X.—On Red Prussiate of Potash.

BY WILLIAM WALLACE.

During the present winter I have been engaged with a series of experiments on the yellow and red prussiates of potash. In the present notice I propose to communicate the results obtained on the following points: 1st, the oxydizing power of ferricyanide of potassium in presence of potash; 2nd, the analysis or valuation of commercial red prussiate of potash; and 3rd, the solubility of ferricyanide of potassium in water at different temperatures.

Oxydizing Power.—The oxydizing power of ferricyanide of potassium, especially in presence of an alkali, has been investigated by several chemists, particularly by Schönbein* and by Boudalt.† The results of my experiments confirm in general those described by Schönbein and others, but in a few cases differences were observed. Several reactions of considerable interest have likewise been added. The action in all cases consists in the conversion of ferricyanide of potassium into ferrocyanide by the absorption of one equivalent of potassium.

In the experiments here referred to, a certain amount of free alkali was invariably present, and the mixtures were generally heated, and when necessary, boiled. The ferrocyanide of potassium produced was obtained in crystals by evaporation, or by the addition of alcohol.

Of non-metallic elementary bodies, iodine was converted into iodic acid, sulphur into sulphuric acid, and phosphorus into phosphoric acid, the latter very slowly. Hydrogen gas was not oxydized.

Of the metals, iron, zinc, bismuth, lead, tin, arsenic, and antimony,

* J. pr. Chem. XX, 128.

† Ibid. XXX, 23.

were rapidly oxydized, but copper and mercury were not sensibly affected. In all cases in which the resulting oxides were soluble in potash, the ferricyanide was rapidly and completely converted into ferrocyanide, the liquid becoming nearly colourless.

Of non-metallic compounds, binoxide of nitrogen was converted into nitric acid, sulphurous and hyposulphurous acids into sulphuric acid (the latter with difficulty), and oxalic acid into carbonic acid.

Of metallic oxides, the protoxides of iron, manganese, cobalt, nickel, lead, and tin, were raised to the state of peroxides, the suboxides of copper and mercury to protoxides, sesquioxide of chromium to chromic acid, oxide of antimony to antimonie acid, and arsenious acid to arsenic acid. The protoxides of zinc and bismuth were not altered. The experiments were performed by mixing ferricyanide of potassium with a salt of the oxide, warming the mixture, and then adding potash in excess.

Of other inorganic compounds, sulphide and iodide of potassium gave up their metal to the ferricyanide, with separation of sulphur and iodine, the sulphide and iodide being present in excess. The sulphur and iodine were dissolved by the potash, but were precipitated on neutralizing the liquid with an acid. A similar action occurred with the sulphides of the heavy metals, especially with those which are soluble in potash. Cyanide of potassium was converted into cyanate of potash.

Most organic compounds which are not of a very stable nature are more or less readily oxidized by ferricyanide of potassium in presence of free alkali. A solution of ferricyanide, with potash, boiled with sugar in excess, was rapidly and completely converted into ferrocyanide, the sugar being oxidized to carbonic acid and water. A similar action was observed to occur with gum, starch, dextrin, and paper, but much less readily than with sugar. When alcohol was treated in the same manner, the greater part of the salt was rapidly converted into ferrocyanide; but a portion was decomposed, with probable formation of cyanate of potash, sesquioxide of iron having been precipitated. The alcohol seemed to be converted into carbonic acid and water.

In the arts, ferricyanide of potassium has been employed for discharging or bleaching indigo and the colouring principles of cochineal and lac-dye. It also destroys litmus, turmeric, and many other colours, but does not bleach them completely.

Valuation of Commercial Red Prussiate of Potash.—This salt is met with in commerce in two states, viz., in crystals and in powder. The latter variety is sometimes prepared by grinding the crystals, but more frequently by exposing finely-pulverized ferrocyanide of potassium to the action of chlorine gas. The product is a mixture of ferricyanide and chloride of potassium. In its preparation, a portion at least of the water of crystallization of the ferrocyanide must be retained, for the dry salt is very little affected by dry chlorine gas; consequently the product, unless purposely dried, must always be contaminated with a certain proportion of water. The chloride of potassium and water were found to amount to about 22 per cent of the powder when freshly prepared. Besides these, there may exist accidental impurities, arising from the employment of impure ferrocyanide, a deficiency of chlorine, and other circumstances; and it might also be largely adulterated with common salt, without materially influencing its appearance. A simple and ready method of estimating its value is therefore of some importance.

Mr. Lieshing* has recently published a very elegant process for the estimation of the amount of pure ferricyanide in the commercial product. He converts the salt into ferrocyanide by the action of sulpharseniate of sodium; but as this reagent is difficult to prepare, the application of Mr. Lieshing's method must necessarily be limited.

Many substances capable of being easily oxidized were tried with the same object, but protochloride of tin in presence of hydrochloric acid was found to be most suitable. The process about to be described is confidently recommended as being exceedingly simple, and as yielding very accurate results. It is based upon the well-known reducing power of proto-compounds of tin; and the tendency which ferricyanide of potassium has to combine with an additional equivalent of alkali-metal, or of hydrogen, forming ferrocyanide of potassium and hydroferrocyanic acid. The decomposition may be thus represented:

A large excess of hydrochloric acid is added, in order to prevent the formation of ferrocyanide of tin. The action is immediate, and takes place at ordinary temperatures.

100 grains of the sample of red prussiate under examination are dissolved in an ounce and a half of water, and three quarters of an ounce of strong hydrochloric acid are added. An alkalimeter is filled with a solution of chloride of tin, having a specific gravity of about

* Chem. Soc. Qu. J. April, 1853.

1.046, and containing in 100 measures about 35.7 grains of tin. The tin solution is added to that of the red prussiate, until the latter loses the green colour that it acquires, and becomes of a bright and distinct violet, or blue tint, without the slightest shade of green. The exact point at which this effect occurs is easily ascertained by placing a drop of the liquid on a slab, after each addition of the tin liquor. The blue colour of the solution is owing to a slight decomposition of the hydroferrocyanic acid produced during the action. A similar experiment is performed with 100 grains of pure and dry ferricyanide of potassium, and the amount of pure salt in the sample is then obtained by a simple calculation.

It was found very convenient to employ a standard solution of chloride of tin, of which each division is equal to 1 or 2 grains of pure ferricyanide. This solution may be preserved without material alteration for a considerable period, if kept in a properly closed vessel.

The accuracy of the process depends upon the extensive colouring power of ferricyanide of potassium. Its solution in 7,000 parts of water is distinctly yellow when spotted upon a slab, and communicates a great tint to blues. In the process just described, a distinct green colouration is observed if 0.2 of a grain of the salt remain unchanged in the solution.

Solubility of Ferricyanide of Potassium.—Gmelin states that this salt requires for solution 3.8 parts of cold water, and a smaller proportion of hot water; while Girardin affirms that it is soluble in 2 parts of cold, and in less than 1 part of hot water. Its solubility at various temperatures has been carefully determined. The results obtained are stated in the following table, which likewise exhibits the specific gravity of the solutions at the temperatures mentioned, compared with water at 60° F.

Temperature.	Sp. gr.	Soluble in parts water.	100 parts of water dissolve
40°	1.151	3.03	33.0
50	1.164	2.73	36.6
60	1.178	2.54	40.8
100	1.225	1.70	58.8
212	1.250	1.29	77.5
220	1.265	1.21	82.6

220° is the boiling-point of the saturated solution. The specific gravity of the salt itself is 1.845.