351. *Phase-rule Studies on Metallic Thiocyanates. Part II. The Systems* $AgNCS–NaNCS–H_2O$, $AgNCS–KNCS–H_2O$, *and* $AgNCS–NH_4NCS–H_2O$ *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 Merrian, *Amer. Chem. J.*, 1902, **28**, 265), and NH_4NCS,AgNCS and $5NH_4NCS$,AgNCS (Cernatescu, *loc. cit.*). The compounds described by Cernatescu and by Wells and Merrian 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 $AgNCS–KNCS–H_2O$ 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_4NCS 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_4NCS aq. and the solution filtered; large dilution with H_2O pptd. the Ag salt, which was washed by decantation with H_2O until free from thiocyanate, collected, again washed with H_2O, 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_2O 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.
AgNCS	NaNCS.	AgNCS.	NaNCS.	
0	58·78	—	—	A
5·09	56·94	0·97	66·86	
9·80	55·42	2·22	66·28	
12·11	54·76	5·06	64·22	A, B
12·14	54·55	19·71	62·69	
12·17	54·73	30·24	60·30	
12·21*	54·80	13·09	60·13	
12·23†	54·78	25·15	57·18	B
12·54†	54·46	36·55	59·06	
12·72	54·34	39·28	46·63	B, C
12·68	54·36	41·78	37·92	C
11·53	48·51	43·74	35·06	
11·21	42·49	48·96	31·37	
11·14	38·31	48·19	30·96	
11·06	25·42	48·87	28·28	
12·61	17·24	58·80	13·10	C, D
10·09	17·55	46·70	10·16	D
1·74	9·19	64·22	3·03	
‡0·00002	0	—	—	

* Plotted for invariant point. † Plotted as one point.

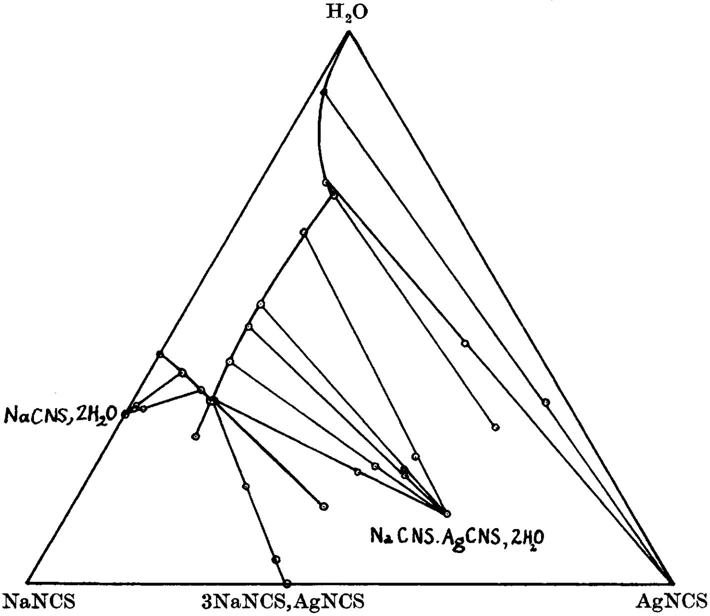
‡ As determined by Kuster and Thiel (*Z. anorg. Chem.*, 1903, **33**, 139), Abegg and Cox (*Z. physikal. Chem.*, 1903, **46**, 11), and Masaki (*Bull. Chem. Soc. Japan*, 1930, **5**, 345).

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

These results are represented graphically in Figs. 1 and 1*a*, which indicate that the double salt 3NaNCS,AgNCS, the short solubility curve of which is shown better in Fig. 1*a*, and the hydrated double salt NaNCS,AgNCS,$2H_2O$ appear in this system at 25°. 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°, 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 $NaNCS,2H_2O$ and with $NaNCS,AgNCS,2H_2O$ without any phase reaction taking place.

The observation (Part I) that the stable form of NaNCS at 25° 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°, using fused $CaCl_2$ or conc. H_2SO_4 as the drying agent. The results of two such expts. are given below.

FIG. 1.



Fused calcium chloride as drying agent.

Rate of loss of H_2O (mg./23 hrs.)	59·3	77·5	75·5	74·8	72·4	71·8	45·8
H_2O, %, in material	30·85	28·03	23·97	19·57	14·67	9·32	3·30

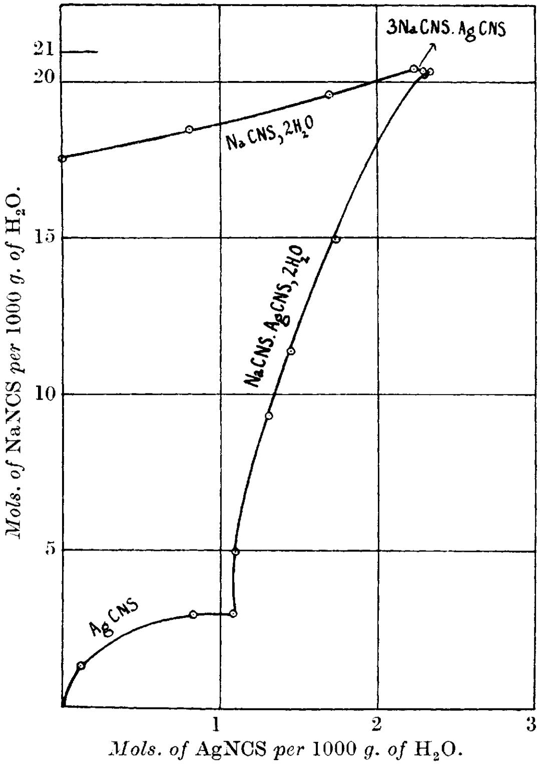
Concentrated sulphuric acid as drying agent.

Rate of loss of H_2O (mg./6 hrs.)	19·8	20·5	21·4	19·6	19·6	20·8	20·3
H_2O, %, in material	31·12	29·73	28·37	26·74	25·19	23·56	21·74
Rate of loss of H_2O (mg./6 hrs.)	21·2	21·6	21·4	20·2	20·0	18·4	19·2
H_2O, %, in material	20·16	18·15	16·29	14·04	11·81	9·50	7·25
Rate of loss of H_2O (mg./6 hrs.)	19·7	14·9	2·0				
H_2O, %, 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°. (The results given above have been corrected for an unavoidable slight gain in wt. which occurred when the NaNCS had to stand over the week-end.)

The double salt NaNCS,AgNCS,$2H_2O$ separated as ill-defined colourless plates, which are either monoclinic or triclinic; *n* 1·65—1·66.

FIG. 1*a*.



The other double salt, 3NaNCS,AgNCS, was not examined further.

System AgNCS–KNCS–H_2O.

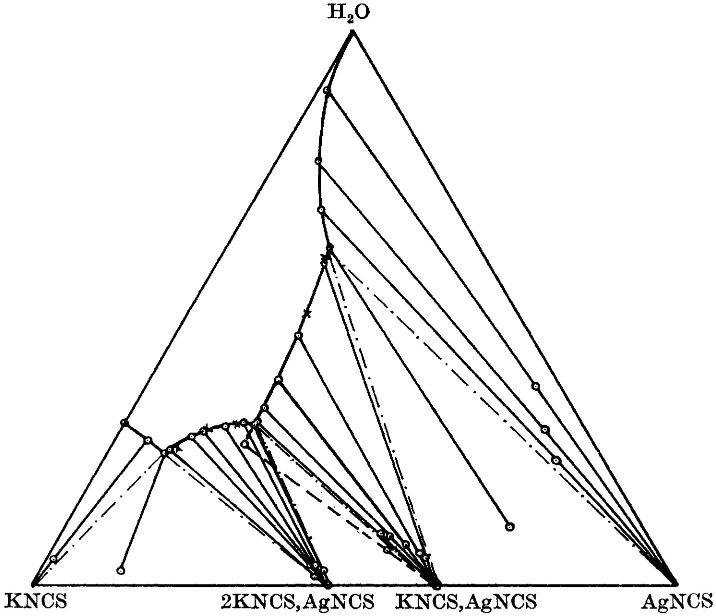
Solutions.		Moist solids.		Solid phase.
AgNCS.	KNCS.	AgNCS.	KNCS.	
0	70·89	—	—	A
5·12	68·77	0·97	94·26	
9·19	66·88	12·73	84·72	A, B
9·22	66·31	43·40	55·09	B
11·78	61·39	41·45	54·96	
13·06	59·29	42·61	54·12	
16·12	55·21	42·44	54·17	
18·74	52·13	42·78	54·28	
20·57	50·53	44·22	53·02	
20·56*	54·09	51·95	41·51	C
20·58	50·01	49·49	41·13	
20·28	47·72	51·11	40·07	
20·04	43·02	54·44	38·15	
19·24	35·88	57·42	36·81	
16·68	25·40	58·89	36·20	
16·10	23·15	69·13	20·28	C, D
11·39	20·98	69·90	7·40	D
6·69	16·97	65·79	6·01	
1·29	9·67	60·27	3·78	
0·00002	0	—	—	

* Metastable.

A = KNCS; B = 2KNCS,AgNCS; C = KNCS,AgNCS; D = AgNCS.

These results are plotted in Fig. 2, which shows the double salts KNCS,AgNCS and 2KNCS,AgNCS to exist at 25°. 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 3KNCS,AgNCS, prepared by Wells and Merrian (*loc. cit.*), to be unstable at 25°. 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 KNCS,AgNCS is concave to the H_2O apex of the triangle, a type of solubility curve which is very rare in three-component aq. systems. The salt KNCS,AgNCS separated as colourless plates which may be orthorhombic, though no very definite figure could be obtained under the microscope; $n > 1{\cdot}748$. The compound 2KNCS,AgNCS crystallised as colourless prisms; n 1·67—1·68.

FIG. 2.



× *Foote.* ⊙ *Author.* —·—·— *Boundaries of solid phase areas as given by Foote.*

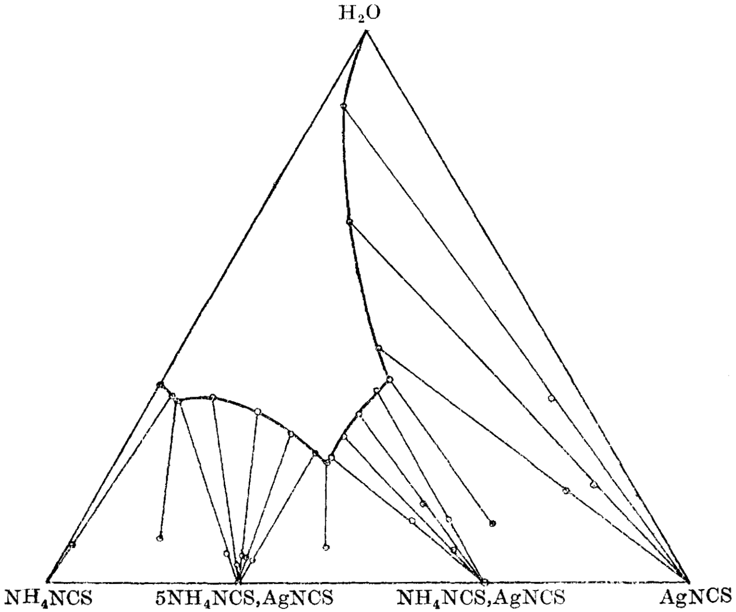
System $AgNCS{-}NH_4NCS{-}H_2O$.

Solutions.		Moist solids.		Solid phase.
AgNCS.	NH_4NCS	AgNCS.	NH NCS.	
0	64·33	—	—	A
3·19	63·37	0·84	92·43	
4·48	62·87	13·97	78·30	A, B
4·51	62·70	25·66	69·18	B
9·46	57·07	28·18	68·48	
17·16	51·42	28·13	66·97	
24·80	48·22	29·13	66·28	
30·38	46·18	30·30	65·69	
33·18	45·13	43·51	50·03	B, C
33·14	44·27	51·44	37·18	C
33·29	40·25	60·34	33·65	
33·44	36·04	51·66	34·17	
34·10	31·10	57·02	31·58	
35·09	28·19	64·19	25·02	C, D
30·88	26·86	72·51	10·81	D
14·92	19·57	76·35	6·04	
3·19	10·66	62·19	4·61	
0·00002	0	—	—	

A = NH_4NCS; B = $5NH_4NCS,AgNCS$; C = $NH_4NCS,AgNCS$; D = AgNCS.

These results when plotted (Fig. 3) indicate the existence, at 25°, of the two double salts $NH_4NCS,AgNCS$ and $5NH_4NCS,AgNCS$ 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 H_2O, whilst the addition of $BaCl_2$ aq. to their aq. solutions gave no ppt. of AgCl. This observation has been confirmed with the double salt $5NH_4NCS,AgNCS$, but from Fig. 3 it will be seen that as addition of H_2O to the compound $NH_4NCS,AgNCS$ results in the formation of AgNCS in the solid phase, it is not possible to prep. an aq. solution of this double salt.

FIG. 3.



The salt $NH_4NCS,AgNCS$ was formed as colourless needles which are probably orthorhombic; $n > 1{\cdot}66$. $5NH_4NCS,AgNCS$ 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 AgNCS decreases in the order $NH_4 > K > Na$.

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 $3NaNCS,AgNCS$, $NaNCS,AgNCS,2H_2O$, $KNCS,AgNCS$, $2KNCS,AgNCS$, $NH_4NCS,AgNCS$, and

$5NH_4NCS,AgNCS$ 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 $3NaNCS,AgNCS$ is very short, whilst that of $KNCS,AgNCS$ 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°, and no indication of the existence of a lower hydrate at this temperature has been obtained.

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