

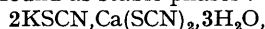
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1. *The Ternary Systems* $\text{NaSCN}-\text{Ca}(\text{SCN})_2-\text{H}_2\text{O}$, $\text{KSCN}-\text{Ca}(\text{SCN})_2-\text{H}_2\text{O}$,
 $\text{NH}_4\text{SCN}-\text{Ca}(\text{SCN})_2-\text{H}_2\text{O}$ and $\text{Ca}(\text{SCN})_2-\text{AgSCN}-\text{H}_2\text{O}$ at 25° .

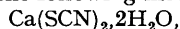
By A. K. MCKERROW, V. J. OCCLESHAW, and (in part) FRANK DRABBLE.

From a study of these condensed ternary systems four new double salts have been found, and the existence of the compound $\text{Ca}(\text{SCN})_2, 2\text{AgSCN}, 2\text{H}_2\text{O}$ confirmed. Some evidence has been obtained showing $\text{Ca}(\text{SCN})_2, 4\text{H}_2\text{O}$ to be dimorphous with a transition point at 23.8° . The solubility of calcium thiocyanate from 0° to 50° has been determined.

THE isotherms of systems of the type $\text{MSCN}-\text{Ba}(\text{SCN})_2-\text{H}_2\text{O}$ in which M was Na, K, NH_4 , and Ag have already been studied at 25° (Parts I, II, and III; J., 1931, 55; 1932, 2404; 1934, 1892). We now describe the isotherms at 25° of the four systems in which barium thiocyanate is replaced by the calcium salt. These systems have not previously been investigated. Wells and Merriam (*Amer. Chem. J.*, 1902, 28, 265) prepared $\text{Ca}(\text{SCN})_2, 2\text{AgSCN}, 2\text{H}_2\text{O}$, the existence of which has now been confirmed, but no double salts between calcium thiocyanate and any of the other three salts are recorded in the literature. The following new double salts, all of which are non-congruent, have been found as stable phases: $3\text{KSCN}, \text{Ca}(\text{SCN})_2, 3\text{H}_2\text{O}$,



$4\text{NH}_4\text{SCN}, \text{Ca}(\text{SCN})_2, 2\text{H}_2\text{O}$, and $7\text{NH}_4\text{SCN}, 6\text{Ca}(\text{SCN})_2, 12\text{H}_2\text{O}$. In the system containing the sodium salt anhydrous sodium thiocyanate was found as a stable solid phase. Marked metastability was encountered in the system containing the potassium salt and the following metastable solid phases were observed:



a solid solution with composition approaching that of the double salt $4\text{KSCN}, \text{Ca}(\text{SCN})_2, 2\text{H}_2\text{O}$, and a second crystalline form of $\text{Ca}(\text{SCN})_2, 4\text{H}_2\text{O}$. This result was not unexpected, since $\text{CaCl}_2, 4\text{H}_2\text{O}$ exists in three forms (see Bassett *et al.*, J., 1933, 151, who give further references). Throughout this paper the variety of calcium thiocyanate tetrahydrate with the smaller solubility at 25° is referred to as the α -form and the second variety as the β -form. The transition temperature was 23.8° . As a check on this value a small part of the $\text{Ca}(\text{SCN})_2, 4\text{H}_2\text{O}$ region in the system containing the silver salt was investigated at 20° , and the β -form recognised as a stable solid phase. Of the other systems, only in the one containing the sodium salt was any attempt made to obtain β - $\text{Ca}(\text{SCN})_2, 4\text{H}_2\text{O}$.

EXPERIMENTAL.

Calcium thiocyanate was a good quality commercial sample which was recrystallised from water until the ratio $\text{Ca}^{2+}/\text{SCN}^-$ was satisfactory. The purification of the sodium and silver salts has already been described (Parts I and II), and the potassium and ammonium salts, which were of "AnalaR" quality, were used without further purification.

Mixtures containing silver thiocyanate were made up as described in Part II, and all other complexes by shaking known proportions of the appropriate salts with definite volumes of water in hard-glass tubes at 25° until a sufficient excess of solid remained. The mixtures were then carefully heated with shaking until solution was complete, and finally rotated in a thermostat regulated at $25^\circ \pm 0.05^\circ$. The period of shaking depended on the nature of the solid phase and varied from a day, when simple salts alone were involved, to at least a week when dealing with some of the double salts. In previous work on thiocyanate systems metastable conditions were often encountered, and in this work the complexes usually required suitable inoculation to induce crystallisation. In all cases the usual precautions were taken to ensure that a condition of equilibrium had been attained.

Because of the viscous character of the mixtures, the nature of the solid phases was determined by the "residue method." Sintered-glass filters were used to separate the liquid and the solid phases for analysis, all filtrations being carried out at the thermostat temperature. The method of analysis used for the system containing silver thiocyanate is described in Part III. With the other systems, calcium and total thiocyanate were determined, and the amount of the second thiocyanate calculated. Calcium was precipitated as oxalate and then determined volumetrically with standard potassium permanganate solution. In carrying out this determination advantage was taken of the suggestion for washing the precipitate made by Bassett (J., 1934, 1270), and allowance was always made for a blank determination. Total thiocyanate was determined by the Volhard method used under the usual standardised conditions. The ammonium thiocyanate solution used was standardised gravimetrically as the silver salt, and then used to standardise the solution of silver nitrate under the conditions observed in the Volhard method. The concentration of the latter solution was occasionally checked gravimetrically as silver chloride.

All results are expressed as g. per 100 g. of saturated solution or moist solid, and the triangular method of plotting has been used throughout. Broken lines on the diagrams indicate metastability. In several of these systems a microscope was used to confirm the conclusions drawn regarding the nature of the solid phases.

The transition temperature of the two forms of calcium thiocyanate tetrahydrate was determined by three methods: (a) thermometrically, (b) dilatometrically, (c) solubility; the values found were 23.4° , 23.8° , and 23.7° , respectively. In method (a) supercooling occurred to a marked degree. With method (b) pure Kahlbaum toluene was used as indicator liquid and the transition point was found from a plot of the rate of volume change against temperature.

Solution		Moist solid.		Solid phase.	Solution.		Moist solid.		Solid phase.
NaSCN.	Ca(SCN) ₂ .	NaSCN.	Ca(SCN) ₂ .		NaSCN.	Ca(SCN) ₂ .	NaSCN.	Ca(SCN) ₂ .	
58.78	0	—	—	A	29.32	32.45	80.37	9.22	B
52.08	7.19	64.42	2.16	A	22.40	39.91	76.83	12.28	B
45.37	15.97	61.05	5.65	A	21.32	41.06	—	—	B
42.98	19.00	58.94	6.46	A	19.57	43.27	65.91	18.40	B
42.99	19.09	72.73	5.89	A, B	16.36	46.46	69.28	16.92	B
m 62.42	0	—	—	B	14.14	49.67	71.03	17.20	B
m 51.47	10.43	—	—	B	11.15	53.03	70.44	17.84	B
m 50.58	11.50	84.50	4.00	B	11.10	53.52	58.78	24.76	B
m 43.83	18.14	90.22	3.06	B	9.88	54.48	9.82	59.29	B, C
41.74	20.59	82.94	6.74	B	8.78	55.11	2.75	64.25	C
38.82	23.13	81.83	7.39	B	5.11	57.57	1.15	65.69	C
37.91	24.07	82.72	6.88	B	3.09	58.49	0.68	64.80	C
32.38	29.71	69.49	14.10	B	—	60.20	—	—	C

A = NaSCN, 2H₂O. B = NaSCN. C = Ca(SCN)₂, 4H₂O. m = Metastablé.

System NaSCN-Ca(SCN)₂-H₂O (with FRANK DRABBLE).—When the results for this system are plotted, Fig. 1 is obtained. The isotherm consists of the solubility curves of NaSCN, 2H₂O, NaSCN, and the α-modification of Ca(SCN)₂, 4H₂O. No solubility curve for the β-form of this salt was found, and there was no indication of double salt formation. In this respect the system resembles the corresponding one containing the barium salt. Fig. 1 shows that anhydrous sodium thiocyanate is stable over a wide area, whereas when barium thiocyanate replaces the calcium salt it occurs only as a metastable phase. In agreement with previous work (de Sweemer, *Natuurw. Tijds.*, 1932, **14**, 231; Parts I and II), no evidence could be found for the existence of the monohydrate of sodium thiocyanate reported by Hughes and Mead (J., 1929, 2282) as being stable below 30.3°, and assumed by Bump (*J. Physical Chem.*, 1932, **36**, 1851). Recalculation of Bump's data to the basis used in this work gives the solubility at 25° as 62.66 g. of NaSCN, and extrapolation of the data given by Hughes and Mead (*loc. cit.*) leads to a value of 62.8 g. It has again been possible to follow the solubility curve of anhydrous sodium thiocyanate throughout the metastable region, the solubility found being 62.42 g. This is in good agreement with the value (62.39 g.) previously found (Part II), and is not far removed from either of the values deduced for this supposed monohydrate.

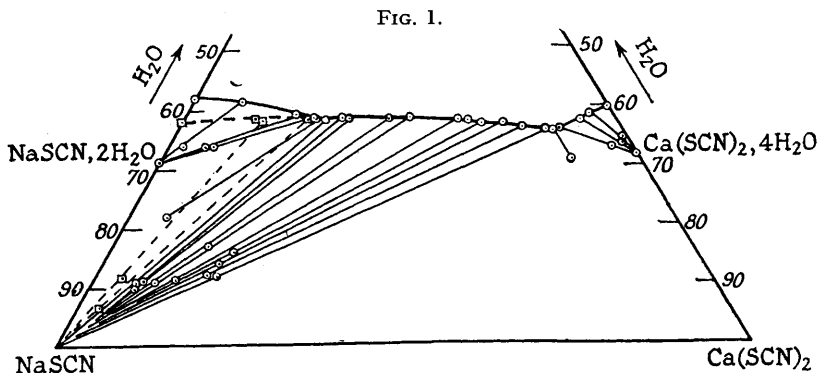
Sodium thiocyanate crystallises as a dihydrate in long thin needles, which are probably hexagonal, with truncated ends. Bump (*loc. cit.*) describes his monohydrate as long, monoclinic needles. Friend ("*Textbook of Inorganic Chemistry*," 1924, II, 147) states that the anhydrous sodium salt is rhombic, but the crystals we obtained, though small and poorly formed, appeared to be hexagonal prisms.

Solution.		Moist solid.		Solid phase.	Solution.		Moist solid.		Solid phase.
KSCN.	Ca(SCN) ₂ .	KSCN.	Ca(SCN) ₂ .		KSCN.	Ca(SCN) ₂ .	KSCN.	Ca(SCN) ₂ .	
70.76	0	—	—	A	18.62	51.82	31.11	46.25	C
66.16	4.01	89.43	1.32	A	17.77	53.18	21.20	53.62	C, α-D
59.32	10.51	85.70	3.93	A	m 21.32	52.10	9.18	61.18	α-D
53.38	16.78	88.92	3.82	A	17.54	53.19	9.52	60.05	α-D
49.34	21.41	86.94	5.42	A	13.81	54.39	8.13	59.95	α-D
45.57	26.61	75.02	12.24	A	10.46	55.68	5.65	61.22	α-D
44.09	29.16	70.78	15.29	A	7.90	56.67	4.61	61.65	α-D
43.75	31.39	72.30	15.49	A	5.23	57.71	2.36	63.83	α-D
43.77	32.21	80.52	11.72	A, B	2.13	58.99	1.04	63.81	α-D
43.56	31.66	58.75	25.90	—	0	60.20	—	—	α-D
42.84	32.11	50.91	31.70	B	m 13.76	54.56	6.46	61.63	β-D
42.07	32.81	51.63	32.15	B	m 10.56	55.89	3.84	63.46	β-D
41.12	33.69	51.92	32.28	B	m 6.40	57.63	2.52	64.25	β-D
40.22	34.22	54.00	32.15	B	m 4.68	58.60	1.40	67.90	β-D
39.06	35.22	47.19	33.63	B	m 2.77	59.55	0.47	66.30	β-D
36.89	37.18	51.33	33.03	B	m x 0	61.10	—	—	β-D
36.28	37.47	43.91	37.20	B, C	m y 0	60.75	—	—	β-D
m 34.17	39.59	44.47	35.80	B	m 43.75	33.61	56.63	28.98	A, E
m 33.53	40.00	46.99	35.23	B	m 41.83	35.31	51.41	32.12	E
m 31.50	41.61	42.98	37.14	B	m 40.38	36.34	56.35	30.94	E
m 43.88	32.56	50.07	32.40	A, C	m 36.74	39.52	51.16	33.96	E
m 42.81	33.38	46.05	37.04	C	m 32.60	43.96	49.82	36.15	E
m 41.91	34.61	44.83	37.48	C	m 29.05	48.50	44.44	41.39	E
m 38.80	36.01	45.30	38.23	C	m 28.30	49.57	28.92	55.25	E, F
35.39	37.95	42.55	38.31	C	m 28.49	49.20	20.25	58.51	F
32.56	40.17	43.48	39.41	C	m 25.26	50.82	14.90	63.37	F
26.55	44.66	39.57	41.08	C	m 23.46	52.14	9.37	66.34	β-D, F
24.00	46.65	39.92	41.11	C	—	—	—	—	—

A = KSCN. m = Metastable.
 B = 3KSCN, Ca(SCN)₂, 3H₂O. x = Estimated from Fig. 2b.
 C = 2KSCN, Ca(SCN)₂, 3H₂O. α-D, β-D = Ca(SCN)₂, 4H₂O.
 E = Solid solution approaching F = Ca(SCN)₂, 2H₂O.
 4KSCN, Ca(SCN)₂, 2H₂O. y = Estimated from data on p. 5.

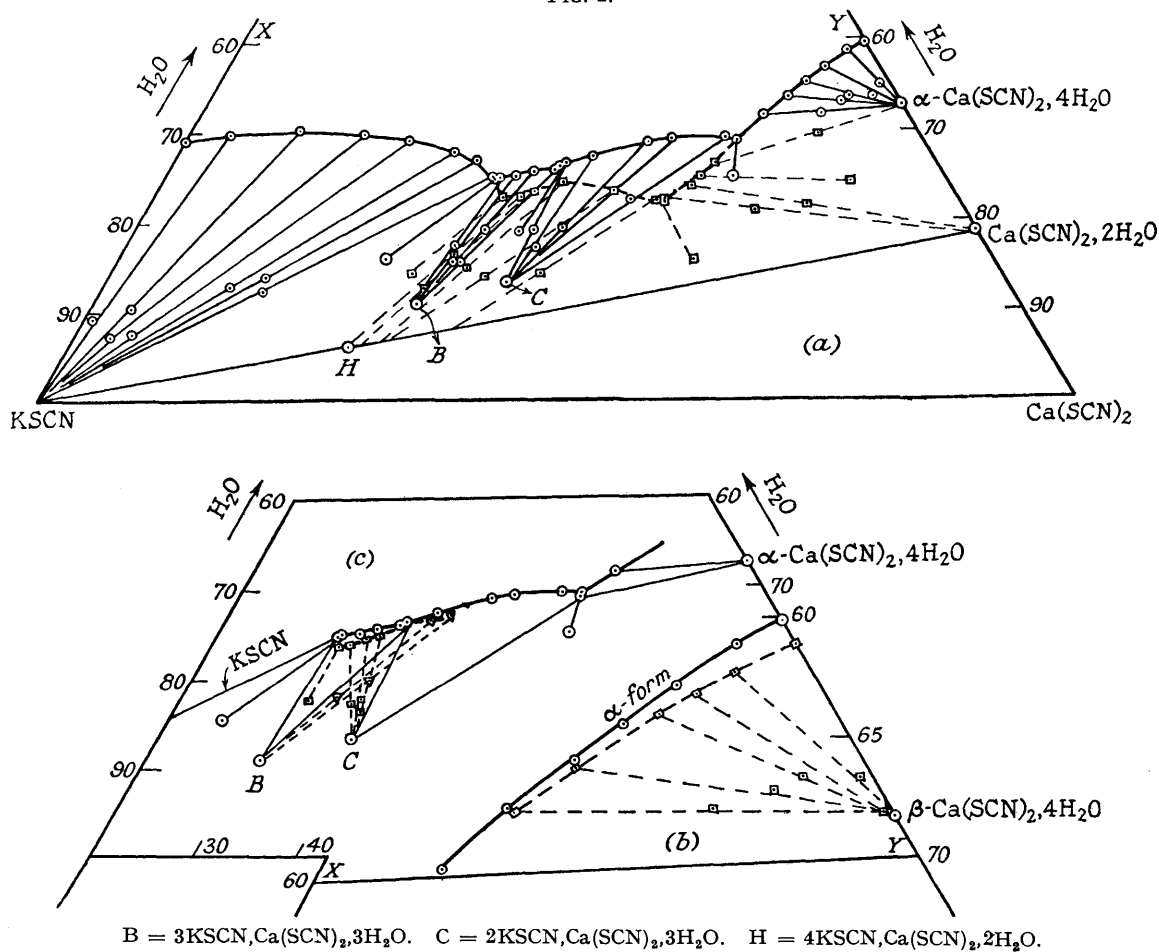
System KSCN-Ca(SCN)₂-H₂O.—To avoid overcrowding, only a selection of the results has been plotted to give the composite Fig. 2. The stable isotherm is made up of four solubility curves corresponding to the solid phases KSCN, 3KSCN, Ca(SCN)₂, 3H₂O, 2KSCN, Ca(SCN)₂, 3H₂O, and Ca(SCN)₂, 4H₂O (Fig. 2a). In addition, the diagram shows solubility curves for the three metastable solid phases already mentioned (Figs. 2a and 2b), and indicates that it was possible to follow the solubility curve of 3KSCN, Ca(SCN)₂, 3H₂O into the metastable region with increasing concentration of calcium thiocyanate, and to prolong the solubility curve of the other stable double salt to its metastable invariant with

potassium thiocyanate (Fig. 2c). The corresponding system containing the barium salt was not so complex and contained only one double salt, *viz.*, $3\text{KSCN}, 2\text{Ba}(\text{SCN})_2, 5\text{H}_2\text{O}$, showing no analogy with either of those now reported.



Potassium thiocyanate crystallises as long, thin, ill-defined needles, and the compound $3\text{KSCN}, \text{Ca}(\text{SCN})_2, 3\text{H}_2\text{O}$ as needle-like crystals which are six- or more-sided and brachydromal. The other stable double salt, $2\text{KSCN}, \text{Ca}(\text{SCN})_2, 3\text{H}_2\text{O}$, separated as thin rectangular plates, occasionally associated with square ones; the solid solution was obtained as thin hexagonal plates, and dihydrated calcium thiocyanate crystallised as hexagonal prisms with basal pinacoid and length 4—8 times the breadth. The α -form of tetrahydrated calcium thiocyanate was obtained as ill-defined rhombs, and the β -form appeared as hexagonal needles with pyramidal ends. Added potassium thiocyanate seemed to exert a stabilising influence on the β -form. As it was not possible to obtain this form at 25° , without addition of about 5% of the potassium salt, its solubility above the transition temperature could only be estimated from its solubility curves by extrapolation. Unmack, Murray-Rust, and Hartley (*Proc. Roy. Soc.*, 1930, *A*, **127**, 228) obtained calcium thiocyanate dihydrate by dehydration of the tetrahydrate, and we have confirmed their observation that attempts to dehydrate it, even at room temperature, result in decomposition.

FIG. 2.

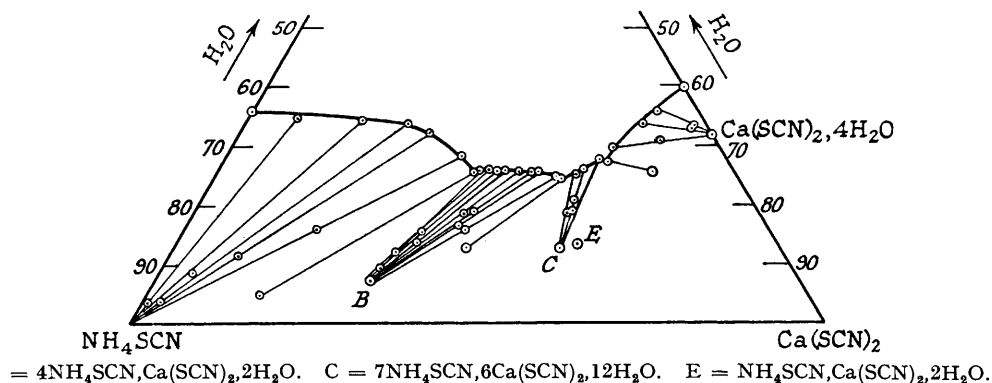


Solution.		Moist solid.		Solid phase.	Solution.		Moist solid.		Solid phase.
NH_4SCN .	$\text{Ca}(\text{SCN})_2$.	NH_4SCN .	$\text{Ca}(\text{SCN})_2$.		NH_4SCN .	$\text{Ca}(\text{SCN})_2$.	NH_4SCN .	$\text{Ca}(\text{SCN})_2$.	
64.33	0	—	—	A	28.15	46.24	44.30	39.40	B
57.85	7.29	95.54	1.09	A	26.87	47.29	42.68	40.70	B
49.18	16.70	86.52	5.00	A	25.95	49.07	43.39	40.89	B
42.72	23.62	93.53	2.83	A	25.50	49.89	41.16	43.01	B, C
40.38	27.52	78.61	10.14	A	25.55	50.13	45.06	42.07	B, C
37.84	34.00	64.68	19.44	A	24.45	50.99	28.15	53.34	C
37.67	37.01	78.81	16.41	A, B	23.31	51.62	27.51	53.78	C
36.98	37.36	58.56	31.85	B	21.38	52.76	25.50	54.04	C
35.04	39.04	55.40	32.53	B	20.55	53.26	25.77	53.68	C
34.35	39.49	54.91	32.28	B	18.40	53.95	26.50	54.53	C
34.13	40.19	49.89	34.61	B	<i>m</i> 16.91	55.22	23.59	55.72	C
32.89	41.58	51.37	34.83	B	17.32	55.64	11.74	62.69	C, D
31.48	43.22	48.28	36.69	B	15.23	55.11	8.01	61.24	D
31.37	43.29	42.43	39.18	B	9.29	57.14	2.19	65.15	D
29.04	45.33	40.84	40.58	B	0	60.20	—	—	D

A = NH_4SCN .
 B = $4\text{NH}_4\text{SCN}, \text{Ca}(\text{SCN})_2, 2\text{H}_2\text{O}$.
m = Metastable.
 C = $7\text{NH}_4\text{SCN}, 6\text{Ca}(\text{SCN})_2, 12\text{H}_2\text{O}$.
 D = $\text{Ca}(\text{SCN})_2, 4\text{H}_2\text{O}$.

System $\text{NH}_4\text{SCN}-\text{Ca}(\text{SCN})_2-\text{H}_2\text{O}$.—Fig. 3 has been constructed from the accompanying results, with the addition of the point representing the compound $\text{NH}_4\text{SCN}, \text{Ca}(\text{SCN})_2, 2\text{H}_2\text{O}$. There are four branches to the isotherm which includes solubility curves for the double salts $4\text{NH}_4\text{SCN}, \text{Ca}(\text{SCN})_2, 2\text{H}_2\text{O}$ and $7\text{NH}_4\text{SCN}, 6\text{Ca}(\text{SCN})_2, 12\text{H}_2\text{O}$ and the two simple

FIG. 3.

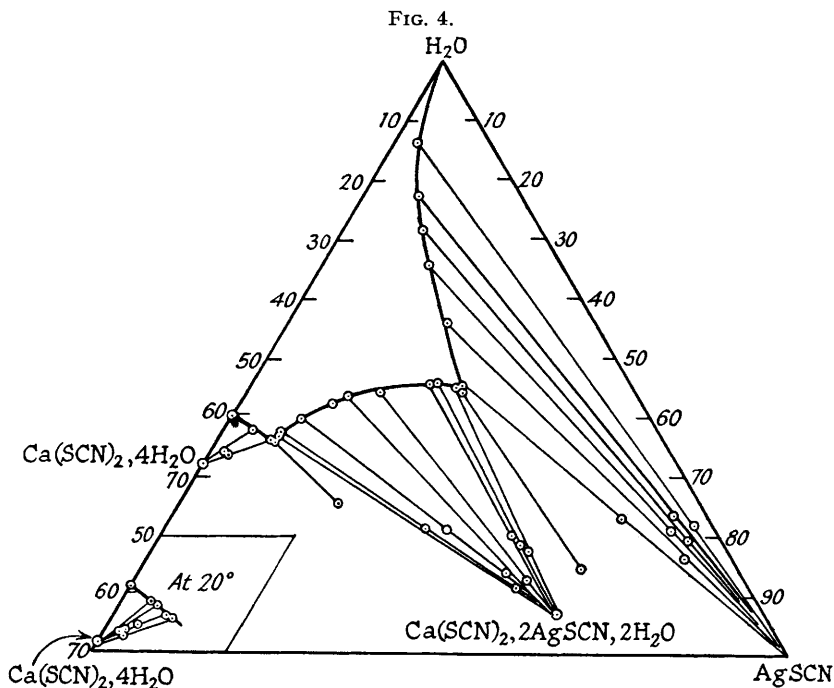


salts. It is improbable that the second double salt is being mistaken for $\text{NH}_4\text{SCN}, \text{Ca}(\text{SCN})_2, 2\text{H}_2\text{O}$. Work on this system was not hampered by metastable conditions and Fig. 3 shows that the tie lines for this second double salt converge sharply to a point representing a compound with the composition stated. Further, points representing the double salts $7\text{NH}_4\text{SCN}, 6\text{Ca}(\text{SCN})_2, 12\text{H}_2\text{O}$ and $\text{NH}_4\text{SCN}, \text{Ca}(\text{SCN})_2, 2\text{H}_2\text{O}$ are too far apart for error in the analytical method used to account for such confusion. When barium thiocyanate replaces the calcium salt the system is of a simpler type, containing but one double salt, *viz.*, $\text{NH}_4\text{SCN}, \text{Ba}(\text{SCN})_2, \text{H}_2\text{O}$, less complex than either of those now reported.

Solution.		Moist solid.		Solid phase.	Solution.		Moist solid.		Solid phase.
$\text{Ca}(\text{SCN})_2$.	AgSCN .	$\text{Ca}(\text{SCN})_2$.	AgSCN .		$\text{Ca}(\text{SCN})_2$.	AgSCN .	$\text{Ca}(\text{SCN})_2$.	AgSCN .	
60.20	—	—	—	α -A	25.15	31.01	22.58	63.08	B, C
58.80	4.03	66.13	1.73	α -A	24.52	30.70	12.56	64.39	C
57.05	7.43	64.31	2.73	α -A	21.72	22.88	6.75	76.88	C
57.03	7.52	52.00	22.67	α -A, B	19.23	15.42	6.23	72.76	C
55.21	8.50	41.14	37.53	B	17.33	11.74	4.80	75.97	C
54.74	8.26	33.52	55.33	B	15.01	8.09	4.69	75.85	C
50.76	10.27	38.43	40.62	B	14.11	3.42	2.82	75.30	C
44.99	13.09	32.54	53.43	B	<i>x</i> —	0.00002	—	—	C
41.95	14.96	—	—	B	* 59.00	—	—	—	β -A
37.02	19.22	31.00	56.11	B	* 57.27	4.24	64.60	2.15	β -A
29.12	25.71	29.59	50.17	B	* 56.85	5.19	63.75	2.72	β -A
27.86	26.74	29.34	52.26	B	* 56.41	7.50	60.95	4.54	β -A
25.47	29.79	28.63	54.10	B	* 55.44	8.73	64.57	3.02	β -A

A = $\text{Ca}(\text{SCN})_2, 4\text{H}_2\text{O}$.
 B = $\text{Ca}(\text{SCN})_2, 2\text{AgSCN}, 2\text{H}_2\text{O}$.
x = Masaki (*Bull. Chem. Soc. Japan*, 1930, 5, 345).
 C = AgSCN .
 * = At 20°.

System $\text{Ca}(\text{SCN})_2-\text{AgSCN}-\text{H}_2\text{O}$.—Fig. 4 is the isotherm obtained from the accompanying data and shows that at 25° only the one double salt, $\text{Ca}(\text{SCN})_2, 2\text{AgSCN}, 2\text{H}_2\text{O}$, exists. This system is less complex than the corresponding one containing the barium salt in which three double salts were found, one of which is of similar composition to the double salt above. This compound crystallises as bladed crystals and exists over a much greater area than its barium analogue.



Further, the solubility curve of $\text{Ca}(\text{SCN})_2, 4\text{H}_2\text{O}$ is comparatively short. The data include a few results obtained for this system at 20° .

Solubility of Calcium Thiocyanate.—The following results were obtained for the solubility (S) at various temperatures.

			β -Form.					
Temp.	0°	8°	16°	20°	23°	25°	25°	
S	55.44	56.11	57.90	59.00	59.80	60.75 *	61.10 *	
			α -Form.					
Temp.	25°	27.5°	30°	35°	41°	45°	50°	
S	60.20	60.26	60.54	60.94	61.69	62.37	63.27	

* See p. 2.

From these results the transition temperature, 23.7° , was obtained.

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