# CLXXXVI.—*The Solubility of Potassium Ferrocyanide in Water at Temperatures up to 25°.*

### By Reece Henry Vallance.

Many investigators have attempted to determine the solubility of potassium ferrocyanide in water at various temperatures, but the results obtained, especially at lower temperatures, do not harmonise (see Vallance, *Chem. News*, 1922, **125**, 7). In the earlier investigations this may have been due in part to a variation in the purity or hydration of the ferrocyanide employed, or to inaccuracy in manipulation; but in recent work it appears more probable that the fault lies in the methods of estimating the amount of salt in the solution. It was deemed necessary at the outset to check the accuracy of the methods in general use, which are : (*a*) titration with potassium permanganate, (*b*) titration with a standard solution of a metallic salt, *e.g.*, of zinc or copper, and (*c*) decomposition of the ferrocyanide into hydrogen cyanide, absorption of the latter by potash, and titration with standard silver nitrate solution.

The first method has been most generally used in solubility determinations, although its accuracy has long been questioned. It does not give good results, since the colour due to a slight excess of the oxidising agent is not easily perceived, and none of the many modifications hitherto proposed was found to be entirely satisfactory.

The second method was not considered suitable for the work in view, since all estimations must be made under exactly similar conditions, and this would be difficult with a series of solutions of different concentrations, of which only limited quantities were available.

The method by which the ferrocyanide is decomposed with evolution of hydrogen cyanide has been used with fairly satisfactory results (Feld, *Chem. Zentr.*, 1903, ii, 1398; Colman, *Analyst*, 1908,

**33**, 261; 1910, **35**, 295), although it is found difficult to avoid loss of the acid (Skirrow, *J. Soc. Chem. Ind.*, 1910, **29**, 319; Williams, *ibid.*, 1912, **31**, 468). Williams showed that solutions of potassium ferrocyanide are catalytically decomposed when boiled with cuprous chloride in the presence of hydrochloric acid. By collecting the evolved acid in alkali, and afterwards titrating with standard silver nitrate, the ferrocyanide originally present may be estimated. This method appeared suitable for the work in view, and was therefore investigated. (The salt used throughout this research was the A.R. trihydrated potassium ferrocyanide, supplied by the British Drug Houses, Ltd.) Great care was taken to avoid loss of hydrogen cyanide, but a series of estimations gave results which were discordant to the extent of 7%, mostly low. In spite of the addition of potassium iodide, the end-point was determined only with difficulty, possibly because of the strong alkali present. Moreover, the method was inconvenient.

Attention was next directed to the method based on the decomposition of complex cyanides by persulphates in presence of mineral acids (Dittrich and Hassel, *Ber.*, 1903, **36**, 1929), 50% of the hydrogen cyanide being evolved and ammonium salts formed. The iron can then be precipitated by ammonia and estimated in the usual way. This method at first appeared satisfactory, but when it was applied to larger quantities (1—4 g.) of the ferrocyanide, the blue precipitate which formed when the acidified mixture of ferrocyanide and ammonium persulphate was heated could not be redissolved, even by the addition of hydrochloric acid and prolonged heating with excess of the persulphate. This method was used for solubility determinations by Harkins and Pearce (*J. Amer. Chem. Soc.*, 1916, **38**, 2714), who admitted that, in spite of the fact that pure hydrogen was passed through the solutions to prevent oxidation, the formation of the blue precipitate sometimes either prevented or vitiated the analyses.

It was found to be impracticable to dry and weigh the ferrocyanide in the anhydrous condition: the loss of water, after heating for definite periods at 105—110°, was always lower than that required by the trihydrate formula, unless the partial decomposition, which was nearly always apparent, became very marked. It is probable, therefore, that the true loss of water would be still lower.

It was thought that it would be more satisfactory if the iron could be converted into the ferric condition, as was attempted in the persulphate method, and many experiments were made in which the salt was heated alternately with concentrated sulphuric acid and concentrated nitric acid. After such treatment, the residue on ignition did not yield a product of constant composition (*e.g.*,

$4K_2SO_4,Fe_2O_3$) and the silica crucibles used were badly attacked. The following method, however, gave excellent results and was used throughout for the solubility determinations.

### *The Estimation of Iron in Potassium Ferrocyanide.*

A weighed quantity of potassium ferrocyanide in a platinum dish was just covered with concentrated sulphuric acid and heated (in a fume-chamber) very gently on a sand-bath until all action had ceased, and then strongly for about ½ hour. After cooling, a little more concentrated sulphuric acid and a few drops of concentrated nitric acid were added, and the heating was repeated, at first gently and then strongly until the residue was dry; this was then cooled, gently warmed with concentrated hydrochloric acid, transferred to a 500 c.c. beaker containing a little hot water, and diluted to about 300 c.c. with water; a few drops of concentrated nitric acid were added, and the mixture was gently boiled until a clear solution was obtained; this was allowed to cool, and made up to 500 c.c. in a flask which had been graduated against a 100 c.c. pipette.

For each estimation, 100 c.c. of the solution were withdrawn by means of this pipette, and the ferric hydroxide was precipitated from the hot solution by addition of ammonium hydroxide. The precipitate was washed several times by decantation, transferred to two filters (in order to facilitate washing), thoroughly washed with hot water until the filtrate was quite free from sulphate and chloride, dried at 110°, ignited, and weighed [Found, for different specimens: Fe, (i) 13·416, (ii) 13·397, (iii) 13·403. Calc. for $K_4Fe(CN)_6,3H_2O$ : Fe, 13·22%].

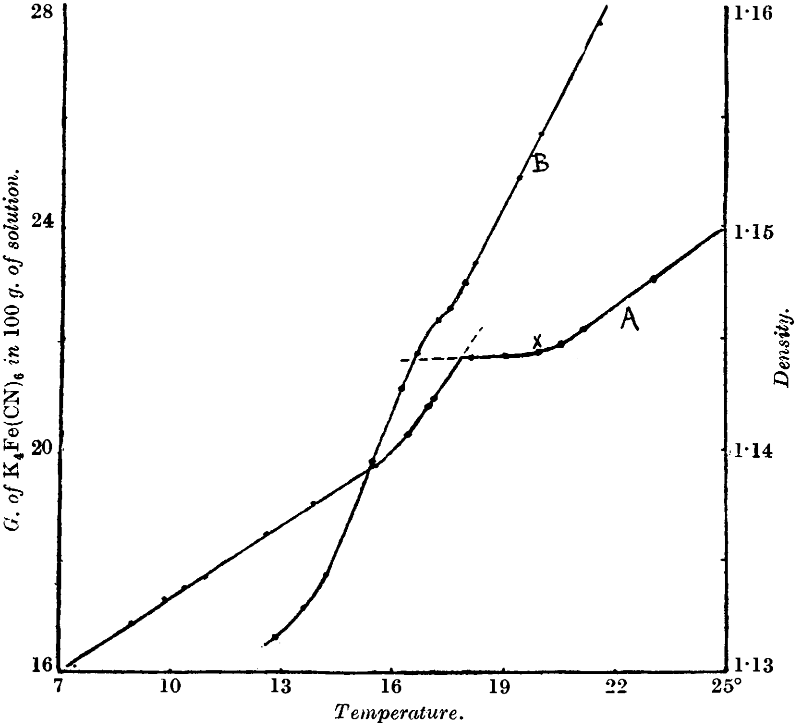
The results, although concordant, were higher than the value required by theory, and to a greater extent than can be accounted for by the low results obtained (p. 1329) for the loss of water on heating.

The method outlined above has also been employed by Friend and Merriman in this laboratory for the estimation of alkali ferricyanides, accurate results being obtained.

### *Determination of the Solubility of Potassium Ferrocyanide at Temperatures up to 25°.*

The method employed was similar to that described by Lumsden (J., 1902, **81**, 350). The solution to be tested was constantly stirred in contact with the salt for about 7 hours, a portion then being drawn by suction from the saturation vessel, through a Gooch filter containing glass wool (previously washed and dried), into a receiving flask. The whole apparatus was sufficiently immersed in a thermostat for the solution to remain under water during the transference, a constant temperature being carefully maintained. A suitable quantity of the filtered solution was immediately weighed into a platinum dish, evaporated to dryness, and the residue decomposed by means of sulphuric acid and estimated by the method already described. The results are in Table I, where *s* represents g. of anhydrous salt in 100 g. of saturated solution. When these results are plotted as in Fig. 1, it is seen that the solubility curve is not continuous, but that a break occurs between 17° and 18°.

Fig. 1.



A. *Solubility curve.* B. *Density curve.*

[x *Value obtained by Briggs* (loc. cit.) *for* " *a* " *salt.*]

TABLE I.

| Temp. | *s*. | Temp. | *s*. | Temp. | *s*. | Temp. | *s*. |
|---|---|---|---|---|---|---|---|
| 7·4° | 16·043 | 12·6° | 18·514 | 17·0° | 20·922 | * 23·1° | 23·074 |
| 8·9 | 16·844 | * 13·8 | 19·067 | 17·9 | 21·687 | * 25·0 | 23·971 |
| 9·8 | 17·309 | 15·5 | 19·715 | 19·0 | 21·725 | | |
| * 10·4 | 17·541 | 16·3 | 20·240 | * 20·4 | 21·953 | | |
| 11·1 | 17·784 | * 16·9 | 20·862 | 21·1 | 22·244 | | |

* Vallance, *loc. cit.*

This points to a change in the solid phase, possibly due to a change in the degree of hydration, but it is of particular interest in view of the long-admitted possibility of the existence of two stereoisomeric forms of potassium ferrocyanide (Briggs, J., 1911, **99**, 1019; 1920, **117**, 1026; Bennett, J., 1917, **111**, 490).

The density of the saturated solution at different temperatures was next examined. A silica pyknometer of about 20 c.c. capacity was employed, and the slight change in capacity with rise in temperature was determined by weighing it full of mercury at two different temperatures. In order to fill the pyknometer with the saturated solution, it was attached to the receiving flask of the solubility apparatus whilst immersed in the thermostat, and the solution was drawn over by suction. The density was calculated from the formula

$$D_{4^\circ}^{t^\circ} = W(1-0\cdot0012/d)/C + 0\cdot0012,$$

where $W$ = apparent weight of solution in air at $t^\circ$, $C$ = capacity of pyknometer at $t^\circ$, $d$ = density of water at $t^\circ$, and 0·0012 = mean density of air.

The results are in Table II.

TABLE II.

| Temp. | $D_{4^\circ}^{t^\circ}$. | Temp. | $D_{4^\circ}^{t^\circ}$. | Temp. | $D_{4^\circ}^{t^\circ}$. | Temp. | $D_{4^\circ}^{t^\circ}$. |
|---|---|---|---|---|---|---|---|
| 12·8° | 1·13153 | 16·2° | 1·14295 | 17·9° | 1·14789 | 21·5° | 1·15811 |
| 13·7 | 1·13307 | 16·6 | 1·14441 | 18·2 | 1·14861 | 25·1 | 1·17041 |
| 14·2 | 1·13430 | 17·2 | 1·14596 | 19·5 | 1·15279 | | |
| 15·4 | 1·13953 | 17·5 | 1·14641 | 20·0 | 1·15435 | | |

Very few determinations have been made by previous workers, but those of Michel and Krafft (*Ann. Chim. Phys.*, 1854, **41**, 478), who give $D^{15^\circ}$ = 1·1441, of Sonstadt (J., 1906, **89**, 343), $D^{8\cdot9^\circ}$ = 1·1191, and of Farrow (J., 1926, 49), $D^{24\cdot9^\circ}$ = 1·1731, are in general agreement with the above figures. The value obtained by Harkins and Pearce (*J. Amer. Chem. Soc.*, 1916, **38**, 2714), $D^{25^\circ}$ = 1·09081, is obviously incorrect. When the results are plotted as in Fig. 1, a slight change in the direction of the curve is observable above 17°.

In order, if possible, to detect an actual transition point, the dilatometric method was employed. The dilatometer contained *m*-xylene as the indifferent fluid, and the long stem was surrounded by the graduated tube of a burette which served as a scale and also protected the capillary from fluctuations of temperature. The instrument was immersed in a thermostat at a definite temperature, and after allowing 15 minutes for the apparatus to assume this temperature, the movement of the meniscus was observed.

For short periods of time there was no appreciable movement at any given temperature, but with longer periods the following results were obtained :

| Temp. | Time (hrs.). | Variation in level of fluid. | Variation per hour. |
|---|---|---|---|
| 29·3° | 24 | −0·60 | −0·025 |
| 21·6 | 26·5 | −0·55 | −0·020 |
| 19·0 | 24 | −0·35 | −0·014 |
| 17·0 | 24 | +0·20 | +0·008 |
| 13·5 | 21 | +0·50 | +0·024 |

It will thus be seen that a simple interpolation gives the equilibrium temperature as 17·7°, which agrees with the transition point indicated by the break in the solubility curve.

The cooling curves of solutions of potassium ferrocyanide of various concentrations over the range 24—13° were found to be quite smooth.

The iron content of a number of samples of crystals, grown at 0° and at temperatures somewhat above 30°, has been determined. The crystals were dried for varying periods between absorbent material under a uniform pressure of 4 lb.; it was found that the composition remained constant after 24 hours. In all cases the results were the same, the iron content approximating to that required by the trihydrate. Further, no differences could be detected in the crystalline form of crystals grown at temperatures above and below the transition point; no crystallographic measurements have been made, however.

Table III shows the densities of the saturated solutions and the solubilities as interpolated at even temperatures.

TABLE III.

| | | G. of $K_4Fe(CN)_6$ | | | | G. of $K_4Fe(CN)_6$ | |
|---|---|---|---|---|---|---|---|
| Temp. | $D^{t^\circ}_{4^\circ}$. | in 100 g. $H_2O$. | in 100 g. sol. | Temp. | $D^{t^\circ}_{4^\circ}$. | in 100 g. $H_2O$. | in 100 g. sol. |
| 7·5° | — | 19·19 | 16·10 | *17·7°* | *1·1471* | *27·62* | *21·64* |
| 10·0 | — | 21·00 | 17·36 | 20·0 | 1·1543 | 28·02 | 21·89 |
| 15·0 | 1·1378 | 24·25 | 19·52 | 25·0 | 1·1701 | 31·53 | 23·97 |

## *Summary.*

1. Various methods of estimating alkali ferrocyanides have been critically examined, and a new process, involving the conversion of the ferrocyanide to the ferric condition by means of concentrated sulphuric and nitric acids, is described. This method is shown to be accurate and suitable for use in solubility determinations. It may also be used for the estimation of ferricyanides.

2. The solubilities of potassium ferrocyanide in water at temperatures up to 25° have been determined and represented by a curve.

A break in the latter indicates a change in the solid phase, the transition point being about 18°.

3. The densities of saturated solutions of the salt have been determined, and the density curve shows a slight change in direction above 17°.

4. By the dilatometric method, the transition point between the two phases is established at 17·7°.

5. Crystals of the salt grown above and below the transition point did not exhibit any apparent difference in crystalline form or in the degree of hydration.

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