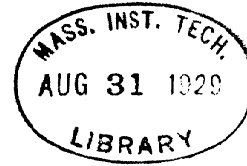


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THE PARTIAL MOLAL VOLUME OF AMMONIA
IN THE
AMMINES OF CALCIUM AND BARIUM CHLORIDES.

by
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INTRODUCTION.

Density data on the amines and the consequent knowledge of the partial molal volume of ammonia in such compounds have been limited to compounds which have comparatively low vapor pressures such as those of the Cobalt, chromium, iron and manganese salts.¹ Such compounds may be isolated in a quite pure state, and density data may be obtained on pure compounds with little modification from the procedure used with ordinary solids.

In the case of compounds such as the amines of the alkaline earth halides, where dissociation pressures run as high as two and a half atmospheres in the case of barium chloride octamine at room temperature, such methods are not applicable. In such cases the pure compound is quite difficult to prepare, and once it is prepared it is apt to lose considerable ammonia forming a mixture of compounds during the process of density measurement.

However, it is not necessary to work with pure amines. The vapor pressure curves show that at equilibrium between a salt and ammonia, at any composition other than those of the compounds there will be two solid phases, either the ammonia free salt and an amine or a mixture of two amines. Take the case of a salt MX forming two amines $MX.aNH_3$ having a molal volume V_1 and $MX.bNH_3$ having a molal

¹ Biltz & Birk, Z. Anorg. Chem. 134, 125, (1921).

Clark, Quick and Harkins, J. A. C. S. 42, 2483, (1920).

Birk, Z. Anorg. Chem. 158, 111, (1926).

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volume V_2 where b is greater than a . It is found by analysis that there are N mols of ammonia per mol of the salt, N being between a and b in value.

$$\frac{b-N}{b-a} = \text{mol fraction MX} \cdot a\text{NH}_3$$

$$\frac{N-a}{b-a} = \text{mol fraction MX} \cdot b\text{NH}_3$$

Let V volume of the two phases per mol of MX used.

$$V = \frac{b-N}{b-a}V_1 + \frac{N-a}{b-a}V_2$$

$$V = \frac{V_2 - V_1}{b-a}N + \frac{bV_2 - aV_1}{b-a} = \left(\frac{\partial V}{\partial N}\right)N + k$$

Consequently the measured volume per mol of the salt used is a straight line function, between the values of the molal volumes of the two compounds forming the mixture, of the number of mols of ammonia per mol of the salt used. The slope of this line is the partial molal volume $\left(\frac{\partial V}{\partial N}\right)$ in the region between the two compounds. If equilibrium is attained between two phases, it is necessary only to start with a definite weight of the salt and after adding ammonia to any desired amount, determine the total volume, and then by analysis find the amount of ammonia combined. By means of plotting a number of these determinations, the molal volumes of the two pure compounds are obtained.

THE AMMINES OF CALCIUM CHLORIDE.

Calcium Chloride according to Huttig² forms a series of four ammines; $\text{CaCl}_2 \cdot \text{NH}_3$, $\text{CaCl}_2 \cdot 2\text{NH}_3$, $\text{CaCl}_2 \cdot 4\text{NH}_3$ and $\text{CaCl}_2 \cdot 8\text{NH}_3$. The first two have low vapor pressures even at somewhat raised temperatures, that for the monamine being 3.1 millimeters at 109°C . and that for the diammine being 38.2 at the same temperature. The tetrammine, however has a vapor pressure of about 305 millimeters at 25°C . while that of the octammine at the same temperature is about 540 millimeters.

Since these pressures are all below one atmosphere, it is possible to use the ordinary pyknometer in determining the densities of these compounds at 25°C . The pyknometers were of about 25 cc. capacity fitted with a ground in thermometer for a stopper and a side arm capillary fitted with a ground glass cap. The two used were repeatedly standardized with distilled water during the course of the work.

The liquids used were kerosene and xylene dried by first allowing them to stand over sodium hydroxide a few days and then over sodium metal for several more days. They were then distilled discarding the first and last tenth. Their densities at 25°C . were obtained by the use of the following formula.

² Huttig, Z. Anorg. Chem. 123, 31, (1922).

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$$D_L = \frac{W_L}{W_W} (D_w - \lambda) + \lambda$$

W_L = weight of pyknometer & liquid - weight pyknometer

W_W = weight pyknometer & water - weight pyknometer

D_L = density of liquid

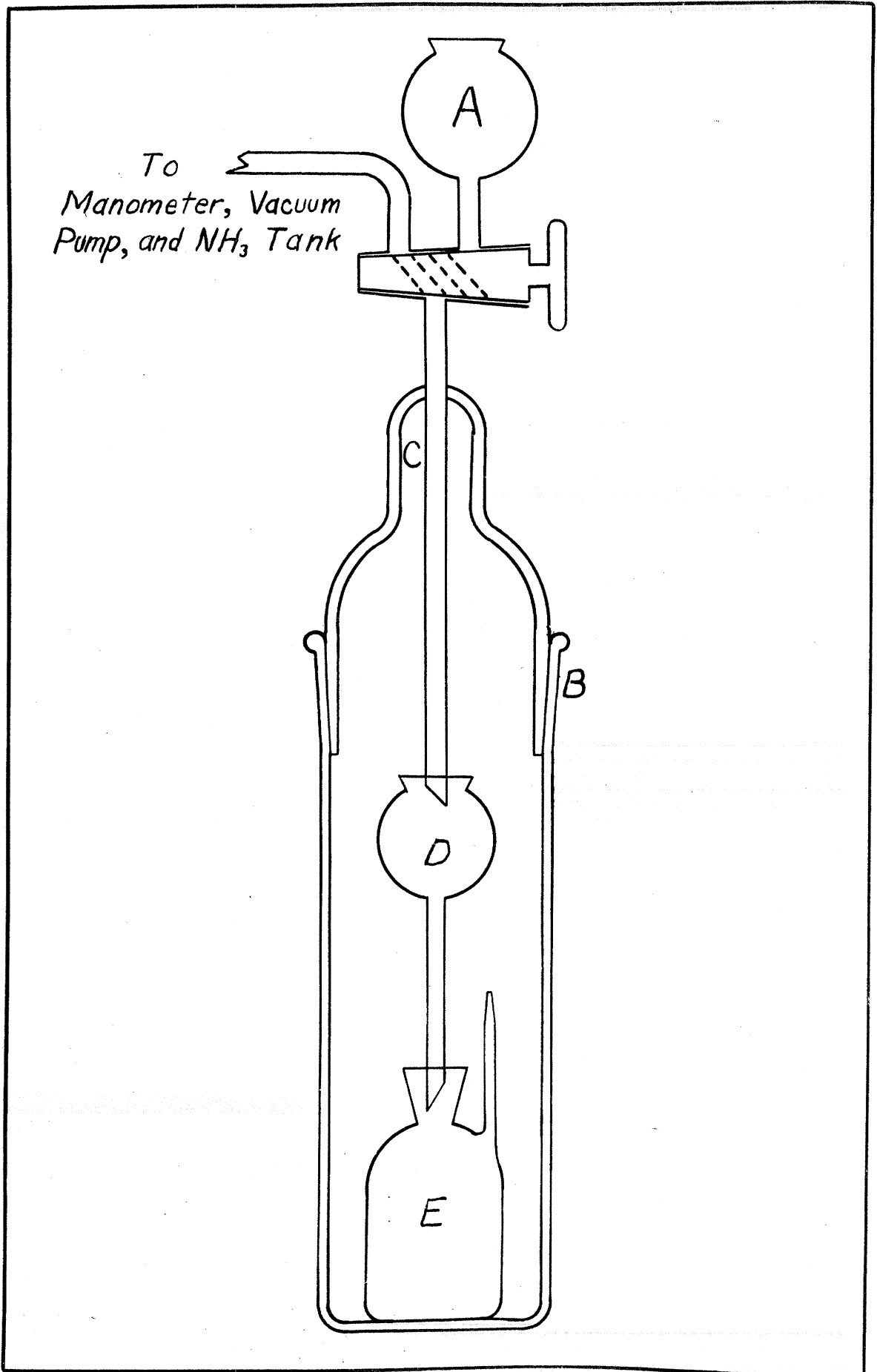
D_w = density of water

λ = .0012 = density of air.

The International Critical Tables value for the density of water was used, 0.997077 at 25 C. The averages of the various determinations were 0.85965 for the density of the xylene, and 0.79781 for the density of the kerosene.

Anhydrous calcium chloride was obtained by the method used by Huttig.² The C. P. anhydrous calcium chloride as obtained on the market was ground to a fine powder together with a small amount of C.P. ammonium chloride. This mixture was placed in a nickel crucible and heated in a sand bath until all the ammonium chloride had volatilized. The preparation was always carried out just before use to prevent the absorption of moisture. Calcium chloride prepared in this way showed no alkalinity and did not form lumps. The ammonia used was anhydrous ammonia which had been standing over sodium for a considerable length of time.

A definite amount of this calcium chloride was then weighed out in a pyknometer as rapidly as possible to prevent the absorption of moisture. This pyknometer, (E) in Figure L, was then placed in a pyrex container with a



large ground glass joint (B) as indicated in the figure. The stopper was so constructed that it could be clamped at (C) to prevent breakage of the connecting tubes on opening for it would frequently open with some difficulty after being evacuated. The tube through the stopper protruded into a thistle tube (D) suspended in the mouth of the pyknometer. This tube allowed the delivery of liquids from thistle tube (A) into the pyknometer, but at the same time prevented entering gas from streaming directly into the pyknometer and blowing out the finely powdered calcium chloride.

After evacuating to less than 0.0005 mm. as read on a MacLeod gauge, the container was surrounded with ice and ammonia passed in at a few centimeters over atmospheric pressure. Larger pressures could not be used for any length of time without loosening the ground glass joint. The time of ammonia absorption was varied from about an hour to about twenty hours depending on the compounds desired. A fairly good estimate of the amount absorbed could be made by the amount of swelling and the change in the rate of absorption. As soon as sufficient ammonia had been introduced it was allowed to stand at approximately its dissociation pressure for times varying from an hour to overnight in order to get equilibrium between the phases.

At this pressure kerosene or xylene in sufficient quantity to somewhat more than cover the compound was introduced through the thistle tube. Since this liquid was warmer than the compound, some ammonia would be expelled

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from the compound which would tend to carry off any traces of other gases which might have accumulated around the compound. On increasing the pressure to atmospheric any ammonia bubbles in the liquid would collapse due to their absorption by the calcium chloride.

The pycnometer was then removed from the container and completely filled with the liquid used and the stopper inserted. It was then suspended in a 25°C. thermostat for about half an hour, after which the cap was put on the capillary and the pycnometer dried on the outside and weighed. The contents of the pycnometer were then washed out into a beaker of distilled water and titrated with one normal hydrochloric acid using methyl orange as the indicator. The acid was standardized with sodium carbonate prepared from C. P. sodium bicarbonate.³ From this titration value the number of mols of ammonia per mol of calcium chloride and the weight of this mixture of two compounds. The density was then calculated by the following formula.

$$D = \frac{W_s}{W_s + W_L - W_{Ls}} (D_L - \lambda) + \lambda$$

W_s = weight of the mixture of compounds

W_L = weight of the pycnometer full of liquid

W_{Ls} = weight of pycnometer with solid and liquid

D_L = density of liquid

λ = 0.0012 = density of air

From this density the volume containing one mol of

³ Treadwell & Hall, "Analytical Chemistry", Vol. 2, p.475.

calcium chloride was calculated by the following relation.

$$V = \frac{M + NM'}{D}$$

$M = 110.99$ = Molecular weight of CaCl_2

$M' = 17.032$ = Molecular weight of NH_3

N = Mols of NH_3 per mol of CaCl_2

D = Density obtained by previous relation

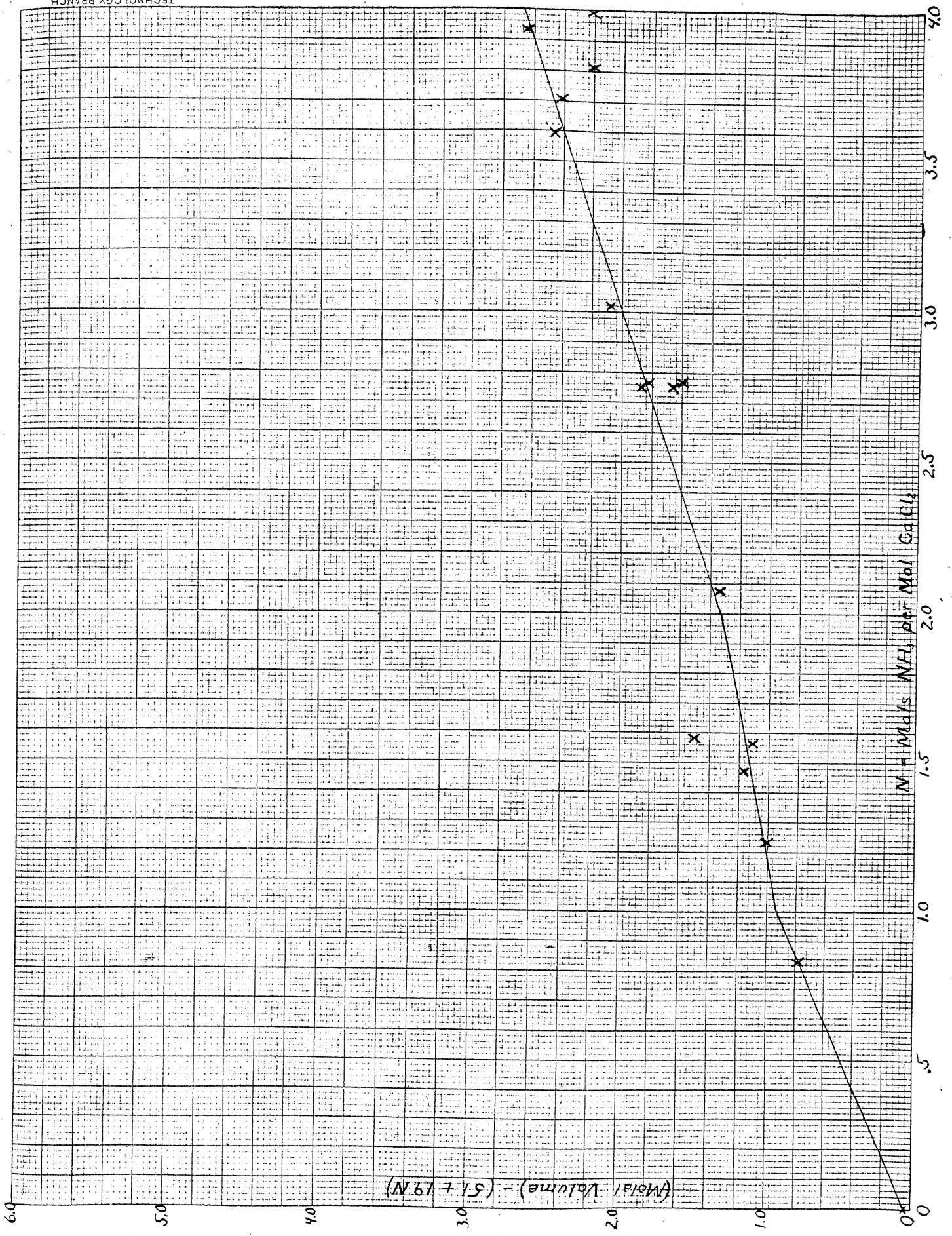
The values of V thus obtained were then plotted against N with the results shown in the graphs and tables given later.

In a few cases gas bubbles were present as they came to the surface when the stopper of the pyknometer was removed for titrating. In these cases, however, the results were considerably higher than the points through which the curve would normally go. Calcium chloride and its amines were not soluble in either kerosene or xylene as was shown by the evaporation of liquid which had been in contact with the solids. Solubility of ammonia in the liquids was found to be small enough, about .01 N. under the conditions of the experiments, to be negligible, especially as it introduces two slight errors of opposite sign which tend to compensate each other. Blank runs showed that the presence of calcium chloride, one of the oils, and ammonium chloride formed during the titration had no appreciable effect on the end point. The reproducibility of the standardization of the pyknometers with water showed them to be influenced little by time or by different pressures of inserting the stopper.

Due to the fact that the points could be fitted

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equally well assuming a hexamine, a rough vapor pressure curve was run at 25°C. in the region of from four to eight mols of ammonia per mol of calcium chloride. Since the vapor pressure remained constant at within five millimeters of 540 mm. throughout the region, the results of Huttig were assumed to be correct.



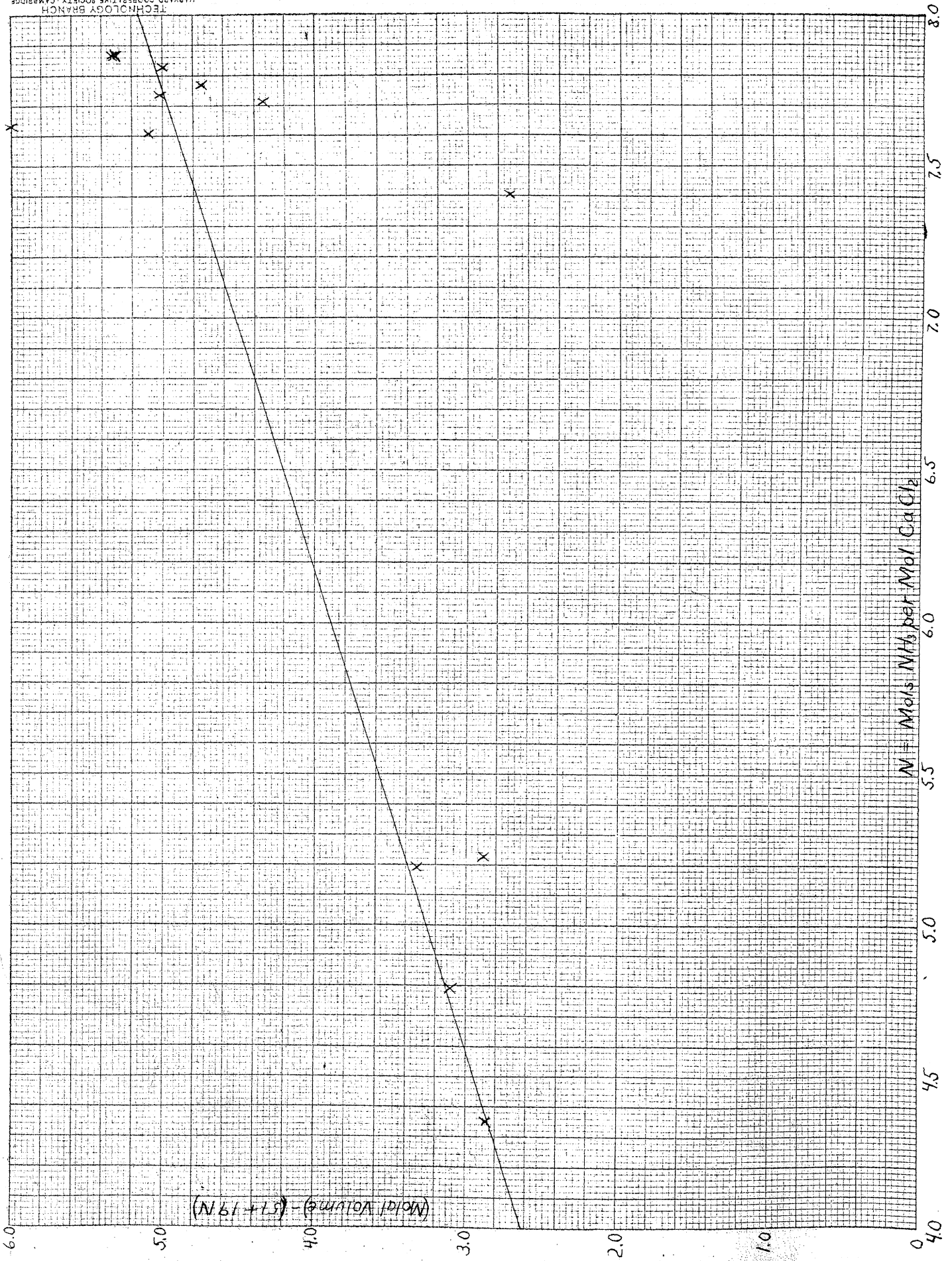


TABLE OF MEASUREMENTS

Wt of CaCl ₂ in grams	Mols of NH ₃ per mol CaCl ₂	Density of Compound	Volume per mol of CaCl ₂
2.0623	7.768	1.1965	203.33
1.9063	7.738	1.1957	203.04
2.2107	7.404	1.2196	194.40
1.6658	7.631	1.1929	202.00
1.7803	7.605	1.1991	200.58
1.5744	7.715	1.2004	201.92
1.8726	7.885	1.1906	205.73
2.3632	7.823	1.1935	204.63
3.2874	4.792	1.3269	145.15
4.4187	3.813	1.4001	125.65
4.4057	3.593	1.4144	121.73
5.2937	3.936	1.3862	128.43
5.0814	5.191	1.3036	152.96
4.9843	2.764	1.5039	105.11
6.7549	3.018	1.4707	110.42
5.7188	2.752	1.5011	105.16
7.1218	2.766	1.5005	105.37
8.4919	1.561	1.6829	81.76
7.1528	1.232	1.7498	75.42
6.4158	2.756	1.5038	105.02
8.1279	1.469	1.6987	80.07
8.4375	1.582	1.6710	82.55
8.8272	2.075	1.5948	91.75
5.9322	5.244	1.3047	153.53
6.5562	3.987	1.3872	128.96

TABLE OF MEASUREMENTS (cont.)

Wt of CaCl ₂	Mols of NH ₃	Density	Mol Volume
5.9894	4.350	1.3556	136.52
8.4714	.830	1.8524	67.55
5.4789	3.707	1.4064	123.82
10.4114	0	2.1750	51.03
8.7591	0	2.1741	51.05
11.3104	0	2.1743	51.05
11.9383	0	2.1734	51.07

Table of Results

Compound	Molal Volume	Density	Average cc. per mol NH ₃
CaCl ₂	51.05	2.1741	
CaCl ₂ .NH ₃	70.93	1.8049	19.88
CaCl ₂ .2NH ₃	90.32	1.6060	19.63
CaCl ₂ .4NH ₃	129.65	1.3816	19.65
CaCl ₂ .8NH ₃	208.16	1.1877	19.64

Partial Molal VolumesRegion, mols/ mol CaCl₂ $\left(\frac{\partial V}{\partial N}\right)$

0 - 1 NH ₃	19.88
1 - 2 NH ₃	19.39
2 - 4 NH ₃	19.66
4 - 8 NH ₃	19.63

BARIUM CHLORIDE OCTAMMINE.

The case of barium chloride was of especial interest since its ammine was used by Lurie and Gillespie ⁴ in studying the fugacity of ammonia in mixtures with nitrogen. The value of twenty cc. per mol was assumed in this work for the partial molal volume of ammonia in the compound in calculating the effect of pressure on the dissociation pressure by means of the Poynting relationship.

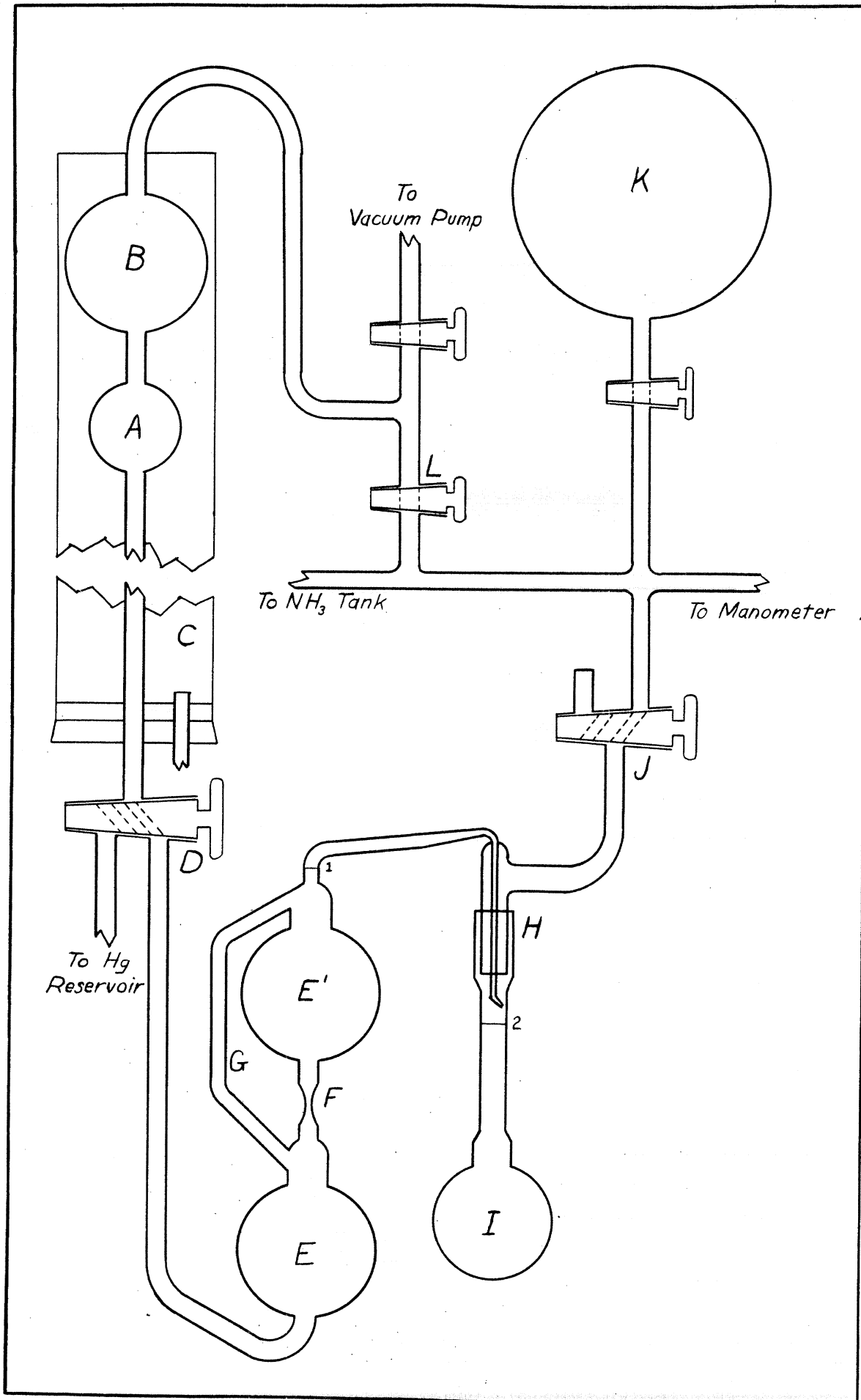
Barium chloride forms but one ammine, an octammine, as was shown by Huttig and Martin ⁵ and checked by Lurie and Gillespie.⁴ The vapor pressure of this compound is quite high being about 2010 mm. at 25 C. This high value makes some modification of the calcium chloride density procedure necessary.

The method adopted was to form the compound in a container of known volume and then to fill the container with kerosene saturated with ammonia at the vapor pressure of the compound. By measuring the amount of the liquid that is required, the volume of the compound is obtained. The ammonia content is subsequently determined by analysis.

Referring to the figure, E and E' were two bulbs, each of approximately 60 cc. capacity. The lower one contained mercury which passed through the stopcock D into the column above. About fifty cc. of kerosene were

⁴ Lurie & Gillespie, J.A.C.S. 49, 1146, (1927).

⁵ Huttig & Martin, Z. Anorg. Chem. 125, 269, (1922).



introduced into these bulbs through the capillary tip at H while the flask I was removed. Into this flask whose volume was about 40 cc. a definite amount of barium chloride was weighed out. It was then sealed on with Kotinsky wax at H. Then the system was evacuated to about the vapor pressure of the kerosene and ammonia then run in to a pressure of about an atmosphere. By repeating this process several times the system was practically freed from air. The bulbs E and E' and the flask I were then surrounded by ice and ammonia passed in at about three atmospheres pressure for from three to five hours. Then, holding the pressure at about 2,100 mm. the ice was removed and a 25°C thermostat with a glass front was substituted.

Bulbs A and B were of about 25 cc. and 75 cc. capacity respectively and the tubing between them and from the lower bulb to the stopcock B, a distance of about 70 cm., were of tubing holding about one cc. per three cm. of length. This column was surrounded by a water bath C, held at 25° by circulating the water through a coil in the thermostat by means of an air lift pump. Heights of mercury in the tubing could be read by means of a meter stick placed directly behind the water bath, with a slider on it such as is on a slide rule except that half the side with the hair line on it was silvered. By the use of this mirror readings could be duplicated to a tenth of a millimeter. The volume of the column at all points between the bulb B and the stopcock D was accurately determined by calibration with mercury.

By running mercury into this column from the bulb E, the kerosene trickled slowly through the capillary F from the upper bulb E' over the sides of the lower bulb which was filled with an atmosphere of ammonia entering through the tube G. When the mercury was run back by applying pressure at the top of the column, the kerosene went back chiefly through the tube G causing a thorough mixing of the liquid. Since there was a volume change of about 50 cc. in the gas phase during the process, a large ballast flask of four or five liters capacity K was attached to make the pressure variation small. By running the kerosene several times between the bulbs E and E' the liquid became saturated with ammonia at about the vapor pressure of barium chloride octamine.

After saturation the kerosene was brought up to the mark l at the top of the bulbs and the height of the mercury in the column adjusted to between A and B by introducing mercury from the reservoir. This height was then read accurately and then sufficient kerosene was forced over through the capillary jet at H to cover the compound in the container I. Any air which might have accumulated around the compound was blown off by letting ammonia escape by the stopcock J. A pressure of about 2,200 mm was then applied and any ammonia bubbles soon collapsed. If there were any air bubbles left, they were shown by bubbles rising as soon as any gas was allowed to escape at J, but if there were none there would be no bubbles rising until the pressure was diminished almost to atmospheric.

When there were no more air bubbles, the kerosene was run over until it filled container I to the mark 2 on the neck which was made of the same size tubing as the column. The height of the mercury in the column was again read, thereby giving with the previous reading a volume which, subtracted from the volume obtained when I contained no barium chloride, gives the volume occupied by the compound.

The thermostat was then removed and a freezing mixture of ice and salt placed around the container I. As soon as it had cooled sufficiently, the pressure was released by opening the stopcock J, and the Kotinsky joint at H broken by heating it gently. The contents of the container were then washed out with distilled water and titrated with two normal hydrochloric acid. Since the amount of ammonia dissolved in the kerosene at the pressure used had previously been determined, the amount of ammonia in the compound could be calculated. Since this correction of the titration value amounted to less than one percent, the error introduced by slight errors in the correction were negligible.

C.P. barium chloride dihydrate was used. After partial dehydration by heating the powdered hydrate, it was ground with ammonium chloride and heated in a nickel crucible on a sand bath in the same way as the calcium chloride. This was the method used by Huttig and Martin. The density of this barium chloride was determined by the standard pycnometer methods for solids. The kerosene and standard acid were prepared like those used with calcium chloride. In order to minimize changes of volume in the apparatus all readings

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were made with the same pressures on all parts of the apparatus.

TABLE OF RESULTS

Molal Volume of Barium Chloride.

BaCl₂ Mol. Wt. 208.29

Weight BaCl ₂	Density	Molal Volume
18.7684	3.8886	53.564
20.7820	3.8889	53.560
19.3984	3.8888	53.561
Averages	3.8888	53.561

Table of Measurements.

Volume of container 40.814 cc. Normality of NH₃ in kerosene .176

Weight BaCl ₂	Mols NH ₃ per BaCl ₂	Observed Volume	Volume per mol	Partial mol vol NH ₃
13.9837	5.573	11.672	173.84	21.58
14.1913	5.729	12.237	179.93	22.00 *
14.4890	6.248	13.088	188.15	21.54
14.3396	4.791	10.755	156.22	21.44
14.0630	5.225	11.221	166.19	21.55
14.2103	5.489	12.120	177.60	22.60 *
14.3435	5.986	12.558	182.37	21.52

* These determinations showed indications of air during the measurement and were excluded in figuring the average.

Results.

Average value $\left(\frac{\partial V}{\partial N}\right)$ for NH ₃ in BaCl ₂ .8NH ₃	21.53
Molal Volume of BaCl ₂ .8NH ₃	225.80
Density of BaCl ₂ .8NH ₃	1.5260

SUMMARY

Methods have been developed for obtaining the densities of amines without isolating the pure amines. The methods are suitable for use with amines having higher dissociation pressures than those which can readily be handled by the usual density procedures for solids.

By these methods the densities of calcium chloride monamine, calcium chloride diamine, calcium chloride tetramine, calcium chloride octamine, and barium chloride octamine were obtained. From these results the partial molal volume of ammonia in these compounds was obtained.