XI.—*The Solubilities of Sodium, Potassium, and Calcium Ferrocyanides. Part I.*

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THIS investigation was undertaken on account of the uncertainty of the solubility data for the ferrocyanides of sodium and potassium, and the lack of data for the calcium salt. Early workers, *e.g.*, Michel and Kraft (*Ann. Chim. Phys.*, 1854, **41**, 482), Étard (*ibid.*, 1894, **2**, 546), and Schiff (*Annalen*, 1860, **113**, 350), obtained values varying from 25 to 40 g. of potassium ferrocyanide in 100 g. of water at 20°. Determinations for the potassium and sodium salts were made at a few temperatures by Conroy (*J. Soc. Chem. Ind.*, 1898, **17**, 104), by Harkins and Pearce (*J. Amer. Chem. Soc.*, 1916, **38**, 2716) at 25° only, by Fabria (*Gazzetta*, 1921, **51**, ii, 374) over the whole range from the cryohydric point to 100°, and by Vallance (*Chem. News*, 1922, **125**, 7) for the potassium salt only, at low temperatures.

Purification of the Salts.—The purest sodium and potassium ferrocyanides obtainable were further purified by rapid crystallisation from hot water. By simple qualitative tests the absence of the most likely impurities, calcium and ammonium, was proved.

The purest calcium salt obtainable, for which we are indebted to Mr. W. G. Adam of the Gas Light & Coke Co., was slightly tinged with blue. It was purified by precipitation with absolute alcohol in the cold (to avoid oxidation) from an air-free saturated solution. The pure lemon-yellow, finely crystalline product was centrifuged, dried in vacuum desiccators, first over charcoal for 24 hours, then over the partly dehydrated salt, and stored in the dark in dark glass-stoppered bottles. No discoloration appeared after 18 months. No trace of sodium, potassium, or ammonium could be detected in the residue left after decomposition of the salt with concentrated sulphuric acid. Determinations of calcium as oxalate in the original and the purified salt proved that no measurable change of composition had resulted from the purification process:

Orig. salt: 16·2, 16·2, 16·2, 16·3, 16·25, 16·1, 16·2, 16·2. Mean, 16·2% Ca.

Recryst. salt: 16·2, 16·25, 16·2, 16·2, 16·2, 16·2, 16·2, 16·3. Mean, 16·2% Ca.

There has been some doubt about the precise number of molecules of water in the calcium salt. The above determinations, which lie much nearer to the theoretical value for a hydration of $11H_2O$ (16·3% Ca) than to that for $12H_2O$ (15·8% Ca), support the conclusion of Berkeley, Hartley, and Burton (*Phil. Trans.*, 1908, **209***A*, 177) that the lower figure is correct. The lower figure is also in accordance with the recent careful determinations of Cumming (J., 1924, **125**, 240).

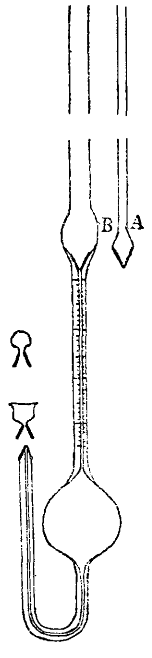
Method of Determining Solubility.—A solution was heated in contact with excess of the solute to the required temperature and after the attainment of equilibrium a definite volume was withdrawn in a weight pipette to be weighed and analysed, and the density calculated.

The ferrocyanide in all three salts was estimated volumetrically with permanganate by the simple method of de Haen (Treadwell, "Quantitative Analysis," p. 632). This method after practice gave concordant results; it is essential to standardise the solution used against standard potassium ferrocyanide and not against the customary oxalic acid. The calcium ferrocyanide was also determined independently as oxalate.

Cumming's method of estimating ferrocyanides with benzidine hydrochloride (J., 1924, **125**, 240) was tried, but it did not appear so suitable for these metallic ferrocyanides as the simple permanganate method and was therefore not employed.

Pure dilute boiling sodium oxalate solution was used in the determination of the calcium salt as oxalate, because ammonium oxalate and oxalic acid as precipitants produced insoluble double calcium ammonium ferrocyanide and insoluble hydroferrocyanic acid, respectively. In the first experiments, in which an alundum cone was used as a filter, no sharp end-point could be obtained on the addition of permanganate, owing to slow diffusion of oxalate from the inner pores of the cone. Gooch crucibles were substituted for the cones, but even then the permanganate readings were not concordant. The asbestos used had no reducing action on permanganate, and experiment also showed that no measurable occlusion occurred at the dilutions used. The cause of the error was traced to the appreciable solubility of calcium oxalate in water. The washing was therefore limited to three fillings of the Gooch, and this procedure was kept constant throughout the experiments.

FIG. 1.



Apparatus.—The solubility vessel consisted of a wide tube of about 200 c.c. capacity, fitted with a rubber bung and stirrer. In order to hold the pipette in place in the solubility vessel the bung carried a short glass tube which was closed when not in use. The temperature of the thermostat was constant to within 0·2°.

The weight pipette, which had a volume of about 4·5 c.c. (Fig. 1), was of a design which has been used for several investigations in this laboratory, but has not previously been described. It is warmed to the temperature of experiment and introduced into the solution with its shorter arm fitted with a glass-wool filter adapted to the ground end. The solution can then be admitted by opening the ground-in plug, A; when it has reached the required level, which can be accurately read by means of the graduations, the plug is replaced. The pipette is then removed, the filter immediately replaced by a ground-on cap, and the whole cleaned and weighed after attaining room temperature. The pipette was repeatedly calibrated with pure mercury to give accurate volume readings for the density determinations.

Owing to the high solubilities of the calcium salt, these solutions were very viscous and consequently difficult to introduce into the pipette. To hasten the filling, slight pressure was applied to the solution in the solubility vessel. The determinations of solubility and density were in almost every case repeated at least once, and, as the data of the table show, the individual solubility experiments very seldom differed from the mean by more than 0·1 unit, or the densities by more than 0·002, except at the highest temperatures, when the experimental difficulties already mentioned make the determinations somewhat less concordant.

Solubilities and Densities.

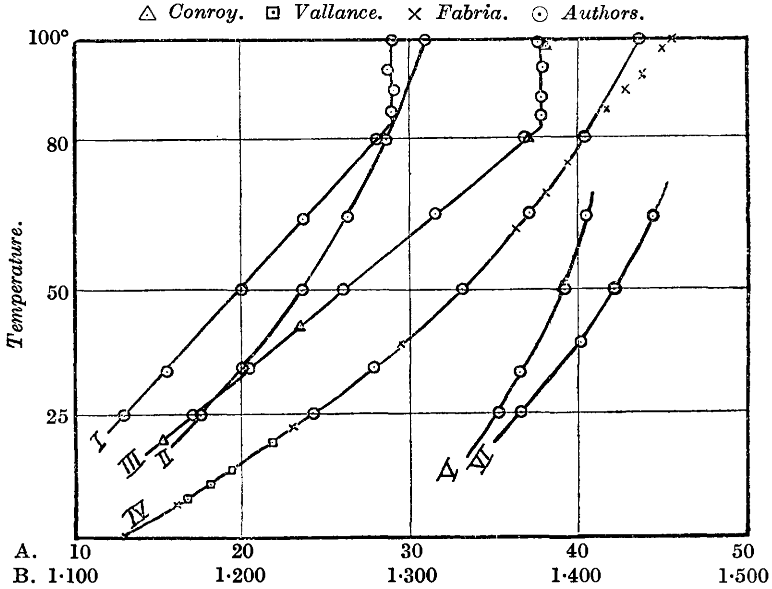
g = grams of anhydrous salt in 100 grams of solution. *d* = density of saturated solutions. The mean values are printed in italics.

	$K_4Fe(CN)_6$.		$Na_4Fe(CN)_6$.		$Ca_2Fe(CN)_6$.	
Temp.	*g.*	*d.*	*g.*	*d.*	*g.*	*d.*
24·9°	23·96	1·1731	17·10	1·1330	36·52	1·3574
	23·83	1·1731	17·15	1·1295	36·42	1·3552
	24·00	1·1734	17·08	1·1312	36·45*	*1·3563*
	24·01	1·1729	*17·11*	*1·1312*	36·36*	
	23·95	*1·1731*			*36·44*	
34·9	28·00	1·2026	20·58	1·1576	39·11	1·3633
	28·08	1·2014	20·58	1·1591	39·30	1·3690
	27·95	1·2015	*20·58*	*1·1584*	39·09*	*1·3662*
	28·01	*1·2018*			39·38*	
					39·22	
49·8	33·26	1·2360	26·16	1·2009	41·98	1·3975
	33·00	1·2340	26·23	1·2000	41·99	1·3964
	33·13	*1·2350*	*26·20*	*1·2004*	42·12*	*1·3970*
					42·06*	
					42·04	
64·7	37·05	1·2627	31·45	1·2432	44·28	1·4071
	36·83	1·2644	31·41	1·2421	44·27	1·4077
	36·94	*1·2635*	*31·43*	*1·2426*	44·72*	*1·4074*
					44·48*	
					44·44	
79·6	40·36	1·2858	36·87	1·2794		
	40·54	1·2850	36·83	1·2779		
	40·45	*1·2854*	*36·85*	*1·2786*		
84·7			37·96	1·2891		
			38·33	1·2942		
			38·15	*1·2916*		
89·6			38·08	1·2959		
94·7			38·25	1·2870		
99·7	43·83	1·3148	37·45	1·2928		
	43·72	1·3082	37·55	1·2849		
	43·78	*1·3115*	37·55	1·2806		
			37·65	*1·2861*		
			37·47			
			37·53			

* As oxalate, the rest as ferrocyanide.

Results of Experiments.—The values obtained for the solubilities of calcium and potassium ferrocyanide lie on two smooth curves (Fig. 2). The values obtained by Vallance and by Fabria (*loc. cit.*) for the potassium salt, which are plotted on our curve for purposes of comparison, are in good agreement with our measurements except at temperatures above 84°, where Fabria's values are considerably higher. To what extent the divergence is due to his having kept his solutions at these high temperatures for as long as 3 hours we are unable to say, but we have repeatedly noticed that solutions of the calcium salt show green coloration on cooling, owing presumably to incipient decomposition. The experimental difficulties with the calcium salt solutions at high temperatures were considerable. The solutions had both high viscosity and high density; the former made the rate of flow into the pipette very slow, and also prevented the very small particles of solid salt from settling rapidly. It was almost impossible to prevent the capillary entrance to the pipette from being blocked, and although five determinations were made for the solubility at 79·6° these are not given, as they show almost the same value as that obtained at 65°.

FIG. 2.



A. *Grams of anhydrous salt in* 100 *grams of solution.*
B. *Density of saturated solution.*

I. *Density of sodium ferrocyanide solutions.* II. *Density of potassium ferrocyanide solutions.* III. *Solubility of sodium ferrocyanide.* IV. *Solubility of potassium ferrocyanide.* V. *Density of calcium ferrocyanide solutions.* VI. *Solubility of calcium ferrocyanide.*

As may be seen from the graph, the solubility curve of sodium ferrocyanide shows a sharp break at 81·7°. This transition temperature does not appear to have been observed before, though it is apparently responsible for the reported transition in the curve for the potassium salt of Étard (*loc. cit.*). Work is in progress on the three-component system calcium ferrocyanide–sodium ferrocyanide–water, and the identity of the lower hydrate of the sodium salt will be investigated. The four points given by Conroy (*loc. cit.*) for the solubility of the sodium salt lie almost exactly on our curve, though, as the number of his determinations was small, the transition point evidently escaped his observation. The density results (Fig. 2) require little comment. No other work appears to have been done on this property of the saturated solutions. The three curves are of the same general form as the corresponding solubility ones. In the case of the sodium salt, the points evidently lie on two curves and are consistent with the transition at 81·7° as given by the solubility curve.

Verification of the Transition Temperature of Sodium Ferrocyanide.—The transition point was verified by the two following methods : 1. *The cooling curve.* On allowing the salt to cool from about 90° to 75° in a jacketed test-tube carrying a copper stirrer and a sensitive thermometer, arrests were observed, in three experiments, at 81·0°, 81·2°, 81·3°, giving a mean value of 81·2°.

2. *Dilatometer.* The dilatometer used was of the ordinary form and had a graduated capillary neck about a foot long. The bulb contained the hydrate ($10H_2O$) and sufficient paraffin to rise to a convenient level in the capillary when the temperature was in the region of 81°. Before the dilatometer was introduced into the thermostat it was heated above 81° so as always to have some of the higher-temperature hydrate present to facilitate the change. In all, six experiments were carried out at temperatures ranging from 80·6° to 82·6°.

At the highest temperature, 82·6°, there was a rapid rise of 1 inch in nearly 3 minutes, and at 81·9° the level of the oil still rose, although at the rate of only $\frac{1}{2}$ inch in $\frac{1}{2}$ hour. In the next three determinations at 81·2°, 81·3°, and 81·3°, respectively, no change in the oil level could be observed. Finally, at 80·6°, there was a fall in the level of $\frac{1}{2}$ inch in $\frac{1}{4}$ hour. These experiments show that the change from the higher-temperature hydrate to the $10H_2O$-hydrate occurs with a volume decrease and vice versa, and that the most probable value of the transition temperature is 81·5°. The values obtained by the less accurate methods, namely, 81·7° by the solubility, and 81·2° by cooling curves, give as a mean value one very close to the most trustworthy value of 81·5°.

Summary.

1. The solubility of sodium, potassium, and calcium ferrocyanide in water has been determined, together with the density of the saturated solutions.

2. Sodium ferrocyanide has a transition point at 81·5°. Neither the potassium nor the calcium salt shows any transition over the

range investigated, the transition point of the potassium salt recorded by Étard being probably due to contamination with sodium ferrocyanide.

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