THE HEAT OF COAGULATION OF FERRIC OXIDE HYDROSOL WITH ELECTROLYTES.[1]

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Introduction.

The pioneers in the field of colloid chemistry, for example Selmi,[2] Graham,[3] and Linder and Picton,[4] attached great significance to the fact that they found no measurable change in temperature accompanying the formation or the coagulation of colloidal dispersions. The formation of a true solution always involves a heat change which it has been customary by way of loose illustrative analogy to regard as being similar in nature to the thermal effect involved in the change of state of a pure substance. In passing into solution, the solid absorbs the analogs of the heats of fusion and of vaporization in order to attain a condition which in many ways resembles that of a gas. In addition there frequently are other phenomena involved such as hydration, ionization and hydrolysis, also associated with energy changes which are usually positive and may more than counterbalance the first effect. But in general the heat of solution of hydrous neutral salts and of non-electrolytes is negative and of the order of some thousands of calories per gram equivalent.

In considering the theory of colloidal dispersion a knowledge of the energy changes involved is important. Many writers maintain that the phenomena of colloidal dispersion are identical with those of true solution save in the final size of the particles; that, in other words, true solution is merely the limiting case of colloidal dispersion. This being the case, colloids must have a "heat of peptization" of the same nature as the heat of crystalloidal solution. It is reasonable to assume that these heat effects arise from the work required to subdivide the solid and are at least roughly proportional to the specific surface developed by the dispersed phase. Taking the diameter of the molecules of a certain substance as $0.1\,\mu\mu$ and the diameter of its colloidally dispersed particles as $10\,\mu\mu$, the "heat of peptization" should then be about one hundredth part of the heat of solution, that is, of the order of some tens of calories per gram equivalent. On the other hand, if crystalloidal solution takes place by a process different from that of colloidal dispersion, we should not

[1] Abstract of a thesis submitted by F. L. Browne to the Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Quoted from Jones, "Nature of Solution," D. van Nostrand Co., 1917, p. 226.

[3] Graham, il. Trans., 151, 220 (1861).

[4] Linder and Picton, J. Chem. Soc., 61, 144, 146, 153 (1892).

expect to find any relation between heat of solution and "heat of peptization."

It is to be understood that by the term "heat of peptization" is meant merely the heat change involved in the subdivision of the solid phase and it is to be distinguished from the heat of wetting, heat of adsorption of substances in solution, or other heat effects due to the presence of substances in true solution. The converse of the "heat of peptization," i. e., the energy change involved in the precipitation of the colloidal dispersion, will be called the "heat of coagulation."

Doerinckel[5] has pointed out that the small amount of literature concerning the heat of coagulation of colloids is contradictory and inconclusive. He found that measurable amounts of heat are evolved on coagulating ferric oxide and silica hydrosols with electrolytes; his sols, however, contained large amounts of electrolytes and the magnitude of the heat effect on coagulation was greatly decreased on partly removing these by dialysis, although he did not seem to attach much significance to this fact. Kruyt and van der Spek[6] extended these experiments to the coagulation of arsenous sulfide hydrosol, finding that no measurable heat change accompanied the coagulation in this case. They concluded that the heat effects during the coagulation of ferric oxide sol are to be attributed to changes in the degree of hydration of the ferric oxide. For the case of arsenous sulfide they pointed out that no measurable amount of heat could be produced by interaction of the electrolytes in the sol and in the coagulant, but they completely ignored this possibility in the case of ferric oxide sol.

Experimental Methods.

The determination of the heat changes accompanying the coagulation of colloids presents unusual difficulty because the magnitude of the heat effect per unit weight of dispersed phase is small, and the concentration of the colloid is usually low, consequently the temperature change to be measured is very small.

The apparatus employed was the familiar "submarine" type of the Richards adiabatic calorimeter.[7] The calorimeter vessel was a silver beaker of 700cc. capacity. This was placed in the "submarine" and the whole immersed in a bath of water constituting the "environment." The water of the environment was kept in rapid circulation by means of two powerful propeller stirrers, and its temperature could be very quickly altered by means of an electrical heating coil or by opening a valve admitting ice-water. A 4-junction copper-constantan thermo-element, connected to a sensitive galvanometer registering by means of a spot of light on a ground-glass scale, was placed with one limb in the liquid in the calorimeter vessel, the other in the environment, so that the difference in temperature between the two could be read at all times. Through-

    [5] Doerinckel, Z. anorg. Chem., 66, 20 (1910); 67, 161 (1910).

    [6] Kruyt and van der Spek, Koll. Z., 24, 145 (1919).

    [7] Richards and Rowe, Proc. Am. Acad., 49, 173 (1913). Daniels, THIS JOURNAL, 38, 1473 (1916). MacInnes and Braham, ibid., 39, 2110 (1917).

out an entire experiment this temperature difference was maintained within $0.006°$ of the desired value; after a sudden change in the temperature of the contents of the calorimeter amounting to $1°$ (very much larger than the temperature changes actually encountered) this temperature difference between environment and calorimeter con-tents could be restored to the desired value within 15 to 30 seconds.

The sample of the colloid to be coagulated was placed in the calorimeter vessel. Within this was suspended a silver cylinder closed at the bottom by a sheet of rubber dam held in place by a rubber band. The solution of the electrolyte used as coagulant was placed in this inner cylinder, or "mixing chamber." By means of mechanical stirrers, both the colloid and the coagulant were vigorously agitated. When the entire contents of the calorimeter had come to the same temperature, the temperature of the environment was so adjusted with respect to that of the calorimeter contents that the temperature of the latter remained constant. This was the case when the environ-ment was very slightly cooler than the calorimeter contents, so that there was a loss of heat to the environment just equal to the heat generated by the operation of the me-chanical stirrers. When this relation between environment and calorimeter tempera-tures had been found and the temperature of the calorimeter contents remained con-stant for a period of 10 minutes or more, the colloid and coagulant were mixed by operating a trigger which slipped off the rubber band holding the rubber bottom of the mixing chamber in place, and the entire silver cylinder was lowered slightly so as to be completely submerged in the mixed liquids in the calorimeter vessel. The same relation between the calorimeter and environment temperature was maintained until the calorimeter temperature again became constant, giving the end-point of the re-action.

The temperature of the calorimeter contents was measured by means of a Leeds and Northrup platinum resistance thermometer and thermometer bridge, the readings being estimated to $0.0001°$. Instead of determining the water equivalent of the calorimeter and the specific heats of the liquids used, at the beginning of each experiment a measured quantity of electrical energy was converted into heat by means of a re-sistance coil submerged in the liquids in the calorimeter, and the resulting rise in tem-perature measured. This gave the amount of energy required to raise the calorimeter and contents $1°$, and by multiplying this by the temperature change resulting upon mixing the liquids, the amount of heat liberated was obtained.

Under certain circumstances the method of operation was not as simple as de-scribed above. The stirring of the liquids in the calorimeter generated a certain amount of heat in consequence of which the temperature of the environment was maintained slightly below that of the liquids in the calorimeter in order that this amount of heat might be lost to the environment. If on coagulating the sol the resistance to the stirrers was greatly increased, heat was generated more rapidly than it was being lost to the environment, and at the end of the reaction the temperature did not remain constant, but rose slowly. In a number of the experiments in which the coagulum was especially gelatinous and bulky this proved to be the case. The difficulty was met by plotting the temperature-time curve for the 20 to 30 minutes following the mixing of the liquids. The temperature rose very rapidly for 1 or 2 minutes, then more slowly, and finally at a constant rate of the order of $0.0002°$ per minute. This constant rise in temperature was due to the added amount of heat generated as a re-sult of the extra resistance to the stirrers. The straignt line forming the last part of the temperature-time curve was extrapolated back to the time of mixing the liquids and the corresponding temperature taken as the end-point of the reaction.

The heat effect observed on mixing a sample of a sol with a solution of an electrolyte in this way included the heats of dilution of the sol with the

water in the electrolyte solution, and of the electrolyte solution with the water in the sol. In separate experiments, another sample of the sol was diluted with a volume of water equal to that of the coagulant, and another portion of the coagulant with a volume of water equal to that of the sol. These heats of dilution were then subtracted from the total heat effect on mixing sol and coagulant to give the "heat of coagulation."

Under the most favorable conditions the temperature difference was measured with an accuracy of 0.0002°, so that, allowing a similar amount for imperfect adiabaticity, the heat change was determined within about 0.25 gram calorie, corresponding to about 0.5 calorie per gram equivalent of ferric oxide for the more concentrated sols used. Where the coagula were very bulky and gelatinous, however, the errors were greater, so that the results cannot be relied upon closer than 1 or 2 calories per gram equivalent of ferric oxide.

Preparation of the Hydrosols.

Graham's method of mixing ferric chloride and ammonium carbonate solutions and dialyzing was used for the preparation of the ferric oxide hydrosols. 400 g. of ferric oxide was dissolved in a liter of water, filtered, and then 1000 cc. of a saturated solution of ammonium carbonate added slowly with constant stirring. Nine liters having been prepared in this way, it was dialyzed through collodion sacks. As soon as the purification had proceeded far enough to permit heating the sol to 80° without causing partial coagulation, the method of hot dialysis[3] was used. Experiment showed that the heat of coagulation of sols of the same purity prepared by hot dialysis and by cold dialysis is the same.

The sols were analyzed for ferric oxide and for chlorine. Following the nomenclature of Neidle, the ratio of gram equivalents of ferric oxide per liter to gram equivalents of chlorine per liter is called the "purity" of the sol.

Results.

Heat of Dilution of Ferric Oxide Hydrosols.—A 9-liter batch of colloid having been prepared, it was given a number for purposes of identification, and subjected to dialysis. As it attained different degrees of purity, samples were withdrawn, analyzed, and divided into portions for measurements of heats of coagulation and of dilution. Table I gives the data obtained on dilut-
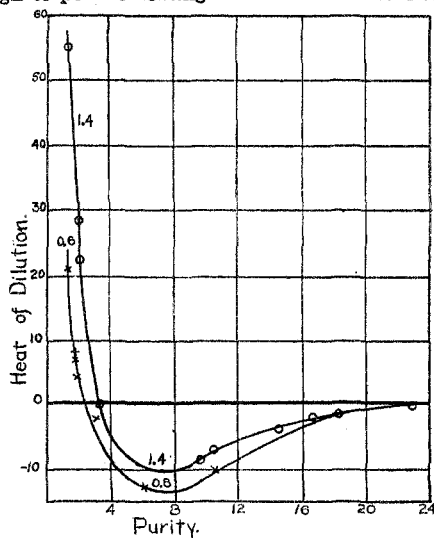

Fig. 1.—The heat of dilution per g. equiv. of Fe_2O_3 as a function of the purity of the sol for ferric oxide hydrosols containing, respectively, 1.4 and 0.6 g. equiv. of Fe_2O_3 per liter. The marked heat effects with the less pure sols disappear when the purity exceeds 22.

[3] Neidle and Barab, THIS JOURNAL, 39, 71 (1917).

ing 340cc. portions of such sols with 240 cc. of water. The first column gives the number of the sol, the second the purity, the third the content of ferric oxide and of chlorine, the fourth the observed

TABLE I.

HEAT OF DILUTION OF FERRIC OXIDE SOL.

340 cc. of sol diluted with 240 cc. of water.

Sol. No.	Purity.	Concentration g. equiv. per liter.		Heat effect calories.	Heat of dilution per g. equiv.	
		Fe_2O_3.	Cl.		Fe_2O_3.	Cl.
8	1.490	1.500	1.007	+29.2	+57.3	+85.4
		0.750	0.504	+ 7.6	+29.7	+44.2
		0.375	0.252	0.0	0.0	0.0
6	1.840	1.443	0.784	+ 4.0	+ 8.1	+15.0
		0.846	0.460	+ 2.1	+ 7.3	+13.4
		0.496	0.270	+ 1.2	+ 7.1	+13.1
8	2.054	1.198	0.583	+ 9.3	+22.8	+46.9
		0.599	0.292	+ 0.9	+ 4.4	+ 9.1
14	2.093	1.446	0.691	+11.8	+23.9	+50.1
6	3.362	1.440	0.428	0.0	0.0	0.0
		0.844	0.251	− 0.6	− 2.1	− 7.0
		0.495	0.147	− 0.3	− 1.8	− 6.0
8	3.373	1.242	0.368	+ 0.3	+ 0.7	+ 2.4
8	6.127	1.455	0.237	− 4.7	− 9.6	−58.7
		0.728	0.119	− 3.2	−12.9	−78.7
6	9.750	1.653	0.169	− 4.3	− 7.7	−74.9
7	10.59	1.578	0.149	− 3.5	− 6.6	−69.8
		0.789	0.075	− 2.5	− 9.4	−99.4
		0.395	0.037	− 1.3	− 9.4	−99.3
7	14.66	1.547	0.106	− 1.4	− 2.7	−40.1
6	16.67	1.428	0.086	− 0.6	− 1.2	−20.6
7	18.30	1.44	0.079	− 0.6	− 1.2	−22.4
7	22.97	1.44	0.063	0.0	0.0	0.0
6	31.88	1.52	0.048	0.0	0.0	0.0

heat effect, and the fifth the heat effect in calories per gram equivalent of ferric oxide and in calories per gram equivalent of chlorine in the sol. For each purity, a curve was drawn showing the heat of dilution per gram equivalent of ferric oxide as a function of the concentration of the sol. By selecting a line of constant concentration and reading its intersections with the curves for the different purities, the data were obtained for Fig. 1, which gives the heat of dilution per gram equivalent of ferric oxide as a function of the purity. Fig. 2 is drawn on the assumption that the heat effects are due entirely to the electrolytes in the sol. Taking the chlorine content as the measure of these electrolytes, the heat of dilution per gram equivalent of chlorine is plotted against the concentration of chlorine in the sol. In this figure is shown also the heat of dilution of ferric chloride solutions of varying concentration, the data for which are given in Table II.

TABLE II.

HEAT OF DILUTION OF FERRIC CHLORIDE.

360 cc. of ferric chloride solution diluted with 255 cc. of water.

Concentration FeCl₃ g. equiv. per liter.	Heat effect calories.	Heat of dilution per g. equiv. FeCl₃.
1.029	+70.5	+190.3
0.515	+18.7	+100.8
0.257	+ 2.9	+ 31
0.129	− 1.8	− 38
0.064	− 2.7	−116
0.032	− 2.2	−191
0.016	− 1.1	−192
0.008	− 0.3	− 90

Heat of dilution of a solution containing 0.0643 g. equiv. of FeCl₃ and 0.0625 g. equiv. of NH₄Cl per liter was −1.95 calorie.

The freshly prepared hydrosols have a positive heat of dilution which rapidly decreases in magnitude as the dialysis proceeds, soon reaching zero and then becoming negative, passing through a minimum at a purity between 7 and 8, finally rising to zero beyond a purity of 21 or 22. Fig. 2 shows that ferric chloride solutions behave similarly on dilution. This suggests that the heat effect observed on dilution of the colloid may be due to the presence of ferric chloride. An observation by Neidle[8] lends support to this view. He noted that when a sol with a purity less than 21 is coagulated with sodium sulfate, for example, and the supernatant liquid tested for ferric ion by means of thiocyanate, a positive test results, but with sols having a purity greater than 21 the test is negative.

The curves in Fig. 2 confirm this assumption. If all the chlorine in the sol represented ferric chloride and the dilution of this salt were the only cause of a heat
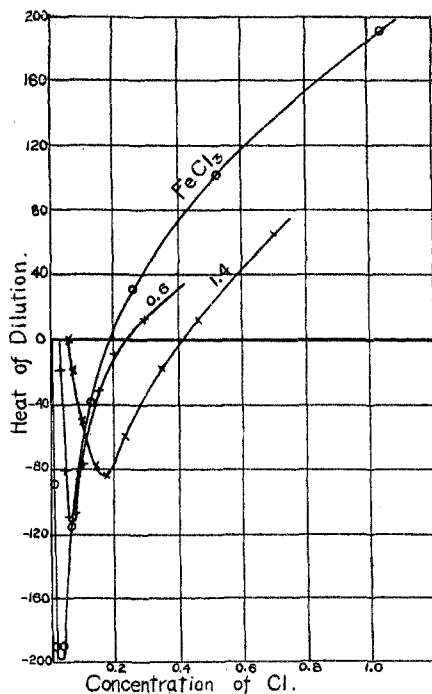

Fig. 2.—The heat of dilution per g. equiv. of Cl in the sol plotted against the concentration of Cl in the sol for ferric oxide sols containing, respectively, 1.4 and 0.6 g. equiv. of Fe₂O₃ per liter, together with the heat of dilution of ferric chloride solutions of varying concentration. The similarity in the shapes of these curves suggests that the heat effects on diluting ferric oxide sols are due to the ferric chloride contained in them.

effect, the curves for the colloids and for the dilution of ferric chloride would coincide. But the first of these assumptions is known to be incorrect, for part of the chlorine represents ammonium chloride, a by-product of the reaction by which the sol was prepared, and a part probably represents hydrochloric acid. In addition the presence of the colloidal ferric oxide undoubtedly results in the adsorption of a part of the electrolytes present. The present state of our knowledge of ferric oxide sol does not permit us to make corrections for these factors quantitatively, but considering them qualitatively we see that, since the heat of dilution of ammonium chloride or of hydrochloric acid in the concentrations present is negligible, the curves for the colloids tend to coincide with that for the ferric chloride solutions. The close similarity in the shapes of the curves together with the fact that after the sols have reached a purity of 21 the heat of dilution is zero, show definitely that the observed heat effects are to be attributed to the electrolytes present in the sol.

When a ferric chloride solution is diluted in the calorimeter there results first a rapid evolution or absorption of heat, depending upon the concentration of the solution used, followed by a slow rise in temperature of the order of magnitude of $0.001°$ per minute. This secondary evolution of heat continues for hours, but during the first 15 or 20 minutes at least it takes place at a constant rate. For present purposes we are interested only in the first large heat change. The temperature of the calorimeter contents was therefore taken at intervals and plotted against the time. The curve became a straight line within a few minutes after the dilution took place, and was extrapolated back to the time of mixing to give the final temperature of the contents of the calorimeter.

Goodwin[9] observed a similar phenomenon in his study of the conductivity of ferric chloride solutions. When a ferric chloride solution is quickly diluted and the conductivity measured at intervals, this is found to increase slowly for a number of hours. Moreover, the diluted solutions which are at first nearly colorless gradually take on the red color characteristic of colloidal ferric oxide. Goodwin explained the phenomenon on the basis of the theory that the hydrolysis of ferric chloride takes place in two steps.

$$\text{Fe}^{+++} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{++} + \text{H}^+ \qquad (1)$$
$$\text{colorless ion}$$
$$x\text{FeOH}^{++} + 2x\,\text{H}_2\text{O} \rightleftharpoons (\text{FeO}_3\text{H}_3)x + 2x\,\text{H}^+ \qquad (2)$$
$$\text{colloidal}$$
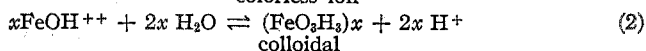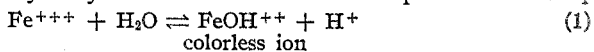
The first step is an instantaneous reaction, but the second requires time. The second step resembles a supersaturation phenomenon in that it proceeds more readily if the solution is first "seeded" with ferric oxide sol, the particles of which are assumed to act as nuclei for the further condensation of ferric oxide.

These experiments on the heat of dilution of ferric chloride solutions

⁹ Goodwin, *Phys. Rev.*, **9**, 251 (1896); **11**, 193 (1900).

indicate that Reaction 1 is strongly endothermal and Reaction 2 exothermal. It should be noted, however, that the thermal data confirm the conclusion that the hydrolysis takes place in two steps, the first a rapid and the second a slow reaction, but do not add any conclusive evidence regarding the nature of the hypothetical intermediate product which Goodwin assumed

TABLE III.

HEAT OF MIXING OF FERRIC CHLORIDE WITH ELECTROLYTES.

360 cc. of $FeCl_3$ solution mixed with 255 cc. of electrolyte.

(For heat of dilution of $FeCl_3$ see Table II.)

Heat of dilution of 255 cc. of electrolytes with 360 cc. of H_2O.

0.1 N $Na_2C_2O_4$	+ 0.6 cal.	0.1 N $K_3Fe(CN)_6$	0.00
0.221 N Na_2SO_4	− 1.32	0.196 N H_2SO_4	+15.2
0.5 N NaCl	− 4.40		

Electrolyte.	Concentration $FeCl_3$.	Heat effect calories.	Heat of mixing.	Heat of mixing per g. equiv. of Cl.
0.1 N $Na_2C_2O_4$	1.029	+ 69.6	− 1.6	− 4.3
	0.515	16.4	− 3.0	− 15.9
	0.257	0.0	− 3.5	− 37.4
	0.129	0.0	+ 1.2	+ 25.1
	0.064	4.6	+ 6.7	+ 289
	0.032	7.6	+ 9.2	+ 794
	0.016	4.6	+ 5.1	+ 886
	0.008	4.4	+ 4.0	+1385
0.221 N Na_2SO_4	1.029	− 61.2	−130.4	− 352
	0.515	−116.9	−133.0	− 717
	0.257	−128.0	−129.5	−1400
	0.129	− 93.3	− 90.2	−1940
	0.064	− 54.8	− 50.8	−2200
	0.032	− 26.8	− 23.3	−2030
	0.016	− 14.6	− 12.2	−2110
	0.008	− 7.4	− 5.8	−2030
0.5 N NaCl	1.029	+ 10.7	− 55.4	− 150
	0.515	− 22.4	− 36.7	− 198
	0.257	− 23.8	− 22.2	− 240
	0.129	− 18.4	− 12.3	− 264
	0.064	− 13.6	− 6.5	− 283
	0.032	− 9.0	− 2.4	− 208
	0.016	− 7.3	− 1.8	− 307
0.1 N $K_3Fe(CN)_6$	1.029	+ 73.2	+ 2.7	+ 7.3
	0.515	+ 14.6	− 4.1	− 22.2
	0.257	− 4.2	− 7.1	− 76.7
	0.129	− 9.2	− 7.4	− 160
	0.064	− 6.6	− 3.9	− 169
	0.032	− 2.9	− 0.7	− 63
0.196 N H_2SO_4	1.029	+118.8	+ 33.1	+ 89
	0.515	54.5	20.6	111
	0.257	27.6	9.5	103
	0.129	19.1	5.7	122
	0.064	18.5	5.9	258
	0.032	18.6	5.6	487

to be FeOH″. From the high heat of formation of water from its ions and the exothermal character of Reaction 2 we should prefer to write it in such a way as to involve the decomposition of fewer molecules of water.

Heat of Mixing of Ferric Chloride with Electrolytes.—The stock ferric chloride solution was 1.029 N and the ratio of equivalents of iron to equivalents of chlorine was 1.000. From this a series of dilutions was prepared, and the heat effect determined on mixing 360 cc. with 255 cc. of the electrolyte solution used for the coagulation of the ferric oxide sols.
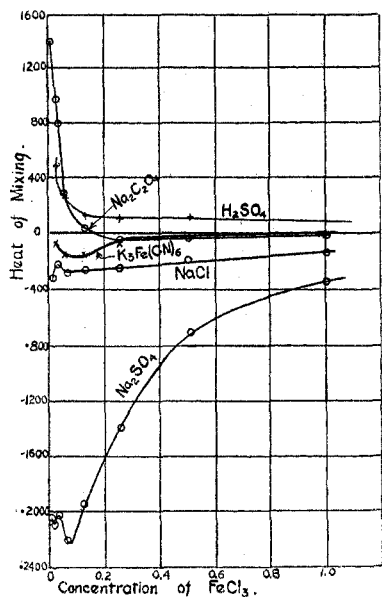

Fig. 3.—The heat of mixing of solutions of electrolytes with solutions of ferric chloride of varying concentration.

From this were subtracted the heats of dilution of 360 cc. of the ferric chloride with 255 cc. of water, and of 255 cc. of the electrolyte solution with 360 cc. of water, the difference being the heat of mixing of the ferric chloride and the electrolyte solution. The data are given in Table III and Fig. 3.

The very significant values for the heats of mixing are undoubtedly to be explained by the influence of the electrolytes upon Reaction 1 in the hydrolysis of the ferric chloride. Moreover, in the coagulation of ferric oxide sols having a purity less than about 22 this heat of mixing of the electrolyte with the ferric chloride present in the sol will be expected to play an important part.

Heat of Coagulation of Sols with Electrolytes.—Since ferric oxide hydrosol is positively charged, the anions are the effective ions in coagulation.

The electrolytes used were sodium oxalate, sodium sulfate, sodium chloride, potassium ferricyanide, sulfuric acid, and sodium hydroxide. With each of these coagulants, the influence of the following factors on the heat of coagulation was determined: (1) the concentration of the hydrosol; (2) the purity of the sol; (3) the concentration of the coagulant.

A large batch of colloid having been prepared and subjected to dialysis, samples were withdrawn at various purities. With each sample a series of dilutions was prepared and observation made of the heat effect accompanying the coagulation with the electrolyte solution being studied. From the total heat effect observed were subtracted the heats of dilution of the sol and of the coagulant to obtain the heat of coagulation. Plotting the results gave a family of curves for sols of the different purities showing

the heat of coagulation as a function of the concentration of the sol. Selecting lines of constant concentration and reading their intersections with the curves for the different purities gave the data from which curves showing the heat of coagulation as a function of the purity, the concen-
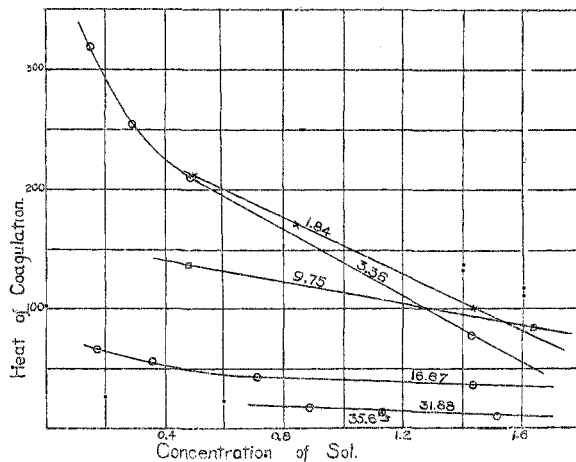

Fig. 4.—The heat of coagulation of ferric oxide sols of varying concentration with 0.1 N $Na_2C_2O_4$. The numbers on the curves give the purity of the sol.

TABLE IV.

HEAT OF COAGULATION OF FERRIC OXIDE SOL OF VARYING CONCENTRATION AND PURITY WITH 0.1 N SODIUM OXALATE.

340 cc. of sol No. 6 mixed with 240 cc. of 0.1 N $Na_2C_2O_4$.

(Heat of dilution of 240 cc. $Na_2C_2O_4$ with 340 cc. H_2O, $+0.6$ cal.)

Purity.	Concentration g. equiv. per liter. Fe_2O_3.	Cl.	Heat effect calories.	Ht. of dil'n of sol.	Heat of coag'l'n per g. equiv. Fe_2O_3.	Cl.
1.84	1.443	0.784	+55.1	+4.0	+103	+189
	0.846	0.495	52.0	+2.1	171	315
	0.496	0.269	27.8	+1.2	214	395
3.362	1.440	0.429	40.5	0.0	81	274
	0.844	0.251	47.1	−0.6	164	552
	0.495	0.147	35.8	−0.3	211	708
	0.290	0.086	25.5	−0.2	254	853
	0.145	0.043	16.3	−0.1	320	1074
	0.073	0.022	14.1	−0.1	550	1850
9.75	1.653	0.170	45.4	−4.3	87	852
	0.485	0.050	21.9	−1.3	137	1340
16.67	1.428	0.086	18.0	−0.6	37	618
	0.714	0.043	11.1	−0.3	45	746
	0.357	0.021	7.6	−0.2	59	979
	0.179	0.011	4.6	−0.1	67	1220
31.88	1.519	0.048	7.1	0.0	13	403
	0.891	0.028	5.9	0.0	19	619
35.6	1.14	0.032	6.9	0.0	16	578

tration of the sol remaining constant, were obtained. Finally, using a sample of colloid having constant purity and concentration, the heat of coagulation with solutions of the electrolyte in varying concentration was measured, correction being made as usual for the heats of dilution of the sol and of the electrolyte. The concentration of the coagulants was varied over wide limits, the most dilute solution lying well below the limiting concentration so that the sols were not coagulated by them.

Tables IV to VI give the data for the heat of coagulation of sols of different purity and concentration with the six different electrolytes. The first column gives the purity of the sol, the second the concentration of ferric oxide and of chlorine in the sol, the third the observed heat effect, the fourth the heat of dilution of the sol and of the coagulant, and the fifth the heat

TABLE V.

HEAT OF COAGULATION OF FERRIC OXIDE SOL OF VARYING CONCENTRATION AND PURITY WITH SODIUM SULFATE.

340 cc. of sol No. 6 or 7 mixed with 240 cc. of Na_2SO_4.

(Heat of dil'n 0.313 N Na_2SO_4 −2.3 cal.; 0.157 N, 0.0 cal.)

Purity.	Concentration g. equiv. per liter.			Heat effect calories.	Ht. of dil'n of sol.	Ht. of coag'l'n per g. equiv.	
	Fe_2O_3.	Cl.	Na_2SO_4.			Fe_2O_3.	Cl.
1.490	1.500	1.008	0.313	− 557.9	+29.2	−1147	−1708
	0.750	0.503	0.157	− 36.9	+ 7.6	− 175	− 260
	0.375	0.252	0.078	− 22.5	+ 0.0	− 177	− 263
2.054	1.198	0.584	0.313	− 85.4	+ 9.3	− 227	− 460
	0.599	0.292	0.157	− 45.5	+ 0.9	− 228	− 468
3.373	1.242	0.369	0.313	− 74.0	+ 0.3	− 171	− 575
	0.621	0.184	0.157	− 37.9		− 179	− 604
6.127	1.455	0.238	0.313	− 26.0	− 4.7	− 38	− 235
	0.728	0.119	0.157	− 7.9	− 3.2	+ 19	+ 118
8.26	1.537	0.186	0.313	+ 17.3	− 5.0	+ 47	+ 389
	0.768	0.093	0.157	+ 12.4	− 3.6	+ 62	+ 515
10.59	1.578	0.149	0.313	+ 21.1	− 3.5	+ 50	+ 531
	0.789	0.075	0.157	+ 14.2	− 2.5	+ 62	+ 658
	0.395	0.137	0.078	+ 9.0	− 1.3	+ 67	+ 712
	0.197	0.018	0.039	+ 5.3	− 0.6	+ 88	+ 934
	0.098	0.009	0.020	+ 3.6	− 0.3	+ 117	+1237
11.76	1.401	0.119	0.313	+ 19.3	− 2.8	+ 51	+ 602
	0.701	0.060	0.157	+ 14.4	− 1.6	+ 67	+ 986
14.66 ·	1.547	0.105	0.313	+ 15.8	− 1.4	+ 37	+ 543
	0.774	0.053	0.157	+ 10.3	− 0.7	+ 42	+ 614
	0.387	0.026	0.078	+ 7.2	− 0.4	+ 57	+ 842
	0.193	0.013	0.039	+ 4.0	− 0.2	+ 63	+ 921
14.77	1.326	0.090	0.313	+ 14.0	− 1.5	+ 39	+ 580
18.30	1.44	0.079	0.313	+ 7.0	− 0.6	+ 20	+ 370
	0.72	0.040	0.157	+ 4.6	− 0.3	+ 20	+ 368
	0.36	0.020	0.078	+ 2.9	− 0.2	+ 25	+ 452
22.97	1.44	0.063	0.313	+ 5.3	0.0	+ 15	+ 354
28.02	1.44	0.051	0.313	+ 5.4	0.0	+ 16	+ 441
39.29	0.77	0.019	0.100	+ 3.6	0.0	+ 13	+ 516

TABLE VI.

HEAT OF COAGULATION OF FERRIC OXIDE SOL OF VARYING CONCENTRATION AND PURITY WITH SODIUM CHLORIDE, POTASSIUM FERRICYANIDE, SULFURIC ACID AND SODIUM HYDROXIDE.

360 cc. of sol with 255 cc. of coagulant.

Coagulant.	Purity.	Concentration g. equiv. per liter.		Heat effect calories.	Ht. of dil'n sol. coagulant.		Hg. of coag'l'n per g. equiv.	
		Fe_2O_3.	Cl.				Fe_2O_3.	Cl.
0.5 N NaCl	2.093	1.446	0.691	− 11.5[a]	+11.8 − 4.4		− 36 −	76
		0.723	0.346	− 17.6[a]	+ 1.2		− 55 −	116
		0.362	0.173	− 13.3[a]	+ 0.1		− 69 −	144
	6.037	1.153	0.191	− 14.3[a]	− 4.2		− 14 −	83
		0.577	0.096	− 9.2[a]	− 2.8		− 9 −	57
		0.288	0.048	− 6.4[a]	− 1.9		− 0.6 −	3
	9.802	1.540	0.157	− 4.2[a]	− 3.6		+ 7 +	70
		0.770	0.079	− 2.2[a]	− 1.1		+ 12 +	117
	15.55	1.305	0.084	− 3.3	− 1.0		+ 5 +	71
		0.653	0.042	− 3.7	− 0.3		+ 4 +	64
	22.96	1.095	0.048	− 3.6	0.0		+ 2 +	49
0.1 N $K_3Fe(CN)_6$	2.093	1.446	0.691	+ 31.5	+11.8	0.0	+ 38 +	79
		0.723	0.346	7.3	+ 0.1		55	116
	6.037	1.153	0.191	4.5	− 4.2		21	126
		0.567	0.096	2.7	− 2.8		27	161
		0.288	0.048	1.5	− 1.9		33	197
	9.802	1.540	0.157	12.2	− 3.8		29	281
		0.770	0.079	8.3	− 1.1		34	331
		0.385	0.039	4.6	− 0.4		36	350
	14.72	1.305	0.089	6.0	− 1.4		16	230
	15.55	1.305	0.089		·		15	228
		0.653	0.042	2.6	− 0.3		12	188
	22.96	1.095	0.048	0.7	0.0		1.8	42
0.199 N NaOH	2.093	1.446	0.691	+462.0[a]	+11.8 − 1.0		+ 870	+1820
		0.723	0.346	430.5[a]	+ 1.2		1653	3460
		0.362	0.173	330.7	+ 0.1		2548	5335
	6.037	1.153	0.191	341.5	− 4.2		835	5045
		0.577	0.096	190.0	− 2.8		934	5662
		0.288	0.048	111.5	− 1.9		1103	6660
	9.802	1.540	0.157	230.5	− 3.8		424	4160
		0.770	0.079	151.8	− 1.1		555	5445
		0.390	0.039	83.0	− 0.4		609	5965
	15.55	0.653	0.042	52.4	− 0.3		229	3556
		0.326	0.021	35.5	0.0		311	4830
	22.96	1.095	0.048	47.3	0.0		123	2830
		0.548	0.024	28.5	0.0		149	3430
0.196 N H_2SO_4	2.093	1.446		+103	+11.8 +15.2		+ 146	
		0.723		68	+ 1.2		200	
		0.367		39	+ 0.1		181	
	6.037	1.153	0.191	103	− 4.2		221	1330
		0.577	0.096	58	− 2.8		220	1325
		0.139	0.048	26	− 1.3		240	1445
	9.802	1.540	0.157	127	− 4.8		209	2045
		0.770	0.078	77	− 1.1		225	2210

TABLE VI (*continued*).

Coagulant.	Purity.	Concentration g. equiv. per liter.		Heat effect calories.	Ht. of dil'n sol. coagulant.	Ht. of coag'l'n per g. equiv.	
		Fe₂O₃.	Cl.			Fe₂O₃.	Cl.
		0.385	0.039	+47	−0.4	+234	+2297
	15.55	0.635	0.042	73	−0.3	249	3870
		0.326	0.021	47	0.0	268	4162
	22.96	1.095	0.048	129	0.0	287	6600
		0.548	0.024	72	0.0	287	6580

^{a} The sols did not coagulate in these experiments.

of coagulation per gram equivalent of ferric oxide and per gram equivalent of chlorine in the sol. Fig. 4 shows the heat of coagulation per gram equivalent of ferric oxide as a function of the concentration of the sol in the case of 0.1 N sodium oxalate as coagulant. The corresponding curves for the o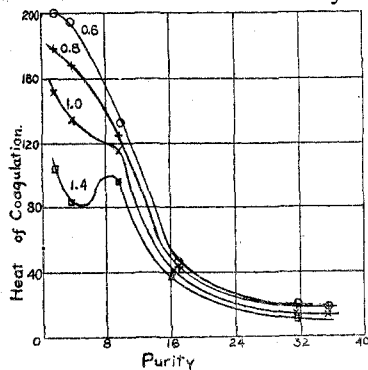ther electrolytes are similar in character. In Fig. 5 the heat of coagulation per gram equiva-lent of ferric oxide is plotted against the purity for sols containing 0.6, 0.8, 1.0, and 1.4 gram equivalents of ferric oxide per liter, the coagulant being 0.1 N sodium oxalate. Fig. 6 gives the heat of coagulation per gram equivalent of ferric oxide as a function of the purity for all six electrolytes used, the concentration of the sol being 1.0 gram equivalent of ferric oxide per liter.

Fig. 5.—The heat of coagulation with 0.1 N Na₂C₂O₄ of ferric oxide sols containing, respectively, 0.6, 0.8, 1.0 and 1.4 g. equiv. of Fe₂O₃ per liter, as a function of the purity of the sol. At the higher purities the heat effects become very small.

These curves show in a striking man-ner that the heat effects are large only when the sol contains large amounts of electrolytes. As these are removed by dialysis, the heat effect falls off very rapidly, eventually falling within the ex-perimental error at a purity of about 23 in the cases of sodium chloride and potassium ferricyanide as coagulants. With sodium sulfate and potassium oxalate at this purity the heat of coagulation is small, but still measurable. The curves could not be car-ried much farther in the direction of greater purity, however, because of the experimental difficulty of preparing such concentrated sols of high purity, and also because the coagulum formed from sols of such high purity becomes so bulky and gelatinous that the contents of the calori-meter can no longer be adequately stirred, and the generation of heat by friction with the stirrers becomes large enough to introduce serious error.

Clearly the observed heat effects are due to the presence of the electro-lytes in the sol and not to the change in the dispersity of the ferric oxide during coagulation. This is shown not only by the fact that the heat

effect disappears when the electrolytes are removed from the sol, but by the great variation in the shape of the curves for the different electrolytes in the region of low purity. With sodium sulfate and sodium chloride the curves have negative as well as positive branches. It seems probable that the heat effects may be attributed entirely to the shift in the equilibrium of Reaction 1 in the hydrolysis of ferric chloride. As has already been pointed out, in our present state of knowledge of ferric oxide sol we do not know very much about the constitution of the sols and the concentrations of the electrolytes present, consequently it is not yet possible to test this theory quantitatively.

Sulfuric acid as coagulant behaves very differently from the other electrolytes in that the heat of coagulation increases with increasing purity. In these experiments, on mixing the sol with the coagulant in the calorimeter, a sudden change in temperature resulted, followed by a slow rise in temperature at a rate of the order of 0.004° per minute continuing indefinitely. The first rapid change in temperature was measured in these experiments. These phenomena are easily understood if we consider that the solution of ferric oxide (sol or gel) in dilute acids takes place through a reversal

Fig. 6.—The heat of coagulation of ferric oxide sols containing 1.0 g. equiv. of Fe_2O_3 per liter with different electrolytes as a function of the purity of the sol.

of the two reactions by which ferric chloride hydrolyzes. In all cases, then, we have the dispersed phase in equilibrium with the intermediate product according to Equation 2, and the latter in equilibrium with ferric ion according to Equation 1. Addition of sulfuric acid by increasing the hydrogen-ion concentration forces the equilibrium of Reaction 1 to the left, decreasing the concentration of the intermediate product, and this in turn causes more of the ferric oxide to pass into solution according to Equation 2.

In Fig. 7 is shown the heat of coagulation of ferric oxide sols of constant purity and concentration with solutions of the six electrolytes of varying
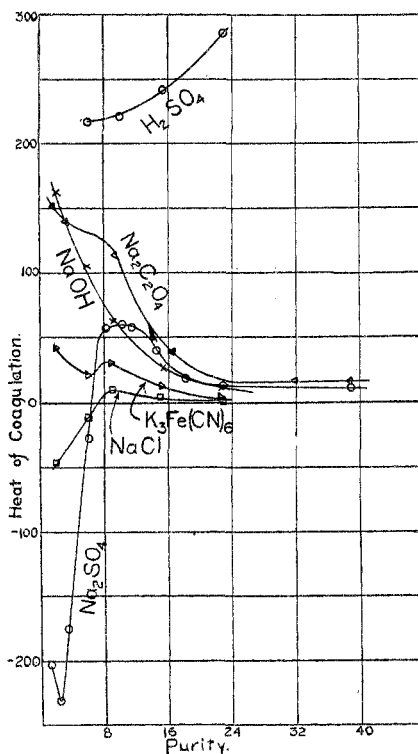
concentration. The data for these curves are given in Table VII. In every case the heat effect increases rapidly at first as the concentration of the coagulant increases, but soon reaches a point beyond which the change is very small. The limiting concentration of the electrolyte in

TABLE VII.

HEAT OF COAGULATION OF FERRIC OXIDE SOL. WITH COAGULANTS OF VARYING CON-CENTRATION.

360 cc. of sol with 255 cc. of coagulant.

Coagulant.	Concn. of coagulant g. equiv. per liter.	Purity of sol.	Concn. of sol g. eq. per liter.	Heat effect calories.	Ht. of dil'n sol.	coagulant.	Ht. of coag'l'n per g. equiv. Fe₂O₃.
Na₂C₂O₄	0.250	11.76	1.337	+ 37.4	−3.0	+ 1.4	+ 81.1
	0.050			22.4		0.0	52.9
	0.040			18.9ᵃ		0.0	45.6
	0.025			14.3ᵃ		0.0	36.0
	0.250	15.85	1.305	+ 13.2	−1.0	+ 1.4	+ 27.3
	0.125			13.3		+ 0.6	29.2
	0.063			11.4		0.0	26.5
	0.031			8.7		0.0	20.5
	0.016			7.0ᵃ		0.0	17.0
Na₂SO₄	1.966	10.97	1.386	−135.4	−3.3	−159.2	+ 57.5
	1.474			− 37.2		− 56.0	47.3
	0.983			− 17.7		− 25.5	23.5
	0.492			+ 11.3		− 5.7	43.8
	0.246			+ 21.0		− 1.6	54.9
	0.123			+ 24.8		− 0.5	60.6
	0.098			+ 27.4		− 0.3	65.7
	0.080			+ 25.6ᵃ		0.0	63.3
	0.061			+ 24.6ᵃ		0.0	53.9
	0.031			+ 8.0ᵃ		0.0	24.0
	0.256	15.48	1.335	+ 14.7	−1.5	− 1.2	+ 36.1
	0.128			16.1		− 0.4	37.5
	0.064			18.9		0.0	42.4
	0.048			17.4		0.0	39.4
	0.032			16.5ᵃ		0.0	37.5
NaCl	0.500	15.55	1.305	− 3.3	−1.0	− 4.4	+ 4.6
	0.210			+ 4.1		0.0	10.9
K₃Fe(CN)₆	0.500	14.72	1.305	− 3.8	−1.4	−10.4	+ 17.0
	0.100			+ 6.0		0.0	15.7
	0.025			+ 3.8ᵃ		0.0	11.1
NaOH	0.511	14.72	1.305	+112.1	−1.4	− 2.6	+247
	0.256			110.2		− 1.2	240
	0.102			97.4		− 0.5	211
	0.051			72.2		0.0	157
H₂SO₄	0.505	15.85	1.305	+138.6	−1.0	+ 26.7	+240
	0.252			126.2		17.6	233
	0.105			113.0		8.8	224
	0.073			92.9		2.1	196
	0.052			76.3ᵃ		1.6	161

ᵃ The sols did not coagulate in these experiments.

each lies between the points marked A and B. It will be seen, therefore, that the curves do not attain their maximum until some time after the limiting concentration has been passed, and that there is no "break" in any of the curves at this point. This confirms the conclusion that the heat effects observed are due entirely to the electrolytes in the sol and
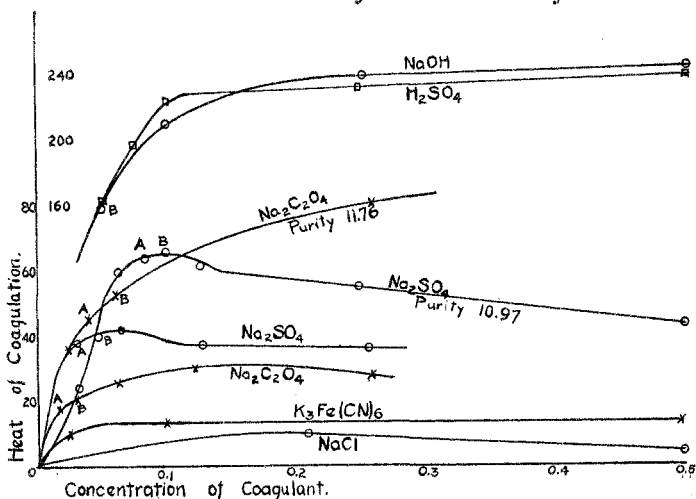

Fig. 7.—The heat of coagulation of ferric oxide sol with different electrolytes as a function of the concentration of the coagulant. The sol contained 1.3 g. equiv. of ferric oxide per liter and had a purity of 15 except where otherwise indicated. The limiting concentration of the electrolyte lies between the points marked A and B.

in the coagulant, and that the act of changing the dispersity of the ferric oxide during coagulation is not associated with any measurable heat change.

Summary.

1. The dilution of ferric oxide hydrosols of varying purity is accompanied by measurable heat effects until the purity exceeds 21 or 22, beyond which point the heat of dilution is zero. If the heat of dilution per gram equivalent of chlorine in the sol is plotted against the chlorine content, the curve is of the same nature as that for the heat of dilution of ferric chloride solutions of varying concentration.

2. The thermal behavior of ferric chloride solutions on dilution confirms the observations of Goodwin based on conductivity to the effect that the hydrolysis of ferric chloride takes place in two steps, the first an instantaneous and the second a slow reaction.

3. The mixing of ferric chloride solutions with common electrolytes involves very significant heat changes.

4. The heats of coagulation of ferric oxide sols of varying purity with sodium oxalate, sodium sulfate, sodium chloride, potassium ferricyanide,

sodium hydroxide, and sulfuric acid have been determined. The curves showing the heat of coagulation as a function of the purity vary widely in shape with the nature of the coagulant, the heat effect being usually positive, but with sodium sulfate and sodium chloride at low purities, negative. As the purity increases the heat of coagulation becomes smaller, finally becoming negligible, except in the case of sulfuric acid. The peculiar behavior of the last electrolyte is due to solution of the ferric oxide.

5. When the heat of coagulation is plotted against the concentration of the coagulating electrolyte, smooth curves are obtained showing no "break" at the point of limiting concentration.

6. The heat effects observed on coagulating ferric oxide sols with electrolytes are to be attributed to the action of the electrolytes in the coagulants upon the electrolytes, particularly ferric chloride, present in the sol. The change in dispersity of the ferric oxide on coagulation does not involve a heat change greater than 1 to 2 calories per gram equivalent of ferric oxide.

7. In the case of ferric oxide hydrosol there exists no "heat of peptization" analogous to the heat of solution of crystalloids.

MADISON, WISCONSIN.

THE STRENGTHS OF COBALTAMMINE BASES AND WERNER'S THEORY OF BASES.

By ARTHUR B. LAMB AND VICTOR YNGVE.

The great strength of many cobaltammine bases has attracted the attention and evoked the surprise of investigators in this field. Cobaltic hexammine hydroxide (luteo cobaltic hydroxide), for instance, is a very soluble, deliquescent substance whose solution is caustic in its properties, absorbs carbon dioxide with avidity, and displaces both ammonia and silver oxide from their salts. Werner,[1] estimating the strengths of various ammine bases qualitatively from their chemical behavior and from the properties of their salts, has arranged certain of them in the order of their strengths, and indeed largely on the basis of these considerations has proposed a new theory of bases and of hydrolysis. We have therefore been interested to obtain quantitative measurements of the strengths of these bases. We have used the conductivity method for this purpose, measuring the conductivities of their dilute solutions at various concentrations and comparing the resulting molecular conductivities with the conductiv-

[1] Werner, "Neuere Anschauungen," 3rd edition, Braunschweig, 1913, p. 265.