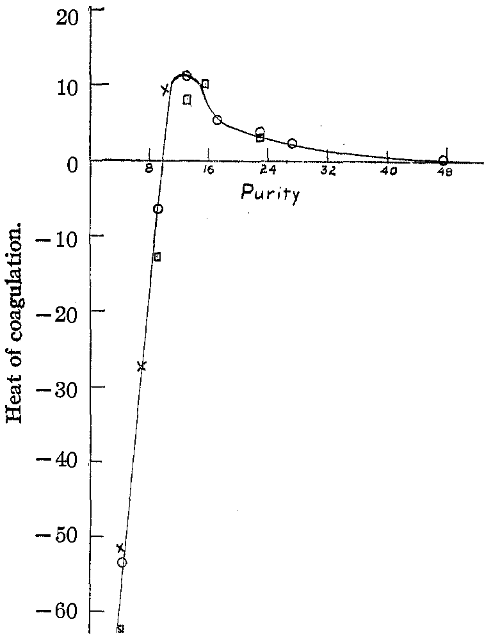

Fig. 1.—Heat of coagulation of 360 cc. of ferric oxide sol prepared by different methods with 255 cc. of 0.2 N sodium sulfate solution as a function of the purity of the sol. The sols contained 0.66 gram equivalents of iron per liter. The heat effects are corrected for the heats of dilution of the sol and of the sodium sulfate. Points indicated by O were obtained with sols prepared after Neidle; those marked X by peptizing ferric oxide in ferric chloride solution; and those marked □ by adding hydrochloric acid to a sol of high purity made by Neidle's method.

The experimental methods of measuring the heats of coagulation have already been described in the paper by Browne and Mathews.[2]

Results and Discussion

Table I gives the heat of coagulation of 360 cc. of ferric oxide sol made by Neidle's method with 255 cc. of 0.2 N sodium sulfate solutions. The first column records the purity of the sol; the second and third, respectively, the total concentrations of iron and of chlorine analytically determined; the fourth the heat effect in gram calories observed on diluting 360 cc. of the sol with 255 cc. of water in the calorimeter; the fifth gives the observed heat of coagulation; and the last gives the heat of coagulation obtained after subtracting the heats of diluting 360 cc. of the sol with 255 cc. of water and 255 cc. of 0.2 N

sodium sulfate solution with 360cc. of water. The data are plotted in Fig. 1.

TABLE I

HEAT OF DILUTION AND OF COAGULATION OF FERRIC OXIDE SOLS MADE BY NEIDLE'S METHOD

360 cc. of sol mixed with 255 cc. of water or 255 cc. of 0.2 *N* sodium sulfate solution[6]

Purity	C_{Fe} G. eq./l.	C_{Cl} G. eq./l.	Total heat of dil. cal.	Heat of coagulation Obs. cal.	Heat of coagulation Corr. cal.
4.44	0.659	0.149	−2.8	−57.4	−53.6
9.11	0.660	0.072	−3.0	−10.3	− 6.3
13.0	0.660	0.051	−3.3	+ 6.8	+11.1
17.1	0.665	0.039	−1.3	+ 3.0	+ 5.3
23.0	0.660	0.029	−0.9	+ 2.1	+ 4.0
27.2	0.659	0.024	−0.8	+ 0.3	+ 2.1
30.4	0.610	0.020	0.0	....	..
47.5	0.66	0.014	0.0	− 1.0	0.0

The curve, Fig. 1, is similar in shape to that found in the previous study by Browne and Mathews for the coagulation with sodium sulfate of sols made by Graham's method (mixing ferric chloride and ammonium carbonate solutions). At the lower purities the points corresponding to given values for the heat of coagulation occur at higher purities than on the old curve, as is to be expected since the sols made by Graham's method contain ammonium chloride which is absent from those prepared according to Neidle. As will be shown later, this ammonium chloride affects the heat of coagulation only slightly, but changes the value for the purity of the sol considerably.

TABLE II

HEAT OF DILUTION AND OF COAGULATION OF FERRIC OXIDE SOL MADE BY PEPTIZING FERRIC OXIDE IN FERRIC CHLORIDE

Mixed as in Table I

Purity	C_{Fe} G. eq./l.	C_{Cl} G. eq./l.	Total heat of dil. cal.	Heat of coagulation Obs. cal.	Heat of coagulation Corr. cal.
1.49	0.152	0.102	+1.0	−67.5	−67.5
3.93	0.405	0.103	−1.9	−54.6	−51.7
7.08	0.764	0.108	−3.0	−31.3	−27.3
10.3	1.154	0.112	−1.4	+ 7.4	+ 9.8

A second series of ferric oxide sols was prepared by peptizing ferric oxide in ferric chloride as already described.[7] The heat of coagulation of these with 0.2 *N* sodium sulfate is given in Table II and the values are plotted in Fig. 1. It will be seen that the points fall on the curve for the sol made by Neidle's method, indicating that sols of the same purity prepared by these two radically different methods have the same consti-

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[6] Heat of dilution of 255 cc. 0.2 *N* Na_2SO_4 with 360cc. water is —1.0 cal.

[7] Browne, THIS JOURNAL, **45** (1923).

tution. The equilibrium is approached in the one case from the side of molecular dispersion and in the other from the side of coarse suspension.

A third series of sols was prepared in the following manner. A large batch of sol was prepared by Neidle's method and dialyzed to a purity of 23. This was divided into 5 portions and to each portion were added the calculated amounts of water and a standard dil. hydrochloric acid solution to give a final total concentration of iron of 0.66 gram equivalents per liter and purities of about 4, 9, 13, 15, and 23, respectively. The purities were checked by analysis. After preparation the sols were set aside for 30 to 50 days to come to equilibrium and the heats of coagulation with 0.2 *N* sodium sulfate solution determined. The results are given in Table III, the last column of which records the time in days elapsing between the addition of the hydrochloric acid to the sol of high purity and the determination of the heat of coagulation. The results also are plotted in Fig. 1. At the purities of 4.08, 9.1, 15.6 and 23.0 the agreement with the results obtained with a sol made by Neidle's method is well within the experimental error, although the value for the heat of coagulation has been changed from +4.0 cal. at purity 23.0 to +10.2 at purity 15.6, and to −64.0 at purity 4.08. At purity 13.1 the agreement is not so close, but the value of the heat of coagulation has increased from +4.0 cal. at purity 23.0 to +7.9 cal. at purity 13.1. If the sol had been allowed a longer time to come to equilibrium this point also would probably have taken its place on the curve.

TABLE III

HEAT OF DILUTION AND OF COAGULATION OF FERRIC OXIDE SOLS MADE BY ADDITION OF HYDROCHLORIC ACID TO A SOL OF HIGH PURITY MADE BY NEIDLE'S METHOD

Mixed as in Table I

Purity	C_{Fe} G. eq./l.	C_{Cl} G. eq./l.	Total heat of dil. cal.	Heat of coagulation Obs. cal.	Corr. cal.	Age Days
4.08	0.654	0.160	+0.2	−64.8	−64.0	30
9.1	0.656	0.072	−2.0	−15.8	−12.8	43
13.1	0.658	0.050	−1.6	+ 5.3	+ 7.9	44
15.6	0.656	0.042	−2.1	+ 7.1	+10.2	51
23.0	0.660	0.029	−0.9	+ 2.1	+ 4.0	..

These experiments confirm the conclusion previously reached by Neidle[4] to the effect that ferric oxide sol represents an equilibrium condition which is defined by the pressure, temperature, concentration and purity and that the process of dialysis can be reversed by carefully adding hydrochloric acid to a sol of high purity and giving it time to come to equilibrium.

It has been pointed out above that in the region of lower purities, a given value for the heat of coagulation occurs at lower purity in the case of a sol made according to Graham than for one prepared by Neidle's method.

This was attributed to the fact that the former contains ammonium chloride which influences the value of the purity greatly but does not greatly alter the heat of coagulation. Table IV records an attempt to convert a sol made by Neidle's method into one of the Graham type by adding ammonium chloride. Sol "Neidle 18^{II}" was prepared by Neidle's method and dialyzed to a purity of 13.0. Its heat of coagulation, corrected, with 0.2 N sodium sulfate solution was +11.1 cal. at a total iron concentration of 0.660 g. eq./l. A 700cc. portion of this sol, having a total iron concentration of 0.700 g. eq./l., was diluted with 84 cc. of 0.5 N ammonium chloride solution and 49 cc. of water, giving the sol "Neidle + NH_4Cl," having a purity of 6.5 and a total iron concentration of 0.660. The heat of coagulation of this sol with 0.2 N sodium sulfate was found to be +6.0 cal., which agrees exactly with the corresponding value for a sol prepared by Graham's method and having the same purity and total iron concentration. A sol made by Neidle's method of purity 6.5 and total ron concentration 0.66·has a heat of coagulation of —31 cal. We may conclude, therefore, that sols made by either method and having the same purity and concentration have the same heat of coagulation, provided that in computing the purity of those made by Graham's method, the chlorine of the ammonium chloride present is deducted from the total chlorine of the sol.

TABLE IV

CONVERSION OF SOL MADE BY NEIDLE'S METHOD INTO ONE OF THE GRAHAM TYPE

Sol	Purity	C_{Fe} G. eq./l.	C_{Cl} G. eq./l.	Heat of coagulation Corr. cal.
Neidle 18^{II}	13.0	0.660	0.0493	+11.1
Neidle + NH_4Cl	6.52	0.661	0.0983	+ 6.0
Graham	6.5	0.66	0.0983	+ 6.0
Neidle	6.5	0.66	0.0983	−31

Sol "Neidle + NH_4Cl" made from 700 cc. "Neidle 18^{II}" containing 0.70 g. eq. of ferric oxide per liter, 84 cc. 0.5 of N NH_4Cl, and 49 cc. of water.

Since ferric oxide sols contain ferric chloride and hydrochloric acid as well as ferric oxide, the heat effects on mixing with sodium sulfate will be due in part to the mixing of the latter with the former electrolytes. It was necessary, therefore, to determine the heat of mixing of the sodium sulfate solution with solutions of hydrochloric acid and of ferric chloride of various concentrations in order to discover how far these effects are responsible for the heat changes during coagulation of the sols. Table V shows the heat of mixing of 255 cc. of 0.2 N sodium sulfate solution with 360 cc. of hydrochloric acid solutions of various concentrations corrected, of course, for the heats of dilution of the hydrochloric acid and the sodium sulfate. These data were plotted for use in the computations which follow. Table VI gives similar data for the mixing of 255 cc. of 0.2 N

sodium sulfate solution with 360 cc. of ferric chloride solutions of various concentrations. These ferric chloride solutions were prepared by diluting a stock 1.0 *N* ferric chloride solution and allowing the diluted solution to stand for about 45 days to come to hydrolytic equilibrium.

TABLE V

HEAT OF MIXING OF HYDROCHLORIC ACID SOLUTIONS OF VARIOUS CONCENTRATIONS WITH 0.2 *N* SODIUM SULFATE SOLUTION

360 cc. of hydrochloric acid mixed with 255 cc. of water or 255 cc. 0.2 *N* sodium sulfate solution[6]

C_{HCl} G. eq./l.	Heat of dil. of HCl cal.	Heat of mixing	
		Obs. cal.	Corr. cal.
0.250	+ 4.0	−103.0	−106.0
0.125	+ 1.4	− 79.2	− 79.6
0.0625	+ 1.0	− 58.4	− 58.4
0.0313	0	− 31.5	− 30.5
0.0156	0	− 15.8	− 14.8
0.0078	0	− 8.0	− 7.0
0.0039	0	− 4.9	− 3.9

In Table VI the first column gives the nominal concentration, N_{FeCl_3}, that is, the total concentration of iron or of chlorine in gram equivalents per liter. The next 2 columns give the actual concentrations of hydrochloric acid and of ferric chloride present as determined in the preceding

TABLE VI

HEAT OF MIXING OF FERRIC CHLORIDE SOLUTIONS OF VARIOUS CONCENTRATIONS WITH 0.2 *N* SODIUM SULFATE SOLUTION

360 c. of ferric chloride mixed with 255 cc. of 0.2 *N* sodium sulfate solution[6]

1	2	3	4	5	6	7	8	9	10	11
			Heat of dilution			Heat of mixing		Heat of mixing due to		
N_{FeCl_3} G. eq./l.	C_{HCl} G. eq./l.	C_{FeCl_3} G. eq./l.	Observed cal.	Corrected cal.	Per g. eq. $FeCl_3$, cal.	Observed cal.	Corrected cal.	HCl cal.	$FeCl_3$ cal.	Heat per g. eq. cal.
0.250	0.060	0.190	+2.4	+2.1	+ 31	−119.4	−120.8	−57.0	−63.8	− 933
0.125	0.035	0.090	−2.8	−2.9	− 89	− 88.5	− 84.7	−35.8	−48.9	−1510
0.0625	0.0173	0.0452	−2.8	−2.8	−172	− 50.1	− 46.3	−17.7	−28.6	−1760
0.0313	0.0091	0.0222	−1.7	−1.7	−212	− 27.6	− 24.9	− 9.3	−15.6	−1950
0.0156	0.0063	0.0093	0	0	. .	− 14.3	− 13.3	− 6.8	− 6.5	−1940
0.0078	0.0048	0.0030	0	0	. .	− 7.8	− 6.8	− 4.8	− 2.0	−1850
0.0039	0.0039	0.0000	0	0	. .	− 4.9	− 3.9	− 3.9	0	

paper. The next 3 columns give, respectively, the observed heat of dilution of the ferric chloride solutions, the heat of dilution corrected for the heat of dilution of the hydrochloric acid present (Col. 2) and the heat of dilution per gram equivalent of ferric chloride. This last is obtained by dividing the values in Col. 5 by the actual amount of ferric chloride in 360 cc. of the solution (0.360 times the corresponding value in Col. 3). Col. 7 records the heat effects observed when 360 cc. of the ferric chloride solution is mixed with 255 cc. of 0.2 N sodium sulfate solution. These values when corrected for the heats of dilution of the ferric chloride (Col. 4) and of the sodium sulfate give the values of Col. 8. The latter are made up in part of the heat of mixing of the sodium sulfate with the hydrochloric acid present in the ferric chloride solutions, Col. 2. These are read from the graph of the data of Table V and recorded in Col. 9. When the latter values are deducted from those of Col. 8 we obtain the heat of mixing of the sodium sulfate with the ferric chloride, Col. 10. The last divided by the total amount of ferric chloride present (0.360 times the values in Col. 3) gives the heat of mixing per gram equivalent of ferric chloride, Col. 11.

We can now examine the heat effects observed during the dilution and the coagulaton of ferric oxide sols with sodium sulfate in more detail. In Table VII, Cols. e and g give, respectively, the heat of dilution and the

TABLE VII

ANALYSIS OF THE HEAT OF DILUTION OF FERRIC OXIDE SOL AND OF ITS HEAT OF COAGULATION WITH 0.2 N SODIUM SULFATE SOLUTION

a	b	c	d	e	f	g
			Heat of dilution			Heat of
Purity	C_{HCl} G. eq./l.	C_{FeCl_3} G. eq./l.	of $FeCl_3$ cal.	of hydrosol Obs. cal.	Corr. cal.	Coag. Corr. cal.
4.44	0.042	0.106	−2.5	−2.8	−0.3	−53.6
9.11	0.020	0.053	−3.0	−3.0	0.0	− 6.3
13.0	0.014	0.038	−2.7	−3.3	−0.6	+11.1
17.1	0.011	0.028	−2.1	−1.3	+0.8	+ 5.3
27.2	0.008	0.016	−1.0	−0.8	+0.2	+ 2.1
30.4	0.007	0.014	0	0	0	....
47.5	0.006	0.008	0	0	0	0

h	i	k	l	m
Heat of mixing with Na_2SO_4 of				
HCl cal.	$FeCl_3$ cal.	H cal.	H/C_{Fe} cal./g. eq.	H/C_{Fe} sum cal./g. eq.
−43	−58	+47.4	+200	+1710
−20	−34	+47.7	+200	+3080
−15	−25	+51.1	+216	+2670
−11	−19	+35.3	+149	+1740
− 8	−12	+22.1	+ 93	+2660
....	....	......	......	......
− 6	− 7	+13.0	+ 55	+3060
				Av. +2487

heat of coagulation (corrected for heat of dilution of sol and coagulant) of sols having the purity shown in Col. a. These data are copied from Table I. Cols. b and c give, respectively, the total amounts of hydrochloric acid and of ferric chloride in the sols. These values are taken from the preceding paper and are based on the assumption that the amounts of these substances present are those which would exist in a ferric chloride solution of nominal concentration, N_{FeCl_3}, equal to the total concentration of chlorine in the sol, C_{Cl}. It is understood that part of this ferric chloride and hydrochloric acid is adsorbed by the ferric oxide, the remainder existing in the dispersion medium.

The concentrations of hydrochloric acid, Col. b, are too low to have a measurable influence on the heat of dilution (see Table V). The values for the heat of dilution of ferric chloride solutions of the concentrations in Col. c are given in Col. d. These are obtained from a graph of the data of Table VI (Col. 10 plotted against Col. 3). When the heat of dilution of the ferric chloride, Col. d, is subtracted from the observed heat effect on dilution of the sol, Col. e, the remainder, Col. f, is scarcely greater than the experimental errors of the calorimetric measurements. Consequently the conclusion reached in the paper by Browne and Mathews to the effect that the heat effects observed on dilution of ferric oxide sols are due entirely to the electrolytes contained therein, is substantiated. The dilution of the ferric oxide contained in the sol does not involve a measurable heat effect.

It will be seen that the above computations involve the assumption that the adsorbed ferric chloride plays the same part on dilution as the ferric chloride contained in the dispersion medium. This is considered entirely reasonable in view of the fact[7] that, although the ferric oxide in these sols is always considered to be highly "hydrous," *all* of the water in the sol acts as solvent for some added solute such as dextrose, as revealed by the freezing-point depression.

Cols. h and i of Table VII give the values for the heats of mixing of 0.2 N sodium sulfate solutions with solutions of hydrochloric acid and ferric chloride, respectively, having the concentrations of Cols. b and c. These data are obtained from Tables V and VI by plotting the values for the heats of mixing against the concentrations, and then reading off the values corresponding to the concentrations given in Cols. b and c of Table VII. When the values of Cols. h and i are deducted from those of Col. g we still have left a heat effect, H, which now is always positive. In Col. l this heat effect is given per gram equivalent of iron in the sol.

It will be seen that the magnitude of this remaining heat effect is practically constant for sols of purity up to about 13, after which it falls off rapidly. This suggests that the heat effect is connected with changes in the adsorption equilibria within the sol during coagulation. In order to obtain some idea of the magnitude of these changes in adsorption equilibria the following experiments were performed. Portions (140 cc.) of ferric oxide sols of varying purity were mixed with 100 cc. each of 0.207 *N* sodium sulfate solution, the coagulated ferric oxide was allowed to settle, and the supernatant liquid analyzed. The results are given in Table VIII. The first 4 columns record, respectively, the purity of the sol, the total amounts of iron and of chlorine contained in 140 cc., and the hydrogen-ion activity (determined by the methods described in the preceding paper). The next 4 columns give, respectively, the total iron, chlorine and sulfate contained in the 240 cc. of supernatant liquid and the hydrogen-ion activity (determined by the indicator method).

TABLE VIII

ANALYSIS OF FILTRATES AFTER COAGULATION OF SOL MADE BY NEIDLE'S METHOD WITH SODIUM SULFATE

140 cc. of ferric oxide sol coagulated with 100 cc. of 0.207 *N* sodium sulfate solution

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sol contained in 140 cc.				Filtrate contained in 240 cc.									
Purity	Total Fe g. eq.	Total Cl g. eq.	a_H g. eq./l.	Total Fe g. eq.	Total Cl g. eq.	Total SO_4 g. eq.	a_H g. eq./l.	Adsorbed Cl in sol g. eq.	Total Cl released g. eq.	Total SO_4 adsorbed g. eq.	$\frac{\text{Cl released}}{\text{total Fe}}$	$\frac{SO_4 \text{ adsorbed}}{\text{total Fe}}$	Sum
1.55	0.210	0.135	......	0.1050	0.1343	0.0150	......	....	....	0.0057	...	...	...
3.92	0.0920	0.0234	$1.8.10^{-2}$	0.0104	0.0208	0.0147	......	0.0074	0.0048	0.0060	0.052	0.065	0.117
8.40	0.0766	0.00911	$0.7.10^{-2}$	0.0006	0.00685	0.0168	Over 10^{-3}	0.0034	0.0011	0.0039	0.014	0.051	0.065
14.6	0.0755	0.00545	$64.\ 10^{-7}$	0	0.00307	0.0165	200.10^{-7}	0.0043	0.0019	0.0042	0.025	0.056	0.081
17.5	0.0648	0.00369	$0.9.10^{-7}$	0	0.00233	0.0168	$0.3.10^{-7}$	0.0031	0.0017	0.0039	0.026	0.060	0.086
22.0	0.0635	0.00288	$1.1.10^{-7}$	0	0.00180	0.0173	$0.8.10^{-7}$	0.0025	0.0014	0.0034	0.022	0.054	0.076
30.4	0.1310	0.00424	$2.8.10^{-7}$	0	0.00238	0.0176	$0.4.10^{-7}$	0.0034	0.0015	0.0031	0.011	0.024	0.035
47.5	0.0882	0.00186	$0.9.10^{-7}$	0	0.0082	0.0195	$0.3.10^{-7}$	0.0014	0.0004	0.0012	0.004	0.014	0.018

Col. 9 gives the amount of chlorine adsorbed by the ferric oxide in 140 cc. of the sol, taken from the data of the preceding paper. Subtracting Col. 6 from Col. 3 leaves the amount of chlorine still adsorbed by the ferric oxide after coagulation, and this difference subtracted from Col. 9 gives the amount of adsorbed chlorine released to the dispersion medium during coagulation or, in other words, the change in adsorbed chlorine compounds during the coagulation. This is recorded in Col. 10. Col. 11 gives the amount of sulfate adsorbed by the ferric oxide during coagulation. This is obtained by subtracting the amount of sulfate found in the supernatant liquid, Col. 7, from the total amount of sulfate used, 0.0207 gram equivalents. Cols. 12 and 13 give, respectively, the chlorine released and the sulfate adsorbed per gram equivalent of total iron in the sol (Cols. 10 and 11 divided by Col. 2), and Col. 14 gives the sum of these two or, in other words the total change in adsorption equilibria during coagulation.

Comparison of Cols. 4 and 8 shows that there is no significant change in the hydrogen-ion activity of the dispersion medium during coagulation[8] and Col. 5 leads to a similar conclusion regarding the ferric-ion concentration. The chlorine that is released to the dispersion medium during the coagulation, therefore, must be present finally as sodium chloride, whereas the absorbed chlorine in the sol before coagulation is partly ferric chloride and partly hydrochloric acid. It follows from this, also, that the adsorbed sulfate must exist finally, at least in part, as ferric sulfate or sulfuric acid adsorbed by the ferric oxide. In other words, the changes in the adsorption equilibria during coagulation involve definite metathetical reactions and consequently will be accompanied by heat effects. These heat effects should be fairly closely proportional to the magnitude of the sum of the chlorine released and the sulfate adsorbed during the coagulation, Col. 14 of Table VIII.

Col. m of Table VII is obtained by dividing the heat effect per gram equivalent of iron (Col. 1) by the sum of the chlorine released and the sulfate absorbed (Col. 14, Table VIII). If the above theory is correct and there is no other source of change in heat energy during the coagulation, the values in Col. m would be expected to be independent of the purity of the sol. It will be seen that while the observed heat of coagulation, Table I, varies with increasing purity from —57.4 to +6.8 and then back to —1.0, the heat effect per gram equivalent of change in adsorbed chlorine and sulfate, Col. m, varies only about 30% from the average value of about +2500 cal. per gram equivalent. In view of the involved character of the computations with the resulting possibility for the accumulation of errors, this is felt to be very satisfactory evidence that the foregoing interpretation is correct.

The conclusion reached in the paper by Browne and Mathews to the effect that the change in dispersity of the ferric oxide during coagulation of the hydrosol with electrolytes does not involve a measurable heat effect, and that the heat effects observed with sols of low purity are due to the interaction of the electrolytes in the sol and in the coagulant, is substantiated. These heat effects arise from the dilution of the ferric chloride

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[8] Pauli and Matula, [*Kolloid-Z.*, **21**, 49 (1917)] similarly found no change in the hydrogen-ion activity of the dispersion medium during coagulation of a ferric oxide hydrosol.

and hydrochloric acid present, to their mixing with the coagulating electrolyte, and to the changes in the adsorption equilibria taking place.

Summary

1. The heat of coagulation of ferric oxide hydrosol of widely varying purity with 0.2 *N* sodium sulfate solution has been investigated, using sols prepared by three very dissimilar methods; (*1*) oxidation of ferrous chloride solution with hydrogen peroxide and dialysis, (*2*) peptization of precipitated ferric oxide in ferric chloride solution, (*3*) addition of various amounts of hydrochloric acid to a sol of high purity made by the first method.

2. The same value for the heat of coagulation at a given purity and total iron concentration is obtained with sols prepared by all three methods, indicating that ferric oxide sols represent an equilibrium which is defined by the temperature, pressure, concentration and purity.

3. The change in dispersity of ferric oxide during coagulation does not involve a measurable heat effect.

4. The heat effects observed during the coagulation of sols of low purity are due to (*1*) dilution of the ferric chloride and hydrochloric acid in the sols, (*2*) mixing of these electrolytes with the coagulating electrolyte, (*3*) changes in the adsorption equilibria.

MADISON, WISCONSIN

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

THE HYDROLYSIS OF METHYL ORTHO-NITROBENZOATE IN ACID SOLUTION

BY GERALD E. K. BRANCH AND DONALD S. MCKITTRICK

Received October 16, 1922

Introduction

The mono-*ortho* substituted benzoic acids, in the presence of hydrogen ion, esterify much more slowly than does the unsubstituted acid. The difference is particularly noticeable when the substituent is a nitro group. The velocity constants as written by Goldschmidt[1] are: benzoic acid, 0.0428; *o*-nitrobenzoic acid, 0.0028; *o*-methylbenzoic acid, 0.011. On the other hand, Kellas[2] found that methyl *o*-nitrobenzoate in alcoholic potash hydrolyzes considerably faster than does methyl benzoate; but he also found that the introduction of a methyl group in the *ortho* position caused a greater slowing up of the alkaline hydrolysis than of the esterification in acid. These results may point to an actual difference in the phenomenon of steric hindrance, in the esterification and hydrolysis reac-

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[1] Goldschmidt, *Ber.*, **28,** 3218 (1895).

[2] Kellas, *Z. physik. Chem.*, **24,** 221 (1897).