CCXCI.—*The Solubility of Potassium Ferricyanide in Water between 0° and 100°.*

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Vallance (J., 1927, 1328) found a break in the solubility curve of potassium ferrocyanide in water at approximately 18°. This did not appear to be connected with any change in hydration of the solid phase, and is of particular interest in view of the long-admitted possibility of the existence of two stereoisomeric forms of the salt (Briggs, J., 1911, **99**, 1019; 1920, **117**, 1026; Bennett, 1917, **111**, 490).

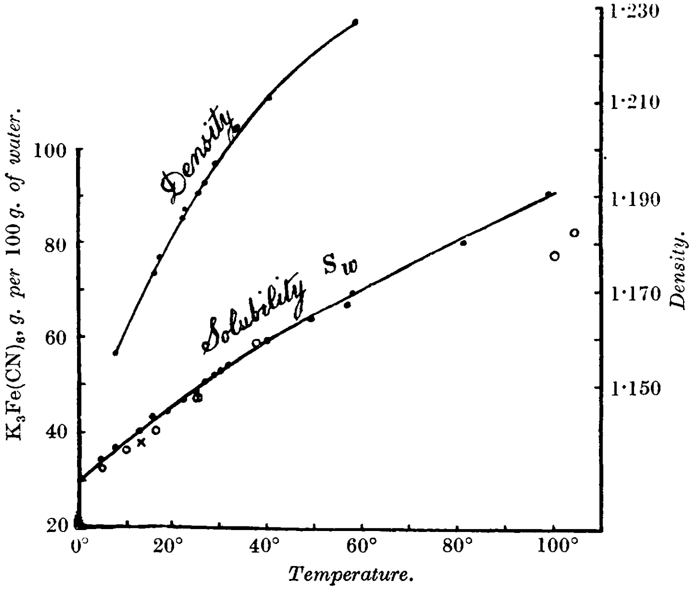
When the solubility curve of potassium ferricyanide is drawn from the six results of Wallace (J., 1855, **7**, 80) and the one datum of Schiff (*Annalen*, 1860, **113**, 150) for 13°, a break would appear to occur between 20° and 40°. The solution-density curve likewise suggests a break. In view of the alleged isomerism of the salt (Locke and Edwards, *Amer. Chem.* J., 1899, **21**, 193, 413; but see Bellucci and Sabatini, *Atti R. Accad. Lincei*, 1911, **20**, 1; Piutti, *Ber.*, 1912, **45**, 1830; Hauser and Biesalski, *Ber.*, 1912, **45**, 2516; Wells, *Amer. Chem. J.*, 1913, **49**, 205; Briggs, J., 1920, **117**, 1026), a further investigation of this point appeared to be desirable.

EXPERIMENTAL.

Pure potassium ferricyanide was recrystallised, and its iron content was estimated by decomposing about 0·5 g. with concentrated sulphuric acid in a platinum dish, heating until the colour that developed had disappeared, adding a small quantity of concentrated nitric acid, and again heating until sulphuric acid fumes were freely evolved. After cooling, the residue was dissolved in dilute hydrochloric acid, diluted to approximately 400 c.c., and the ferric hydroxide precipitated with ammonia, filtered, re-dissolved, reprecipitated, ignited, and weighed [Found: Fe, (i) 17·08, (ii) 17·01. Calc.: Fe, 16·96%].

Determination of Solubility.—The method employed in preparing a saturated solution was similar to that described by Lumsden (J., 1902, **81**, 350). The solution was stirred continuously in contact with the finely crushed salt for about 6 hours, a portion being withdrawn by suction from the saturation bottle through glass wool into a receiving flask, the usual precautions for submersion in the thermostat being observed to ensure complete uniformity of temperature. A measured volume of the filtered solution was diluted to 250 c.c., and 25 c.c. were evaporated to dryness; from the iron content, determined as indicated above, the amount of ferricyanide was calculated.

FIG. 1.



Solubility and density curves of K$_3$Fe(CN)$_6$.

○ Wallace's data.

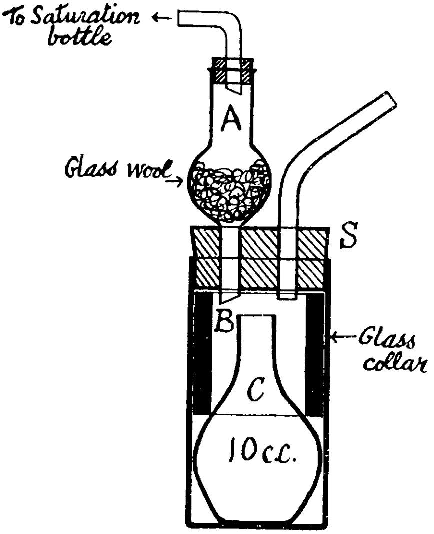
× Schiff's datum [38 g. K$_3$Fe(CN)$_6$ per 100 g. H$_2$O].

⌽ Grube's result (*Z. Elektrochem.*, 1914, **20**, 342).

The results are given in Fig. 1 and Table I, where S_w and S_s represent g. of anhydrous salt per 100 g. of water and of solution respectively.

Determination of Density.—For the determination of the density of the saturated solution, the apparatus shown in Fig. 2 was attached to the saturation bottle, and the liquid sucked over. The apparatus consisted of a 10 c.c. glass density bottle, *C*, standing inside a closely fitting cylindrical bottle, and kept in position either with a glass rod through the rubber stopper *S*, or by a loose glass collar as shown in the figure. The volume of *C* and its variation with temperature had previously been ascertained. The end *B* of the filter tube *A* was adjusted not to pour direct into *C* but outside it, and then to flow into it as the containing bottle filled up. The rubber stopper was now removed, and the glass stopper inserted in the density bottle, which was then washed and set aside to cool, being covered with a small tube to prevent evaporation through the capillary.

FIG. 2.



After a density determination the solution was frequently used for a solubility determination so that both data were obtained from the one sample. The results (in air) are given in Table I.

TABLE I.

Temp.	S_w.	S_s.	$D_{4^\circ}^{t^\circ}$ (in air).	Temp.	S_w.	S_s.	$D_{4^\circ}^{t^\circ}$ (in air).
0·1°	30·24	23·22	—	28·3°	52·14	34·27	—
4·7	34·21	25·49	—	28·9	—	—	1·1971
7·8	36·95	26·96	1·1567	29·8	53·02	36·65	—
12·8	40·22	28·68	—	31·5	54·21	35·15	—
15·7	43·58	30·35	1·1738	33·1	—	—	1·2045
16·75	—	—	1·1766	39·9	59·27	37·22	1·2115
18·7	44·85	30·96	—	49·0	64·25	39·12	—
21·8	—	—	1·1855	56·25	67·80	40·41	—
22·1	47·22	32·08	1·1872	58·0	69·78	41·10	1·2269
25·0	48·80	32·80	—	81·0	80·82	44·70	—
25·3	—	—	1·1905	99·0	90·83	47·60	—
26·3	50·74	33·66	1·1928				

Discussion.—The density and solubility data (S_w) are shown in Fig. 1. The curves are regular, giving no indication of a break. The solubility curve conforms to the equation

$$S_w = 30{\cdot}4 + 0{\cdot}80t - 0{\cdot}0020t^2.$$

With the exception of the value at 37·8°, Wallace's figures are lower than ours, particularly that at 100°, probably owing to the fact that he estimated his ferricyanide volumetrically by reduction with stannous chloride, a method that is less accurate than the gravimetric. The very low results at 100° and above may possibly be in part due to hydrolysis. Even warm solutions smell of hydrocyanic acid, and at 100° the odour is very marked. Hydrolysis would be likely to affect the volumetric method more seriously than the gravimetric. In order to reduce the disturbing effect of any such change we were careful to use fresh solutions for each of our determinations. Schiff's result is a little low. Grube states that one litre saturated at 25° contains 385·5 g. of salt, and if our mean value (1·1905) be adopted for the density at this temperature, S_w is 47·89, a value slightly lower than ours, *viz.*, 48·80.

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