107. *The Solubility of Silver Thiocyanate in Aqueous Ammonia.*

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GINTL (*Ber. Wien. Akad.*, 1869, **60**, 474), by dissolving silver thiocyanate in warm aqueous ammonia, isolated the compound $AgCNS,NH_3$ (compare also Weith, *Z. Chem.*, 1869, 381; Gössmann, *Annalen*, 1856, **100**, 76), described as glistening plates which rapidly lost ammonia on exposure to air. Apart from the four approximate determinations of Abegg and Cox (*Z. physikal. Chem.*, 1903, **46**, 1), however, no measurements of the solubility of silver thiocyanate in aqueous ammonia appear to have been made. The solubility isotherm at 25° has therefore been determined over a wide range of ammonia concentrations from N upwards, and the compositions of the solid phases, evident from Fig. 1, have been investigated.

EXPERIMENTAL.

Materials.—Silver thiocyanate, prepared by precipitation from ammonium thiocyanate and silver nitrate (A. R.), was freed from any possible contamination with chloride by employing excess of thiocyanate and digesting the precipitate with the mother-liquor. It was then thoroughly washed, and in some experiments dried at 110°, whilst in others it was used in the moist condition. No difference of final solubility was ever observed corresponding to this difference in treatment, though the dried samples came to equilibrium more slowly and frequently gave, at first, metastable points on the prolongation of the silver thiocyanate curve in regions where the stable solid is a compound with ammonia. In all these cases the solubility decreased steadily, on continued stirring, to the normal value.

Solubility Measurements.—Method. Ammonia solution and silver thiocyanate were placed in a flask having two necks, one of which was closed by a bung until required for sampling, while the other carried an electrically driven stirrer mounted in a liquid seal. Heavy paraffin was used as sealing liquid, since with mercury, which was tried at first, contamination of the solution sometimes occurred. The flask was mounted in a thermostat maintained at $25\cdot00° \pm 0\cdot01°$ (for details of thermostat, see Hume, *J. Opt. Soc. Amer.*, 1929, **19**, 158), and the mixture was stirred violently for some hours before each analysis.

Sampling was carried out as follows. A small flask, fitted with a bung and stopcock, was weighed and then partially evacuated. It was connected through a small sintered-glass filter to a sampling

tube which was introduced into the solubility flask. By opening the stopcock, a suitable quantity of the solution could be drawn into the flask. The tube and filter were now disconnected, the stopcock opened momentarily to admit air up to atmospheric pressure, and the flask and its contents weighed. Before use, the connecting tube and filter were warmed to the thermostat temperature, and the suspended solid in the solubility flask allowed to settle, thus guarding against clogging the filter and allowing rapid sampling. This minimised the risk of error due either to cooling of the solution or to the evaporation of ammonia from it. As a check, samples were occasionally taken from the supernatant clear liquid without use of the filter, and these gave results in agreement with those obtained by the ordinary method.

The samples were titrated with standard nitric acid, bromophenol-blue being used as indicator, and the precipitated thiocyanate was collected on a Gooch crucible, washed, dried at 110° (the most satisfactory temperature according to van Name, *Amer. J. Sci.*, 1900, **10**, 451), and weighed. With the more concentrated solutions it was necessary to guard against loss of ammonia during the titration. This was effected by attaching a funnel to the sampling flask, and running into it a suitable quantity of the standard acid. On opening the stopcock, the absorption of ammonia vapour produced a sufficient reduction of pressure to draw the acid into the flask without the possibility of loss of ammonia. In this way the bulk of the ammonia was neutralised, and the titration could be completed in the usual manner.

Results. Each solution was analysed several times with intervals of stirring, and each result quoted is the mean of at least two final concordant analyses. The ammonia concentrations were reproducible to 0·2%, the silver thiocyanate concentrations to 0·3%. The results are collected in Table I, concentrations of both substances being expressed in g.-mols. per 1000 g. of solution.

TABLE I.

Solid phase.	$[NH_3]$.	$[AgCNS]$ × 10^3.	Solid phase.	$[NH_3]$.	$[AgCNS]$ × 10^3.
AgCNS	1·026	5·17	AgCNS,NH$_3$	3·684	19·91
	1·587	8·54		3·767	20·31
	1·840	10·01		4·335	22·84
	2·178	12·34		4·504	23·41
	2·276	12·92		5·27	27·24
AgCNS,½NH$_3$,½H$_2$O (?)	2·440	13·76		5·36	27·71
	2·581	14·54		6·60	34·89
	2·848	15·90		7·35	39·66
	2·915	16·35		7·47	40·62
	3·049	17·34		8·94	51·8
AgCNS,NH$_3$	3·217	17·80		9·91	62·0
	3·325	18·42		11·36	79·1
				14·69	159·6

A plot of the two variables shows " breaks " at concentrations of ammonia very near the two points $[NH_3] = 2 \cdot 276$ and $3 \cdot 049$. This is depicted in Fig. 1, which gives the curve between N and $4N$. The evidence for the compositions of the solid phases is described in the next two sections.

Solid Phases.—Experiments without reference substances. The analysis of the solid phases proved more difficult than had been anticipated. Any direct analysis was out of the question owing

FIG. 1.
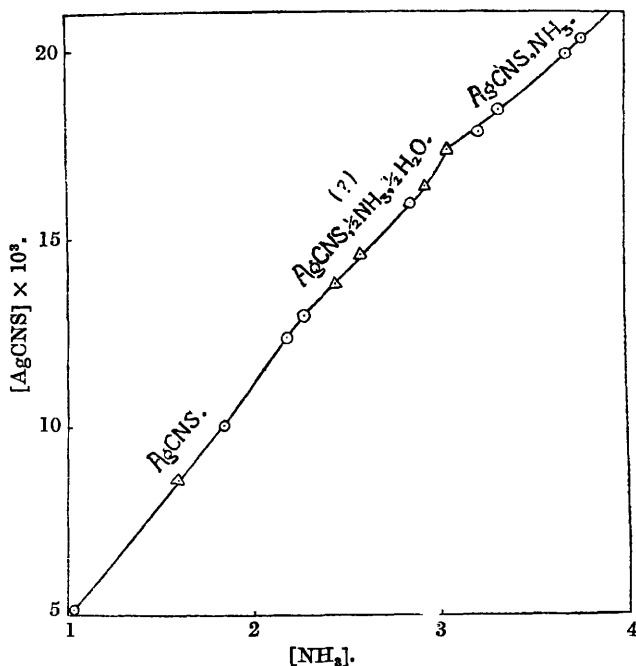
△ *Solid phase was analysed at these points.*

to the rapidity with which they decomposed on being separated from the mother-liquor, and except in the case of the phase richest in ammonia, this difficulty was enhanced by the slimy character of the suspensions obtained.

It thus became clear at an early stage that indirect methods must be adopted. A large number of rough analyses were carried out during the solubility measurements, by a method depending on the assumption that the solid phases contained no water. These were supplemented by a number of experiments involving the use of a reference substance.

The first series was carried out as follows. After equilibrium had been attained, and the composition of the solution fixed (in determining a point on the solubility curve), a sample was taken in the usual way except that the filter was omitted. A suspension of solid and solution was thus obtained, of known total weight. Matters were so arranged as to have as large a proportion of the former as possible, but in the majority of cases this was only about 10% of the whole. The total ammonia and total thiocyanate in the sample were then determined, and hence the weight of water by difference. If all the water was assumed to be present in the liquid phase (of known composition), the weights of ammonia and of silver thiocyanate present in the solid phase could be calculated. This procedure involved a considerable multiplication of errors, especially in view of the small proportion of solid phase. On the other hand, the importance of errors due to the incorrectness of the assumption that the solid contains none of the water is reduced for the same reason. The probable experimental error in the ammonia : silver thiocyanate ratio was 1—5%, and if the solid contained equal numbers of molecules of silver thiocyanate and water, an apparent value for this ratio of from 80% to 95% of the correct value would be obtained (according to the concentration of the solution).

An example will show the method of calculation :

Percentage composition of solution : NH_3, 16·92 ; AgCNS, 1·032. Hence H_2O by difference, 82·05.

Weight of sample (liquid plus solid)   ...   91·82 g.
Total ammonia.................................   14·73 ($\pm$ 0·02) g.
Total silver thiocyanate   ....   10·37 g.
Hence total water in sample ....   66·72 g.

Thus, associated with 66·72 g. of H_2O in solution we have : NH_3, 13·76 ($\pm$ 0·02) g., and AgCNS, 0·84 g. ; and the solid phase consists of : NH_3, 14·73 − 13·76 = 0·97 ($\pm$ 0·02) g. ; AgCNS, 10·37 − 0·84 = 9·53 g. The molecular ratio NH_3/AgCNS in solid = 0·99 ($\pm$ 0·02). (If the solid contains one molecule each of AgCNS, NH_3, and H_2O, calculation shows that this ratio becomes 1·22.)

These experiments gave the following results. On the highest part of the curve, ammonia : silver thiocyanate ratios of from 0·95 to 1·02 (mean 0·985) were obtained. The margin of experimental error was 1—5%, while recalculation on the assumption that the solid phase contained 1 mol. of water per mol. of silver thiocyanate gave a mean ratio of 1·10. This may be taken to imply fairly definitely that the solid phase is $AgCNS,NH_3$ and cannot contain more than a small proportion of water.

On the lowest portion of the curve the results indicated silver thiocyanate as solid phase, the amount of ammonia apparently associated with the solid being within the experimental error.

On the intermediate section the results were less definite. The $NH_3 : AgCNS$ ratios were less concordant, varying from about 0·4 to 0·49. This suggested that the solid phase consisted of $AgCNS,\frac{1}{2}NH_3,xH_2O$, where x is probably less than 1.

A further series of experiments was now undertaken with a view to obtain more accurate values of the $NH_3 : AgCNS$ ratio, and at the same time to determine experimentally the water content of the solid phases.

Experiments with reference substance. It was decided to bring to equilibrium in a closed vessel a weighed amount of pure dry silver thiocyanate and a weighed amount of an ammonia solution of previously determined composition. The solution would contain a known concentration of some suitable reference substance, and from changes in concentration of this and of the ammonia it would be possible to calculate the composition of the new solid formed. It was hoped to work with about equal weights of solid and solution, and thus to reduce the multiplication of errors (due to determination as difference) to a factor of about 2. This, however, proved impracticable, for a suspension of silver thiocyanate or its ammine in less than about three times its weight of water forms a slimy mud which cannot be satisfactorily manipulated. The multiplying factor was thus from 4 to 7, as against from 5 to 20 in the experiments already described.

Unexpected difficulty was experienced in finding a suitable reference substance; one, that is, which could be accurately estimated, and would neither react with the substances present nor be appreciably adsorbed from a dilute solution by a relatively large bulk of a finely divided solid. After various substances had been tried and rejected, potassium thiocyanate in about $0·1N$-concentration was chosen, and appeared satisfactory on the whole, though there were indications of a slow loss of thiocyanate from the solution on prolonged shaking with the solid.

The solutions were shaken with the solid for two days, and then samples were analysed. Sampling was carried out in the same way as in the solubility measurements, except that there was an additional preliminary filtration, to prevent clogging, by means of a glass-wool filter at the opening of the sampling tube. The samples were titrated with standard nitric acid, and the precipitated silver thiocyanate collected and weighed, the potassium thiocyanate in the filtrate being then determined either gravimetrically or volumetrically, the bromophenol-blue already present being used

as an adsorption indicator (compare Garrick, *Proc. Leeds Phil. Soc.*, 1931, **2**, 301).

An example will illustrate the results obtained. Initial composition of solution (weight normalities) :

KCNS 0·1102, NH$_3$ 6·676.

Composition of mixture : AgCNS 48·87 g. ; solution 125·58 g. Final composition of solution (weight normalities) :

KCNS 0·1147, NH$_3$ 4·529.

As the concentration of KCNS increased from 0·1102 to 0·1147, the total weight of solution phase must have decreased by this ratio. Hence, total weight of final solution is

0·1102/0·1147 × 125·58 = 120·6 g.

Now, knowing the total weight and the compositions of both the initial and the final solution, we can calculate how much water and ammonia have been taken up by the solid :

	Initial soln., g.	Final soln., g.	Taken up by solid, g.
Total weight	125·58	120·6	—
KCNS	1·345	1·345	—
NH$_3$	14·27	9·30	4·97
AgCNS	—	0·21	—
H$_2$O (by diff.) ...	109·97	109·75	0·22

The solid thus contains AgCNS 48·66 g., NH$_3$ 4·97 g., H$_2$O, 0·22 g. This gives as composition of the solid : AgCNS, 0·997NH$_3$,0·04H$_2$O, and is typical of the results obtained on the highest part of the curve, confirming to within 1% the formula AgCNS,NH$_3$, and showing the absence of appreciable quantities of water.

On the middle section, however, the results were less satisfactory. Equilibrium was attained very slowly, and when a very long time was allowed for reaction, there were indications that the solution was slowly losing thiocyanate, possibly by adsorption. The results approximated to the formula AgCNS,½NH$_3$,½H$_2$O, but the variations were wider than could be accounted for by the experimental error, the ammonia being usually low, and the water high. The extremes were NH$_3$ 0·48—0·505, H$_2$O 0·54—0·63. There was no indication of a progressive variation with the concentration of the solution, such as would be found if a range of solid solutions was formed.

It may be therefore concluded that the solid phase stable above [NH$_3$] = 3·049 is AgCNS,NH$_3$; that stable between [NH$_3$] = 2·276 and 3·049 appears to be AgCNS,½NH$_3$,½H$_2$O, but this is regarded as requiring further investigation.

Summary.

1. The solubility of silver thiocyanate, at 25°, in aqueous ammonia solutions of concentration from 1 to 14N, has been measured,

2. The curve indicates the existence of two solid phases containing ammonia.

3. Evidence bearing on the compositions of these phases has been obtained.

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