

ium ion closer together. In view of this small uncertainty it is thought fairer to leave the values as recorded above, *i. e.*, 58.6 and 59.1.

### Summary

The conductivities of hydrazine picrate, trinitro-*m*-cresylate and perchlorate have been measured at 25°, likewise sodium picrate and potassium perchlorate. At low concentration the slope of the curve obtained by plotting equivalent conductivity against square root of the concentration is quite close to that calculated from the equation of Onsager.

From these results the mobility of the hydrazinium ion has been calculated.

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## DENSITIES, AND PARTIAL MOLAL VOLUMES OF AMMONIA, FOR THE AMMINES OF CALCIUM AND BARIUM CHLORIDES

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### Introduction

Density data for ammines 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.<sup>1</sup> Such compounds may be isolated in quite a pure state, and density data may be obtained for pure compounds with little modification from the procedure used with ordinary solids.

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

However, it is not necessary to work with pure ammines. The vapor pressure curves show that at equilibrium between a salt and ammonia, at any composition other than that of the compounds, there will be two solid phases, either the ammonia-free salt and an ammine or a mixture of two ammines. Consider the case of a salt MX forming two ammines: MX-

<sup>1</sup> Biltz and Birk, *Z. anorg. Chem.*, **134**, 125 (1921); Clark, Quick and Harkins, *This Journal*, **42**, 2483 (1920); Birk, *Z. anorg. Chem.*, **158**, 111 (1926).

$a\text{NH}_3$  having a molal volume  $V_1$ , and  $\text{MX}\cdot b\text{NH}_3$  having a molal volume  $V_2$ , where  $b$  is greater than  $a$ . Let there be found by analysis  $N$  moles of ammonia per mole of the salt  $\text{MX}$ ,  $N$  being between  $a$  and  $b$  in value. Then the mole fraction of  $\text{MX}\cdot a\text{NH}_3$  in the mixture of the two solids will be  $(b - N)/(b - a)$ ; and that of  $\text{MX}\cdot b\text{NH}_3$  will be  $(N - a)/(b - a)$ .

Let  $V$  be the volume of the two phases per mole of  $\text{MX}$ . Then the partial molal volume of ammonia in the solids is  $(\partial V/\partial N)$ . It is this quantity that should be used in the Poynting equation to calculate the effect of pressure on the decomposition pressure of solids that evolve a gas.<sup>2</sup> We have then

$$V = V_1(b - N)/(b - a) + V_2(N - a)/(b - a) \quad (1)$$

and

$$V = N(V_2 - V_1)/(b - a) + (bV_1 - aV_2)/(b - a) \quad (2)$$

Hence the measured volume per mole of the salt is a straight-line function, between the values of the molal volumes of the two compounds forming the mixture, of the number of moles of ammonia per mole of salt. The slope of this line is the partial molal volume in the region between the two compounds. If equilibrium is obtained between the phases, it is necessary only to start with a definite weight of the salt and to add ammonia in successive portions, the total volume and the quantity of combined ammonia being determined after each addition. By plotting  $V$  against  $N$ , the molal volumes of the two pure compounds are obtained as intercepts, and the partial molal volume as a slope.

### The Ammines of Calcium Chloride

Calcium chloride forms according to Hüttig<sup>3</sup> 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 high temperatures; that for the monamine being 3.1 mm. of mercury at  $109^\circ$ , and that for the diamine being 28.2 mm. at the same temperature. The tetrammine, however, has a vapor pressure of about 305 mm. at  $25^\circ$ , while the octammine has a vapor pressure at the same temperature of about 540 mm.

Since these pressures are all below one atmosphere, it is possible to use the ordinary pycnometer to determine the densities of these compounds at  $25^\circ$ . The pycnometers were of about 25-cc. capacity and were fitted with a ground-in thermometer as stopper and a side-arm capillary fitted with a ground-glass cap. Two were used, and were repeatedly standardized with distilled water during the course of the work.

The liquids used were kerosene and xylene, dried by allowing them to stand first over sodium hydroxide for a few days and then over sodium metal for a like period. They were then distilled and the first and last

<sup>2</sup> Gillespie, *Proc. Am. Acad. Arts Sci.*, **66**, 153 (1930).

<sup>3</sup> Hüttig, *Z. anorg. Chem.*, **123**, 31 (1922).

tenths were rejected. Their densities at 25° were obtained by the use of the familiar formula

$$D_L = W_L(D_w - 0.0012)/W_w + 0.0012 \quad (3)$$

The "International Critical Tables" value for the density of water was used: 0.997077. The average results of the density determinations were 0.85965 for the xylene and 0.79781 for the kerosene.

Anhydrous calcium chloride was obtained by the method used by Hüttig. The c. p. anhydrous material as obtained on the market was ground to a fine powder, together with a small quantity 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 been driven off. 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 formed no lumps. The ammonia used was anhydrous ammonia which had been standing over sodium for some months.

A definite quantity of this calcium chloride was weighed out in a pycnometer as rapidly as possible to prevent absorption of moisture. This pycnometer, designated by E in Fig. 1, was then placed in a Pyrex container having a large ground-glass joint B. The stopper was constructed so that it could be clamped at C to prevent breakage of the connecting tubes on opening against the pressure of the atmosphere. The tube through the stopper protruded into a thistle tube D suspended in the mouth of the pycnometer. This tube allowed the delivery of liquids from thistle tube A into the pycnometer, but prevented gas from streaming directly into the pycnometer and blowing out the finely-powdered calcium chloride.

After evacuation to better than 0.0005 mm. as read on a McLeod gage, the container was surrounded with ice, and ammonia was introduced 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 one hour to about twenty hours, depending on the compounds desired. A fairly good estimate of the quantity absorbed could be made by the amount of swelling and the change in the rate of absorption (judged by the pressure). As soon as sufficient ammonia had been introduced, the system was allowed to stand at approximately its dissociation pressure for periods varying from an hour to overnight, in order to obtain equilibrium.

Fig. 1.—Apparatus for calcium chloride amines.

At this pressure, kerosene or xylene was introduced through the thistle tube in sufficient quantity to somewhat more than cover the compound. Since the liquid was warmer than the compound, some ammonia was expelled, carrying off any traces of other gases which might have accumulated around the compound. On increasing the pressure to atmospheric pressure, any ammonia bubbles in the liquid collapsed, being absorbed by the unsaturated solid.

The pycnometer was then removed from the container and completely filled with the given liquid and the stopper inserted. It was then suspended in a thermostat at 25° for half an hour, after which time 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 1 *N* hydrochloric acid, using methyl orange. The acid was standardized with sodium carbonate from sodium bicarbonate.<sup>4</sup>

From the titration value the number of moles of ammonia per mole of calcium chloride and the weight of the mixture of solid compounds were obtained. The density of the mixture of solid compounds was calculated by the familiar formula

$$D = \frac{W_s}{W_s + W_L - W_{Ls}} (D_L - 0.0012) + 0.0012 \quad (4)$$

From this density, the volume containing one mole of calcium chloride was calculated from the relation

$$V = (M + NM')/D \quad (5)$$

where *M* is the mol. wt. of CaCl<sub>2</sub>; *M'* that of NH<sub>3</sub>; *N* is the number of moles of NH<sub>3</sub> per mole of CaCl<sub>2</sub>; and *D* is the density determined by the use of equation (4).

The values of *V* thus obtained were then plotted against *N* (using a deviation plot), with the results shown in the graph and table given later.

In a few cases gas bubbles were present and came to the surface when the stopper of the pycnometer was removed for the titration. In these cases the results were considerably higher, the points being much above the line established by other measurements: small errors due to undiscovered bubbles seemed not to occur. Calcium chloride and its ammines were not soluble in either kerosene or xylene, as was shown by the evaporation of liquid which had been in contact with the solids. The solubility of ammonia in the liquids was found to be so small, about 0.01 *N* under the experimental conditions, as to be negligible, especially as it introduces two slight errors of opposite sign which tend to compensate. Blank runs showed that the presence of calcium chloride, either oil, and ammonium chloride (formed during the titration) had no appreciable effect on the end-point. The reproducibility of the standardization of the pycnometers with water showed them to be influenced little by time or by different pressures of inserting the stopper.

Because of the fact that the experimental points could be fitted equally well by the assumption that a hexamine exists, in addition to the compounds found by Hüttig, the vapor pressure-composition curve was approximately determined at 25° for values of *N* from 4 to 8. The vapor pressure remained constant at 540 ± 5 mm. throughout the region, and the results of Hüttig were therefore assumed correct in drawing the lines.

### Barium Chloride Octamine

The case of barium chloride was of interest because of its use by Lurie and Gillespie<sup>5</sup> in studying the thermodynamic properties of ammonia in

<sup>4</sup> Treadwell and Hall, "Analytical Chemistry," 6th ed., 1924, Vol. II, 475.

<sup>5</sup> Lurie and Gillespie, THIS JOURNAL, 49, 1146 (1927).

mixtures with nitrogen. They assumed the value 20 cc. per mole for the partial molal volume of ammonia, for use in the Poynting relation.

Barium chloride forms but one ammine, the octammine, as was shown by Hüttig and Martin.<sup>6</sup> The vapor pressure is quite high, 2049 mm., at 25°.<sup>7</sup> This high value makes some modification necessary for determining the density.

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 volume of kerosene required, the volume of the compound was obtained. The ammonia content was subsequently determined by analysis.

In Fig. 2, E and E' are two bulbs, each of approximately 60 cc. capacity. The lower bulb contained mercury which extended through the stopcock D into the column above. About 50 cc. of kerosene was introduced into these bulbs through the capillary tip at H while the flask I was removed. Into this flask, whose volume is about 40 cc., a definite quantity of barium chloride was introduced and weighed. The flask was then sealed on with de Khotinsky wax at H. The system was evacuated to about the vapor pressure of the kerosene, and ammonia was admitted to a pressure of about 1 atm. By repeating the evacuation and loading with ammonia several times, the system was practically freed from air. The bulbs E and E' and the flask I were then surrounded with ice, and ammonia was admitted at about 3 atm. for from three to five hours, according to the composition desired. With the pressure at about 2100 mm., the ice was removed and a thermostat at 25° with a glass front was substituted.

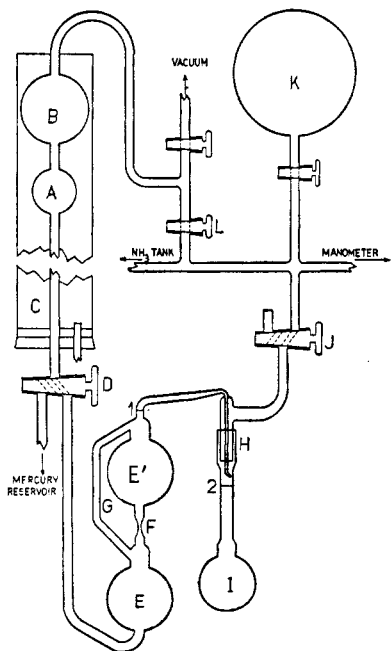


Fig. 2.—Apparatus for barium chloride octammine.

Bulbs A and B are of about 25 cc. and 75 cc. capacity, respectively, and the tubing between them and from the lower bulb to the stopcock D—a distance of about 70 cm.—was of tubing holding about 1 cc. in 3 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. The height of mercury in the tubing could be read by means of a meter stick placed directly behind the water-bath, carrying a slider like that of a slide rule, except that half the under side was silvered. By the use of this mirror readings could be duplicated to 0.1 mm. The volume of the column at all points between B and D was accurately determined by calibration with mercury.

By running mercury into this column from the bulb E, the kerosene was caused to

<sup>6</sup> Hüttig and Martin, *Z. anorg. Chem.*, **125**, 269 (1922).

<sup>7</sup> Gillespie and Lurie, *THIS JOURNAL*, **53**, 2978 (1931).

trickle 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 returned 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 K of 4 to 5 liters capacity was attached to make the variation of the pressure 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  $\text{BaCl}_2 \cdot 8\text{NH}_3$ .

After saturation, the kerosene was brought up to the mark 1 at the top of the bulbs and the height of the mercury adjusted between A and B by introducing mercury from the reservoir. This height was then read accurately and sufficient kerosene was then forced over through the capillary jet at H to cover the compound in the container I. Any air that might have accumulated around the compound was blown off by letting ammonia escape by the stopcock J. A pressure of about 2200 mm. was then applied, and any ammonia bubbles soon collapsed. If there were any air bubbles left, they were later shown by the rising of bubbles as soon as any gas was allowed to escape at J; but if there were none, no bubbles rose until the pressure was diminished almost to that of the room. When there were judged to be 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 read again, thereby giving, with the previous height reading in connection with the calibration, a volume. When this volume was subtracted from the volume measured when I contained no solid, the volume occupied by the compound was obtained.

The thermostat was then removed and a freezing mixture of ice and salt placed around I. After the cooling, the pressure was released by opening the stopcock J, and the joint at H was broken by gently heating the wax. The contents of the container were then washed out with distilled water and titrated with 2 *N* hydrochloric acid. Since the quantity of ammonia dissolved in the kerosene at the given pressure had previously been determined, the quantity of ammonia in the compound could be calculated. This correction of the titration value amounted to less than 1%, and the error introduced by slight errors in the correction was 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 for calcium chloride. This method was used by Hüttig and Martin. The density of this barium chloride was determined by the standard pycnometer method for solids. The kerosene and standard acid were prepared in the same manner as for the experiments with calcium chloride. In order to minimize changes of volume in the apparatus, all readings were made with the same pressures on all parts of the apparatus.

TABLE I  
EXPERIMENTAL RESULTS AT 25°

Compound	Density	Molal volume	Average molal volume of $\text{NH}_3$	Partial molal volume of $\text{NH}_3$
$\text{CaCl}_2$	2.1741	51.05		
$\text{CaCl}_2 \cdot \text{NH}_3$	1.8049	70.93	19.88	19.88
$\text{CaCl}_2 \cdot 2\text{NH}_3$	1.6060	90.32	19.63	19.39
$\text{CaCl}_2 \cdot 4\text{NH}_3$	1.3816	129.65	19.65	19.66
$\text{CaCl}_2 \cdot 8\text{NH}_3$	1.1877	208.16	19.64	19.63
$\text{BaCl}_2$	3.8888	53.561		
$\text{BaCl}_2 \cdot 8\text{NH}_3$	1.5260	225.80	21.53	21.53

### Results

Twenty-eight determinations of density were made of solids containing calcium chloride and ammonia, seven of solids containing barium chloride and ammonia (in five of which the formation of air bubbles was successfully avoided), four of pure calcium chloride and three of pure barium chloride; all at 25°, as established by platinum thermometry. Table I gives the density and molal volume of the compound, the average volume of ammonia in cc. per mole and the partial molal volume of ammonia in the two solids,

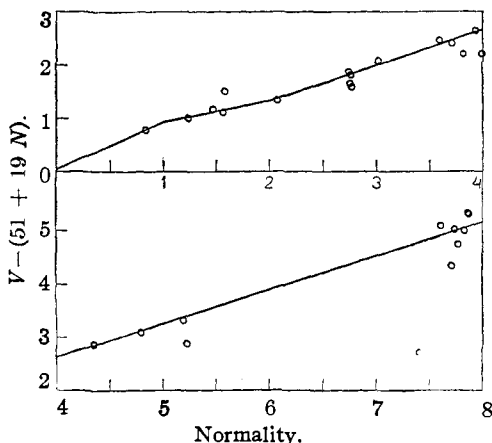


Fig. 3.—Deviation plot of the quantity  $V - (51 + 19N)$  against  $N$  for the calcium chloride amines (in two sections).

the symbol of one of these being entered on the same line of the table as the partial molal volume, and the symbol for the other being entered on the line above. In the cases of barium chloride and of the first ammine of calcium chloride, the partial molal volume and the average volume of ammonia are the same, but they are, in general, not the same. Figure 3 shows the deviation plot (in two sections) used for calcium chloride amines. Using the symbols defined above, the quantity  $V - (51 + 19N)$  was plotted against  $N$ , and straight lines drawn between the values of  $N$ : 0-1, 1-4 and 4-8. The following molecular weights were used in the calculations:  $\text{CaCl}_2$ , 110.99;  $\text{BaCl}_2$ , 208.29;  $\text{NH}_3$ , 17.032.

### Summary

Methods have been developed for obtaining the densities of amines without isolating the pure ammine. The methods are suitable for use with compounds having decomposition pressures too high for the usual density procedures for solids.

By these methods the densities of calcium chloride monammine, diammine, tetraammine and octammine, and of barium chloride octammine were obtained. The densities of calcium and barium chlorides were also determined. From the results the partial molal volume of ammonia in these compounds was calculated: it differs but little from the average molal volume of ammonia in the solids.

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