17. *The System Ammonia–Sulphur Dioxide–Water at 25°.*

By L. M. Hill.

A partial study has been made of the solid–liquid equilibria in the system ammonia–sulphur dioxide–water at 25°. The work has been confined to the solubility curve for hydrated ammonium sulphite $(NH_4)_2SO_3,H_2O$ at pressures not exceeding one atmosphere. The practical limits for this pressure restriction were found to be solutions containing 23% NH_3, 6% SO_2 and 16% NH_3, 50% SO_2. The monohydrate dissolves congruently and can exist with solutions containing excess of either NH_3 or SO_2. A strong tendency towards supersaturation was encountered.

The system ammonia–sulphur dioxide–water forms an interesting study since the first two components are gaseous at room temperatures and pressure. In this respect it resembles the system ammonia–carbon dioxide–water which has already been partly described by different workers.

The most extensive published study of the system under consideration is contained in four papers by Terres and Hahn [*Gas- u. Wasserfach*, 1927, **70**, (*a*) 309—312, (*b*) 339—342, (*c*) 363—367, (*d*) 389—395]. The solubility results are mainly recorded in (*c*), though (*b*) and (*d*) contain relevant matter. Consideration of the system was limited to solutions which have the normal sulphite monohydrate and anhydrous hydrogen sulphite as their solid phase. Isotherms within this range were reported at 0°, 20°, 30°, 40°, 50°, and 60°.

Discontinuities in the monohydrate curve exist in each of the above-mentioned isotherms, and become less evident at the higher temperatures. These irregularities could not be explained on the basis of changes in the chemical composition of the solid phase, and structural changes in the molecule were suggested. Terres and Hahn also included some vapour-pressure measurements in their work.

Apart from the above-mentioned study, no other workers seem to have investigated the ternary system with its variable ammonia and sulphur dioxide concentrations, but there are records of the solubilities of the different sulphites in water. These isolated binary solutions give single points on ternary curves. Included in this category there are results at 25° by Ishikawa with Murooka and with Hagisawa (Seidell, "The Solubility of Inorganic and Metal Organic Salts", 1940, Vol. 1, 1120, 1121). Other results at 25° are by Hunt (*J. Amer. Chem. Soc.*, 1932, **54**, 3511) and by Terres and Overdick (*Gas- u. Wasserfach*, 1928, **71**, 106) and 60° and 85° points are to be found in the work of Silbermann and Ivanov (*J. Appl. Chem. U.S.S.R.*, 1941, **14**, Nos. 7—8, 941).

EXPERIMENTAL.

A full examination of this system would have involved the determination of the composition and pressure of the vapour phases which contained all the components. The work was, however, restricted to the equilibrium conditions between solids and solutions whose total vapour pressure did not exceed one atmosphere.

The solubility mixtures were prepared from freshly distilled water, reagent ammonia solution (*d* 0·88), gaseous ammonia, where required, and gaseous sulphur dioxide. Each mixture was placed in an 8-oz. bottle fitted with a glass stirrer whose bearing was sealed by a shallow mercury lute. Before the mixture was stirred in a thermostatically controlled water-bath, the air in the upper part of the bottle was displaced by coal-gas in order to reduce to a minimum the oxidation of the sulphite. A little stannous chloride solution was also used in a few instances to inhibit oxidation, but as the results showed that it failed to achieve its object the addition was discontinued. As the results in the table show, a small and variable amount of sulphate was present in each equilibrium solution in spite of efforts to prevent oxidation.

System NH_3–SO_2–H_2O *at* 25° Solid phase : $2NH_3,SO_2,2H_2O$.

	Solution. G. per 100 g.			Moist solid. G. per 100 g.		
$d^{25°}_{15°}$.	NH_3.	SO_2.	SO_3.	NH_3.	SO_2.	SO_3.
0·964	23·8	6·5	0·2	24·6	34·8	Nil
1·007	19·9	9·3	—	23·7	40·5	—
1·061	17·4	13·5	Nil	22·4	36·6	Nil
1·101	16·1	15·9	0·3	—	—	—
1·109	15·8	16·4	0·1	—	—	—
—	13·8	19·0	Nil	18·5	30·9	Nil
1·150	13·8	19·2	0·1	—	—	—
—	11·9	20·7	0·7	20·7	38·3	Nil
—	12·1	21·0	—	—	—	—
1·201	11·5	22·0	0·3	—	—	—
1·234	11·8	27·3	0·2	—	—	—
1·278	12·4	33·3	0·3	17·1	38·6	0·2
1·342	13·4	41·4	0·8	19·8	44·6	0·9
1·358	13·8	43·2	0·2	20·8	45·7	1·3
1·371	14·1	44·9	0·4	19·6	46·4	0·5
1·411	14·8	49·2	0·5	19·6	48·6	0·5

A strong tendency for the initial mixtures to remain as clear supersaturated solutions was encountered in many cases, and this was dealt with by "seeding" with a few crystals of hydrated sulphite as soon as some of this had been prepared.

After the solubility mixtures had been stirred long enough to establish equilibrium—tests demonstrated that an overnight period of 17 hours was generally sufficient for this—stirring was stopped in order to allow the solid phase to settle. The clear liquor for analysis was then sampled in a dry pipette and transferred rapidly to a stoppered weighing bottle. In most cases a sample of filtered moist solid phase "residue" was taken and also analysed.

The samples of solution and moist solid were transferred by water to measuring flasks and aliquot proportions were analysed by the following methods :

(1) Sulphite by titration with N/10-iodine solution.

(2) Total sulphur (sulphite + sulphate) determined gravimetrically as barium sulphate after the sulphite had been oxidised to sulphate by bromine in hydrochloric acid solution.

(3) Alkalinity. Titration with N-sulphuric acid, methyl-orange being the indicator (the hydrogen sulphite is neutral to this indicator).

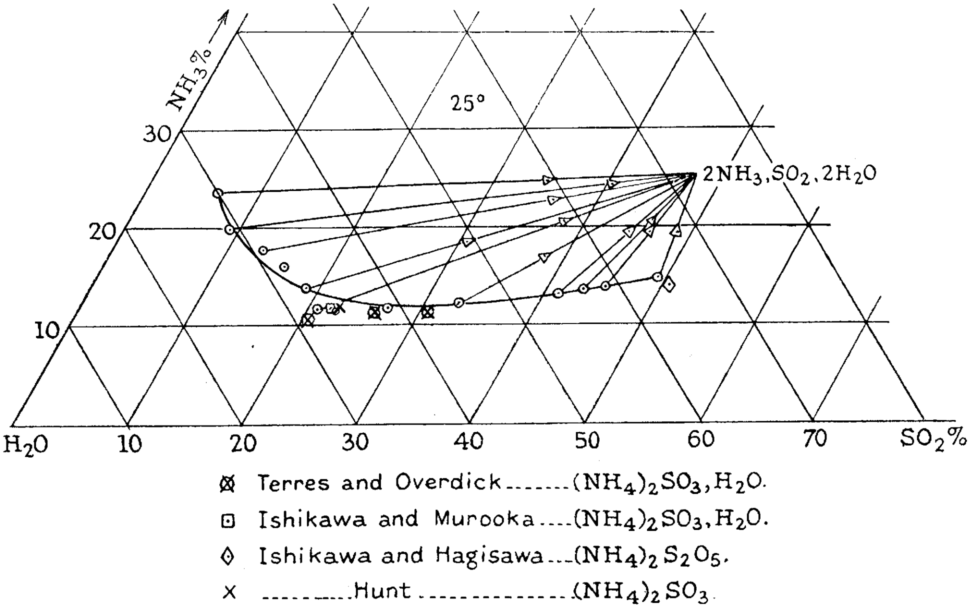
(4) Ammonia. Two methods were employed to varying extents. (*a*) Direct method in which the solution was boiled with sodium hydroxide and the liberated ammonia collected in N-sulphuric acid. (*b*) Indirect method in which ammonia was calculated from determinations (1), (2), and (3)—in equivalents, NH_3 = Alkalinity + $\frac{1}{2}$ sulphite iodine titre + sulphate. The agreement between 4*a* and 4*b* was reasonably good.

It was found that if further oxidation were to be avoided, the sulphite determination (1) had to be carried out as soon as possible after the sample was taken from the solubility bottle.

The composition of solutions and the corresponding residues are given in the table and plotted in the figure. The solid phase deduced graphically by plotting solution and moist solid compositions is in each case ammonium sulphite monohydrate ($2NH_3,SO_2,2H_2O$) as reported by Isikawa and Murooka for the binary system. The solubility points exhibit some irregularities and these are probably due in varying degrees to the characteristics of the system which have already been mentioned, *i.e.*, volatility of the components, difficulty of preventing oxidation, and supersaturation with respect to the solid phase.

It is possible that solutions with high sulphur dioxide concentrations may lie on a metastable extension of the monohydrate curve. This possibility is supported by the results of Terres and Hahn who, though not working at 25°, obtained at 20° and 40° two solid-phase points each containing about 44% of SO_2.

The shape of the 25° isotherm for solutions containing less than 19% of SO_2 is at variance with the isotherms of Terres and Hahn, who suggest irregular, looped curves with a SO_2 minimum of 16% in their work at 20°. In the absence of further evidence no opinion can be expressed on the cause of this disagreement.



The author wishes to acknowledge the help of Mr. W. Edge with this investigation.

IMPERIAL CHEMICAL INDUSTRIES RESEARCH DEPARTMENT,
ALKALI DIVISION, NORTHWICH, CHESHIRE.

[*Received, February 25th,* 1947.]