

HEATS OF SOLUTION IN LIQUID AMMONIA

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A thesis, presented to the Department of Chemistry  
of Union College, in partial fulfillment of the requirements  
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## INTRODUCTION

The work on liquid ammonia is done at Union College under the direction of Dr. Frederic C. Schmidt. The apparatus was designed by Kraus, Ridderhof and Schmidt<sup>1</sup>. Previous work at Union is reported in the Journal of the American Chemical Society<sup>2</sup>, and in various departmental theses.

This paper will present the heat of solution of methyl ammonium chloride as a function of the concentration at  $-33.^{\circ}$ . The heats of other amine and imine hydrochlorides, organic salts will also be included, as will the preparation of certain organic salts and calibration data.



## HISTORICAL

The notice of liquid ammonia as a solvent was first reported in the Annalen in 1839. The first serious study was begun by Franklin and Cady in 1896<sup>3</sup>. Franklin investigated the field for purely academic reasons. Charles A. Kraus saw the opportunity to further his studies on solutions with liquid ammonia as a solvent, and began thermodynamic studies of this solvent.

Heats of solution were studied first by Kraus and Ridderhof<sup>1</sup>, and Kraus and Prescott<sup>4</sup> at Brown. Their method was relatively crude. They merely approximated an amount of ammonia dropped in some salt and measured the ammonia driven off. On high heat values their work is thoroughly reliable.

Schmidt<sup>5</sup> introduced the idea of measuring the sample into a sealed fragile glass bulb, which is broken under the liquid when thermal and barometric pressure is obtained. He also introduced the idea of the pipette into the system.

In previous years at Union Dr. Schmidt, assisted by Sottysiak, Kluge, Studer<sup>2</sup>, studied the effect of concentration on the molar heat of solution of the ammonium halides, several metallic halides, the alkali and alkaline earth metals, and various other compounds.

In 1936 two new calorimeters of Nonex glass were prepared by the General Electric Company. These have been found to be entirely satisfactory.

The apparatus at Union was constructed by Dr. Frederic C. Schmidt.



### APPARATUS

The apparatus (Figure I) is essentially an adiabatic calorimeter. Commercial ammonia, obtained from the Mathieson Alkali Company, contains 1/2% water. It is therefore dried over sodium and stored in a small supply tank. The system is evacuated to 10 or less by a vacuum pump, driven by a 1/2 horsepower motor. Ammonia is then drawn from the small supply tank into pipette P, where it is condensed against a pressure head of about 200 mm. Hg. The temperature is at  $-33^{\circ}$  C. since a Dewar of boiling liquid  $\text{NH}_3$  surrounds the pipette. The pipette has been previously calibrated to deliver 29.79 gm. of ammonia to the calorimeter.

The known volume of ammonia is evaporated from the pipette into the calorimeter. The calorimeter is one of two made of Nonex glass by the General Electric Company in 1936. It is the same in all details as the one described by Kraus and Schmidt<sup>5</sup>. Since the calorimeter constant and radiation constant have been determined for the twin<sup>2</sup>, the same volumes were used for this calorimeter. In the calorimeter the  $\text{NH}_3$  is again condensed at  $-33^{\circ}$  C. and about 900 mm. Hg.

Efficient stirring is effected by a magnetic stirrer. A soft iron case is suspended by a steel spring within a solenoid. To the case is attached a glass rod with a glass chain on the bottom. The current in the solenoid is controlled by a mechanical make and break device.

The sample is introduced into the calorimeter in fragile glass bulbs attached to the end of a crushing rod. When temperature and pressure equilibrium are reached the bulb is broken.

The major heat effect vaporizes some of the ammonia, which is absorbed in water; then titrated with standard sulfuric acid. The minor heat effect is measured by means of a copper constantan thermocouple cali-



brated by E. M. F. pressure readings on the apparatus, and reference to pressure temperature reports of the Bureau of Standards<sup>6</sup>.

The chemicals used were for the most part commercial products. The ammonia, supplied by the Mathieson Alkali Company, was dried over Na or  $\text{NaNH}_2$  before used in the calorimeter.

The methyl ammonium chloride was obtained from the Eastman Kodak Company. Any water or methyl amine and/or hydrochloric acid was removed by vacuum before sealing the bulb. An analysis for the chloride concentration was made and revealed satisfactory purity.

O-Toluidene-picric acid was prepared by mixing equivalent amounts of o-toluidene and picric acid in hot alcoholic solution<sup>7</sup>. This method is described by Fuoss as a general preparation of picrates. The resulting compound was recrystallized from alcohol. It decomposed at 186-188° C.

Aniline hydrochloride was prepared by treating vacuum distilled aniline with gaseous HCl in ether solution.

The sulfuric acid used was prepared by diluting the concentrated Graselli acid with distilled water. It was 0.1047 N. This value was determined by three independent investigators against three different primary standards.



TABLE I

Data for Heat of Solution of Methyl Ammonium Chloride in  
Liquid Ammonia

<u>Sample</u>	<u>Gm. NH<sub>3</sub></u> <u>evolved</u>	<u><math>\Delta t</math></u>	<u><math>\Delta p</math></u>	<u>Total</u> <u><math>\Delta H</math></u>	<u>Molar</u> <u><math>\Delta H</math></u>	<u>Mols NH<sub>3</sub></u> <u>per mol salt</u>
0.5907	.1051	0.26	0.00	45.08	5160	199.5
1.1835	.2114	0.42	0.00	86.48	4941	99.4
1.4709	.1940	1.08	1.00	107.80	4956	80.2
2.0151	.4026	0.36	0.50	146.67	4922	58.0
1.7501	.3235	0.37	0.00	121.15	4678	66.8

### DISCUSSION OF RESULTS

Interpretation of the results shows that methyl ammonium chloride has a positive heat of dilution approaching 5200 cal/mole in the very dilute region. The general shape of the curve is in agreement with the  $\text{NH}_4\text{Cl}^2$  curve, but with lower values for the heat effect. This effect is to be expected as the introduction of the methyl group lowers the acid properties of the ammonium salt.

An interesting study would be the comparison of ethyl ammonium chloride and di-methyl ammonium chloride, as these are isomeric one with the other.



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