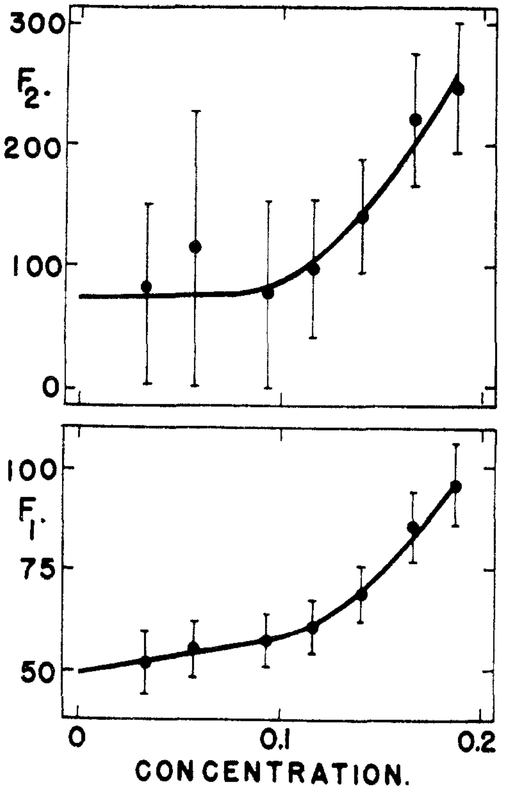

Fig. 1.—Variations of functions F_1 and F_2 with the concentration of pyrophosphate (in moles per l.). See data in Table I.

was changed, and this caused a variation of the liquid junction potential. However, the resulting error was probably small (less than 0.001 volt) since a saturated solution of potassium chloride was used in the junction.

Summarizing, the existence of various pyrophosphate complexes of Tl(+1) was demonstrated. The species $Tl(P_2O_7)^{-3}$ is predominant in the neighborhood of *p*H 13, but complexes of a higher order also exist; their formation constants, however, can only be determined in a very approximate manner by the polarographic method.

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The Systems Ammonia–Sulfamide and Sulfuric Acid–Sulfamide

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Several studies[1,2] of the behavior of acid amides toward basic and acidic solvents have been carried out in recent years. As part of this program, we were interested in investigating the binary systems ammonia–sulfamide and sulfuric acid–sulfamide.

Experimental

Materials.—Anhydrous sulfuric acid was prepared by adding the calculated amount of fuming sulfuric acid to chemically pure concentrated sulfuric acid which had been checked to assure the absence of nitric acid. The purity of the anhydrous sulfuric acid thus obtained was checked by determining its freezing point. The freezing point of our product was 10.3° (lit. 10.31°). The freezing point was rechecked before each sample of the acid was taken.

Anhydrous ammonia of the synthetic grade with a stated purity of 99.9% was used. Its purity was also checked by its freezing point; found −77.8° (lit. −77.74°).

Sulfamide was prepared by the reaction of sulfuryl chloride with an excess of anhydrous ammonia in the vapor state. A stream of dry nitrogen was passed through a dilute solution of sulfuryl chloride in petroleum ether. The gas stream (containing entrained sulfuryl chloride) was then passed into a reaction flask into which a large excess of gaseous ammonia was being passed. The solid products of the reaction were dissolved in water which was made slightly acidic with hydrochloric acid. After the solution had stood for at least 48 hours, the solution was evaporated to a very small volume under an infrared lamp in a current of dry air. The height of the lamp was adjusted so as to maintain a temperature between 50 and 60° in the evaporating solution. The small volume of remaining solution was then placed in a vacuum desiccator over calcium chloride to crystallize. The dried crystals were extracted with ethyl acetate, the ethyl acetate evaporated, and the crystals obtained dried in a vacuum desiccator. The sulfamide was further purified by another recrystallization from ethyl acetate. The product melted sharply at 91.5° (uncor.) (lit. 91.5–93.0°). Yields approximating 30 to 35% based upon the sulfuryl chloride used were obtained.

The System Sulfuric Acid–Sulfamide.—It was observed immediately that when samples of anhydrous sulfuric acid and sulfamide are mixed a clear solution is obtained, but that, if the solution stands for from 15 to 30 minutes at room temperature, a white solid begins to appear. This crystalline white solid was removed and shown by analysis and determination of the melting point to be virtually pure sulfamic acid. The reaction was also carried out in pure nitromethane and it was shown that, in the presence of excess sulfuric acid, the solvolytic reaction represented by the equation

$$SO_2(NH_2)_2 + SO_2(OH)_2 \longrightarrow 2SO_2(NH_2)(OH)$$

takes place quantitatively to yield sulfamic acid, which may be filtered off and isolated. Typical analytical results are listed in Table I.

TABLE I

	Experimental	Calcd. for $SO_2(NH_2)(OH)$
Sulfur(VI), %	31.8, 32.2, 32.1	33.0
Equiv. wt.	96.3, 96.5, 96.4	97.1

Melting point 203° (uncorrected) (lit. 205).

The System Ammonia–Sulfamide.—This binary system was investigated by the cryoscopic method and a phase diagram for the system constructed. The freezing point cell used is shown in Fig. 1. The thoroughly cleansed and dried cell was flushed out with dry nitrogen and the two side arms stoppered. A weighed sample of sulfamide was introduced through side arm B, the side arm sealed, and the whole cell and contents weighed. The desired amount of ammonia was introduced into the cell through side arm A and condensed by a Dry Ice–$CHCl_3$–CCl_4 cooling mixture. The rate of condensation of ammonia was followed by means of a flowmeter in the line. After the desired quantity of ammonia had been condensed, the side arm A was sealed, and the cell allowed to come to room temperature and weighed. The freezing points of the mixtures thus obtained were determined by means of cooling curves recorded, as described in previous publications from this Laboratory, on a Micromax self-recording potentiometer connected to a copper-constantan thermocouple placed in the well (C) of the cell. Constant stirring was provided by an intermittently actuated solenoid around the neck of the cell and a glass stirrer (E) which contained an iron slug (D) in its upper end. The thermocouple was covered with 2,3-dimethylpentane to minimize convection effects in the thermocouple well. The precautions observed and the techniques used in taking the freezing points were essentially the same as described in previous publications from this Laboratory.[3] The freezing

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[1] H. H. Sisler, A. W. Davidson, R. Stoenner and L. Lyon, THIS JOURNAL, **66**, 1888 (1944).

[2] H. H. Sisler, C. A. VanderWerf and S. Stephanou, *ibid.*, **68**, 2538 (1946).

[3] B. Rubin, H. H. Sisler and H. Schechter, *ibid.*, **74**, 877 (1952).

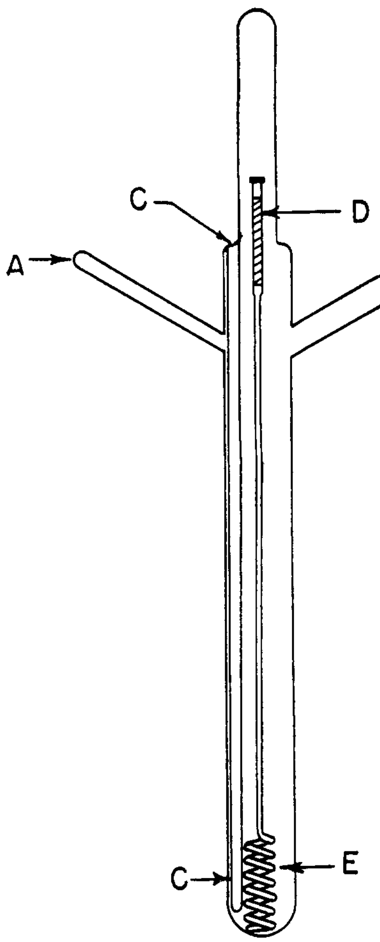


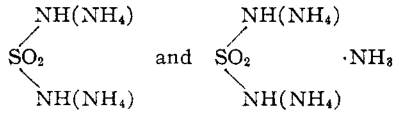
Fig. 1.—Freezing point cell.

points were each determined at least twice and are believed to be correct within 1.5°. Each portion of the curve was checked at least twice and no more than seven consecutive points were determined without cleaning out the cell completely.

The results of this phase study are represented graphically in Fig. 2. This figure indicates the formation of two previously unreported compounds, *viz.*, $SO_2(NH_2)_2 \cdot 2NH_3$ and $SO_2(NH_2)_2 \cdot 3NH_3$, with melting points of −15.8° and −12.5°, respectively. It came as something of a surprise that the 1:1 compound is not indicated. Eutectics were observed at −21.8° and 59.5 mole % of ammonia, at −19.0° and 69.1 mole % of ammonia, and at about −78.0° and about 97 mole % of ammonia.

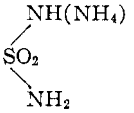
Discussion and Conclusions

The complete solvolysis of sulfamide in solution in anhydrous sulfuric acid prevents (or at least makes very difficult) the determination of whether or not sulfamide acts as a base toward sulfuric acid. With reference to the sulfamide–ammonia system, one might be tempted to interpret the formation of the compounds $SO_2(NH_2)_2 \cdot 2NH_3$ and $SO_2(NH_2)_2 \cdot 3NH_3$ as indicating that sulfamide acts as an acid toward anhydrous ammonia. The two compounds would thus be formulated



$$SO_2\begin{matrix}\diagup NH(NH_4)\\ \diagdown NH(NH_4)\end{matrix} \quad \text{and} \quad SO_2\begin{matrix}\diagup NH(NH_4)\\ \diagdown NH(NH_4)\end{matrix} \cdot NH_3$$

If this is the correct interpretation, however, it is difficult to understand why no evidence for the compound $SO_2(NH_2)_2 \cdot NH_3$, or



$$SO_2\begin{matrix}\diagup NH(NH_4)\\ \diagdown NH_2\end{matrix}$$

was obtained. There is no question, however, about the existence of the two new compounds, whatever may be the nature of their structures.

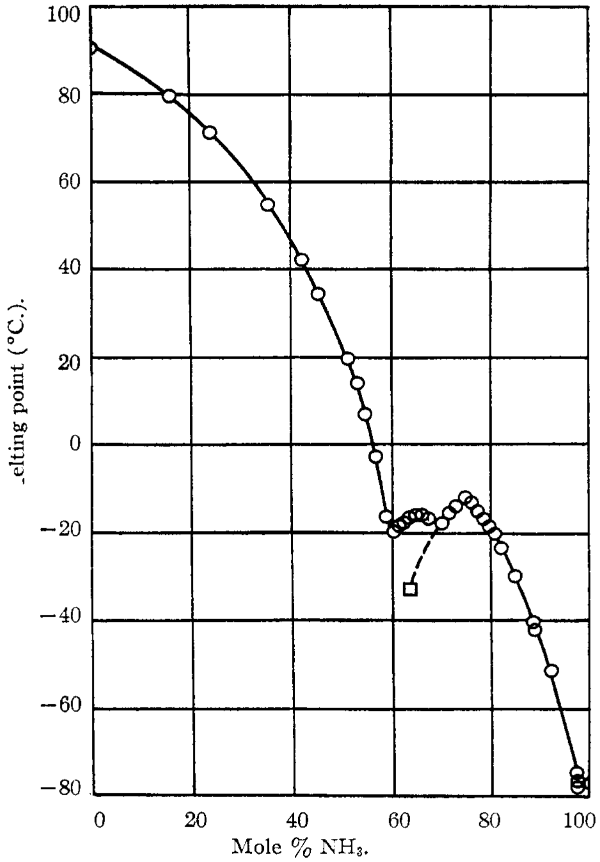


Fig. 2.—The system sulfamide–ammonia.

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Precipitate-Ion Exchange Reactions Using Nickel-63

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A number of solid–fluid exchange reactions have been carried out in the past.[1] The purpose of these experiments was to investigate the exchange of nickel(II) ions in aqueous solution with nickel(II) in a number of insoluble compounds.

Experimental

Preparation of Compounds.—The insoluble nickel(II) compounds were prepared by the procedures described in the literature references cited in the footnotes of Table I.

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(1) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 351–364.