416. *Phase-rule Studies on Metallic Thiocyanates. Part III. The Systems* $Ba(NCS)_2$–NH_4NCS–H_2O *and* $Ba(NCS)_2$–$AgNCS$–H_2O *at* 25°.

By VINCENT J. OCCLESHAW.

THESE systems, which have not previously been investigated, have been studied for comparison respectively with those containing barium and silver thiocyanates (Parts I and II; J., 1931, 55; 1932, 2404). No double salt between the first pair of thiocyanates is recorded in the literature, but Wells and Merrian (*Amer. Chem. J.*, 1902, **28**, 265) prepared $Ba(NCS)_2,2AgNCS,2H_2O$ by dissolving silver thiocyanate in a concentrated aqueous solution of the barium salt. The existence of new *double salts* $Ba(NCS)_2,NH_4NCS,H_2O$; $Ba(NCS)_2,AgNCS,2H_2O$; $Ba(NCS)_2,3AgNCS,2H_2O$ is now demonstrated.

Barium thiocyanate was purified by recrystallisation as described in Part I, the silver salt was obtained and purified as detailed in Part II, and the ammonium salt, an " A.R." product, was used without further purification.

The various mixtures were made as described in Parts I and II (*locc. cit.*), but as most of the solutions, other than those with which silver thiocyanate was in equilibrium, were very concentrated and viscous, the mixtures were rotated, for periods varying up to 7 days, in a thermostat regulated at 25° ± 0·05°. Also, since the systems under examination readily form metastable mixtures, inoculation with the appropriate equilibrium solid phases had to be resorted to in order to ensure the attainment of stable equilibrium. Those mixtures in which silver thiocyanate was the solid phase were treated as described in Part II.

To analyse the system containing ammonium thiocyanate the weighed amounts of solution and moist solid withdrawn were made up to convenient volumes, and in aliquot portions

barium was determined as sulphate, and total thiocyanate gravimetrically as the silver salt. From these results the percentages of barium and ammonium thiocyanates could be obtained. With the system containing silver thiocyanate two samples of solution and moist solid were withdrawn; in one, total thiocyanate was determined as above, and in the other barium thiocyanate was determined by Volhard's method, the silver nitrate solution used having been standardised gravimetrically as silver chloride. The amount of silver thiocyanate was then obtained by difference. All results are expressed as g. per 100 g. of solution or moist solid.

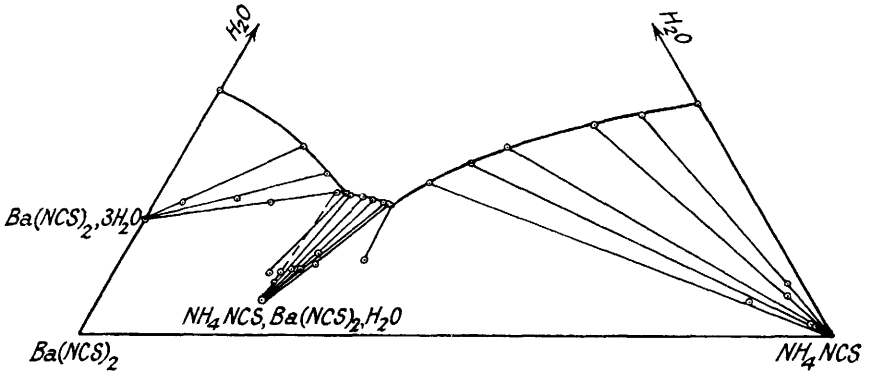
System $Ba(NCS)_2$–NH_4NCS–H_2O.

Solutions.		Moist solids.		Solid phase.	Solutions.		Moist solids.		Solid phase.
NH_4NCS.	$Ba(NCS)_2$.	NH_4NCS.	$Ba(NCS)_2$.		NH_4NCS.	$Ba(NCS)_2$.	NH_4NCS.	$Ba(NCS)_2$.	
64·33	—	—	—	A	26·73	52·36	23·59	65·89	B
57·72	8·38	89·93	1·96		25·64	53·37	22·16	69·85	
52·36	15·31	90·55	2·90		*m* 23·53	54·61	22·11	68·36	B and C
42·72	28·88	96·45	1·61		24·69	53·65	20·84	69·87	
38·95	34·60	95·94	1·95		24·70	53·47	15·59	64·27	C
34·73	41·66	85·96	8·53		20·75	54·51	10·89	68·25	
31·85	48·33	38·47	50·10	A and B	15·48	55·51	3·71	76·03	
31·52	48·43	26·22	62·96	B	0	62·61	—	—	A
31·00	48·52	23·83	67·82		*m* 32·19	48·05	67·19	23·53	
30·78	48·96	25·52	62·16		*m* 29·90	52·12	75·16	17·38	A and C
29·64	49·68	24·11	65·67		*m* 29·76	52·54	27·61	60·06	
29·52	49·76	25·42	62·98		*m* 28·47	54·08	16·78	65·80	C
28·85	50·36	23·80	66·25		*m* 35·83	53·67	9·46	73·24	
27·41	51·63	23·34	66·58		*m* 25·28	53·57	8·21	72·59	

A = NH_4NCS; B = $Ba(NCS)_2,NH_4NCS,H_2O$; C = $Ba(NCS)_2,3H_2O$. *m* = Metastable.

Fig. 1 shows the isotherm obtained by plotting the results for the mixtures in stable equilibrium on a triangular diagram, but not all results given for the double salt have been

FIG. 1.



incorporated. This isotherm includes the solubility curve of a new hydrated *compound* $Ba(NCS)_2,NH_4NCS,H_2O$, which separates only from solutions containing 31·85—24·69% of ammonium thiocyanate and 48·33—53·65% respectively of the barium salt. Crystals of this substance have rather a prismatic habit with the length about twice the breadth; the terminations show two faces, one of which is considerably larger than the other. They are anisotropic, the extinction with the length of the crystals being 18°, and biaxial, appearing to be monoclinic and having a refractive index > 1·65. In cold, dry weather this double salt can be air-dried [Found: NCS, 49·83; $Ba(NCS)_2$, 73·16; NH_4NCS, 21·34. $Ba(NCS)_2,NH_4NCS,H_2O$ requires NCS, 50·10; $Ba(NCS)_2$, 72·93; NH_4NCS, 21·90%].

So strong is the tendency for mixtures in this system to attain metastable equilibrium that it has been possible to trace the solubility curves of the two simple salts to their intersection in a metastable invariant point. In addition, metastable conditions were obtained in one instance where the solid phase was the hydrated double salt and the saturated solution contained 23·53% of ammonium thiocyanate with 54·61% of the barium salt.

Although the separate solubilities of ammonium and barium thiocyanates at 25° have

almost identical values, these two salts do not conform with Kuklin's theorem (*J. Russ. Phys. Chem. Soc.*, **1929**, **61**, 667) : at mutual saturation, a condition which is really metastable, their solubilities are not proportional to their separate solubilities. The ratio of the latter is 1·028, the ammonium salt having the greater solubility, whereas at mutual saturation the ratio is 0·567.

System $Ba(NCS)_2$–AgNCS–H_2O.

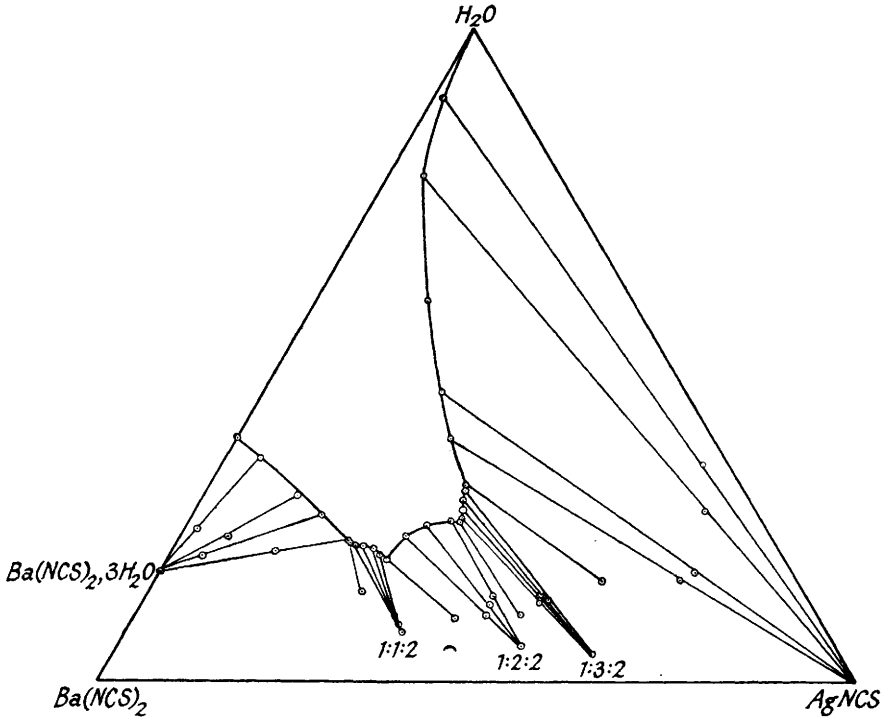
Solutions.		Moist solids.			Solutions.		Moist solids.		
$Ba(NCS)_2$.	AgNCS.	$Ba(NCS)_2$.	AgNCS.	Solid phase.	$Ba(NCS)_2$.	AgNCS.	$Ba(NCS)_2$.	AgNCS.	Solid phase.
62·61	0	—	—		39·54	35·79	38·80	49·78	1 : 2 : 2; 1 : 3 : 2
61·39	4·29	74·87	1·60		39·02	35·79	35·19	52·59	
58·91	12·58	71·31	6·26	A	38·41	35·13	34·92	51·90	
57·36	17·04	76·19	4·20		37·49	34·58	34·62	52·13	1 : 3 : 2
55·99	22·58	66·36	13·63		37·13	34·28	34·59	51·19	
55·91	22·98	57·92	28·09	A; 1 : 1 : 2	36·78	34·01	34·00	53·51	
55·20	23·91	55·42	36·48		36·04	33·79	25·44	58·87	1 : 3 : 2; B
54·14	25·01	55·60	34·25	1 : 1 : 2	34·50	27·99	15·04	69·13	
53·23	26·35	55·31	36·67		32·20	23·24	12·86	70·15	
52·61	27·89	55·73	35·53		27·00	14·67	—	—	B
52·01	29·17	47·52	42·57	1 : 1 : 2; 1 : 2 : 2	18·18	4·47	6·58	67·14	
47·74	29·81	43·32	46·40		9·68	0·75	3·28	63·42	
44·28	31·67	41·97	45·97	1 : 2 : 2	0	* 0·00002	—	—	
40·61	34·70	40·65	45·83						

A = $Ba(NCS)_2,3H_2O$; B = AgNCS; 1 : 1 : 2 = $Ba(NCS)_2$,AgNCS,$2H_2O$; 1 : 2 : 2 = $Ba(NCS)_2$,$2AgNCS,2H_2O$; 1 : 3 : 2 = $Ba(NCS)_2$,$3AgNCS,2H_2O$.

* Determined by Masaki (*Bull. Chem. Soc. Japan*, 1930, **5**, 345).

By plotting the above results, Fig. 2 is obtained; it indicates the existence of the three double salts denoted above as 1 : 1 : 2, 1 : 2 : 2, and 1 : 3 : 2 in this system at 25°. For the

FIG. 2.



last compound, which has a high molecular weight compared with its water content, the points representing the di- and the mono-hydrate lie very close together in Fig. 2, but on a larger scale it is clearly seen that the tie lines indicate the existence of the dihydrate rather than

any other. These salts exist in equilibrium with saturated solutions containing respectively 55·91—52·01% $Ba(NCS)_2$ with 22·98—29·17% AgNCS; 52·01—39·54% $Ba(NCS)_2$ with 29·17—35·79% AgNCS; and 39·54—36·04% $Ba(NCS)_2$ with 35·79—33·79% AgNCS. Thus the area of existence of the 1 : 2 : 2 salt is larger than that of either of the other two. No congruent point occurs on the solubility curve of any of these double salts.

All three double salts are colourless and characteristically crystalline. The 1 : 1 : 2 salt separates as square plates with the edges and corners truncated; the crystals are anisotropic and show extinction straight with edge; also they are biaxial and the optical properties suggest that they are monoclinic rather than orthorhombic as their habit suggests. The refractive index is $> 1{\cdot}65$.

Crystals of the 1 : 2 : 2 salt are prismatic, the length being about three times the breadth. They are anisotropic and show extinction straight with a long edge. In addition, they are biaxial and either monoclinic or triclinic. Their refractive index is $> 1{\cdot}73$.

The 1 : 3 : 2 salt crystallises as flat, nearly rectangular plates, with the shorter edge inclined at an angle of 96° to the longer. All four angles are cut off by smaller sides, those cutting the acute angles being better developed than the other two. The crystals are anisotropic, the extinction angle with the longer edge being about 9°. They are biaxial and appear to be monoclinic. The refractive index is $> 1{\cdot}65$. On filtration, the crystals felt together to form a scintillating solid.

Each of these double salts can be air-dried in cold dry weather but is deliquescent above about 15°. After being air-dried, a sample of the 1 : 2 : 2 salt gave NCS, 37·66; $Ba(NCS)_2$, 40·65; AgNCS, 54·41% [Calc.: NCS, 37·39; $Ba(NCS)_2$, 40·81; AgNCS, 53·39%].

Like the double salts containing silver thiocyanate (Part II), the above compounds are stable to light. As they react almost immediately with methylene iodide, the determination of their refractive indices is difficult.

Summary.

The new double salts $Ba(NCS)_2,NH_4NCS,H_2O$, $Ba(NCS)_2,AgNCS,2H_2O$, and $Ba(NCS)_2,3AgNCS,2H_2O$ have been found to occur, and the existence of $Ba(NCS)_2,2AgNCS,2H_2O$ has been confirmed. They all decompose on attempted recrystallisation from water.

These double salts, all of which have refractive indices greater than 1·65, are anisotropic and biaxial, with optical properties that suggest they are monoclinic.

The double salts containing silver thiocyanate are stable to light.

The solubility curves of ammonium thiocyanate and barium thiocyanate trihydrate have been traced to their intersection in a metastable invariant point, but the data obtained do not conform with Kuklin's theorem.

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