

**351.** *Phase-rule Studies on Metallic Thiocyanates. Part II. The Systems AgNCS–NaNCS–H<sub>2</sub>O, AgNCS–KNCS–H<sub>2</sub>O, and AgNCS–NH<sub>4</sub>NCS–H<sub>2</sub>O at 25°.*

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THE following double salts containing silver thiocyanate and an alkali-metal or ammonium thiocyanate have been described: NaNCS, AgNCS and 3NaNCS, AgNCS (Cernatescu, *Bull. Soc. Sci. Acad. Roumaine*, 1921, **6**, 53), KNCS, AgNCS and 2KNCS, AgNCS (Foote, *Amer. Chem. J.*, 1903, **30**, 341; *Z. physikal. Chem.*, 1903, **46**, 79), 3KNCS, AgNCS (Wells and Merriam, *Amer. Chem. J.*, 1902, **28**, 265), and NH<sub>4</sub>NCS, AgNCS and 5NH<sub>4</sub>NCS, AgNCS (Cernatescu, *loc. cit.*). The compounds described by Cernatescu and by Wells and Merriam were prepared by dissolving silver thiocyanate in aqueous solutions of alkali-metal or ammonium thiocyanate, whilst Foote obtained evidence for the existence of his compounds from a study of the system AgNCS–KNCS–H<sub>2</sub>O at 25°, finding the salt 3KNCS, AgNCS to be unstable and to break down into a mixture of 2KNCS, AgNCS and potassium thiocyanate at this temperature. As this system was not studied by use of the "residue" method and was not completed at the silver thiocyanate end, it has been reinvestigated by means of this method; the two ternary aqueous systems each containing the thiocyanates of silver and either sodium or ammonium have also been studied to determine the stability of the known double salts at 25°.

EXPERIMENTAL.

KNCS and NH<sub>4</sub>NCS were A.R. chemicals and were used without further purification; NaNCS was purified by the method described in Part I (J., 1931, 55); for this work all samples were recryst. from EtOH before use. AgNCS was obtained by purification of residues which had accumulated from numerous gravimetric determinations and therefore contained little impurity. These residues were dissolved in NH<sub>4</sub>NCS aq. and the solution filtered; large dilution with H<sub>2</sub>O pptd. the Ag salt, which was washed by decantation with H<sub>2</sub>O until free from thiocyanate, collected, again washed with H<sub>2</sub>O, then with EtOH, and dried in an air-oven at 120°.

Except when AgNCS was the equilibrium solid phase, the various mixtures were made up from weighed amounts of the appropriate solids with sufficient H<sub>2</sub>O to give 1–1.5 g. of solid phase after equilibrium had been attained. These mixtures were first heated at 40° until homogeneous and then shaken for at least 2 days—equilibrium was usually attained in less than 1 day—in a thermostat regulated at 25° ± 0.05°. Where AgNCS was the stable solid phase, the mixtures were made up by shaking excess of this salt with solutions of the second thiocyanate kept at 40°, after which they were shaken in the thermostat until equilibrium, as determined by duplicate analysis of the solution at 2-day intervals, had been attained. As in Part I, when NaNCS was

the solid phase in equilibrium, the mixtures were inoculated with the dihydrated Na salt to hasten attainment of equilibrium. Inoculation with the stable solid phases was resorted to with the system containing KNCS, as a tendency to form metastable mixtures was observed in this case also.

After equilibrium had been reached and the solid phase had settled, weighed samples of solution and moist solid (obtained as in Part I) were analysed by the following method. To determine total thiocyanate, one sample was suitably diluted with  $H_2O$ , a slight excess of  $AgNO_3$  aq. added, and the pptd.  $AgNCS$  filtered off, washed, and dried as before. In a second sample, the thiocyanate radical was destroyed by boiling with fairly conc.  $HNO_3$  aq. in a flask with a ground-in air condenser, excess of acid was removed by evaporation nearly to dryness, and, after addition of  $H_2O$ , the Ag was titrated (Volhard) by  $NH_4NCS$  which had been standardised gravimetrically as  $AgNCS$ .

The two mixtures at the extreme  $AgNCS$  end of the system containing the K salt were analysed by treatment with a large excess of  $H_2O$  to ppt. all the  $AgNCS$ , which was filtered off, washed, and dried to constant weight as before. The filtrate and washings were made up to 500 c.c., and the remaining thiocyanate determined volumetrically by Volhard's method, the  $AgNO_3$  solution used having been standardised gravimetrically as  $AgCl$ . As  $AgNCS$  is sol. in dil. thiocyanate solutions, these results are believed to be in error by about 2%.

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

*System  $AgNCS-NaNCs-H_2O$ .*

Solutions.		Moist solids.		Solid phase.	Solutions.		Moist solids.		Solid phase.
$AgNCS$	$NaNCS$ .	$AgNCS$ .	$NaNCS$ .		$AgNCS$ .	$NaNCS$ .	$AgNCS$ .	$NaNCS$ .	
0	58.78	—	—	A	12.68	54.36	41.78	37.92	C
5.09	56.94	0.97	66.86		11.53	48.51	43.74	35.06	
9.80	55.42	2.22	66.28		11.21	42.49	48.96	31.37	
12.11	54.76	5.06	64.22	A, B	11.14	38.31	48.19	30.96	C, D
12.14	54.55	19.71	62.69		11.06	25.42	48.87	28.28	
12.17	54.73	30.24	60.30	B	12.61	17.24	58.80	13.10	D
12.21*	54.80	13.09	60.13		10.09	17.55	46.70	10.16	
12.23†	54.78	25.15	57.18	B, C	1.74	9.19	64.22	3.03	
12.54†	54.46	36.55	59.06		‡0.00002	0	—	—	
12.72	54.34	39.28	46.63						

\* Plotted for invariant point.

† Plotted as one point.

‡ As determined by Kuster and Thiel (*Z. anorg. Chem.*, 1903, **33**, 139), Abegg and Cox (*Z. physikal. Chem.*, 1903, **46**, 11), and Masaki (*Bull. Chem. Soc. Japan*, 1930, **5**, 345).

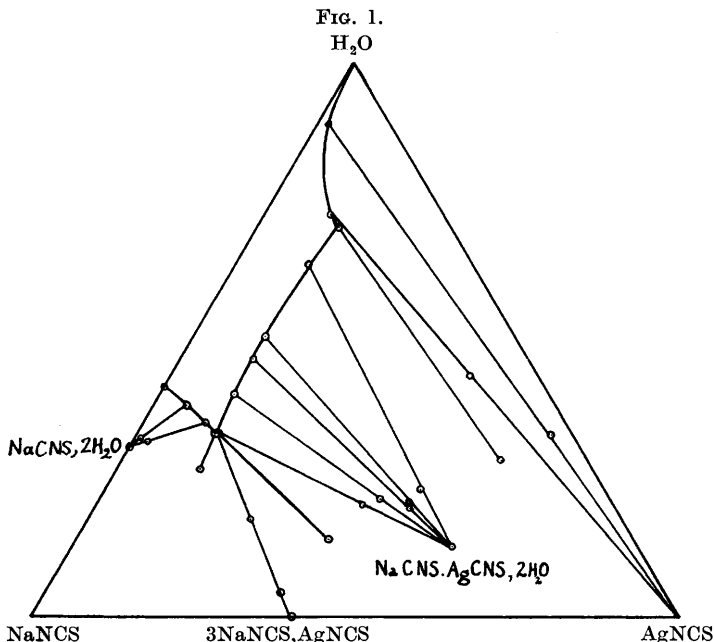
A =  $NaNCS, 2H_2O$ ; B =  $3NaNCS, AgNCS$ ; C =  $NaNCS, AgNCS, 2H_2O$ ;

D =  $AgNCS$ .

These results are represented graphically in Figs. 1 and 1a, which indicate that the double salt  $3NaNCS, AgNCS$ , the short solubility curve of which is shown better in Fig. 1a, and the hydrated double salt  $NaNCS, AgNCS, 2H_2O$  appear in this system at  $25^\circ$ . The former exists over a very small area, only separating from satd. solutions containing from 12.21 to 12.72%  $AgNCS$  and 54.80 to 54.34%  $NaNCS$ , whilst the area of existence of the second double salt is wide: with satd. solutions containing 54.34—17.24%  $NaNCS$ , in which the concn. of  $AgNCS$  varies only from 12.72 to 11.06 to 12.61%. In order to make quite certain that the double salt  $3NaNCS, AgNCS$  was a stable solid phase at  $25^\circ$ , mixtures in which it appeared to be the stable solid phase, as well as mixtures representing the invariant points at each end of its solubility

curve, were inoculated with  $\text{NaNCS}\cdot 2\text{H}_2\text{O}$  and with  $\text{NaNCS}\cdot\text{AgNCS}\cdot 2\text{H}_2\text{O}$  without any phase reaction taking place.

The observation (Part I) that the stable form of  $\text{NaNCS}$  at  $25^\circ$  is its dihydrate has been confirmed. Additional evidence in support of this fact has been obtained by measuring the rate of dehydration of the dihydrate at  $25^\circ$ ,



using fused  $\text{CaCl}_2$  or conc.  $\text{H}_2\text{SO}_4$  as the drying agent. The results of two such expts. are given below.

*Fused calcium chloride as drying agent.*

Rate of loss of $\text{H}_2\text{O}$ (mg./23 hrs.) .....	59.3	77.5	75.5	74.8	72.4	71.8	45.8
$\text{H}_2\text{O}$ , %, in material	30.85	28.03	23.97	19.57	14.67	9.32	3.30

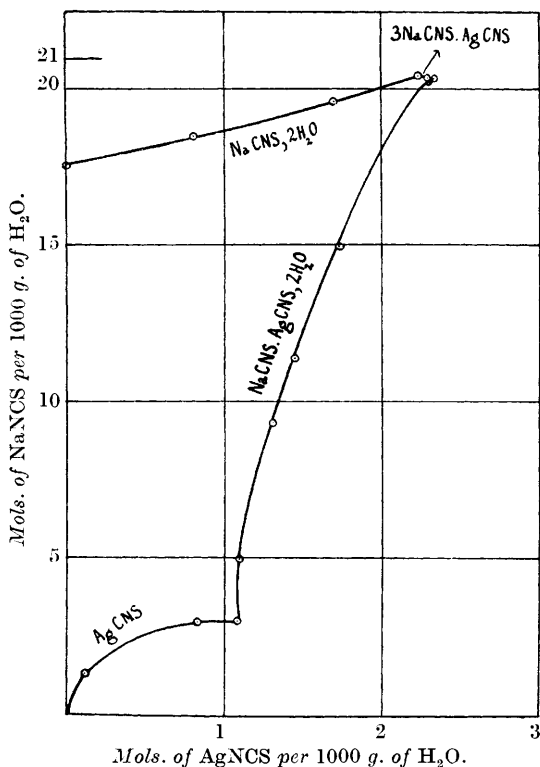
*Concentrated sulphuric acid as drying agent.*

Rate of loss of $\text{H}_2\text{O}$ (mg./6 hrs.) .....	19.8	20.5	21.4	19.6	19.6	20.8	20.3
$\text{H}_2\text{O}$ , %, in material	31.12	29.73	28.37	26.74	25.19	23.56	21.74
Rate of loss of $\text{H}_2\text{O}$ (mg./6 hrs.) .....	21.2	21.6	21.4	20.2	20.0	18.4	19.2
$\text{H}_2\text{O}$ , %, in material	20.16	18.15	16.29	14.04	11.81	9.50	7.25
Rate of loss of $\text{H}_2\text{O}$ (mg./6 hrs.) .....	19.7	14.9	2.0				
$\text{H}_2\text{O}$ , %, in material	5.00	2.34	0.23				

As dehydration always took place at the existing barometric press., variations in the latter have affected the results, but when these are plotted no indication is given of the existence of a lower hydrate at  $25^\circ$ . (The results given above have been corrected for an unavoidable slight gain in wt. which occurred when the  $\text{NaNCS}$  had to stand over the week-end.)

The double salt  $\text{NaNCS}, \text{AgNCS}, 2\text{H}_2\text{O}$  separated as ill-defined colourless plates, which are either monoclinic or triclinic;  $n$  1.65—1.66.

FIG. 1a.



The other double salt,  $3\text{NaNCS}, \text{AgNCS}$ , was not examined further.

*System  $\text{AgNCS}-\text{KNCS}-\text{H}_2\text{O}$ .*

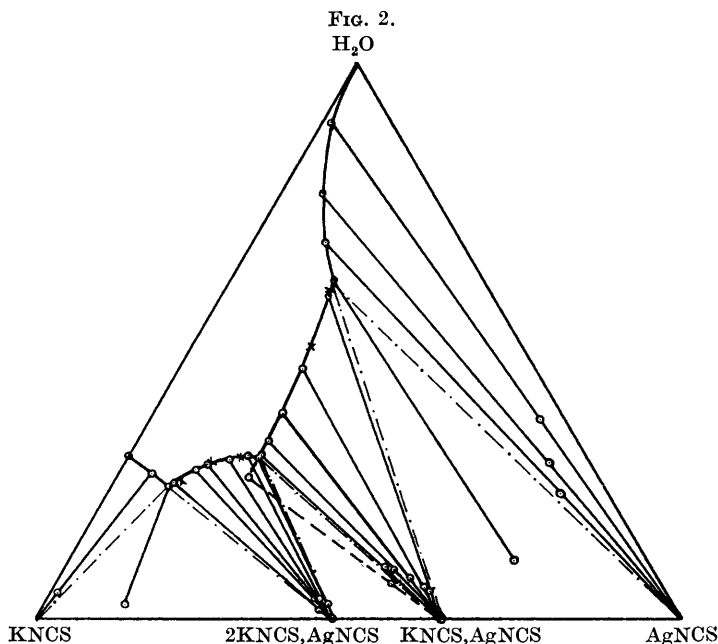
Solutions.		Moist solids.		Solid phase.	Solutions.		Moist solids.		Solid phase.
AgNCS.	KNCS.	AgNCS.	KNCS.		AgNCS.	KNCS.	AgNCS.	KNCS.	
0	70.89	—	—	A	20.56*	54.09	51.95	41.51	B
5.12	68.77	0.97	94.26		20.58	50.01	49.49	41.13	
9.19	66.88	12.73	84.72	A, B	20.28	47.72	51.11	40.07	C
9.22	66.31	43.40	55.09	20.04	43.02	54.44	38.15		
11.78	61.39	41.45	54.96	B	19.24	35.88	57.42	36.81	C, D
13.06	59.29	42.61	54.12		16.68	25.40	58.89	36.20	
16.12	55.21	42.44	54.17	16.10	23.15	69.13	20.28	D	
18.74	52.13	42.78	54.28	11.39	20.98	69.90	7.40		
20.57	50.53	44.22	53.02	6.69	16.97	65.79	6.01	D	
				1.29	9.67	60.27	3.78		
				0.00002	0	—	—		

\* Metastable.

A = KNCS; B =  $2\text{KNCS}, \text{AgNCS}$ ; C =  $\text{KNCS}, \text{AgNCS}$ ; D = AgNCS.

These results are plotted in Fig. 2, which shows the double salts  $\text{KNCS}, \text{AgNCS}$  and  $2\text{KNCS}, \text{AgNCS}$  to exist at  $25^\circ$ . As many as possible of the results given

by Foote (*loc. cit.*) for this system are also shown on the diagram; the results now obtained confirm his observations. Foote found the double salt  $3\text{KNCS}, \text{AgNCS}$ , prepared by Wells and Merrian (*loc. cit.*), to be unstable at  $25^\circ$ . In the present work, in only one case, where no great care was taken over the temp. of prepn. of the mixture and with a shorter shaking period than was usually employed, a mixture in which the solid phase was this double salt was obtained, but this proved to be metastable. It will also be noted that the solubility curve of the double salt  $\text{KNCS}, \text{AgNCS}$  is concave to the  $\text{H}_2\text{O}$  apex of the triangle, a type of solubility curve which is very rare in three-component aq. systems. The salt  $\text{KNCS}, \text{AgNCS}$  separated as colourless plates which



× Foote. ○ Author. ---- Boundaries of solid phase areas as given by Foote.

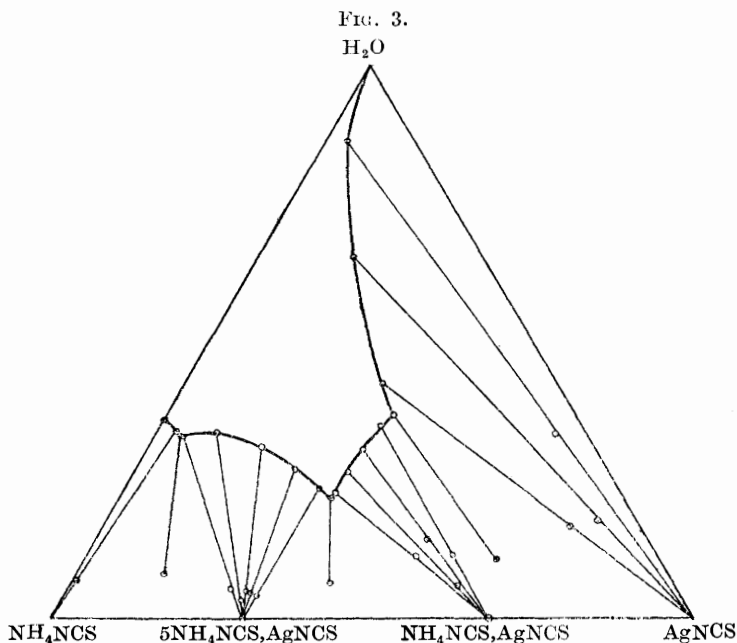
may be orthorhombic, though no very definite figure could be obtained under the microscope;  $n > 1.748$ . The compound  $2\text{KNCS}, \text{AgNCS}$  crystallised as colourless prisms;  $n 1.67-1.68$ .

*System*  $\text{AgNCS}-\text{NH}_4\text{NCS}-\text{H}_2\text{O}$ .

Solutions.		Moist solids.		Solid phase.	Solutions.		Moist solids.		Solid phase.
AgNCS.	$\text{NH}_4\text{NCS}$	AgNCS.	$\text{NH}_4\text{NCS}$ .		AgNCS.	$\text{NH}_4\text{NCS}$ .	AgNCS.	$\text{NH}_4\text{NCS}$ .	
0	64.33	—	—	A	33.14	44.27	51.44	37.18	C
3.19	63.37	0.84	92.43		33.29	40.25	60.34	33.65	
4.48	62.87	13.97	78.30	A, B	33.44	36.04	51.66	34.17	C, D
4.51	62.70	25.66	69.18	B	34.10	31.10	57.02	31.58	
9.46	57.07	28.18	68.48		35.09	28.19	64.19	25.02	D
17.16	51.42	28.13	66.97	30.88	26.86	72.51	10.81		
24.80	48.22	29.13	66.28	14.92	19.57	76.35	6.04	D	
30.38	46.18	30.30	65.69	3.19	10.66	62.19	4.61		
33.18	45.13	43.51	50.03	B, C	0.00002	0	—	—	

A =  $\text{NH}_4\text{NCS}$ ; B =  $5\text{NH}_4\text{NCS}, \text{AgNCS}$ ; C =  $\text{NH}_4\text{NCS}, \text{AgNCS}$ ; D =  $\text{AgNCS}$ .

These results when plotted (Fig. 3) indicate the existence, at 25°, of the two double salts  $\text{NH}_4\text{NCS}, \text{AgNCS}$  and  $5\text{NH}_4\text{NCS}, \text{AgNCS}$  and that a congruent point occurs on the solubility curve of the latter salt. Both these salts, as prepared by Cernatescu (*loc. cit.*), are described (*Chem. Abs.*, 1921, **15**, 1262) as well-formed cryst. compounds which are decomp. by much  $\text{H}_2\text{O}$ , whilst the addition of  $\text{BaCl}_2$  aq. to their aq. solutions gave no ppt. of  $\text{AgCl}$ . This observation has been confirmed with the double salt  $5\text{NH}_4\text{NCS}, \text{AgNCS}$ , but from Fig. 3 it will be seen that as addition of  $\text{H}_2\text{O}$  to the compound  $\text{NH}_4\text{NCS}, \text{AgNCS}$  results in the formation of  $\text{AgNCS}$  in the solid phase, it is not possible to prep. an aq. solution of this double salt.



The salt  $\text{NH}_4\text{NCS}, \text{AgNCS}$  was formed as colourless needles which are probably orthorhombic;  $n > 1.66$ .  $5\text{NH}_4\text{NCS}, \text{AgNCS}$  crystallised as colourless plates which under the microscope appeared to be tetragonal;  $n$  1.67—1.675.

The triangular diagrams show clearly that the effect of the thiocyanates in increasing the solubility of  $\text{AgNCS}$  decreases in the order  $\text{NH}_4 > \text{K} > \text{Na}$ .

#### *Summary.*

The three ternary aqueous systems containing silver thiocyanate and the thiocyanate of either sodium, potassium, or ammonium have been investigated at 25°.

The double salts  $3\text{NaNCS}, \text{AgNCS}$ ,  $\text{NaNCS}, \text{AgNCS}, 2\text{H}_2\text{O}$ ,  $\text{KNCS}, \text{AgNCS}$ ,  $2\text{KNCS}, \text{AgNCS}$ ,  $\text{NH}_4\text{NCS}, \text{AgNCS}$ , and

$5\text{NH}_4\text{NCS}$ ,  $\text{AgNCS}$  have been found to exist at this temperature, but of these only the last is stable in contact with its saturated solution.

The solubility curve of  $3\text{NaNCS}$ ,  $\text{AgNCS}$  is very short, whilst that of  $\text{KNCS}$ ,  $\text{AgNCS}$  is concave to the water apex.

These double salts are all definitely crystalline and colourless and have refractive indices between 1.65 and 1.75.

In increasing the solubility of silver thiocyanate, the ammonium salt has the greatest and the sodium salt the least effect. The dehydration of sodium thiocyanate dihydrate has been studied at  $25^\circ$ , and no indication of the existence of a lower hydrate at this temperature has been obtained.

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