CLX.—*The System Calcium Ferrocyanide–Sodium Ferrocyanide–Water. Part II.*

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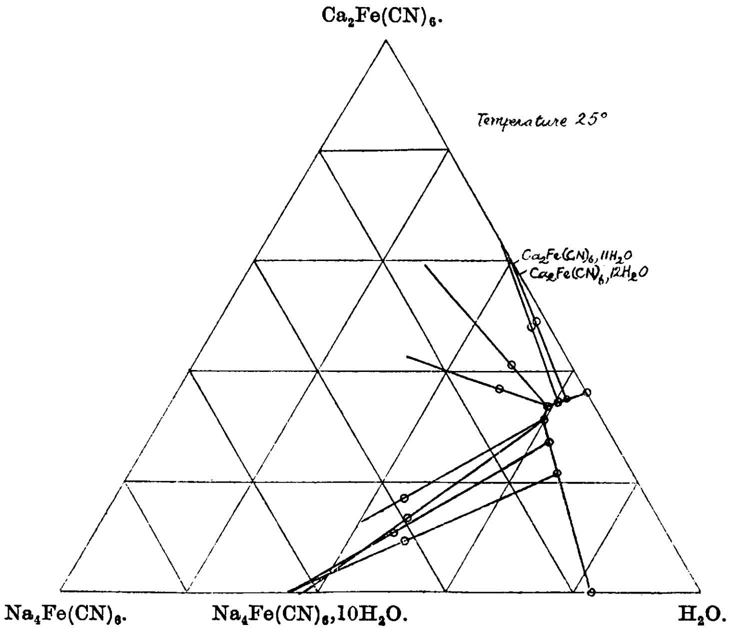
THE solubility equilibria of the systems calcium ferrocyanide–water and sodium ferrocyanide–water were described by the author in a previous paper (J., 1926, 49), in which it was shown that $Na_4Fe(CN)_6,10H_2O$ undergoes transformation into a less hydrated form at 81·5°. The present paper deals with the three-component system calcium ferrocyanide–sodium ferrocyanide–water, which was investigated with the view of determining by the " Rest " method the formula of the sodium salt which is stable at higher temperatures. This object was not attained, as the two ferrocyanides gave the double salt $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$. This salt, which is of the same type as the well-known double salts of calcium and potassium or ammonium ferrocyanides, has been obtained by Wyrouboff (*Ann. Chim.*, 1870, **21**, 283) by crystallisation from solutions of the mixed components, but the product so prepared was evidently not pure, since Wyrouboff's analyses led him to formulate it as $CaNa_3Fe(CN)_6$. Crystals of the double salt now obtained have been examined by Dr. T. V. Barker, who finds that their crystallographic properties agree with those stated by Wyrouboff.

FIG. 1.



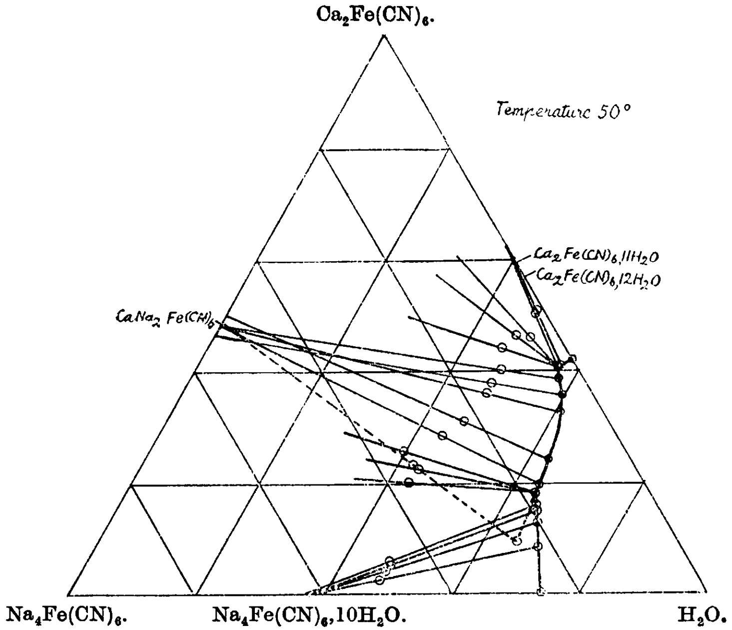
Nevertheless, the system was of some interest and was investigated in detail. The range of the solubility determinations of the calcium salt was extended from the cryohydrate to 90°, and it was found, like the sodium salt, to suffer transformation to a lower state of hydration.

EXPERIMENTAL.

System Calcium Ferrocyanide–Water.

Determination of the solubility of the pure calcium salt at 90° gave 44·2 g. of anhydrous salt per 100 g. of solution, a value almost identical with that obtained at 65°, *viz.*, 44·4 g. In the course of the former experiments five independent determinations of the solubility at 80° were made, giving a mean value of 44·0. These experiments clearly indicate a change of the ordinary hydrate into a form which is stable at higher temperatures and the solubility of which is practically independent of temperature. From cooling curves it appears that the lower limit of stability of the new form is 59·7°. The complete solubility curve of calcium ferrocyanide is now given from −11·6° to 90° as g. of anhydrous salt in 100 g. of solution.

FIG. 2.



Temp. ...	−10·1°	24·9°	34·9°	49·8°	59·7°	64·7°	79·6° & 90°
Conc. ...	30·45	36·44	39·22	42·04	44·20	44·44	44·37

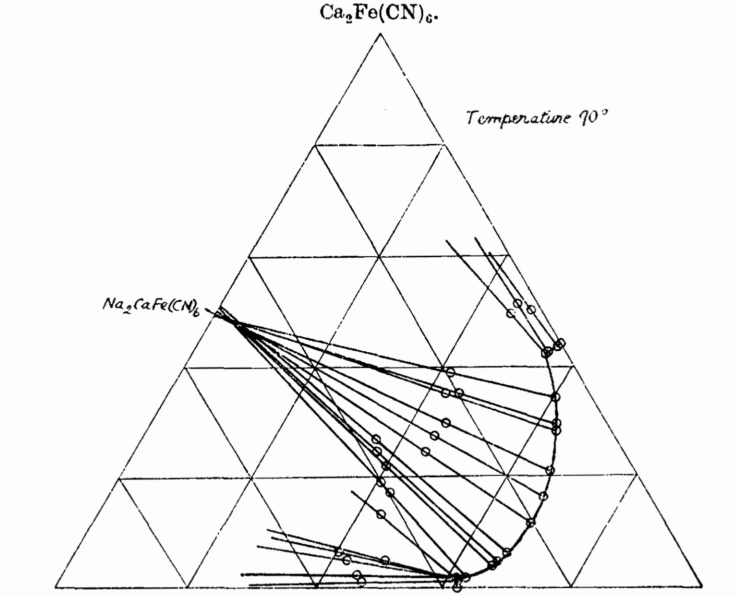
System Calcium Ferrocyanide–Sodium Ferrocyanide–Water.

The composition of the solutions and of the wet solids in equilibrium with them were determined by the methods previously described in detail (*loc. cit.*), *viz.*, the total ferrocyanide by permanganate, and the calcium volumetrically by the oxalate method. The withdrawal of solutions by means of the weight pipette previously described enabled density as well as solubility determinations to be made. The experiments were carried out at 25°, 50°, and 90°, and the results obtained are in the following tables, and represented in Figs. 1, 2, and 3. The values represent weights of anhydrous salt per 100 g. of solution in columns 2 and 3, and per 100 g. of wet solid in columns 5 and 6. The triple-point values are starred. (*M* represents metastable state.)

Determination of Invariant Points.

1. The transition point of pure calcium ferrocyanide was found by means of cooling curves to be 59·7°, and in the presence of the solid double salt to be 58·2°. The solubility of the pure salt was 44·2 g. in 100 g. of solution.

FIG. 3.



2. The transition point of pure sodium ferrocyanide, determined by the same method, was 81·5°, and when the solid double salt was present, it was 81·16°. The composition of the solution at the former temperature was 37·5 g. of $Ca_2Fe(CN)_6$ in 100 g. of solution, and at the latter 3·14 g. of $Ca_2Fe(CN)_6$, 34·74 g. of $Na_4Fe(CN)_6$, and 62·14 g. of water.

3. The melting point of the calcium ferrocyanide cryohydrate was found to be —10·1° and its composition was 30·45 g. of anhydrous salt per 100 g. of solution, which had *d* 1·198.

		Solutions.			Solids.		
	D.	$Ca_2Fe(CN)_6$.	$Na_4Fe(CN)_6$.	H_2O.	$Ca_2Fe(CN)_6$.	$Na_4Fe(CN)_6$.	H_2O.
	At 25°.						
	1·356	37·16	—	62·84	—	—	—
	1·369	35·27	3·67	61·05	49·00	1·23	49·76
	1·373	35·10	4·79	60·11	48·71	3·01	48·33
*	1·381	33·24	7·55	59·21	42·22	9·55	48·24
	—	33·40	7·33	59·27	37·76	14·66	47·60
*	—	31·30	8·46	60·24	17·31	37·37	45·27
	—	31·60	8·75	59·65	13·97	38·25	47·71
	1·344	28·02	9·64	62·34	11·40	42·26	46·41
	—	22·22	11·50	66·27	9·88	41·76	48·38
	1·130	—	17·04	82·96	—	—	—
	At 50°.						
	1·392	42·20	—	58·00	—	—	—
	—	40·71	2·53	56·78	50·51	1·42	48·08
	—	40·51	2·91	56·58	49·30	1·83	49·90
*	1·436	39·95	2·65	57·38	46·46	6·54	46·98
	1·438	40·10	2·91	57·00	43·98	9·85	46·17
	—	38·70	3·30	57·94	40·10	11·31	48·61
	—	36·07	4·73	59·20	37·79	14·65	47·59
	1·363	33·08	6·50	60·44	36·63	15·90	47·46
	1·332	24·40	12·99	62·61	32·07	23·11	44·81
	1·314	20·05	16·24	63·71	29·45	27·73	42·83
	1·308	17·28	18·49	64·24	26·32	31·20	42·46
*	1·311	18·13	18·00	63·87	23·39	34·04	42·51
	1·310	17·93	18·44	63·62	20·58	37·22	42·22
M	1·280	9·53	25·25	65·26	23·88	34·18	41·91
	1·300	16·26	18·65	65·10	6·09	47·17	46·79
	1·296	15·57	19·37	65·52	5·71	47·38	46·96
	1·281	13·18	20·10	66·74	4·59	48·41	47·01
	1·255	9·13	22·11	68·76	3·01	49·61	47·38
	1·200	—	26·20	73·80	—	—	—
	At 90°.						
	1·401	44·40	—	55·60	—	—	—
	1·400	43·96	0·34	55·70	50·35	1·71	47·88
	1·396	42·74	2·77	54·50	50·81	2·99	46·20
*	—	42·42	3·12	54·44	49·16	4·47	46·37
	1·335	34·74	5·02	60·27	39·05	19·22	41·73
	1·313	30·17	7·43	62·39	35·52	19·90	44·57
	1·307	29·09	8·08	62·82	35·66	22·55	41·80
	1·307	21·34	13·09	65·56	30·27	25·50	44·26
	1·249	16·64	16·28	67·07	28·32	28·21	43·56
	—	14·88	18·18	66·94	27·40	29·73	42·86
	1·238	11·99	20·29	67·71	25·50	31·15	43·36
	1·238	11·44	20·49	68·13	23·56	29·52	46·90
	1·242	6·54	26·83	66·61	25·94	35·85	38·20
	1·240	6·49	26·72	66·67	29·03	37·10	33·89
	1·252	4·88	29·48	65·53	25·60	37·79	36·62
	1·256	3·83	31·36	64·97	23·33	39·02	37·64
	1·266	2·89	33·55	63·59	21·47	38·35	40·19
	1·279	2·20	35·36	62·46	19·08	40·36	40·56
	1·284	2·21	35·77	62·02	17·45	39·81	42·73
	1·302	1·46	38·97	59·58	13·97	43·54	42·47
*	1·285	1·88	37·04	61·05	6·87	53·15	39·95
	1·285	1·81	36·81	61·38	5·63	47·55	46·81
	1·288	1·72	36·97	61·31	2·41	52·52	45·03
	1·288	1·37	37·35	38·73	1·30	54·55	44·13
	1·290	—	38·00	62·00	—	—	—

4. The cryohydric temperature of sodium ferrocyanide was estimated as −1·40° and the concentration as 6·81 g. in 100 g. of solution. The density, by extrapolation, is 1·130.

5. The cryohydric temperature for the three-component system was −11·6°, and the concentrations were $Ca_2Fe(CN)_6$, 28·9; $Na_4Fe(CN)_6$, 3·587; H_2O, 67·51%.

Discussion.

At all three temperatures investigated, the double salt is stable, and the range of stability increases markedly with rise in temperature. The range of solutions in equilibrium with the double salt $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$ moves over very much towards the calcium side at lower temperatures. The solubility curve for the double salt is continued into the metastable region at 50° as shown in the diagram.

The values obtained at 25° and 50° confirm the accepted formula of the sodium salt as $Na_4Fe(CN)_6,10H_2O$, and provide additional evidence that the formula of the calcium salt is $Ca_2Fe(CN)_6,11H_2O$ and not $Ca_2Fe(CN)_6,12H_2O$, as might be expected. The evidence at 90° is less satisfactory, as the range of solutions with which the simple salt is in equilibrium is in both cases very limited. The values obtained are sufficient to show that at this temperature the stable forms of the two salts are less highly hydrated than at the lower temperatures, but precise formulation must await the investigation of other systems. Both at 90° and at 50° the tie-lines clearly indicate a formula $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$ for the double salt. At 50°, both the single salts are highly hydrated; the tendency of the double salt to combine with water is thus markedly less than that of the single salts. In its temperature coefficient of solubility it also diverges considerably from the behaviour of the hydrated components, for its solubility clearly falls with increase in temperature. This fact is also probably connected with the absence of hydration, since the dehydrated forms of the single salts have no appreciable temperature coefficient of solubility.

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