

On the other hand, irregular fluctuations of several millivolts are obtained when the junction is at the end of a thin tube dipping into a wider one.

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PREPARATION OF NEGATIVE COLLOIDAL FERRIC OXIDE BY HYDROLYSIS OF PRUSSIAN BLUE

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Hydrolysis of a solution of ferric chloride yields a positive ferric oxide sol. In order to account for the character of the electrical charge on this sol, Powis¹ offers the following explanation. While both ferric ions and chloride ions are adsorbed by the colloidal particle, the former are preferentially adsorbed, and since they are relatively more positive than the chloride ions are negative, the micelle acquires a positive charge. The same author points out the fact that, in general, colloidal suspensions of the hydroxides of multivalent metals are positive. This is because they are prepared by dialysis or hydrolysis of one of their salts having a univalent anion.

Frequent mention is made in the literature of negative colloidal ferric oxide.² The general methods of preparation have consisted, in the main, of operations in one or in two steps. In the latter case a positive sol is prepared and then recharged by allowing it to come into contact with a solution containing some negative ion which is sufficiently adsorbed to give to the micelle a negative charge. The other mode of operation, while essentially the same, is different in that the positive form is not isolated but is recharged in the same system in which hydrolysis is performed. Thus Powis¹ prepared negative ferric oxide by allowing a dilute solution of ferric chloride to flow into an excess of sodium hydroxide solution.

Von Kohei Hakozaki² has shown that positive colloidal iron oxide can be recharged negatively by the addition of potassium ferrocyanide. The tetravalent ferrocyanide ions are not only highly negative but they also have a large volume and are probably only slightly hydrated. The last two factors enable these ions to be strongly adsorbed and the first likewise contributes to make them very effective in reversing the charge on a positive iron oxide sol. From these facts it was suggested to us that if hy-

¹ Powis, *J. Chem. Soc.*, 107, 818 (1915).

² Fischer, *Biochem. Z.*, 27, 223 (1910); Dhar and Sen, *J. Phys. Chem.*, 27, 376 (1923); Dhar, Sen and Gosh, *ibid.*, 28, 457 (1924); Kruyt and van der Spek, *Kolloid-Z.*, 22, 81 (1918); 25, 17 (1919); von Kohei Hakozaki, *ibid.*, 39, 319 (1926).

hydrolysis of a ferric salt in the presence of this easily adsorbable highly negative ion could be achieved, a negative iron oxide sol might result.

Ferric ferrocyanide was selected as the salt to be hydrolyzed on the strength of the following observations. When a dilute solution of ferric chloride is dropped into a boiling solution of potassium ferrocyanide, a deep blue negative sol of Prussian blue results. Similarly, a negative sol of Prussian blue is obtained when small crystals of the salt are shaken with cold water. Apparently Prussian blue is soluble enough to give Fe^{+++} ions and $\text{Fe}(\text{CN})_6^{----}$ ions, which, on being adsorbed by the molecules of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, yield a negative colloid. In verification of this assumption it was found that by making a fresh dilute suspension of Prussian blue in water and dropping this suspension slowly into five liters of vigorously boiling distilled water the resulting product first became bluish, then faded to colorless or pale yellow. The fading indicated the start of hydrolysis of Prussian blue. Further addition of the salt gave a product that changed in color from yellow to orange and finally to a dull red. Tests applied to this red solution proved it to be a negative colloid.

The best results have been obtained by preparation according to the following method. A fresh suspension of 2 g. of Prussian blue is made in one liter of distilled water and allowed to drop slowly into five liters of boiling distilled water. After the addition of the first ten drops the operation is stopped until hydrolysis commences. This action becomes apparent as the color changes from blue to a faint yellow. The initial change from blue to yellow normally requires thirty or forty minutes. However, if a small amount (5 cc.) of positive or negative colloidal ferric oxide is added to the receiving flask containing the boiling water, the change takes place in less than five minutes. Dropping is resumed after the start of hydrolysis and is continued until the liter of suspension has been added, the complete operation requiring five hours. Boiling distilled water is added at intervals to offset the loss of water resulting from the prolonged boiling. After all of the Prussian blue is added, the sol has become chocolate colored. If it is now allowed to stand for fourteen hours, a slight settling is noted in the bottom of the flask and the sol has changed to a greenish color. Boiling at this point entirely destroys the green color and turns the sol permanently red. The green coloration may be avoided by boiling for thirty or forty minutes after the addition of the last drop of Prussian blue, but there is always a slight settling of a brownish-black residue after the sol has stood for fourteen hours or longer.

The sol prepared in the above manner was dialyzed at a temperature of 80–90° for twenty-four hours. It showed no signs of settling at the end of this period and only a slight trace of settling was shown after the dialyzed sol had stood for three weeks. However, excessive dialysis produced instability. Thus, after five or six days of cold dialysis or three days of hot dialysis, the sol flocculated.

In appearance the stable sol is somewhat cloudy in reflected light but is red and perfectly clear in transmitted light providing the Prussian blue has been added at a slow rate. If addition of the salt has been too rapid, *i. e.*, less than five hours has been required for the complete operation, the sol is turbid in transmitted light. Qualitative analysis of the coagulum from the turbid sol for nitrogen by the sodium fusion test shows the element to be

present. However, analysis of the clear sol gives no evidence of nitrogen. In the latter case it may be assumed that hydrolysis is complete, the final product being, most likely, hydrated ferric oxide. Similarly in the case of the turbid sol it may be assumed that hydrolysis is incomplete, there being present in the final product both ferric oxide and complex iron cyanide compounds.

The particles of the clear sol are plainly visible in the ultramicroscope. Using this instrument their mean diameter was found to be 89μ when measured according to the technique developed by Ayres in this Laboratory and to be presented by him in a later communication. Migration toward the anode during cataphoresis indicates that the particles carry a negative charge. The value of the zeta potential was found to be 29.5 millivolts when measured under a potential gradient of 5.11 volts per cm. The method employed in the cataphoretic experiments was a modification of that used by Burton.³ It was found that by replacing the distilled water in the U-tube above the sol with the ultrafiltrate from the sol better results were obtained.

The following flocculation values were obtained on a sol which contained 0.1 g. of iron per liter and which had been dialyzed at a temperature of from 80 to 88° for twenty-four hours. Since the sol particles are negatively charged, the cation is the effective agent in producing flocculation. ("Flocculation value" as here used denotes the number of millimoles of electrolyte per liter which produced complete flocculation in four hours, the reaction taking place in a volume occupying 4 cc.)

TABLE I
FLOCCULATION VALUES

Electrolyte	NaCl	BaCl ₂	AlCl ₃
Flocculation value	40.0	0.9	0.045

In Table II an irregular series is shown with thallic chloride, since this salt in its higher concentrations gives a non-flocculating zone where the charge on the sol is positive.

TABLE II
DATA WITH THALLIC CHLORIDE

ThCl ₄ per liter, mml.	Flocculation	Dir. of migr. in cataphoresis	ThCl ₄ per liter, mml.	Flocculation	Dir. of migr. in cataphoresis
50	Complete		0.1	Complete	
10	Partial		0.08335	Complete	
5	None	Toward cathode	.0625	Complete	
2.5	None	Toward cathode	.05	Partial	
1.0	None	Toward cathode	.025	Partial	
0.5	None	Toward cathode	.0125	None	Toward anode
0.25	None	Toward cathode	.01	None	Toward anode
0.1667	Complete		.005	None	Toward anode
0.125	Complete				

³ Burton, *Phil. Mag.*, [6] 11, 434 (1906).

The upper flocculation zone corresponds to the flocculation of a positive sol, the lower to that of a negative sol. All those cases in which complete flocculation occurred when 2 cc. of electrolyte was added to 2 cc. of sol and allowed to stand for four hours are listed as the "Complete" flocculation zone under the column headed "Flocculation." All other cases in which complete flocculation occurred or which showed turbidity at the end of seventy-two hours are placed in the "Partial" flocculation zone. "No flocculation" corresponds to the samples in which no turbidity was manifest at the end of seventy-two hours.

A comparison of the properties of this sol is being made with the properties of a sol that has been recharged with potassium ferrocyanide. The effect of H^+ ion concentration on an irregular series for colloidal ferric oxide is being studied using potassium ferrocyanide as the recharging agent.

Summary

1. Negative colloidal hydrous ferric oxide has been prepared by hydrolysis of a suspension of Prussian blue.
2. Some of the properties of the sol have been studied.

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

TEMPERATURE-CONDUCTANCE CURVES OF SOLID SALTS. III. HALIDES OF LITHIUM

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The temperature-conductance curves of the solid halides of sodium and potassium have been investigated^{2,3} and found in most cases to exhibit two distinct slopes when plotted to the axes $\log k$ (logarithm of the specific conductance) against $1/T$ (reciprocal of the absolute temperature). It was suggested by one of the writers² that the change of slope is probably significant of a change in the mechanism of conduction. Pursuant of this suggestion, transference experiments were performed upon sodium chloride⁴ which indicated that only the sodium ion takes part in the conduction process over the temperature range of the lower slope, while in the higher temperature range both ions contribute to the conduction.

With the assumption that the conductance of a solid is proportional to the number of ions in its lattice which have an energy greater than a

¹ This paper is an abstract of a thesis submitted by D. C. Ginnings in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Phipps, Lansing and Cooke, *THIS JOURNAL*, **48**, 112 (1926).

³ Phipps and Partridge, *ibid.*, **51**, 1331 (1929).

⁴ Phipps and Leslie, *ibid.*, **50**, 2412 (1928).