VII.—*Phase-rule Studies on Metallic Thiocyanates. Part I. The Systems* $Ba(CNS)_2$–$NaCNS$–H_2O *and* $Ba(CNS)_2$–$KCNS$–H_2O *at* 25°

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NEITHER the solubilities of metallic thiocyanates nor their double salts have hitherto received much attention. The majority of the double salts are of the types $M^{I}CNS,M^{II}(CNS)_2,xH_2O$ and $2M^{I}CNS,M^{II}(CNS)_2,xH_2O$, where M^{I} is usually an alkali metal, but little is known as to the conditions for their formation or of their stability in solution. No double salts of the alkali-metal thiocyanates with those of the alkaline-earth metals have been described, and results are now given of a study of two ternary aqueous systems, each containing the thiocyanates of barium and an alkali metal at 25°.

EXPERIMENTAL.

The potassium thiocyanate used was of A.R. quality. The sodium and barium thiocyanates were prepared by repeated crystallisation of the commercial materials from water, followed by drying over fused calcium chloride, until the ratios Ba : CNS and Na : CNS were satisfactory. Certain commercial samples of barium thiocyanate contained a little of the ammonium salt, and in some cases were purified by boiling with a slight excess of barium hydroxide solution until ammonia ceased to be evolved; carbon dioxide was passed through the cold solution to eliminate the excess of barium hydroxide, and the solution was boiled, filtered, and evaporated to crystallisation. After a further recrystallisation the barium thiocyanate was sufficiently pure for use. As the sodium thiocyanate after purification still contained some sodium carbonate, the material used in the determination of the solubility of this salt and in making up the mixtures on the sodium thiocyanate side of the system was further purified by recrystallisation from 96% alcohol and then dried at 130° (Found : CNS, 71·64. Calc. : CNS, 71·64%).

The various mixtures were made up from weighed amounts of the appropriate solids together with ordinary distilled water in such quantity as to give a saturated solution at 25° as well as just sufficient solid phase for accurate analysis. According to Hughes and Mead (J., 1929, 2282), there is a transition point in the system $NaCNS-H_2O$ at about 30°, so in the system containing this salt, where the solid phase was probably hydrated sodium thiocyanate, the various mixtures were heated until homogeneous, and the resultant solution was cooled to 30° (approx.), any solid separating being just dissolved by the addition of a little water, and then rotated in a thermostat regulated at 25° ± 0·05° for 2—7 days. As this procedure did not always give the stable solid phase, it was modified as follows : the mixtures were made up from weighed amounts of solids with sufficient water to give unsaturated solutions at 25°; dry filtered air at 25° was drawn through the solutions at this temperature until sufficient solid phase separated, whereupon the mixtures were shaken in the thermostat for periods varying from 2 days to 4 weeks. Even so, the mixtures, in most cases, had to be inoculated with hydrated sodium thiocyanate to induce separation of the stable solid phase. In the potassium thiocyanate system the mixtures, after homogeneity had been attained by warming, were cooled to 35° and treated and shaken in the thermostat as above. A few points on the diagram of this system were confirmed by using mixtures prepared by the second method.

When equilibrium had been attained, the solid phase was allowed to settle and convenient amounts of solution and moist solid were withdrawn, a warmed pipette with a glass-wool filter being used for the former, and a sintered-glass filter to retain the latter. After being weighed, the solution and moist solid were made up to convenient volumes and analysed. In each system barium and total thiocyanate radical were determined, the former as sulphate and the latter gravimetrically as the silver salt (Treadwell, " Analytical

Chemistry," Vol. II, 7th edn., p. 303). As an occasional check, the thiocyanate was oxidised by bromine water and the resultant sulphate determined as barium sulphate, but there is no doubt that the first method is quite accurate.

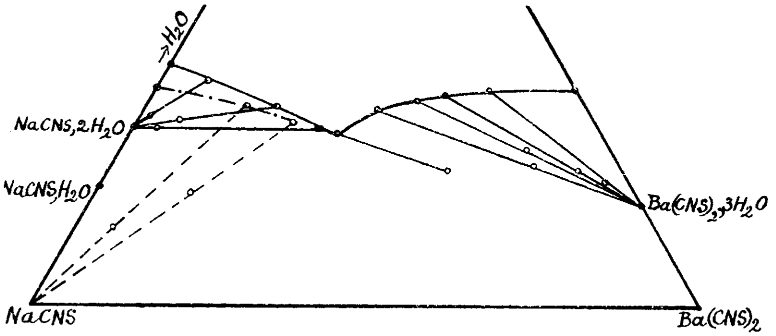
All results are expressed as g. per 100 g. of solution and moist solid respectively.

System $Ba(CNS)_2$–NaCNS–H_2O.

	Solution.			Moist solid.		
No.	$Ba(CNS)_2$.	NaCNS.	H_2O.	$Ba(CNS)_2$.	NaCNS.	H_2O.
1	62·61	0	37·39	—	—	—
2	49·83	12·96	37·21	74·91	3·20	21·89
3	43·53	19·93	36·54	69·76	6·62	23·62
4	39·73	24·64	35·63	60·61	12·23	27·16
5	34·93	31·11	33·96	63·05	12·54	24·41
6	30·94	39·33	29·73	50·64	25·93	23·43
7	27·99	41·52	30·49	—	—	—
8	27·99	41·60	30·41	3·59	66·10	30·31
9	19·77	46·03	34·20	6·19	61·93	31·88
10	7·07	54·14	38·79	1·52	66·06	32·42
11	0	58·78	41·22	—	—	—
12	23·21	45·09	31·70	14·33	66·31	19·26
13	15·18	50·60	34·22	5·91	80·98	13·11
14	0	62·39	37·61	—	—	—

(Nos. 12, 13, and 14 refer to mixtures which are really metastable.)

FIG. 1.



These results are plotted in Fig. 1, from which it will be seen that no double salt exists in this system at 25°, and that the dihydrate of sodium thiocyanate is the stable solid phase when this salt is in equilibrium with the various saturated solutions. Hughes and Mead (*loc. cit.*) find that the monohydrate of sodium thiocyanate is the stable form below 30·3°, but this result could not be confirmed. From the data given by these authors, the solubility of sodium thiocyanate at 25° is 60·2 g. per 100 g. of solution, whereas the value now obtained is 58·78, which is the mean of four closely agreeing determinations on solutions which had been shaken in contact with solid phase for from 2 days to a month. When the solubility of sodium thiocyanate was determined by shaking excess of the anhydrous salt with water until equilibrium was attained, values of 62·34 and 62·40 were obtained; and in two cases, in which an unsaturated solution was evaporated by passage of dry filtered air at 25° and then shaken in the thermostat, values of 62·37 and 62·46 were obtained, giving a mean of 62·39.

When a solubility curve is constructed from the data given by Hughes and Mead (*loc. cit.*), and the branch for which the stable solid phase is anhydrous sodium thiocyanate is extrapolated to 25°, a solubility of 62·80 g. per 100 g. of solution is obtained, from which it appears that the solubility of 62·39 corresponds to solutions in contact with anhydrous salt, if allowance is made for the difference in the methods used. When such solutions were inoculated with dihydrate, this hydrate immediately separated, and the solubility fell to 58·78. In one case after inoculation, the solid phase in equilibrium with one of these solutions was separated and dried by pressure between filter-paper. It was found to have CNS, 49·03 (Calc. for $NaCNS,2H_2O$: CNS, 49·60%).

Either by not cooling the various mixtures to 30° before shaking them in the thermostat, or by evaporating unsaturated solutions at 25° by the method already given, it has been possible to trace the curve, where solutions are in metastable equilibrium with anhydrous sodium thiocyanate, for some distance from the $NaCNS-H_2O$ side of the diagram. When, however, such mixtures were inoculated with dihydrate and shaken, the solid phase became sodium thiocyanate dihydrate, and the solutions, after equilibrium had been attained, were found to correspond to points on the upper curve of the diagram. In view of the readiness with which anhydrous sodium thiocyanate absorbs moisture when exposed to the atmosphere, it is somewhat remarkable that it should change so very slowly into its dihydrate, the stable form at 25°, when in contact with these aqueous solutions. During the purification of sodium thiocyanate, this dihydrate, which readily forms supersaturated solutions, was obtained. Prepared in this way, and freed from as much mother-liquor as possible by suction, it had CNS, 48·56; kept over partly dehydrated dihydrate in a vacuum for 4 days, it had CNS, 49·43; and kept thus for a further 20 days, it had CNS, 49·38. Another sample, prepared and dried in the same way, had CNS, 49·67 (Calc. for dihydrate : CNS, 49·60%). The transition temperature of this dihydrate, determined dilatometrically, was 30·4°, and that determined thermometrically was 30·3°.

Further work on the system $NaCNS-H_2O$ is in progress.

System $Ba(CNS)_2$–KCNS–H_2O.

	Solutions.			Moist solid.		
No.	$Ba(CNS)_2$.	KCNS.	H_2O.	$Ba(CNS)_2$.	KCNS.	H_2O.
1	62·61	0	37·39	—	—	—
2	55·72	14·45	29·83	74·78	4·40	20·82
3	53·14	19·46	27·40	73·41	6·04	20·55
4	52·84	19·50	27·66	55·84	27·81	16·35
5	46·60	26·04	27·36	57·29	32·91	9·80
6	43·66	28·95	27·39	55·30	32·13	12·57
7	39·45	34·02	26·53	51·94	33·27	14·79
8	39·10	34·47	26·43	49·86	33·37	16·77
9	37·04	37·18	35·78	52·86	33·44	13·70
10	31·73	43·92	24·35	46·65	36·64	16·71
11	30·75	45·00	24·25	44·66	38·54	16·80
12	28·96	47·67	23·37	49·06	36·83	14·11
13	28·68	48·28	23·04	26·76	63·37	9·87
14	22·78	52·42	24·80	5·63	88·24	6·13
15	10·24	62·32	27·44	1·97	92·15	5·88
16	0	70·89	29·11	—	—	—

The results for this system are plotted in Fig. 2. Foote (*Amer. Chem. J.*, 1903, **30**, 341) gives 70·53 g. per 100 g. of solution as a mean value for the solubility of potassium thiocyanate at 25°, but the value now obtained is 70·89. From the diagram for this system, it appears that a *double salt* corresponding closely to the formula $3KCNS,2Ba(CNS)_2,5H_2O$ exists over a fairly wide area, whereas when potassium thiocyanate forms double salts with the thiocyanates of other bivalent metals, these are usually of the type $KCNS,M(CNS)_2,xH_2O$ or $2KCNS,M(CNS)_2,xH_2O$.

FIG. 2.

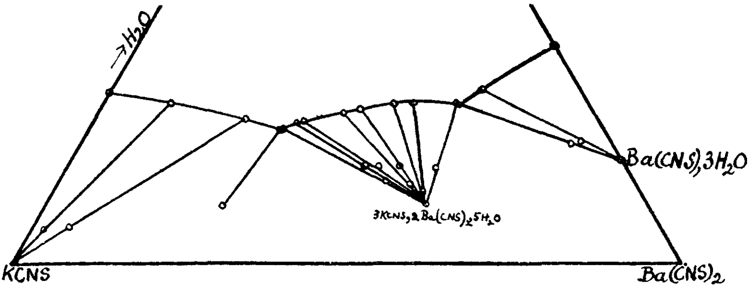


Fig. 2 shows this double salt to be capable of crystallisation from water without decomposition, so it was prepared by making a solution containing the constituent salts in the proportion indicated by the formula, and allowing it to crystallise at 25°. Two samples prepared in this way were freed from as much mother-liquor as possible by suction, dried in air in cold weather, and analysed (washing with water could not be carried out on account of the high solubility of the substance) [Found: KCNS, 32·91, 33·09; $Ba(CNS)_2$, 57·29, 56·63; H_2O (by diff.), 9·80, 10·28. $3KCNS,2Ba(CNS)_2,5H_2O$ requires KCNS, 32·91; $Ba(CNS)_2$, 56·99; H_2O, 10·12%].

Summary.

The ternary systems $Ba(CNS)_2$–NaCNS–H_2O and $Ba(CNS)_2$–KCNS–H_2O have been investigated at 25°.

The solubilities of the thiocyanates of barium, sodium, and potassium are 62·61, 58·78, and 70·89 g. respectively per 100 g. of solution.

The dihydrate is the stable solid phase of sodium thiocyanate at 25°, its transition temperature being about 30·3°. The metastable solubility curve of anhydrous sodium thiocyanate has been traced for some distance in the ternary system, and the solubility of the anhydrous salt found to be 62·39 g. per 100 g. of solution. Double-salt formation has not been found in the system containing sodium thiocyanate.

In the system containing potassium thiocyanate, a double salt, $3KCNS,2Ba(CNS)_2,5H_2O$, exists over a wide area and is stable in aqueous solution.

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