

CHEMISTRY

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The address of Chairman H. T. Briscoe on Two Decades in the History of Chemistry and the paper on The Preparation of Acetyl Bromide, by M. T. Bruton and Ed. F. Degering, are published by title only. Karl Means, Butler University, was elected chairman for 1940.

The Adsorption of Potassium Ferrocyanide and Ferric Sulfate by Prussian Blue

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Studies concerning the composition of Prussian blue precipitates formed by the interaction of the ferric and ferrocyanide ions have led to interesting and, in some instances, conflicting conclusions. It has been shown that, when the reactants are mixed, oxidation-reduction reactions and adsorption occur which prevent the formation of the stoichiometric compound, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. Bhattacharya and Dhar¹ report experiments that indicate that this compound is formed when a solution of ferric chloride is added to a solution of potassium ferrocyanide. They further point out that, when the precipitate is allowed to age in contact with the supernatant liquid, the composition of the precipitate changes to approach an equilibrium mixture as a result of either oxidation-reduction or adsorption processes or both. It is pointed out that Prussian blue is primarily susceptible to adsorption processes.

The simple compound, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, is formed, according to Müller,² only if the solutions of ferric iron and ferrocyanide are of definite concentrations. In most cases the precipitate consists of a complex mixture, the exact composition of which depends upon the conditions under which it is prepared. Woringer³ states that commercial iron blue is a complex compound, $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_3[\text{Fe}_3(\text{CN})_6]_3$, which is formed as the result of the mutual oxidation and reduction of the ferric and ferrocyanide ions. Schmidt and Rassow⁴ are of the opinion that Prussian blue is a ferric ferrocyanide in which part of the iron is replaced by potassium and two molecules of water in intermolecular combination. Davidson and Welo⁵ state that the formulas for the "soluble" and "insoluble" blues are $\text{KFe}[\text{Fe}(\text{CN})_6]$ and $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, respectively. Justin-Mueller⁶ suggests the formula, $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}} : (\text{CN})_6 : \text{Fe}^{\text{II}}]_3$

¹Bhattacharya, A., and Dhar, N. R., *Z. für anorg. und allgem. Chem.*, **213**:240-8 (1933).

²Müller, E., *Journ. prakt. Chem.*, **84**:353-69 (1911).

³Woringer, P., *Chem.-Ztg.*, **36**:78 (1912).

⁴Schmidt, P. F., and Rassow, B., *Z. Angew. Chem.*, **37**:333-4 (1924).

⁵Davidson, D., and Welo, L. A., *Journ. Phys. Chem.*, **32**:1285-9 (1931).

⁶Justin-Mueller, E., *Bull. Soc. Chim.*, **49**:1285-9 (1931).

From experiments carried out by Ihne and Kanning⁷ concerning the composition of iron blue, it was concluded that Prussian blue prepared by the oxidation of the so-called "white paste" (primarily ferrous ferrocyanide with adsorbed alkali ferrocyanide) consists of ferric ferrocyanide in combination with the alkali ferrocyanide as an adsorption product. The extent of the adsorption of the soluble ferrocyanide was found to depend upon the relative concentrations and proportions of the ferrous and ferrocyanide ions used in the preparation of the ferrous ferrocyanide.

The experiments reported in this paper are for the purpose of determining quantitatively the adsorptive capacity of Prussian blue for potassium ferrocyanide and ferric chloride in an effort to add to the already existing data concerning the fact that Prussian blue, when prepared, contains contaminating substances as adsorption products. The adsorption experiments were performed on Prussian blue precipitates, prepared and dried in a specific manner. The effect of ageing the prepared precipitate was also studied.

Experimental

Preparation of the Prussian blue precipitates.—The Prussian blue was prepared by adding 2,625 ml. of 2N ferric sulfate solution to 2,500 ml. of 2N potassium ferrocyanide solution. The mixture was stirred thoroughly and divided into two equal parts.

One part of the mixture was filtered with suction, washed free of soluble ions and dried at a temperature of 95°C. for 50 hours. The dried Prussian blue was then pulverized and again dried for 95 hours at 95°C. This product was ground in an agate mortar until it passed a 100 mesh sieve and is designated "fresh" Prussian blue.

The second portion of the precipitated Prussian blue was transferred to a large flask and maintained at a temperature of 98°C. for 240 hours. After this "ageing" process, the precipitate was filtered, washed, dried, and pulverized in the same manner as was the first portion. This particular sample was designated "aged" Prussian blue.

Determination of adsorptive capacities of the Prussian blues.—The capacity of each of the two Prussian blues for adsorbing potassium ferrocyanide and ferric sulfate was determined at varying concentrations of the adsorbate. The procedure employed for the adsorption determinations was the same in each instance.

A sample of the powdered Prussian blue, weighing 10.000 gm. was placed in 100 ml. of the solution of the adsorbate contained in a 125 ml. Erlenmeyer flask which had previously been immersed in a constant temperature bath at 25°C. The flask was then stoppered, shaken vigorously, and replaced in the constant temperature bath for 30 minutes. During this time, the contents of the flask were thoroughly mixed by shaking every five minutes. As is customary, adsorption equilibrium was assumed to be attained after 30 minutes.

When adsorption was complete, the contents of the flask were passed through a parlodion ultrafilter which served to separate well

⁷Ihne, R. E., and Kanning, E. W., *Ind. Eng. Chem.*, 31:88-9 (1939).

the Prussian blue from the solution of the adsorbate. The concentration of the filtrate from the ultrafiltration process was then determined which, when subtracted from the concentration before adsorption, yielded data from which the extent of the adsorption was calculated. Both the ferric and ferrocyanide ions were determined by titration in acid solution with potassium permanganate.

In order to avoid errors due to the dilution of the filtrate by water retained by the ultrafilter in its preparation or to the adsorption of ferric or ferrocyanide ions by the ultrafilter material, blank determinations were carried out. It was found that no change in concentration of the adsorbate solutions occurred when passed through the ultrafilter. It was also found by actual test that no detectable quantity of Prussian blue would pass the ultrafilter.

Data and Results

The results obtained for the adsorption of potassium ferrocyanide by the "fresh" Prussian blue are presented in Table I. The extent of adsorption is represented by the values of X/M and is expressed as milli-equivalents of potassium ferrocyanide adsorbed per gram of Prussian blue. The table also includes the logarithms of the factors, C , and X/M , where C is the final concentration of adsorbate. The data in Table II shows the adsorption of ferric sulfate by the "fresh" Prussian blue. The curves in Fig. 1 are the graphical representations of the adsorption of potassium ferrocyanide (curve I) and ferric sulfate (curve II) by the "fresh" Prussian blue. The curves are obtained by plotting the values of X/M as ordinates and the final adsorbate concentration, C , as abscissae. The logarithm curves, obtained by plotting $\log C$ and $\log X/M$ are presented in Fig. 3, in which curve I represents the adsorption of the ferrocyanide and curve II the adsorption of ferric sulfate.

The results obtained for the adsorption of potassium ferrocyanide and ferric sulfate by the "aged" Prussian blue are presented in Tables III and IV, respectively. The adsorption curves for the "aged" sample

TABLE I.—Adsorption of Potassium Ferrocyanide by "Fresh" Prussian Blue

Initial Conc. of $K_4Fe(CN)_6$ (g.eq./l)	Final Conc. of $K_4Fe(CN)_6$ (g.eq./l) (C)	Log C	X/M	Log X/M
3.020	2.300	0.362	7.20	0.847
1.924	1.302	0.115	6.22	0.793
1.000	0.517	-0.287	4.83	0.684
0.500	0.117	-0.937	3.83	0.583
0.252	0.010	-2.000	2.42	0.384
0.1124	0.0012	-2.921	1.21	0.083
0.0504	0.0016	-2.796	0.488	-0.312

TABLE II.—Adsorption of Ferric Sulfate by “Fresh” Prussian Blue

Initial Conc. of $\text{Fe}_2(\text{SO}_4)_3$ (g.eq./l)	Final Conc. of $\text{Fe}_2(\text{SO}_4)_3$ (g.eq./l) (C)	Log C	X/M	Log X/M
2.76	2.663	0.0425	0.975	-0.011
1.93	1.863	0.270	0.705	-0.152
1.0125	0.969	-0.014	0.435	-0.362
1.011	0.960	-0.018	0.510	-0.292
0.5055	0.485	-0.315	0.210	-0.678
0.249	0.237	-0.625	0.120	-0.921
0.1134	0.1014	-0.994	0.120	-0.921
0.0564	0.0444	-1.353	0.120	-0.921

TABLE III.—Adsorption of Potassium Ferrocyanide by “Aged” Prussian Blue

Initial Conc. of $\text{K}_4\text{Fe}(\text{CN})_6$ (g.eq./l)	Final Conc. of $\text{K}_4\text{Fe}(\text{CN})_6$ (g.eq./l) (C)	Log C	X/M	Log X/M
2.637	1.940	0.288	6.97	0.843
1.918	1.385	0.141	5.33	0.727
1.449	0.959	-0.018	4.90	0.690
0.999	0.639	-0.195	3.60	0.556
0.498	0.259	-0.587	2.39	0.378
0.260	0.1108	-0.955	1.50	0.176
0.0493	0.00012	-3.921	0.49	-0.310

of Prussian blue are shown in Fig. 2; curve III represents the adsorption of potassium ferrocyanide and curve IV the adsorption of ferric sulfate. The log curves for the adsorption experiments with the “aged” Prussian blue are shown in Fig. 3; curve III represents the log C-log X/M relation for potassium ferrocyanide and curve IV the corresponding relation for ferric sulfate.

Discussion of Results

From the data presented, it is apparent that positive adsorption from solution has occurred in all experiments. Both the “fresh” and the “aged” samples of Prussian blue possess a much greater adsorptive capacity for potassium ferrocyanide than for ferric sulfate. In Table I it is seen that, at an initial adsorbate concentration of 3.020 equivalents per liter, 1 gram of the adsorbent adsorbs 7.2 milli-equivalents or

TABLE IV.—Adsorption of Ferric Sulfate by “Aged” Prussian Blue

Initial Conc. of $\text{Fe}_2(\text{SO}_4)_3$ (g.eq./l)	Final Conc. of $\text{Fe}_2(\text{SO}_4)_3$ (g.eq./l) (C)	Log C	X/M	Log X/M
2.910	2.843	0.454	0.67	-0.174
2.433	2.375	0.375	0.60	-0.222
1.922	1.881	0.274	0.41	-0.387
1.415	1.382	0.141	0.33	-0.481
0.963	0.939	-0.027	0.24	-0.720
0.506	0.493	-0.307	0.13	-0.886
0.225	0.212	-0.674	0.13	-0.886

0.66 gm. of potassium ferrocyanide. The adsorption of ferric sulfate by the “fresh” Prussian blue was very slight, the maximum value of X/M being 0.975 milli-equivalents per gram of the adsorbent.

The adsorptive capacity of the “aged” sample of Prussian blue for the two salts studied was in general less at the same concentrations of adsorbate than that for the “fresh” sample. This difference in the adsorptive capacities of the two samples of the adsorbent can be seen by a comparison of curves I and II in Fig. 1 and curves III and IV in Fig. 2. The adsorptive capacity of the two samples of the Prussian blue for ferric sulfate is only slight; however, the adsorption of this salt by the “aged” adsorbent is slightly greater than that by the “fresh” sample. The data for the adsorption of ferric sulfate is considered subject to slight error because of the extremely small differences between the initial and final adsorbate concentrations.

Two explanations might serve to explain the effect of “ageing” the Prussian blue on its adsorptive capacity. The decreased capacity as a result of “ageing” at an elevated temperature could be due to a change in the physical nature of the adsorbent. The “ageing” process no doubt causes a general increased particle size, resulting in a decreased adsorbent surface. The effect of the “ageing” process by the formation, during the digestion period, of an equilibrium mixture of Prussian and Turnbull’s blue has been suggested by experiments conducted by Bhattacharya and Dhar.¹ Turnbull’s blue in general possesses less adsorptive capacity for the ferrocyanides, which would account for the effect of “ageing” of the precipitate studied. It is of interest to note (see curves I and II, Fig. 3) that the adsorptive capacity of the “fresh” Prussian blue exceeds that of the “aged” sample up to a potassium ferrocyanide concentration of about 2.0 N, beyond which the “aged” sample possesses the greater adsorptive capacity for this salt. It is difficult to explain this discrepancy.

The fact that adsorption has actually occurred in these experiments, especially in those involving the adsorption of potassium ferrocyanide, is evidenced by the nature of the curves that are obtained when the

concentration of the adsorbate is plotted against the quantity of adsorbate removed from solution. According to the adsorption equation, a parabolic curve should be obtained which yields a straight line when the logarithms of the coordinate factors are plotted. The curves in Figs. 1, 2, and 3 indicate that a process of adsorption is concerned in the removal of potassium ferrocyanide and ferric sulfate from solution by the two Prussian blues.

Summary

From the experiments performed, data are obtained that indicate a large adsorptive capacity of precipitated Prussian blue for potassium ferrocyanide and a comparatively small adsorptive capacity for ferric sulfate.

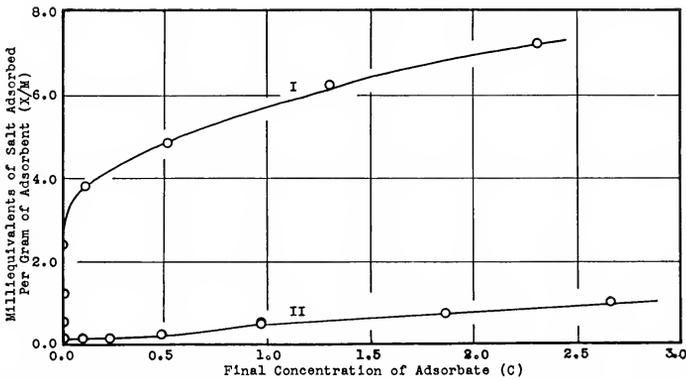


Fig. 1. Adsorption of potassium ferrocyanide and ferric sulfate by "fresh" Prussian blue. Curve I. Adsorption of potassium ferrocyanide. Curve II. Adsorption of ferric sulfate.

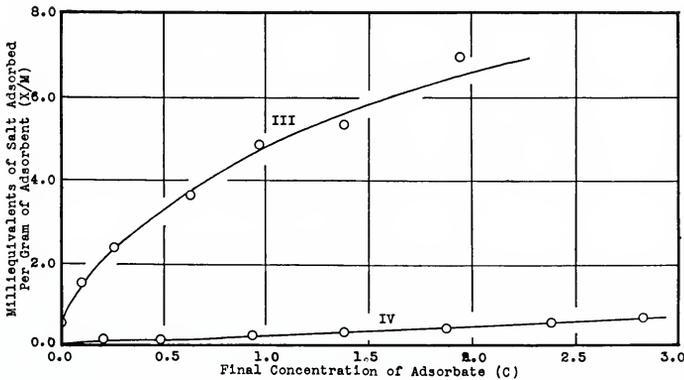


Fig. 2. Adsorption of potassium ferrocyanide and ferric sulfate by "aged" Prussian blue. Curve III. Adsorption of potassium ferrocyanide. Curve IV. Adsorption of ferric sulfate.

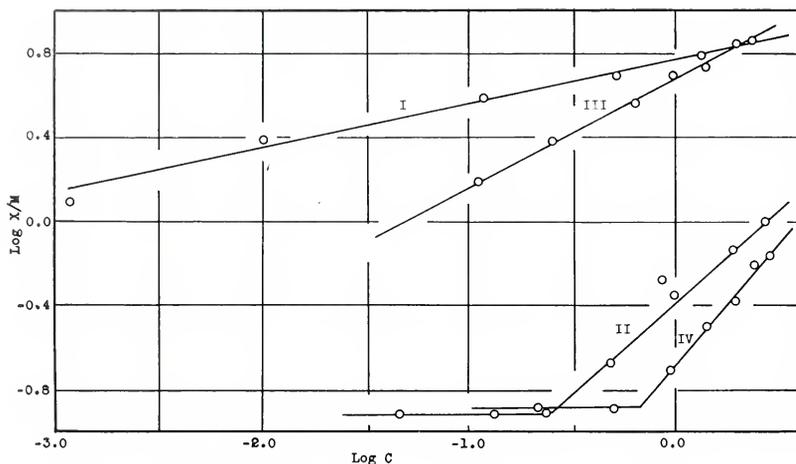


Fig. 3. Log X/M-log C relationship for the adsorption of potassium ferrocyanide and ferric sulfate by Prussian blue. Curves I and II. Adsorption of potassium ferrocyanide and ferric sulfate. Respectively by the "fresh" Prussian blue. Curves III and IV. Adsorption of potassium ferrocyanide and ferric sulfate. Respectively by the "aged" Prussian blue.

"Ageing" the precipitated Prussian blue for 240 hours at 98°C. produced an adsorbent which possessed a lesser adsorptive capacity for both potassium ferrocyanide and ferric sulfate.

The fact that the X/M-C curves follow the general form of the Freundlich adsorption isotherm is evidence that a true process of adsorption occurs in the removal of the two salts (potassium ferrocyanide and ferric sulfate) from solution by contact with dried Prussian blue.

The data presented in this and other papers seem to indicate that the explanation of the composition of precipitated Prussian blue should include the possible existence of the rather large quantities of soluble ferrocyanides and also small quantities of ferric salts adsorbed by the primary precipitate. Although the deviation of the composition of Prussian blue from the basic compound, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, may not be accounted for entirely on the basis of the adsorption of soluble salts by the primary precipitate, the process of adsorption seems to play a very important part in the definition of the composition of the product obtained from the interaction of ferrocyanide and ferric ions.