

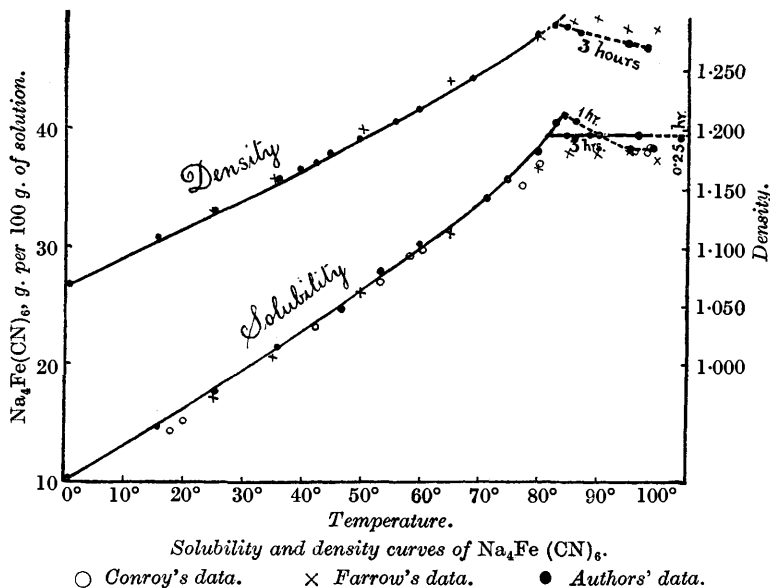
CCCIII.—*The Solubility of Sodium Ferrocyanide in Water between 0° and 104°.*

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THE first systematic investigation of the solubility of sodium ferrocyanide in water was carried out by Conroy (*J. Soc. Chem. Ind.*, 1898, **17**, 103), who evaporated his solutions to dryness and kept the residues at 110° until they attained constant weight. In some cases the results were checked volumetrically. But desiccation

methods with complex cyanides are frequently inaccurate in consequence either of incomplete expulsion of water (analysis A, p. 2328) or of decomposition (analysis B), although it may happen by chance that numerically correct results are obtained when imperfect dehydration is counterbalanced by loss through decomposition. Conroy's results above 90° were somewhat irregular, probably for the above reason, and when plotted they show a break near 80°, to which, however, he made no reference.

FIG. 1.



Miss Farrow (J., 1926, 49) redetermined the solubility of the salt between 24.9° and 99.7°, using de Haën's permanganate volumetric method, and fixed the transition point by dilatometric and cooling-curve measurements at a mean value of 81.5°.

The accuracy of volumetric methods has long been questioned, and it seemed desirable that these data should be checked and extended to 0° by a series of gravimetric determinations of the iron present in solution. The method employed was a modification of that first used by Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413; Vallance, J., 1927, 1328), and has been successfully applied to potassium ferricyanide by Friend and Smirles (J., 1928, 2242). The densities of the solutions were determined with the apparatus described by the latter authors.

The results are expressed in the table as g. of anhydrous salt per 100 g. of solution. The solution was stirred in contact with excess of crystals for $2\frac{1}{2}$ —3 hours at temperatures below the transition point, but for various periods above 80° .

The densities and solubility data are shown in Fig. 1, together with those of Farrow and of Conroy, the latter of whose data, expressed as g. per 100 g. of water in the original memoir, have been recalculated for the purpose of comparison. The saturated solution in contact with crystals of the salt boiled at $104.2^\circ/751$ mm.

The following results show the uncertainty of data obtained by desiccation methods, as employed by Conroy, the result being sometimes too high and sometimes too low, probably for the reason already given. Two solutions of sodium ferrocyanide were prepared and treated as follows :

| | Result calculated as g. of $\text{Na}_4\text{Fe}(\text{CN})_6$, | |
|--|---|--------|
| | A. | B. |
| (i) Taken to dryness on water-bath and weighed as anhydrous salt | 1.0460 | 0.5032 |
| (ii) Heated in electric oven at 110 — 120° and weighed as anhydrous salt | 1.0455 | 0.5010 |
| (iii) Decomposed with sulphuric acid and weighed as Fe_2O_3 | 1.0292 | 0.5108 |

The solubility and density increase steadily with the temperature from 0° to about 80° . Between 25° and 65° the results agree well with those of Conroy and Farrow, but above 65° they are somewhat higher, although the solubility shows remarkable constancy between 84.2° and 96.6° for the 3-hour periods. As rise of temperature tends to increase the rate of decomposition of ferrocyanide solutions, it appeared possible that the difference between our results and those of Conroy and Farrow might be due, in part at least, to a variation in the period of stirring in contact with the crystals of the salt. Experiments were therefore carried out to determine the effect of varying this period. In Series II, portions of the solution were removed after 1, 2, 3, and 4 hours, respectively, and their ferrocyanide contents were determined, not only gravimetrically, but also volumetrically by the permanganate method as used by Farrow. The permanganate, however, was standardised by titration with sodium ferrocyanide solution, the concentration of which was checked gravimetrically; our experience shows that standardisation of permanganate by direct titration with a given weight of alkali ferrocyanide crystals is less accurate than the gravimetric method in consequence, presumably, of variation in the water content of the crystals.

| Temp. | Na ₄ Fe(CN) ₆ , g. per 100 g. soln. | | L ₄ ^s (in air). | Temp. | Na ₄ Fe(CN) ₆ , g. per 100 g. soln. | | L ₄ ^s (in air). |
|--|--|-------|--|----------------------------------|--|------|--|
| | Grav. | Vol. | | | Grav. | Vol. | |
| Series I; 3 hours' stirring. | | | | | | | |
| 0·65° | 10·23 | — | 1·0680 | 71·0° | 34·34 | — | — |
| 16·7 | 14·69 | — | 1·1079 | 74·25 | 35·82 | — | — |
| 25·35 | 17·63 | — | 1·1303 | 79·5 | 38·26 | — | 1·2809 |
| 35·75 | 21·54 | — | 1·1572 | 82·35 | — | — | 1·2892 |
| 39·4 | — | — | 1·1665 | 82·4 | 40·69 | — | — |
| 42·0 | — | — | 1·1728 | 84·0 | 41·28 | — | — |
| 44·3 | — | — | 1·1794 | 84·2 | 39·57 | — | 1·2875 |
| 46·6 | 24·80 | — | — | 85·0 | 39·30 | — | — |
| 49·55 | — | — | 1·1921 | 86·7 | — | — | 1·2824 |
| 53·0 | 28·11 | — | — | 88·4 | 39·57 | — | — |
| 55·4 | — | — | 1·2078 | 94·3 | — | — | 1·2738 |
| 59·6 | — | — | 1·2180 | 96·6 | 39·69 | — | — |
| 59·75 | 30·35 | — | — | 97·8 | — | — | 1·2688 |
| 68·7 | — | — | 1·2446 | | | | |
| Series II; 1, 2, 3, 4, and 4 hours' stirring, respectively. | | | | Series III; 1 hour's stirring. | | | |
| 85·0 | 40·84 | 40·84 | — | 85·0 | 40·84 | — | — |
| „ | 40·37 | 40·57 | — | 90·0 | 39·51 | — | — |
| „ | 39·30 | 39·19 | — | 95·3 | 38·61 | — | — |
| „ | 38·78 | 39·49 | — | 99·1 | 38·67 | — | — |
| „ | — | 38·47 | — | Series IV; 0·25 hour's stirring. | | | |
| | | | | 104·2 | 39·27 | — | — |

The "apparent" solubility is seen to fall as the period of stirring is increased, approaching asymptotically a minimum value. The "true" solubility is thus difficult to ascertain, as a certain period of stirring is essential to ensure saturation. A third series of experiments was therefore carried out between 85° and 100° in which the period of stirring was 1 hour. The solubilities fell with rise of temperature to a constant value at 95° (see Fig. 1, broken line), which, however, was slightly lower than the constant value in the 3-hour tests, but was practically identical with that of Conroy and Farrow. It would thus appear that if sufficient time is allowed (which time diminishes with rise of temperature), a condition of more or less partial equilibrium is reached, the exact value of which depends upon local conditions, being possibly dependent upon a series of factors, such as the rate of access of oxygen, the ease of escape of hydrogen cyanide, etc. (compare Tananaeff, *Z. anorg. Chem.*, 1928, **172**, 403). One hour would thus appear to be sufficient at 95°, and the lower value obtained in the 1-hour tests is probably connected with the fact that a different apparatus was used from that in the 3-hour tests. For practical purposes, therefore, it may be accepted that the apparent solubility of the salt between 85° and 104° is approximately constant at about 38·5—39·5 g. of anhydrous salt per 100 g. of solution, the value depending

upon local conditions at the time. The "true" solubility of the pure salt in contact with its pure solution will be somewhat higher than this. By extrapolation from Series II the true solubility at 85° is estimated at 41.5 g.

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