

HEATS OF SOLUTION IN LIQUID AMMONIA

by

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Approved by Federic C. Schmidt

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## INTRODUCTION

Water, chemically speaking, is the most important individual substance known. Water occupies an outstanding position among solvents. In its capacity as a solvent for salts and as an ionizing agent, it is in a class by itself. Of all known liquids, ammonia most closely resembles water in those properties which make water outstanding among solvents<sup>1</sup>. As a solvent ammonia is secondary to water, however; many salts insoluble in water dissolve readily in liquid ammonia. Solutions of salts in liquid ammonia are excellent conductors of electricity. Ammonia unites with salts to form ammonia of crystallization. It solvates ions. It is an associated liquid. Its physical constants are all out of proportion for a substance of such simple composition, that is, high critical pressure, high boiling point, and low cryoscopic and ebullioscopic constants.

Liquid ammonia has been recognized as an ideal reaction medium by many workers. A large chemical manufacturing company has erected a plant for running reactions in liquid ammonia<sup>2</sup>. The need for physical chemical data, notably heats of solution, becomes quite apparent.

Definite calorimetric work on heats of solution in liquid ammonia was started by Kraus and Ridderhof<sup>3</sup>, who designed a quartz adiabatic calorimeter for measuring heats of solution in liquid ammonia at the boiling point, in which the major heat effect is measured by the amount of ammonia vaporized or condensed by the process of solution. The calorimetric measurements were improved by Kraus and Prescott<sup>4</sup> and Kraus and Schmidt<sup>5</sup>. The calorimeter used in the present research is essentially similar to the one used by Kraus and Schmidt; however, the calorimeter proper was constructed of Nonex glass.

The work covered in this thesis describes the exothermic heats of solution over a wide range of concentration of the alkali metals, lithium and potassium; the alkaline earth metals, calcium, barium, strontium; and ammonium iodide.

### APPARATUS

The apparatus used by Schmidt<sup>5</sup> in measuring exothermic heats of solution was constructed in this laboratory and used in this investigation. Figure I is a schematic diagram of the apparatus.

The Calorimeter: The calorimeter is similar to one designed by Ridderhof<sup>5</sup> for calorimetric measurements in liquid ammonia. The calorimeter proper consists of a Nonex glass tube 20 mm. in diameter and 40 cm. long. The lower part of the calorimeter is protected from heat flow by a vacuum jacket A, which is silvered on the inside. This silvering operation cut the heat flow into or out of the calorimeter to a minimum, and due to the shortness of time of solution (an average of 2.5 minutes), any correction necessary for radiation is insignificant. The top of the calorimeter is provided with a ground glass joint B into which fits a cap C, made of Nonex glass. The cap has sealed onto it three tubes, D, E, F, through which pass respectively the thermocouple H, a bulb crusher G, and a magnetically operated glass stirrer I. The stirrer consists of a glass chain K, suspended from a glass rod L, which is attached to a soft iron bar hung inside of a piano wire spring R. The spring is suspended within a glass tube which is sealed to the cap C. The stirrer is operated by making and breaking a current passing through a solenoid, which surrounds the glass tube containing the soft iron bar, by means of a mechanical circuit breaker. The motion of the stirrer is kept uniform by damping due to friction of the spring on the walls of the glass tube. This friction is sufficient to keep the iron bar from oscillating. The by pass J is inserted to keep the meniscus of the mercury in the manometer from oscillating because of the pumping action of the iron bar. The calorimeter is kept nearly adiabatic by surrounding it with a bath of boiling liquid ammonia in a silvered Dewar tube L.

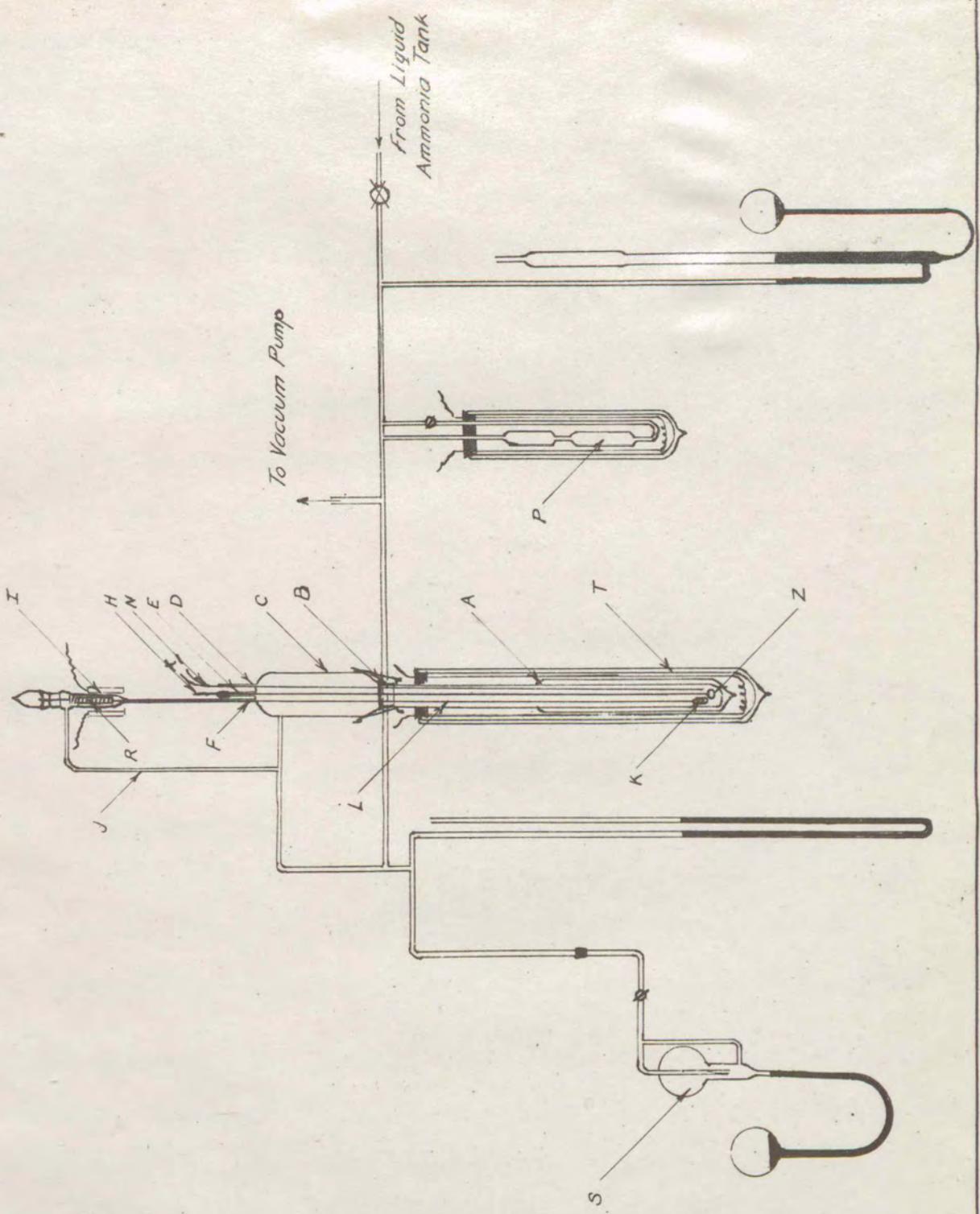


fig. I

### Determination of Calorimeter Constant

50 grs. of distilled water at 25° C. was placed into the calorimeter. An approximately 2 ohm constantan resistance coil was placed in the water. The coil was heated by means of storage batteries. The time of heating, the voltage across the coil, and the amperage were accurately measured. By means of a thermocouple the temperature of the water was measured at the start and the finish of a determination.

The difference between the calories input and the calories output divided by the temperature rise of the water expresses the calorimeter constant in calories per degree.

Table I

### Data on Determination of Calorimeter Constant

Det.	Volts	Amps.	Time	Cals. Input	ΔT	Cals. Output	Difference in cals.	Cal. Constant
1	2.40	5.65	180 sec.	585.1	9.65° C.	482.5	100.6	10.40
2	2.47	5.65	240 "	800.1	15.30° C.	660.0	140.1	10.60
3	2.45	5.64	240 "	792.5	15.08° C.	654.0	138.5	10.57

Average calorimeter constant = 10.52 cals./deg. at T = 25° C.

Calorimeter constant was corrected to 9.16 cals./deg. at T = -33.45° C.

The Thermocouple: The thermocouple was one designed by Prescott<sup>4</sup>, and consists of a fine copper-constantan wire couple. The couple has a coefficient of 0.0314 millivolts per degree as calibrated against vapor pressure of ammonia by use of Bureau of Standards' publications<sup>5</sup>. The thermocouple was used in conjunction with a "Queen" Standard Potentiometer, manufactured by the Gray Instrument Company, and a Leeds and Northrup type R galvanometer having a sensitivity of 10.5 millimicrons per unit volt. The thermocouple was calibrated by obtaining time-pressure and time-electromotive force curves

and obtaining electromotive force-temperature values for these two determinations from data furnished by the Bureau of Standards<sup>6</sup>.

The Pipette: The pipette is shown as P in the diagram. A pipette was used, so that a fixed weighed amount of solvent could be delivered to the calorimeter each time. The pipette was calibrated by filling with mercury to a fixed mark and weighing. The result of the calibration is given in Table II.

Table II

Data on Calibration of Liquid Ammonia Pipette

Weight of Mercury I	604.94 g.
II	604.72 g.
Mean	604.83 g.

$$1 \text{ gr. Hg} = 0.07586 \text{ c.c.}^7$$

$$604.83 \times 0.07586 = 44.67 \text{ c.c.}$$

$$1 \text{ c.c. NH}_3 \text{ weighs } 0.6818 \text{ grs.}^8$$

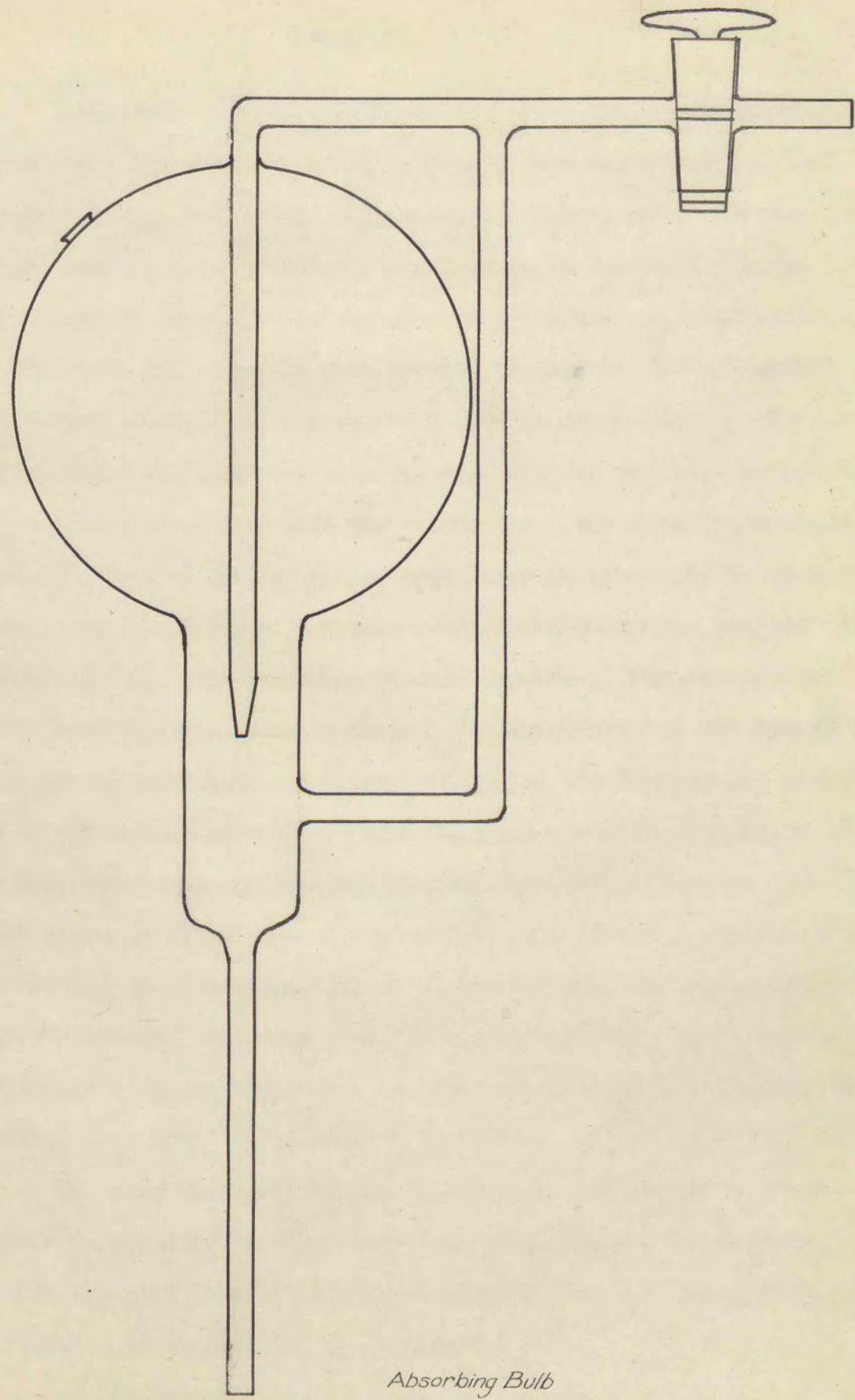
$$44.67 \times 0.6818 = 30.46 \text{ grs. NH}_3$$

Volume of system at room temperature and 1 atmosphere pressure is equivalent to approximately 0.67 g. NH<sub>3</sub>.

Pipette delivers to calorimeter each time 29.79 g. NH<sub>3</sub>.

Ammonia Absorbing Flask: Since exothermic heats of solution are measured by the amount of ammonia evolved by solution, an absorbing flask is necessary to collect the ammonia evolved. The flask is shown as S in figure I, and in detail in figure II. This flask is somewhat different from the flask used in previous experimental determinations. As to whether this type is more efficient is still questionable. However, it was found to be quite satisfactory in its performance. The flask is adjusted, when the calorimeter has come to equilibrium, by dropping the mercury in the flask until it just closes off the constricted opening of the inner tube. The levelling bulb is made fast. Water

is placed in the flask on top of the mercury seal. This appears to be an ideal arrangement for absorbing the ammonia because with a very slight increase in pressure in the system, the ammonia gas bubbles through and is absorbed by the water. The outer tube acts as a check valve.



*Absorbing Bulb*

J.S.

*fig II*

PROCEDURE

A measurement is made by first exhausting the pipette system to a pressure of a few microns. The pipette P is then surrounded by a bath of liquid ammonia kept boiling by a nichrome wire heating coil. The required amount of ammonia, dried previously over sodium, is condensed into the pipette. A fragile bulb Z, exhausted and sealed after a weighed amount of solute had been placed into it, is sealed onto the bulb crushed H. The calorimeter system is then exhausted to a pressure of from 15 to 25 microns. The boiling liquid ammonia bath is removed from the pipette P and the measured amount of liquid ammonia is distilled into the calorimeter. The condensation is aided by means of a bath of boiling liquid ammonia in the Dewar Tube T. When all the ammonia is condensed, all stopcocks are closed except the one into the absorbing flask S. The absorption flask is adjusted. The stirrer I is started. Electromotive force readings of the temperature of the solvent are taken on the potentiometer. The warm junction of the thermocouple is kept in a bath of melting ice and water. When the system is at equilibrium as shown by the constancy of the temperature readings, the bulb is broken. There is a sudden change in temperature and pressure<sup>5</sup>. Any ammonia evolved is absorbed by the water in S. The determination is finished when the temperature readings are again constant. The pressure in the system invariably comes back to the same level or a very few m.m. from it. This small pressure difference is negligible.

The water from S is drained into a volumetric flask. S is then thoroughly washed with distilled water and the washings added to the volumetric flask. The ammoniated water is made up to volume and titrated with standardized sulfuric acid using methyl red as an indicator.

Table III lists the constants used in calculating heats of solution, and Table IV shows a typical calculation.

Table III

Constants Used in Calculation of a Heat of Solution

1. Specific heat of liquid ammonia at boiling point <sup>6</sup>	1.067 cals./deg.
2. Heat of Vaporization <sup>9</sup>	327.7 cals./gr.
3. Calorimeter Constant	9.16 cals./deg.
4. Radiation Constant <sup>10</sup>	0.125 cals./deg./min.
5. Pressure equivalent in grams of NH <sub>3</sub> <sup>5</sup>	1 cm. Hg = 0.00608 grs. NH <sub>3</sub>

Table IV

Data and Calculation of a Typical Determination

Heat of Solution of Ammonium Iodide in Liquid Ammonia

Grams NH <sub>4</sub> I	Ammonia Evolved	ΔT Solution	Time in Minutes	ΔP
4.2692 g.	1.7045 g.	1.34°	2.5	0

1. Effect due to evolution of ammonia:

$$\text{Grams NH}_3 \times \text{Heat of vaporization}$$

$$1.7045 \text{ grs.} \times 327.7 \text{ cals./gr.} \quad 558.56 \text{ cals.}$$

2. Effect due to solvent:

$$\text{Grams solvent} \times \text{Specific heat} \times \Delta T \text{ solution}$$

$$29.79 \text{ grs.} \times 1.067 \text{ cals./gr.deg.} \times 1.34 \text{ deg.} \quad 42.60 \text{ cals.}$$

3. Effect due to calorimeter:

$$\text{Calorimeter constant} \times \Delta T \text{ solution}$$

$$9.16 \text{ cals./deg.} \times 1.34 \text{ deg.} \quad 12.27 \text{ cals.}$$

$$\text{Total heat effect} \quad 615.45 \text{ cals.}$$

$$\text{Heat of Solution of one gram mole} \quad 20,828 \text{ cals.}$$

Because of the short time of solution any correction due to radiation is negligible. Since the pressure change is zero, this correction is obviously non-existent.

TABLE V.

## DATA ON HEATS OF SOLUTION OF METALS IN LIQUID AMMONIA

29.79 grams of ammonia used in each sample

Compound	Weight of Sample	NH <sub>3</sub> evolved upon solution	Mols NH <sub>3</sub> per mol of sample	$\Delta T_{OC}$	Time in minutes	$\Delta H$ Total in cal/s.	$\Delta H$ Molar in cal/s.
Lithium	0.1769 g.	0.5831 g.	67.6	0.29	3.0	202.9	7362
	0.2955	1.0350	39.7	0.18	3.5	345.6	8144
	0.4100	1.4160	28.2	-0.58	5.0	487.9	8260
	0.4822	1.8040	25.6	-0.26	5.0	585.1	8421
	0.5448	1.9120	20.9	0.48	5.0	646.4	8380
Potassium	1.2918	0.00	52.9	0.0	0.0	0.0	0
	1.7200	0.00	39.8	0.0	0.0	0.0	0
Calcium	0.1907	0.1418	366.0	0.0	5.0	48.47	9784
	0.2470	0.1905	282.0	0.0	1.5	62.36	10116
	0.2779	0.2544	251.0	-0.21	0.5	74.77	10780
Barium	0.3850	0.1068	621.0	-0.10	2.0	50.90	11024
	0.5477	0.2089	435.0	-0.45	3.0	50.05	12547
	0.7469	0.2776	519.0	-0.35	5.0	77.55	14258
	0.8011	0.3137	282.0	-0.22	2.0	95.80	14298
	1.3658	0.5292	175.0	-0.32	4.0	160.32	16124
Strontium	0.3000	0.2401	507.0	-0.47	2.0	59.40	17351
	0.3831	0.2624	597.0	-0.19	4.0	78.44	17940
	0.6606	0.4744	246.0	-0.72	4.0	125.98	18200
	0.9720	0.6747	155.0	-0.15	2.5	214.90	19580

TABLE VI.

## DATA ON HEATS OF SOLUTION OF AMMONIUM IODIDE IN LIQUID AMMONIA

Sample	Weight of Sample	Amount of <u>NH<sub>3</sub></u>	NH <sub>3</sub> evolved upon solution	Mols NH <sub>3</sub> per mol of sample	ΔT°C.	Time in minutes	ΔH Total in cals.	ΔH Molar in cals.
1	0.1561 g.	29.79 g.	0.0116 g.	1666.0	0.20	1.0	11.98	12759
2	0.3495	29.79	0.0358	726.5	0.43	2.0	30.89	12819
3	0.4512	29.79	0.0611	562.1	0.55	2.0	42.56	13875
4	0.6809	29.79	0.1014	372.2	0.75	1.0	65.11	15435
5	1.6081	24.89	0.4147	129.5	0.91	1.0	166.00	14978
6	2.1453	24.89	0.6740	98.6	0.81	3.5	247.93	16758
7	2.7640	24.89	0.9175	74.0	0.56	2.5	318.74	16710
8	4.2892	29.79	1.7045	56.1	1.54	2.5	613.43	20828

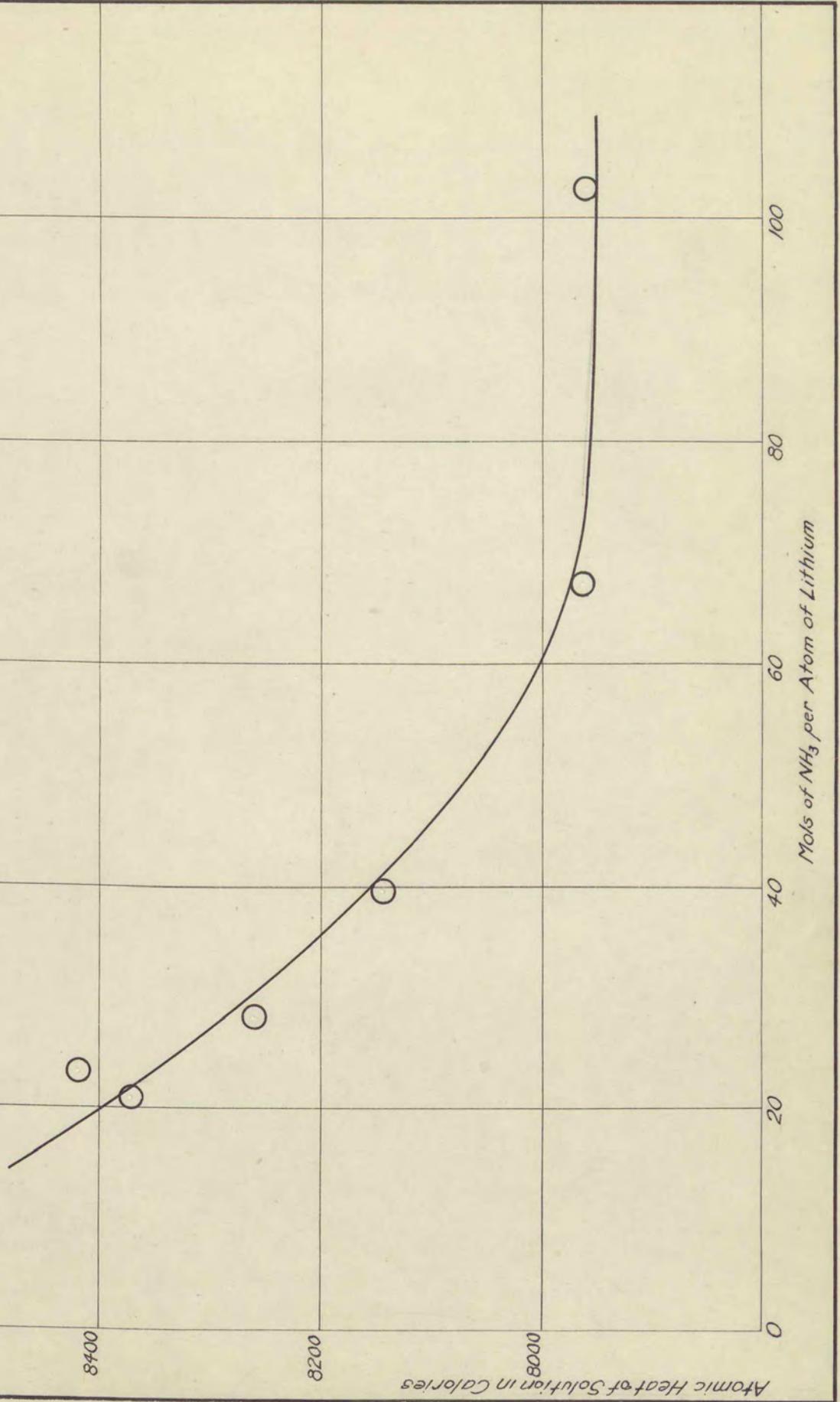


fig. III

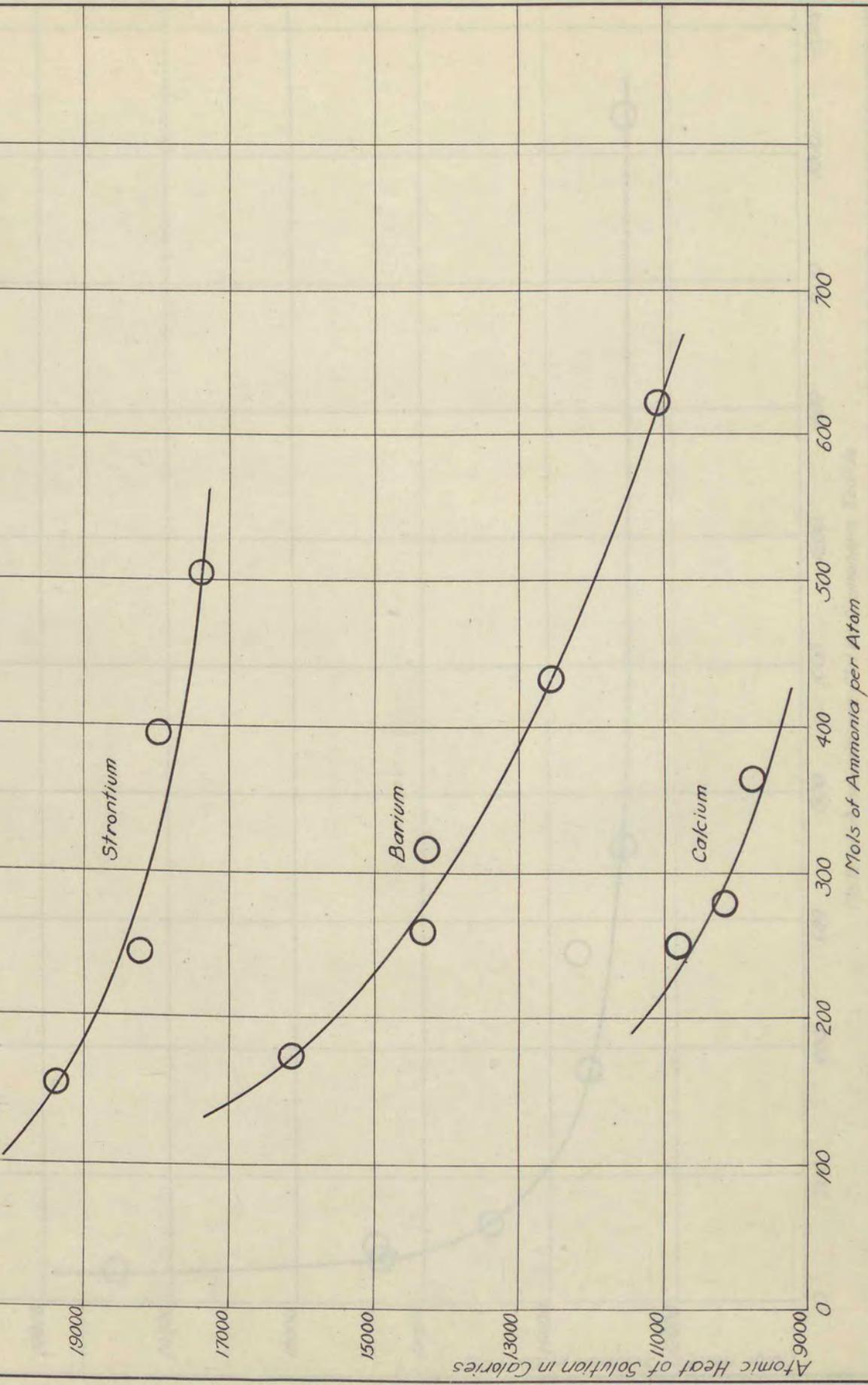


Fig. IV

### DISCUSSION

In Tables V and VI are listed the data obtained for various heats of solution. In Figures III, IV and V are plots of the heat of solution curves. The curves are drawn with molar heats of solution in calories as ordinates against mols of ammonia per mol of sample as abscissa.

In the normal process of solution, the first effect upon the solute is the degradation of the crystal lattice, by the solvent, into simpler particles, namely molecules or atoms<sup>11</sup>. The subsequent effect is the ionization, in the case of electrolytes, of said molecule or atom, and then in some cases a solvation of each ion to a greater or less degree by the solvent. The heat of solution is therefore the sum of all the energies, both negative and positive, of all these processes.

Lithium, unlike sodium<sup>5</sup>, shows a rather highly positive or exothermic heat of solution. This is probably due to the formation of a highly solvated lithium ion. As seen in Figure III, with increasing dilution, the heat of solution becomes less and approaches a constant value. This negative heat of dilution is due to the increasing importance of one of the factors discussed above.

Potassium shows no heat of solution. Two results are reported here, however; they are consistant with other published determinations<sup>5</sup>. In making a determination it was observed that there was absolutely no change in temperature when the potassium dissolved in liquid ammonia. In all probability there is a very small heat effect. The conclusion to be drawn is that all the energies discussed above just balance each other.

Work done by other investigators in this laboratory has shown metallic cesium and rubidium to have no heat of solution<sup>12</sup>.

Calcium, barium and strontium all have very high heats of solution. Kraus<sup>13</sup> has shown that calcium forms a hexa-ammoniate. This heat of formation is a large factor in the heat of solution.

Barium and strontium also form ammoniates. Figure III shows that all three metals have negative heats of dilution.

Ammonium iodide shows an extremely high heat of solution, unlike ammonium chloride and ammonium bromide<sup>10</sup>. This ammoniated acid differs markedly from the latter two, in that it exhibits a negative heat of dilution. The only difference between these three compounds is in their anions. The negativity of the heat of dilution may be explained in this manner: the iodide ion upon being solvated exerts a heat effect in direct opposition to that of solution. The solvation heat effect of chloride and bromide ions, therefore, is assumed to be in direct addition to that of solution. That the above ions are solvated in aqueous solutions have been proven by transport experiments in water<sup>14</sup>. Since water and ammonia exhibit many similar properties, it can be assumed that the solvation of these ions also occurs in liquid ammonia.

SUMMARY

This investigation completes the data on all of the metals soluble in liquid ammonia. Data has also been presented on ammonium iodide. This, with the exception of ammonium nitrate, completes the investigation of the strong inorganic acids which are soluble in liquid ammonia. The data on ammonium nitrate is incomplete as this paper is written.

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