36. Dissociation Pressures of Compounds of Ammonia and Trideuterammonia with some Metallic Salts.

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Measurements of the dissociation pressures of compounds of ammonia and trideuterammonia with eleven metallic salts, *viz.*, $CaCl_2$, $CaBr_2$, $BaBr_2$, $FeCl_2$, $NiCl_2$, $MnCl_2$, LiCl, LiBr, LiI, NaI, $CuSO_4$, are described, and from the results the heats of decomposition of the various ammines and deuterammines are calculated.

In all, 64 systems of the type $M,xN(H \text{ or } D)_3 = M,yN(H \text{ or } D)_3 + (x - y)N(H \text{ or } D)_3$ have been observed in the temperature range −50° to 300°. The effect of isotopic replacement is demonstrated and briefly discussed.

The densities of $NiCl_2,6NH_3$ and $NiCl_2,6ND_3$ have been accurately measured in order to demonstrate the molecular volume isotope effect.

The addition compounds (ammines) of ammonia and anhydrous salts vary considerably in stability, and may be divided roughly into two classes : (*a*) those stable in aqueous solution, and (*b*) those decomposed by water. Compounds of the second type are generally ammines of uni- and bi-valent metals, *e.g.*, $NiCl_2,6NH_3$, $FeCl_2,6NH_3$, $CaCl_2,8NH_3$, $CuCl,3NH_3$, and $CuSO_4,5NH_3$, and at ordinary temperatures are mostly in equilibrium with pressures of ammonia of the same order as the dissociation pressures of the hydrates. There are gradations of stability, and $NiCl_2,6NH_3$ and the corresponding ammines of the bivalent transition elements, for example, can exist in aqueous solution in presence of a large excess of ammonia. The ammines in which we are interested range in stability from this nickel compound to $BaCl_2,8NH_3$, which at 20° has a decomposition pressure of 2 atm.

The dissociation pressures of compounds of ammonia with the halides of silver and the chlorides of magnesium, calcium, zinc, and mercury were measured by Isambert (*Compt. rend.*, 1868, **66**, 1259; 1878, **86**, 968), who also determined the heats of dissociation calorimetrically. The heat of dissociation of the compound of ammonia with silver chloride was calculated by Horstmann (*Ber.*, 1876, **9**, 749) from the slope of the pressure–temperature curve ($\Delta p/\Delta T$).

Measurements of limited scope on ammines of various salts were made by several workers (Bonnefoi, *Ann. Chim. Phys.*, 1901, **23**, 317; Baud, *Compt. rend.*, 1901, **132**, 553; Girardet, *Bull. Soc. chim.*, 1910, **7**, 1028), and systematic investigations by Ephraim (*Z. physikal. Chem.*, 1913, **81**, 513; *Ber.*, 1919, **52**, 940), who showed that the stability of an ammine, as measured by the temperature at which it gives a pressure of 100 mm., is inversely proportional to the atomic volume of the metal atom.

Ephraim and Müller (*Ber.*, 1921, **54**, 973), with hexammines of nickel salts with MoO_4'', WO_4'', CrO_4'', SeO_4'' and SO_4'', found that the anion with the largest molecular volume gives the most stable complex. Ephraim and Bolle (*Ber.*, 1915, **48**, 638) found that nickel salts of univalent anions show decreasing stability in the order ClO_4', I′, Br′, ClO_3', Cl′. With zinc salts the order was I′, Br′, Cl′, ClO_4', NO_3', and ClO_3'. Zinc is not strictly comparable with nickel, since its lowest ammine is a tetrammine, whereas nickel gives a diammine. Ephraim's later work (*Z. anorg. Chem.*, 1925, **147**, 24; *Ber.*, 1926, **59**, 1219) was concerned with more detailed investigation of the lower ammines and with the higher stable ammine complexes.

Biltz and Hüttig and their collaborators dealt mainly with the complete investigation of all the ammines formed by each salt. The results were summarised and discussed by Biltz (*Z. anorg. Chem.*, 1923, **130**, 93). The relation of stability to heat of dissociation q, was discussed by Biltz and Biltz and Grimm (*ibid.*, 1925, **145**, 63), who showed that the best term of comparison was $U + q$, where U is the lattice energy of the pure salt. It was shown that : (1) For the same number of molecules of ammonia, $U + q$ falls with increasing radius of the cation and also of the anion when the ion has the same number of electrons in the outer quantum group; (2) a cation with 10 outer electrons gives a higher value than one in the same period with 8 (Cu > K; Zn > Ca); (3) for cations with the same outer electron group $U + q$ for any given number of molecules of ammonia increases with the electrovalency; (4) the differences between the $U + q$ values with the same number of ammonia molecules but a different halogen fall with increase in ammonia content when the cation has 8 outer electrons, but rise when it has 18 or 20. These results agree with Fajans's rule (*Z. Elektrochem.*, 1928, **34**, 502). Ammines of silver and cuprous halides, which form compounds with ½, 1, 1½, 2, and $3NH_3$ and thus do not fit into the above scheme, were explained by assuming that an associated salt molecule and not the ion is the unit to which the ammonia is attached.

It has been shown for a number of salt deuterates (Partington and Stratton, *Nature*, 1936, **137**, 1075; Schacherl and Behounek, *ibid.*, 1936, **138**, 406; Lange and Sattler, *Z. physikal. Chem.*, 1937, **179**, 427; Bell, J., 1937, 459; 1940, 72; Miles and Menzies, *J. Amer. Chem. Soc.*, 1938, **60**, 87) that the dissociation pressure in the temperature range 20—80° is smaller than that of the corresponding hydrates, and that the heat of dissociation is greater for deuterium oxide than for water, the difference being greater than could be accounted for by the different heats of evaporation of these two.

Ubbelohde (*Trans. Faraday Soc.*, 1936, **32**, 525) showed that the effect of the substitution of deuterium for hydrogen depends on the nature of the link, and that the effects described should be, and are, accompanied by a contraction of the crystal lattice, which leads to a greater work of removal of deuterium oxide than of water. Robertson and Ubbelohde (*Nature*, 1937, **139**, 504) found by the *X*-ray method that with oxalic acid dihydrate lattice expansion occurs, which can be explained by assuming that water is attached by a hydrogen bond, the resonance associated with which would be less complete in the deuterium compound. In agreement with this, Bell (*loc. cit.*, 1940) showed that the vapour pressure and heat of dissociation of this compound are affected by isotopic substitution in the opposite sense to ordinary salt hydrates.

EXPERIMENTAL.

The experiments involved measurements of the vapour pressures of pure ammonia and deuterammonia, and of the dissociation pressures of the ammines and deuterammines of several salts, some density measurements on the light and heavy ammines of nickel chloride being also made.

(i) *Preparation of Ammonia.*—The pure, dry gas was prepared by two methods: the action of water on magnesium nitride was first used, but later the gas was evolved by heating a mixture of pure ammonium chloride and calcium oxide in a 250-c.c. Pyrex distilling flask connected with three large U-tubes filled with sodium hydroxide pellets and all sealed together. Following these were two condensing traps, the first containing sodium, and finally a trap permanently attached to the storage vessel. Beyond this was a trap leading to the manometer, a side arm leading to the "Hyvac" pump (suitably protected by sulphuric acid towers), and a final condensing bulb. The apparatus, first pumped out to 5 mm., was filled with ammonia to a pressure of 50 cm. by gently warming the generating flask. This gas was pumped off, and the process repeated twice. The tap leading to the pump was then closed and the trap cooled in solid carbon dioxide–alcohol until about 10 c.c. of liquid ammonia collected in it. Despite a large excess of calcium oxide in the generating flask, a considerable amount of water had by this time collected in the first arm of the first U-tube; beyond this, however, the sodium hydroxide was not attacked. When the liquid was collected, the first part of the apparatus was sealed off. The liquid was kept overnight in contact with the sodium, with which it formed an almost black solution, and was then cautiously distilled into the second trap by warming to give a pressure of about 20 cm. and cooling the second trap to −79°, at which temperature the vapour pressure of ammonia is 4·5 cm. The last 2 c.c. of liquid were rejected by sealing away the first trap. A second and third distillation were carried out in the same way into the third and then into the furthest trap, beyond the storage vessel, which was then sealed off, and the ammonia bulb isolated. From this the ammonia was evaporated into the vacuous 3-l. storage flask to a pressure of 80 cm. A 2-l. flask with a rubber bung was connected to the joint on the storage vessel, and was evacuated and filled with ammonia to form a reserve supply which could be transferred to the main storage vessel. In some later experiments the U-tubes containing soda pellets were replaced by a bubbler containing very concentrated sodium hydroxide solution, followed by a straight tube, 1·5 cm. diam. and 75 cm. long, containing soda pellets, followed by pieces of metallic sodium.

(ii) *Preparation of Deuterammonia.*—Bruyne and Smith (*J. Amer. Chem. Soc.*, 1935, **57**, 1203), Taylor and Jungers (*ibid.*, 1933, **55**, 5057), Smits, Muller, and Kröger (*Z. physikal. Chem.*, 1937, *B*, **38**, 177), Frivold, Hassel, and Rustad (*Physikal. Z.*, 1937, **38**, 191) have used the reaction $Mg_3N_2 + 6D_2O = 3Mg(OD)_2 + 2ND_3$. The heavy water (99·6% D_2O) we used was in 10 g. ampoules from the Norsk Hydro, and about 8 g. produced enough ND_3 to fill the 3-l. flask at 74 cm., almost corresponding with the theoretical yield. For our purposes Kahlbaum's magnesium nitride was not sufficiently pure, as the ammonia evolved from it with water had a smell of acetylene; the method finally adopted for the preparation of the pure nitride was to heat magnesium turnings in a boat inside a seamless iron tube through which passed a stream of dry cylinder nitrogen. A boat of thick nickel foil was quickly attacked, but one of stainless-steel sheet about 2 mm. thick, bent into the form of an open rectangular box 15 cm. long and 1·5 cm. square section, was used to prepare in all about 200 g. of the nitride and showed no evidence of attack. In each experiment about 15—20 g. of magnesium turnings were used, and by suitable temperature regulation nearly all the product was yellow and gave a perfectly white residue with water.

The heavy ammonia was prepared in the apparatus shown in Fig. 1. The 200-c.c. flask on the left was fitted with a ground glass joint carrying a dropping tube surmounted by a small tap and vessel *A* to contain the heavy water. The bulb of the flask was half-filled with magnesium nitride in small lumps. The delivery tube led to a large U-tube filled with nitride, mostly in fine powder but with some lumps to prevent blocking. After this came a sodium trap 1 and three condensation traps 2—4, beyond which was a manometer and a vessel 5 containing clean sodium. The manometer and this vessel were attached by interchangeable joints, but the rest of the apparatus was sealed together. Before assemblage, each part was thoroughly cleaned and dried, and a current of warm, dry air was passed through the whole apparatus after it had been sealed together. The apparatus was evacuated while the parts containing magnesium nitride were heated with a small flame. On standing overnight the pressure had increased to 5 mm. and the pumping out was repeated until the pressure did not increase on standing. The heavy water was then introduced into *A* by the small syphon, also shown in Fig. 1 (cf. Partington and Towndrow, *Trans. Faraday Soc.*, 1939, **35**, 553). The heavy water in *A* was protected by the small phosphoric oxide tube shown. The heavy water was dropped on the nitride while the U-tube was cooled in alcohol–solid carbon dioxide. As each drop reacted, steam was evolved. This condensed in the upper part of the flask and was kept from spreading into the side tube by immersing the lower part of the flask in ice water, the nitride being brought in contact with the condensed water by shaking the flask, which could be moved vertically about 2 cm. When about 8 g. of heavy water had been added, the generating flask was heated with a free flame for 30 mins. to as high a temperature as possible and was then sealed off at S_1. The rest of the apparatus was then heated by a flame to drive all moisture quickly into contact with the nitride. The apparatus was left overnight, and the ammonia then distilled into the sodium trap, and the first part of the apparatus removed by sealing off at S_2. Distillation was continued into the remaining traps, traps 2 and 3 being sealed off and removed when the liquid had left but the glass was still very cold. The ammonia was finally distilled into the trap 5. Tap T_4 was closed, and the trap 4 and storage flask evacuated before ammonia was allowed to evaporate. The gas remaining in the connecting tubes and trap 5 was condensed in trap 4 and allowed to pass into the flask.

(iii) *Dryness of the Ammonia.*—It was realised that one of the main problems would be to ensure that the ammonia and deuterammonia were quite free from moisture. The presence of only 1% of water in the ammonia might cause a serious error in the pressure measurements, and when passing from the highest to the lowest ammine most of the water would remain in the solid phase and so raise the water–ammonia ratio as high as 1·20. Gillespie and Lurie (*J. Amer. Chem. Soc.*, 1931, **53**, 2978) dried ammonia by leaving the liquid in a steel bomb with sodium for some months. It is doubtful whether this long period is necessary. In our work the liquid ammonia was condensed into a trap containing a

FIG. 1.
Apparatus used in the Preparation of Deuterammonia.

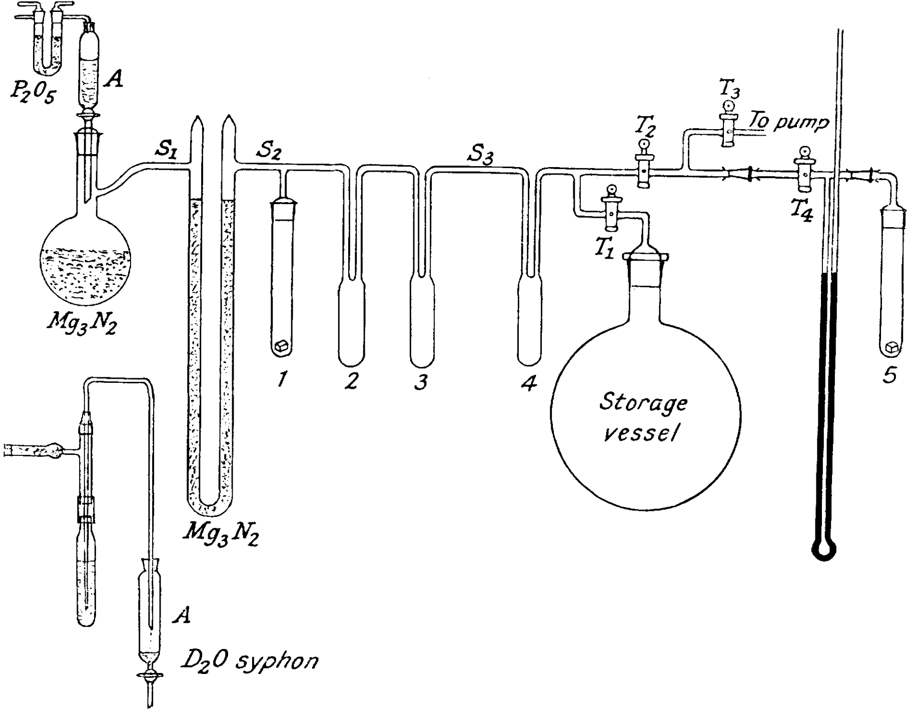


FIG. 2.
Apparatus used in the Preparation of the Ammines.

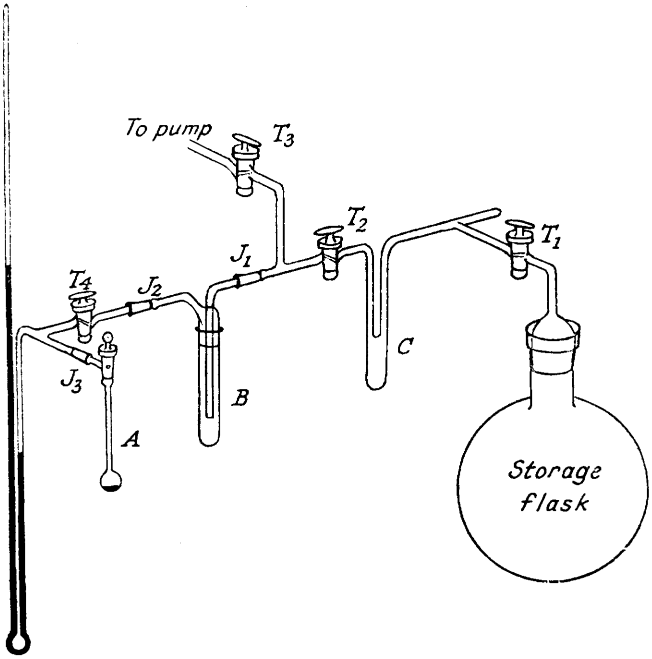
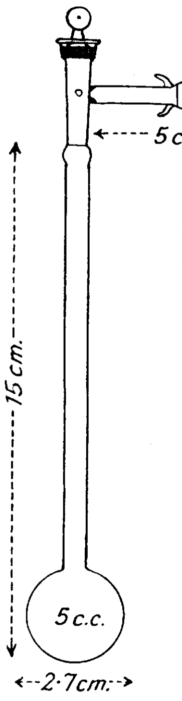


FIG. 3.
The Ammine Bulb.



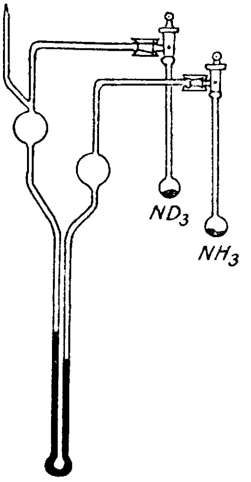


FIG. 5.
The Differential Tensimeter.

few fragments of sodium and left for 24 hours. One possible source of failure with this method is a tendency for moisture to collect as ice on the tube at a place level with the surface of the cooling bath, and so be spared contact with the sodium. To avoid this the sodium was made to cover the walls of the tube to a height well above this position by causing a concentrated solution of sodium in liquid ammonia to evaporate quickly, whereupon the crystallising sodium creeps and can, by a suitable rate of evaporation, be brought to any required height in the tube.

(iv) *Measurement of the Vapour Pressure of the Two Ammonias* (NH_3 *and* ND_3).—To check the purity of the gases, the vapour pressures were measured between −80° and −30°. The ammonia was condensed into an ammine bulb shown in Fig. 3, which was attached to a manometer by a ground joint. The apparatus was the same as for use with the ammine and is shown on the left of Fig. 2. The temperature of the bulb was maintained by immersion in a bath of cold alcohol in a 1-l. Dewar vessel. The experiment was begun with excess of solid carbon dioxide mixed with the alcohol, and the temperature raised by adding small quantities of warm alcohol with vigorous stirring. The temperature could be kept fixed within very narrow limits and was measured by a carefully calibrated six-junction copper–constantan thermocouple (Hart, Thesis, London University, 1941, pp. 18—23). The same couple was used for all low-temperature measurements, including dissociation measurements with several ammine systems.

The results for light ammonia agree well with those in the " International Critical Tables "; the deviations were negligible and nowhere equivalent to a temperature error of more than 0·1°. The b. p. from the $\log_{10} p$–$1/T$ line ($T_0 = 273{\cdot}1°$) is −33·4° (I.C.T., −33·35°). The results with trideuterammonia are shown in Table I and agree well with those of Taylor and Jungers (*loc. cit.*), the b. p., −31·0°, being the same as that given by them.

TABLE I.

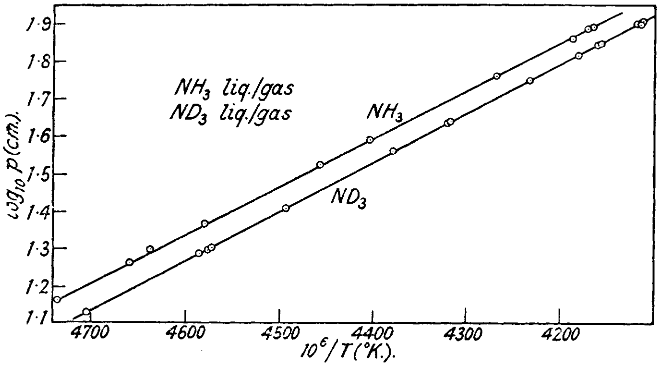
Vapour Pressures of Ammonia and Deuterammonia.

$NH_{3\ \text{liq.}}/NH_{3\ \text{gas.}}$				$ND_{3\ \text{liq.}}/ND_{3\ \text{gas.}}$					
t.	*p*, cm.	*t*.	*p*, cm.	*t*.	*p*, cm.	*t*.	*p*, cm.	*t*.	*p*, cm.
−62·4°	13·60	−46·0°	38·67	−60·5°	13·40	−44·7°	36·20	−32·6°	69·78
−57·4	18·34	−38·8	57·25	−54·9	19·34	−41·6	43·50	−32·5	70·22
−55·4	19·90	−34·3	72·10	−54·6	19·77	−41·5	43·96	−30·10	79·28
−54·7	23·25	−33·4	76·23	−54·4	20·01	−36·9	55·80	−30·3	79·58
−48·7	33·20	−33·1	77·64	−50·5	25·50	−33·9	65·02	−30·00	79·88

The results are shown in log p–$1/T$ plots in Fig. 4. The equations of the lines are $\log_{10} p_{NH_3} = 8{\cdot}162 - 1266/T$ and $\log_{10} p_{ND_3} = 8{\cdot}280 - 1308/T$, the pressure being in mm. of mercury.

FIG. 4.

Vapour Pressure of Liquid NH_3 *and* ND_3.



(v) *Preparation and Analysis of the Anhydrous Salts.*—Ammines of metallic calcium and of the following salts were investigated: $CuSO_4$, $CaCl_2$, $CaBr_2$, $BaCl_2$, $BaBr_2$, $FeCl_2$, $NiCl_2$, $MnCl_2$, LiCl, LiBr, LiI, NaI.

(*a*) *Copper sulphate.* Even very pure specimens of recrystallised copper sulphate blackened on dehydration, and the anhydrous salt was prepared from electrolytic copper foil. This was dissolved in redistilled nitric acid, the product heated to dryness in a porcelain dish, ignited, and the oxide dissolved in dilute A.R. sulphuric acid. The solution was evaporated, the pentahydrate twice recrystallised and then dehydrated by first heating the fine powder in a vacuum at 100° to give the monohydrate, and then heating this at 300° for some hours in a Hyvac pump vacuum. The product was ground quickly, and the final process repeated until analysis corresponded with $CuSO_4$.

(*b*) *Calcium chloride.* Each sample of anhydrous salt was prepared immediately before use by heating a finely powdered mixture of dry " AnalaR " calcium chloride and pure ammonium chloride in a porcelain or platinum boat in a combustion tube through which a stream of very dry nitrogen was passed. The product was of 99·9% purity, the 0·1% deficiency being moisture absorbed during transference. The salt in the ammine bulb was further dehydrated by evacuation while the bulb was heated with a small flame.

(*c*) *Calcium bromide.* A.R. Calcium carbonate was dissolved in a large excess of pure hydrobromic acid solution (constant-boiling, redistilled), the solution neutralised with ammonia, and evaporated to dryness on a water bath. The solid was ground and heated in an air oven at 150°. This left an intimate mixture of calcium and ammonium bromides, which was converted into anhydrous calcium bromide in the same way as the chloride. The product was perfectly white and dissolved in water to give a clear solution with a neutral reaction. Two samples used analysed 99·85% and 99·90% purity.

(*d*) *Barium bromide.* " AnalaR " Barium bromide crystals were finely ground and dried at 100° for some hours. Before use, the almost completely dry product was heated to a high temperature in a small evacuated Pyrex flask. The salt analysed to the theoretical result.

(*e*) *Ferrous chloride.* Anhydrous ferrous chloride was prepared by heating B.D.H. " extra pure " iron wire in a current of dry hydrogen chloride, as described by Partington and Skeen (*Trans. Faraday Soc.*, 1934, **30**, 1062). Analysis gave the theoretical result.

(*f*) *Nickel chloride.* Pure nickel chloride was recrystallised three times, the dry product finely ground, dried in a desiccator over calcium chloride, and further dehydrated at 150° for some hours, during which it was occasionally removed and reground. The product contained $NiCl_2$, 99·0%, and apparently retained some moisture. Further purification was effected by subliming in a current of dry hydrogen chloride, by very strong heating in a short length of Vitreosil tubing. The final product was a very voluminous, flaky, brown powder with a decided lustre, which absorbed moisture only very slowly. Analysis gave the theoretical result.

(*g*) *Manganous chloride.* Kahlbaum's manganous chloride " for analysis " was finely ground and dried, first in a desiccator over phosphoric oxide for some days, and then at 150°. The flesh-coloured powder was finally dehydrated in vacuum in a small Pyrex bulb heated to the softening point. The rose-coloured product gave the theoretical analysis.

(*h*) *Lithium chloride.* " AnalaR " Lithium chloride was finely ground, dried at 150°, and kept in a phosphoric oxide desiccator before use. Analysis gave the theoretical result and the solution was quite neutral.

(*i*) *Lithium bromide.* The slightly acid solution of " AnalaR " lithium carbonate in redistilled hydrobromic acid was evaporated almost to dryness, and the salt twice recrystallised. Dehydration was carried out first at 100° and then by heating the finely ground material in a current of nitrogen, as with calcium chloride. When dehydrated in air the product gave a slightly alkaline solution. The samples gave the theoretical analysis.

(*j*) *Lithium iodide.* Kahlbaum's hydrated material was a moist, very deliquescent, brownish powder. Dehydration of this proved very difficult (cf. King and Partington, *Trans. Faraday Soc.*, 1927, **23**, 522). The hydrate in a platinum boat was exposed to a rapid current of warm, dry nitrogen, at first without heating the solid. After an hour the material was white. The part of the tube containing the boat was then heated gently at first, the temperature being slowly raised until the solid showed signs of melting, and this temperature was maintained for some hours. The product gave a slightly alkaline reaction with water. A typical sample contained LiI, 99·9%, and the discrepancy was no doubt due in part to moisture absorbed in transference. The solid in the ammine bulb was finally dehydrated *in situ* by heating in a vacuum.

(*k*) *Sodium iodide.* Pure sodium iodide (cf. King and Partington, J., 1926, 20) was recrystallised twice and dried in an air oven. It analysed pure.

(vi) *Preparation of the Ammines.*—The apparatus for the preparation of the ammines is shown in Fig. 2 and the ammine bulb *A* in detail in Fig. 3. These bulbs were of Pyrex or soda glass according to the heating bath used. Each had an interchangeable cone-ground joint which could fit into a socket on a manometer, an extra condensation trap, or the storage vessel. All interchangeable joints, size OO, were made tight with hard vacuum grease (W. Edwards and Co.). The small combined tap and stopper on the ammine flask was lubricated, as were all other taps, with the corresponding " soft " vacuum grease, and all taps were protected by mercury in the flanges. The mercury manometer shown in Fig. 2 is of the closed-end type, one of three designs used. Another had an open end, and a third was of constant-volume type. They were read by a cathetometer or a travelling microscope.

The condensation trap had a wide joint so that freshly cut sodium could be quickly introduced in an almost untarnished state. These traps had interchangeable ground joints. The trap *C* served to return ammonia to the storage flask, as described above.

After the ammonia bulb and trap had been carefully cleaned and dried, just sufficient soft vacuum grease to lubricate the tap when in position was applied, and the bulb and trap were weighed with a counterpoise of a similar shape. The anhydrous salt was introduced through a funnel, and the bulb closed. The salt was finally dehydrated at 300° in a vacuum till the weight was constant, the bulb being weighed vacuous, with the grease on the ground joint removed.

The bulb was connected as shown in Fig. 2. The apparatus to the left of T_2 was evacuated to less than 0·01 mm., T_3 was closed, and the apparatus tested for leak for about 30 mins. Meanwhile, ammonia was withdrawn from the storage flask and condensed in *C*, T_1 was closed, and T_2 opened, and, with the tap on *A* closed, the ammonia distilled into *B*, into which a small piece of sodium had previously been introduced. The finally dried ammonia was evaporated from *B* into contact with the anhydrous salt by opening the tap on *A*. The actual process of combination between the ammonia and the salt required different conditions according to the nature of the salt, and details for each ammine are given later. The bulb *A* was then removed, vacuum grease cleaned from the joint, and the whole reweighed. From the weights, the composition of the solid could be calculated. Before pressure measurements were begun, a little ammonia was removed, so that both solid phases could be present, and any ammonia absorbed on the finely divided solid removed. With deuterammonia, where it was desired to retain the gas, the same procedure was adopted as when larger quantities of gas were removed in passing from a higher to a lower ammine. The ammine flask was attached through a manometer to the storage flask, as in Fig. 2, and with the flask tap closed, the manometer and connecting tube were evacuated through T_3. This tap was then closed, and with T_1 and T_2 closed, *C* was cooled in alcohol–solid carbon dioxide or preferably (since the vapour pressure of ammonia at the temperature of solid carbon dioxide is still 5 cm.) in liquid air. T_2 was then opened and the requisite quantity of ammonia passed from *A* into *C* by warming *A* with the tap open. The gas in the tubing of the manometer and between T_4 and T_2, about 10 c.c., was also condensed in *C*. Thus about 0·001 g. of ammonia could be removed from *A* at each step. With the trap *B* or a similar bulb in position larger amounts could be removed at each stage. By using liquid air almost all loss of trideuterammonia could be avoided.

(vii) *The Pressure Measurements.*—The ammine flask with the joints suitably lubricated was firmly bound to the manometer with soft-iron wire round the hooks shown in Fig. 3, the manometer was attached to the vacuum line, and with the ammine bulb tap closed and the manometer tap open, the manometer was evacuated. The tap was then closed and the manometer moved to a position where the ammonia bulb could fit into a thermostat or other heating apparatus.

A differential apparatus used in comparing the equilibrium pressures of light and heavy ammines is shown in Fig. 5.

For temperatures between 0° and 50° an electrically operated water thermostat regulated by a mercury–toluene bulb regulator to ±0·02° was used. Below room temperature a constant-level device was used, and ice-cold water was siphoned in from a bucket containing excess of ice and water. Up to 80° a water thermostat was occasionally used with a thick layer of heavy paraffin to reduce evaporation. For isolated measurements a smaller gas-regulated thermostat was available, with a small spiral regulator giving temperature to ±0·02°. In the range 50—150° a 30-l. oil thermostat was used. The oil was a good-quality, water-white, vegetable oil. This was well stirred, and the temperature regulated by a xylene–mercury regulator up to 140°, and by an aniline regulator above this. Both regulators were of the spiral pattern. The oil was still quite clear after 6 months' almost continuous use, and up to 100° there was no fuming. Mineral oil smoked above 100° and deposited a sediment. The temperature could be maintained to ±0·02° above 80°; below this the viscosity of the oil prevented efficient stirring.

For temperatures of 180—300° a small furnace was used. The temperature bath, contained in a Pyrex or Hysil beaker suspended from the top of the furnace tube, was large enough to take both light and heavy ammine bulbs, and a third equal bulb, symmetrically placed, contained the standardised Anschütz thermometer or platinum and platinum–rhodium thermocouple. The readings of the thermometer and couple agreed to 0·1°. The furnace tube was of non-transparent silica in one piece, the upper half of 8 cm. diameter, the lower of 4 cm., and the winding of nichrome wire was covered by a thick layer of heat-resisting cement. A rectangular box of asbestos sheet held the tube and lagging. The temperature regulation was by a mercury-filled regulator, as shown in Fig. 6, operating a relay which could short-circuit the last 10 ohms of resistance in series with the furnace. Over long periods the temperature control had a maximum variation of ±0·1°, as measured on the thermometer in the bath.

The heating bath was the eutectic mixture of lithium, sodium, and potassium nitrates (30, 16, and 54%, respectively),

m. p. 120°. This could be used up to 300°. Above 200°, soda glass was rapidly attacked, but Pyrex and Hysil glasses withstood the highest temperature used.

(viii) *The Ammine Systems*.—(*a*) *Copper sulphate ammines*. On admitting ammonia to anhydrous copper sulphate, the violet pentammine is immediately formed, and the green diammine is not seen during the synthesis. It was not possible to prepare the *pure* pentammine with gaseous ammonia. After 24 hours a solid of composition $CuSO_4,3{\cdot}5$—$4{\cdot}5NH_3$ was obtained, which absorbed ammonia only very slowly. By condensing liquid ammonia on the partly amminated material, allowing it to evaporate at atmospheric pressure, and repeating the operation several times, the pure pentammine could be prepared. It was insoluble in liquid ammonia, and on evaporation a fine powder remained, which occupied about five times the volume of the anhydrous salt.

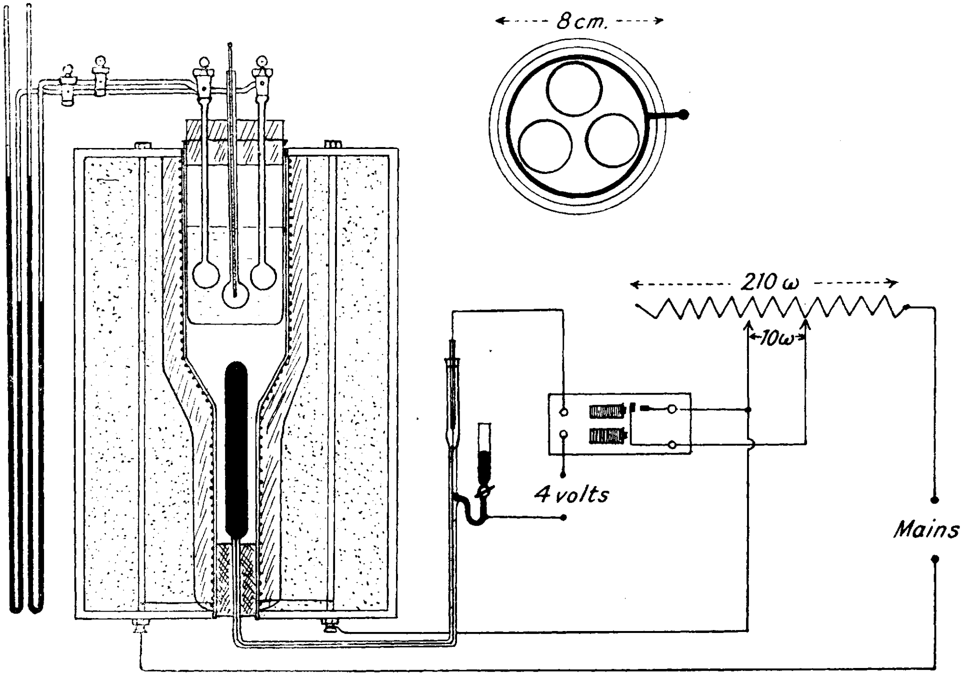
The diammine and monoammine were prepared by decomposing the pentammine as described above.

Preparation of the heavy ammines followed the same lines. The two sets of compounds had the same colour, whereas $CuSO_4,5H_2O$ and $CuSO_4,5D_2O$ differ appreciably in colour.

The pressure measurements with $CuSO_4,5/4NH_3$* were not in good agreement with those of Ephraim (*Z. physikal. Chem.*, 1913, **83**, 196) or of Foz and Le Boucher (*Anal. Fís. Quím.*, 1932, **30**, 21), the results of these workers being also in marked disagreement. Our measurements are in good agreement with some previously made by Mr. C. H. Bottoms in this laboratory, and two further samples of the ammine gave results in perfect agreement with the earlier ones. The equilibrium at each temperature was established in 36—48 hours, and the pressures were much higher than those found by the above authors, especially at the lower temperatures. Measurements with two samples of heavy ammine gave results in good agreement. The isotope effect is quite large.

FIG 6.

Furnace and Temperature Regulator.



With the tetrammine–diammine system, results in the range 100—160° were obtained with little trouble and the results with ammonia were in reasonable agreement with those of previous workers.

The diammine–monoammine systems were measured in the range 220—280°. The isotope effect is much smaller than with the higher systems.

Attempts to measure the 1/0 systems were abandoned, since at the high temperatures necessary (280—320°) decomposition and blackening began, as found by Foz and Le Boucher (*loc. cit.*).

(*b*) *Calcium chloride ammines.* Absorption of gaseous ammonia by the salt became extremely slow when the composition $CaCl_2,7NH_3$ was reached, but with liquid ammonia the pure octammine could be prepared in a few minutes. A sample prepared with gaseous ammonia at 0° for 30 hours gave the same pressures as one made with liquid ammonia. The octammine is a voluminous, fine white powder which occupies several times the volume of the anhydrous salt.

Calcium chloride forms compounds with 8, 4, 2 and 1 NH_3 but not (as is often erroneously stated) with $6NH_3$. The 8/4 system gave easily reproducible results with both ammonia and trideuterammonia in the range 0—30°, the pressures reaching stationary values in 24—36 hours. Two different ammine preparations were measured in both cases. There was little tendency for ammonia to be reabsorbed at ordinary temperature, so equilibrium could only be reached from the lower pressures. The results for the light ammine were in good agreement with those of Hüttig (*Z. anorg. Chem.*, 1922, **123**, 31); earlier results differ fairly considerably. The results in the table are for both preparations, and the two sets of measurements agreed remarkably well.

With these systems an example is given of the rate of attainment of equilibrium :

	2 hrs.	4 hrs.	16 hrs.	30 hrs.	36 hrs.
p_{NH_3}, cm., at 20·0°	39·0	40·08	41·62	41·73	41·73
p_{NH_3}, cm., at 25·0°	50·2	52·20	56·20	56·42	56·45

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* The symbol x/y indicates a system of two solids containing 1 mol. of salt with x and with y mols. of NH_3 or ND_3.

In one or two cases the temperature was maintained for 8 days after the first constant pressure was attained and the results proved that the equilibrium pressure was reached in 36 hours, but with the tetrammine, equilibrium was not usually reached in less than 4 days. In the case of the deuterammine the slow approach was more pronounced, and early experiments gave apparent equilibrium values considerably below the true ones. Both preparations of ammine behaved similarly.

The decomposition pressures of the diammine were measured between 120° and 170°. Equilibrium was attained very slowly, and the results were not reproducible with any accuracy. On cooling to room temperature (pressure 1 mm. at 100°) reabsorption of ammonia was almost negligible. The measurements, and those with the monoammine, were soon abandoned.

(*c*) *Calcium bromide ammines.* The octammines were prepared as described above, and their appearance was similar to that of the corresponding chloride compounds. The octammine decomposed to form a hexammine, in contrast with the chloride. The pressures of the octammine were easily measured in the 0—30° range and gave equilibrium in 24 hours. The isotope effect is quite large. The hexammine–diammine system also gave easily reproduced and quickly obtained equilibrium pressures (constant in 8—12 hours). The isotope effect was quite small. The temperature range was 30—80°; the hexammine is more much stable than tetramminocalcium chloride.

The diammine–monoammine equilibrium was measured in the range 180—220°. The 1/0 system gave similar results in the higher range 200—250°. In these two systems equilibrium was usually attained in 8—12 hours, and the results were reproducible. The isotope effects are rather small and about the same as with the 6/2 system. The results for the ammonia systems are in excellent agreement with measurements of Hüttig (*loc. cit.*), especially with the first two systems.

(*d*) *Barium bromide ammines.* The octammines were prepared without difficulty as described above. The salt forms compounds with 8, 4, 2 and 1 NH_3. The dissociation pressures of the first three light ammines agreed well with those of Hüttig and Martin (*Z. anorg. Chem.*, 1922, **125**, 269). The corresponding heavy ammines gave pressures only slightly lower, and the isotope effects are quite small. With the two higher systems pressure equilibrium was rapidly attained; with the 2/1 system this took several days, but the results were reproducible. Attempts were made to measure the 1/0 decomposition, but equilibrium was approached extremely slowly and no reliable results could be obtained.

(*e*) *Ferrous chloride ammines.* Ferrous chloride is an example of a class of salt (the bivalent halides of the transition elements) which gives as the highest ammine a hexammine, which decomposes to a di- and then to a mono-ammine. The hexammine was prepared by condensing ammonia on the anhydrous salt and allowing it to evaporate at a pressure of about 0·5 atm. The anhydrous salt absorbs ammonia rapidly, and in 30 mins. pure hexammine was obtained as a very fine, green-tinged, white powder. Although the anhydrous salt did not react appreciably with ammonia gas at room temperature, yet once compound formation began, the solid absorbed ammonia quite rapidly. The 6/2 systems were measured between 50° and 110°. Equilibrium pressures were reproducible and attained in 4—6 hours.

The results for ammonia do not agree very well with those of previous workers. The graph (Fig. 7) shows these and illustrates why it was necessary to re-measure all the light systems rather than to accept previous results. The results of Ephraim (*loc. cit.*) and Girardet (*loc. cit.*), considered by Biltz and Hüttig (*Z. anorg. Chem.*, 1920, **109**, 111) to be in good agreement, differ by more than those for our light and our heavy systems. Equilibrium pressures in the 2/1 systems, measured in the 220—275° range, were reproduced with reasonable accuracy and indicate a small isotope effect. In the 1/0 system results were obtained with ease in the 250—290° range. Equilibria were rapidly obtained (1 hour) and were reproducible. The isotope effect is again small.

(*f*) *Nickel chloride ammines.* In the preparation of the hexammine a very interesting effect was observed. The anhydrous salt did not react with gaseous ammonia, and even when excess of liquid was condensed on the solid no combination occurred at low temperature. At about −30°, when excess of liquid still remained but the gas pressure was slightly above 1 atm., combination began and proceeded rapidly to the green diammine and then to the violet hexammine On the first occasion the combination, once begun, proceeded so rapidly and with the evolution of so much heat that the remaining ammonia suddenly vaporised with a mild explosion. The partly amminated salt absorbed ammonia gas rapidly and in about 1 hour the pure hexammine could be prepared. Two preparations of both isotope ammines were made. The first pair were pale violet, but the second preparations were much lighter and almost white. A mere trace of moisture gives a much darker colour, and a sample of incompletely dehydrated nickel chloride (5% H_2O) gave an ammine which was quite blue. The hexammine dissociations were measured in the range 100—170°. The initial results at lower temperatures gave some trouble, since at first, high pressures were obtained which could not be reproduced. This was due to some effect which was removed on standing. At 100° the freshly prepared ammonia system gave a pressure of 5·3 cm. After 3 days this had decreased to 4·52 cm., and on cooling and reheating became 3·70 cm. After removal of a little gas and a further 3 days' standing the value 3·29 cm. was the highest obtained. Finally, a reproducible value of 3·26 cm. was found. After this, the pressures at higher temperatures were quite reproducible. The same behaviour was found with the deuterammine and with the second preparation of the materials. The final results for these systems were very satisfactory, and those with ammonia agreed well with those of earlier workers (Biltz and Fetkenheuer, *Z. anorg. Chem.*, 1913, **83**, 163). The results in the table are, at lower temperatures, measurements with both independently prepared ammines, and at higher temperatures the measurements are those with the later preparations.

The 2/1 systems were measured between 230° and 280°. The equilibrium pressures were quite slowly attained (24 hours), but were reproducible and constant over the whole of the composition range between diammine and monoammine. Below the monoammine the pressure fell off gradually with composition and results were not reproducible. The trideuterammonia system behaved similarly.

(*g*) *Manganous chloride ammines.* The anhydrous salt absorbed ammonia fairly rapidly at −30°, and in the presence of excess of liquid ammonia the hexammine was prepared in a short time as a fine white powder. Measurements on the 6/2 system gave quite accurate reproducible equilibrium pressures. Biltz and Hüttig (*Z. anorg. Chem.*, 1920, **109**, 89) found that between $MnCl_2,6NH_3$ and $MnCl_2,5NH_3$ the pressure decreased continuously, but we did not find this. From a composition of $MnCl_2,5{\cdot}72NH_3$ to $MnCl_2,2{\cdot}3NH_3$ the equilibrium pressure was quite constant. The same was found with the isotopic system. The results for the isotope pressures were confirmed by the tensimeter.

With the two pairs of lower systems, 2/1 and 1/0, the results were similar to the corresponding nickel chloride systems. The 2/1 system gave reproducible, quickly reached, equilibrium pressures, whereas the 1/0 system showed a continuous fall in pressure between the two limits of composition. The 2/1 system was measured in the range 180—250° and the results are considered accurate.

(*h*) *Lithium chloride ammines.* This salt forms a pentammine, with a dissociation pressure of 1 atm. at about −10°, readily prepared by condensing a slight excess of liquid ammonia on the salt. The pure tetrammine was prepared from the pentammine by leaving the ammine flask in connection with the storage vessel with the bulb cooled at 0°.

The 5/4 decomposition was not measured. The 4/3 equilibrium measurements were made in the short range 0—14°, but the accuracy with which each measurement could be made and reproduced compensated for this. At each temperature only 30 mins. were required to attain equilibrium. With the 3/2 system, equilibrium was quickly established and the results were accurately reproducible. The measurements of the two light systems agreed quite well with those of Biltz and Hansen (*Z. anorg. Chem.*, 1923, **127**, 1) and of Bonnefoi (*loc. cit.*), but we found no break in the pressure–composition curve corresponding with a monoammine. The pressure for the diammine lay midway between the values given by these workers for the supposed 2/1 and 1/0 systems. Our results with two further, independently prepared samples of the ammine were closely reproducible, as the following measurements made on the three samples at 50° show.

Sample I.

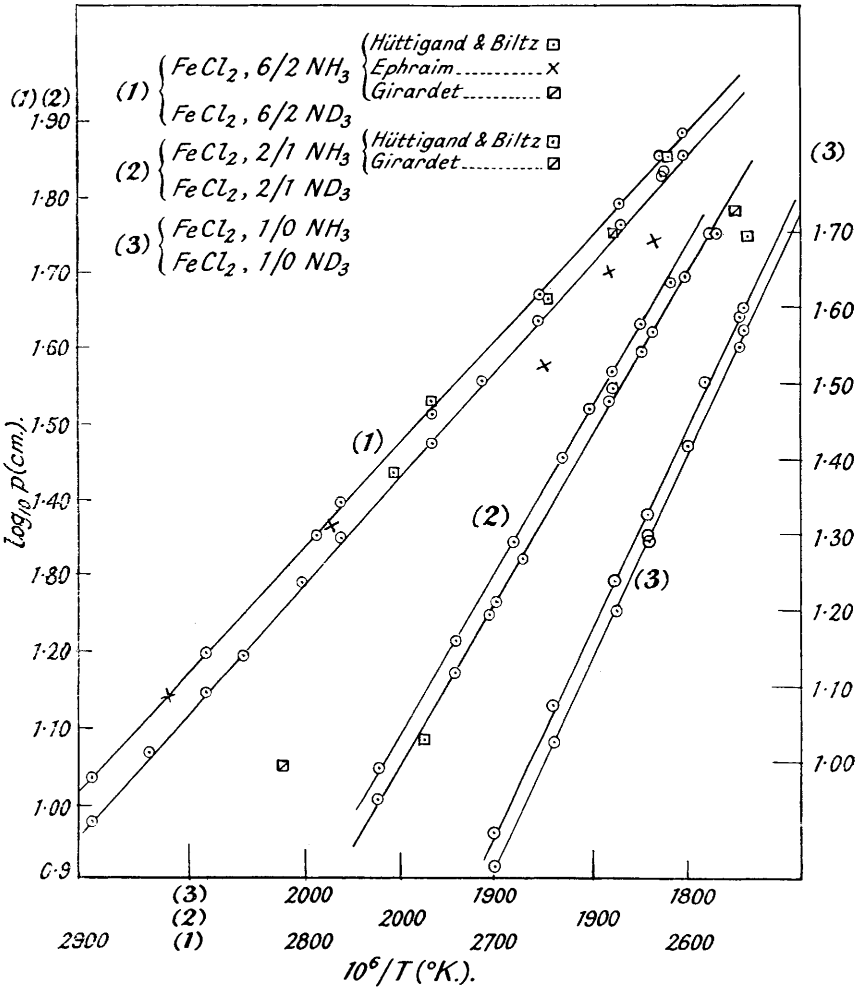
p_{NH_3}, cm.	12·45	12·50	12·37	12·35	12·45	12·2
Mols. NH_3 per mol. LiCl	1·98	1·34	1·20	0·71	1·56	0·35

Sample II. $p_{1\cdot21NH_3}$ = 12·61 cm. *Sample III.* $p_{0\cdot72NH_3}$ = 12·48 cm.

In this 2/1 system equilibrium was established in 4—8 hours, rather longer than is required by the higher systems. The isotope effect is largest in the case of the 4/3 system.

Fig. 7.

Ferrous Chloride Ammines and Deuterammines.



(*i*) *Lithium bromide ammines.* This salt forms definite compounds with 7·5 and 6 molecules of ammonia (Bonnefoi, *loc. cit.*), but these were not considered suitable, as their decomposition pressue is not much lower than the vapour pressure of liquid ammonia at the same temperature. The pentammine was prepared in the same manner and with the same facility as that of the chloride, and measurements on it were made in the range −50° to 20°. The pressures required not more than 1 hour to reach equilibrium and were accurately reproducible. With the low-temperature method described it was easily possible to maintain the temperature to ±0·2° during this time, and to make a series of measurements covering the whole range in the course of one day. The results given were found in several series of measurements, which when plotted as $\log_{10} p$ against $1/T$ gave the same line. The measurements of Biltz and Hansen (*loc. cit.*) agree only roughly with ours. The deuterammine behaved in a manner identical with the light ammine and the isotope effect was accurately measurable.

The other ammines found by Biltz and Hansen (*loc. cit.*), whose investigations extended to both lithium bromide and iodide, were compounds of LiBr with 4, 3, 2, and $1NH_3$. We confirmed the existence of each of these, and pressure measurements were made with each system formed by them.

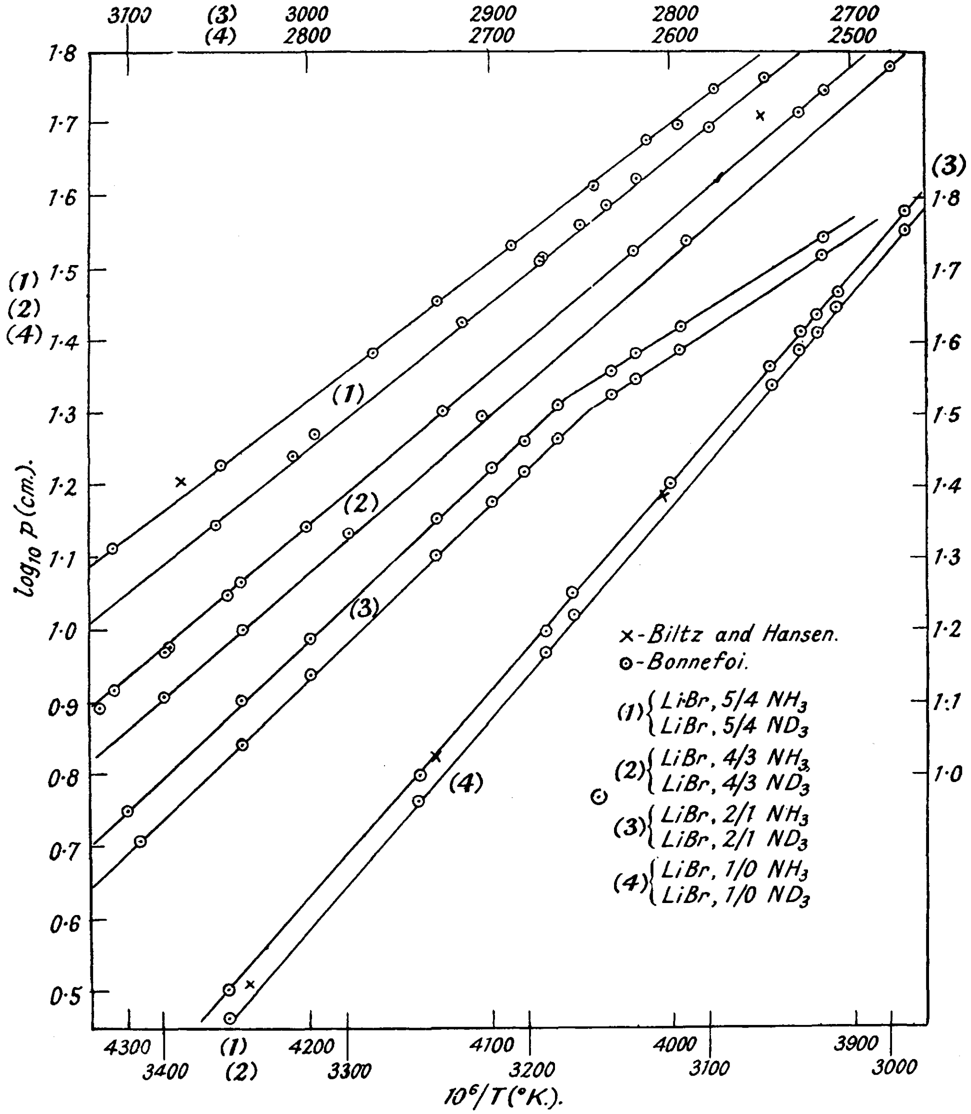
The 4/3 equilibrium was measured in the range 18—60° and gave accurately reproducible results. The 3/2 system gave apparently accurate results up to *ca.* 75°, above which the pressure rose more steeply with temperature than before.

Corresponding with this, the ammine became semi-liquid, and at about 85° completely liquid. The logarithmic plot showed a sharp break at 75°, and above this the line became steeper. This is due to melting of the diammine, and above this temperature its heat of fusion must be added to the heat of dissociation to give the total heat absorbed in passing from solid $LiCl,3NH_3$ to liquid $LiCl,2NH_3$. The results at and above the m. p. were not very accurately reproducible, and in the table, values are given only for the solid reaction. The isotope effect for this system is unexpectedly small.

The results for the 2/1 system were more satisfactory. In agreement with the above, m. p.'s of 78·1° for the light and 79·3° for the heavy compound were found, and the pressure rose more slowly with temperature above the m. p., indicating that the diammine was melting at this temperature. Reproducible results could be found several degrees above the m. p.

Fig. 8.

Lithium Bromide Ammines and Deuterammines.



while there was still solid monoammine in contact with fused diammine, but at 105° the substance became homogeneous liquid, all the monoammine having dissolved. The system was then no longer univariant and no further pressure measurements were made. On cooling the fused mixture, the previous results could be exactly reproduced at lower temperatures. Equilibrium in presence of the solids was reached in about 6 hours, but in less than 30 mins. when liquid was present.

With the monoammine, measurements over the range 80—130° could be made, and no melting was encountered. The results were reproducible, and equilibrium was attained in 1—2 hours.

The results for these systems agree roughly with those of Biltz and Hansen (*loc. cit.*) who also mentioned the existence of the m. p. They assumed, however, that the triammine melted at 78°, and apparently did not investigate the trend of the pressure–temperature increase above the m. p.

(*j*) *Lithium iodide ammines.* The pentammine was prepared in the same manner as the corresponding bromide compound. The pressure measurements on the 5/4 system followed the same course as that of the bromide system and gave similar results. The 4/3 system gave results reproducible with great accuracy, and the logarithmic plot showed a transition point at 74·4° for NH_3 and 75·8° for ND_3, indicating that one component was melting. The course of the log

p–$1/T$ line showed that the triammine melted at the stated temperature, and it was possible to make several pressure measurements on the resulting system of solid tetrammine up to the point where the system became homogeneous owing either to melting of the tetrammine or to complete solution of this compound in liquid triammine. From the graphs, the heat of fusion of the triammine could be calculated. The results for the solid system give the isotope effect with unusual accuracy.

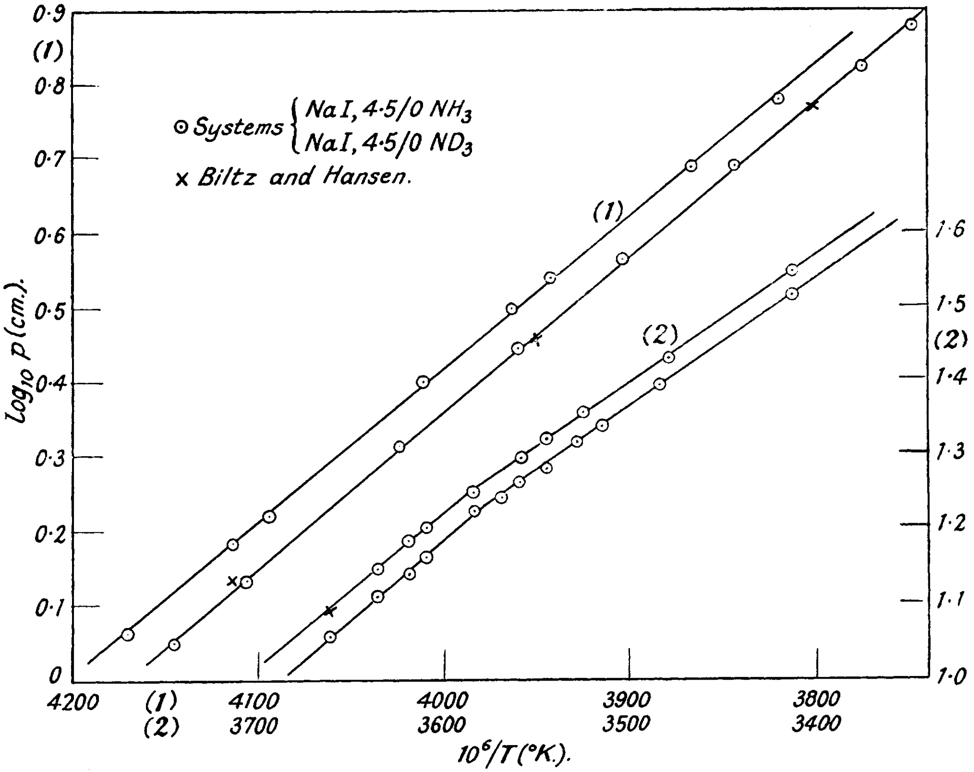
The next lower system, between triammine and diammine, clearly showed the same m. p., since the log p–$1/T$ line swung through the same angle as for the previous system, but in the opposite direction, showing that the decomposing ammine was melting. The calculated heats of fusion, as seen from the table, agree very well with those from the previous measurements. Measurements could be continued for several degrees above the m. p., but no sharp change was found to indicate fusion of the diammine. The logarithmic plot showed a slow change at the point when the system became entirely liquid.

The equilibrium measurements on the 2/1 system gave results of more interest. The ammine remained solid and gave a linear logarithmic plot up to 101·1° (NH_3) and 102·3° (ND_3), whereat the solid began to melt; above this a few measurements indicated that the monoammine and not the diammine had melted. Only a few results could be obtained above the m. p., since at 105—108° the systems became entirely liquid.

The pressures found for the solids extended over only 10° and 20—80 mm., but they enabled the heats of decomposition to be calculated with reasonable accuracy.

FIG. 9.

Sodium Iodide Ammine and Deuterammine : (1) Solids ; (2) Liquids.



Attempts to measure the dissociation of the monoammine were unsuccessful, since below the m. p. the pressures were quite small and could not be reproduced accurately. Above the m. p. the system soon became homogeneous, although the exact point at which the solid (LiI) disappeared depended on the composition of the system.

Biltz and Hansen (*loc. cit.*) observed the two m. p.'s at the same temperatures (80° and 101°) for the light ammines, but they wrongly assigned the higher to the diammine and gave 138° as that LiI,NH_3. The latter point is probably a transition in the p–T curve for some composition corresponding to the final dissolution of LiI in fused LiI,NH_3.

(*k*) *Sodium iodide ammines.* This salt was stated by Biltz and Hansen (*loc. cit.*) to form a hexammine at very low temperatures, and a compound $NaI,4{\cdot}5NH_3$ which seemed to give pressures suitable for measurement in the range −10° to +10°. The fact that sodium chloride forms a pentammine, and evidence put forward by Distanov (*J. Gen. Chem., U.S.S.R.*, 1938, **8**, 783), suggest that the iodide compound is really a pentammine. Biltz and Hansen's evidence for the existence of $NaBr,5{\cdot}25NH_3$ also seemed to indicate a slight error. The pressure–composition results for the NaI–NH_3 systems which they found indicate the formation of $NaI,4{\cdot}5NH_3$:

Mols. of NH_3 per mol. of NaI	5·07	4·84	4·61	4·48	4·44
p, cm.	10·5	10·5	10·5	2·7	2·2

and we also find that even below the composition of the pentammine the system still gives the equilibrium pressure of the higher system. The apparent composition when the pressure at 0° fell from a value greater than 1 atm. to 13 cm. varied between 4·8 and 4·4 mols. of NH_3, and thus it was not possible either to confirm accurately the results of Biltz and Hansen or to support our suggestion that a pentammine might be formed.

The ammine was prepared by condensing liquid ammonia on the pure salt. The deutero-compound showed the same behaviour as the ammonia compound in respect of the composition. The measurements of pressure presented no difficulty, the accuracy and speed of attainment of equilibrium being equal to that possible in the case of a pure liquid. Measurements were made in two parts, between −30° and −10° in the low-temperature apparatus and between 0° and 30° in the water thermostat. It was found that at 6·2° (NH_3) and 6·6° (ND_3) the ammine melted, but above this temperature the system remained heterogeneous and measurements were reproducible as far as 30°. The isotope effects could be calculated with great accuracy for the heats of decomposition of the solid–liquid ammine to the pure salt and for the heats of fusion of the ammine. The measurements of Biltz and Hansen were below 0° only, but agreed roughly with ours.

Results.—The results of all measurements are shown in Table II and some are given in Figs. 7, 8, and 9, in which $\log_{10} p$ (in cm.) is plotted against $10^6 \times (1/T)$. The linearity of the graphs is in agreement with previous results for heterogeneous systems (Scheffer, *Proc. Acad. Sci. Amsterdam*, 1917, **19**, 636). The values of $\Delta p_{\text{mm.}}$ give the amounts to be added to the values of p (in cm.) to give the value of p found from the log p plots.

TABLE II.

Pressure–Temperature Data.

$CuSO_4,5/4NH_3$.

t	40·0°	40·9°	46·0°	56·0°	58·0°	66·0°	68·0°	75·0°	78·0°	80·0°
p, cm.	3·20	3·50	5·10	9·85	11·22	19·10	21·10	35·00	40·10	43·6
$\Delta p_{\text{mm.}}$	−0·07	0	0·8	−1·0	−1·6	1·0	−3·0	3·3	4·0	−5·0

$CuSO_4,5/4ND_3$.

t	40·2°	48·7°	49·5°	57·8°	59·0°	62·0°	77·2°	78·0°	79·6°	84·2°	85·6°
p, cm.	2·70	4·80	4·93	8·32	9·79	11·75	30·84	33·50	35·70	48·50	52·41
$\Delta p_{\text{mm.}}$	0	1·2	0	−1·3	1·3	0	−3·0	6·0	−6·0	7·0	0

$CuSO_4,4/2NH_3$.

t	102·4°	105·0°	114·1°	116·1°	120·0°	122·0°	124·0°	128·0°	132·6°
p, cm.	5·25	5·88	9·20	11·18	12·20	13·50	15·24	18·21	22·80
$\Delta p_{\text{mm.}}$	3·0	0·9	0	0	0	−1·0	−0·7	0	3·0

$CuSO_4,4/2ND_3$.

t	107·4°	111·5°	119·6°	129·0°	134·3°	134·9°	150·0°	164·0°
p, cm.	5·27	6·46	9·65	15·42	20·40	21·50	43·43	77·80
$\Delta p_{\text{mm.}}$	2·0	0·8	−0·7	−3·6	0	3·3	2·0	0

$CuSO_4,2/1NH_3$.

t	219·5°	230·0°	246·0°	251·8°	256·5°	260·8°	269·0°	271·4°
p, cm.	5·56	8·32	15·34	19·72	23·05	26·62	34·17	37·00
Δp_{mm}	−1·0	−1·8	−2·0	3·0	0	2·0	0	0

$CuSO_4,2/1ND_3$.

t	224·0°	251·8°	260·8°	273·8°
p, cm.	5·95	17·80	24·63	36·55
Δp_{mm}	0	1·0	3·0	−1·0

$CaCl_2,8/4NH_3$.

t	0·0°	17·5°	18·3°	19·0°	20·0°	21·0°	22·0°	23·0°	25·0°	28·0°
p, cm.	10·50	35·08	37·28	38·80	41·73	44·58	47·32	50·11	56·45	66·07
$\Delta p_{\text{mm.}}$	0	−1·0	0	0	1·0	1·0	1·0	0	0	−8·0

$CaCl_2,8/4ND_3$.

t	0·0°	18·30°	19·45°	20·00°	22·80°	25·10°	26·80°	27·00°	28·80°
p, cm.	17·86	29·67	32·36	33·60	39·74	46·26	51·55	53·00	58·85
$\Delta p_{\text{mm.}}$	0	−1·0	0	1·0	−2·0	−1·0	6·0	−1·0	6·0

$CaCl_2,4/2NH_3$.

t	0·0°	21·90°	22·50°	24·90°	26·80°	28·00°	30·80°	36·50°
p, cm.	5·15	23·90	24·89	28·50	32·73	34·62	42·02	58·20
$\Delta p_{\text{mm.}}$	−0·4	2·0	2·2	−3·0	1·2	−3·1	6·0	−3·0

$CaCl_2,4/2ND_3$.

t	0·0°	20·00°	21·30°	24·60°	26·50°	28·00°	28·25°	28·80°	30·30°	33·30°	35·0°
p, cm.	3·81	16·80	18·20	23·02	25·90	28·50	28·90	29·71	33·50	39·24	44·40
$\Delta p_{\text{mm.}}$	−1·5	0	−2·1	2·2	0	0	0	−2·1	4·0	−4·0	3·4

$CaBr_2,8/6NH_3$.

t	0·0°	14·85°	18·30°	20·00°	22·75°	26·80°
p, cm.	13·00	36·20	46·95	50·30	61·95	77·70
$\Delta p_{\text{mm.}}$	1	−4·4	8·2	−5·2	9·0	0

$CaBr_2,8/6ND_3$.

t	0·0°	19·00°	21·00°	23·70°	26·80°
p, cm.	10·50	40·80	46·80	55·93	68·03
$\Delta p_{\text{mm.}}$	−0·9	1·6	0	−0·8	0

$CaBr_2,6/2NH_3$.

t	30·10°	51·60°	56·10°	61·30°	70·10°	77·60°
p, cm.	2·96	10·90	14·55	18·80	30·50	43·60
$\Delta p_{\text{mm.}}$	0	−2	1·5	0	4·0	0

$CaBr_2,6/2ND_3$.

t	33·20°	49·60°	57·90°	62·40°	70·70°	78·40°
p, cm.	3·34	9·18	14·62	18·80	29·30	43·45
$\Delta p_{\text{mm.}}$	0	0·5	−0·3	0	2·0	0

$CaBr_2,2/1NH_3$.

t	178·0°	183·0°	201·0°	211·0°	222·5°	226·0°
p, cm.	13·00	16·50	31·05	44·70	63·50	72·30
$\Delta p_{\text{mm.}}$	0	0	−2·5	2·0	−4·0	2·0

$CaBr_2,2/1ND_3$.

t	184·2°	206·0°	212·0°	227·0°
p, cm.	15·50	34·40	42·50	69·20
$\Delta p_{\text{mm.}}$	1	0	0	−2

$CaBr_2,1/0NH_3$.

t	207·5°	220·0°	232·0°	241·8°	256·0°	257·0°	260·0°	261·0°
p, cm.	9·60	15·30	24·00	32·00	54·70	55·00	61·30	62·30
$\Delta p_{\text{mm.}}$	0	0	−2	−3	0	4	−1	0

$CaBr_2,1/0ND_3$.

t	208·5°	220·0°	226·7°	238·5°	240·9°	254·5°
p, cm.	9·12	14·30	18·50	28·60	30·40	49·40
$\Delta p_{\text{mm.}}$	0	0	2	1	−1	2

$BaBr_2,8/4NH_3$.

t	0·0°	19·40°	21·90°	26·80°	28·70°	30·8°
p, cm.	9·05	30·70	34·90	46·70	51·50	57·80
$\Delta p_{\text{mm.}}$	0	1·0	−2·5	1·0	0	1·0

$BaBr_2,8/4ND_3$.

t	0·0°	19·30°	21·30°	24·60°	28·80°
p, cm.	7·91	28·08	32·65	39·00	49·40
$\Delta p_{\text{mm.}}$	−1·0	1·0	1·0	0	−2·0

$BaBr_2,4/2NH_3$.

t	19·30°	21·30°	24·60°	28·80°	32·10°
p, cm.	23·75	27·00	32·70	41·40	49·46
$\Delta p_{\text{mm.}}$	0	1·0	1·0	0	0

$BaBr_2,4/2ND_3$.

t	23·60°	26·80°	29·90°	34·40°
p, cm.	28·15	34·40	41·50	52·70
$\Delta p_{\text{mm.}}$	−1·0	0	1·0	−1·0

$BaBr_2,2/1NH_3$.

t	34·40°	40·0°	41·60°	46·60°
p, cm.	16·50	23·60	26·20	35·30
$\Delta p_{\text{mm.}}$	0	−2·0	0	2·0

$BaBr_2,2/1ND_3$.

t	36·50°	40·00°	46·50°	50·10°
p, cm.	17·50	22·50	33·30	42·30
$\Delta p_{\text{mm.}}$	−2·0	1·0	−5·0	3·0

TABLE II.—(*Continued.*)

$FeCl_2$,6/2NH_3.

t	46·70°	70·30°	80·9°	84·80°	86·40°	92·80°	100·50°	106·60°	109·90°
p, cm. ...	2·82	10·78	18·0	22·40	25·00	32·70	46·50	61·20	70·65
Δpmm. ...	0	−2·6	2·2	−1·5	3·5	−1·1	−2·1	0	0

$FeCl_2$,6/2ND_3

80·90°	86·40°	92·80°	100·50°	106·60°	109·90°
15·70	22·60	29·90	43·00	57·40	66·60
−1·5	4·0	−3·0	−5·0	4·3	0

$FeCl_2$,2/1NH_3.

t	224·0°	234·0°	239·5°	242·0°	243·0°	247·0°	249·0°	251·0°	252·5°	253·5°	255·5°	260·0
p, cm. ...	11·20	16·37	20·02	22·17	22·50	26·60	30·40	28·92	31·80	33·10	36·32	41·82
Δpmm. ...	0	0	0	2·0	0	0	0	4·1	−3·4	−1·0	2·0	4·0

$FeCl_2$,2/1ND_3.

t	224·0°	234·0°	239·5°	243·0°	249·0°	255·5°	260·0°	267·0°	271·0°	275·0°
p, cm. ...	12·80	14·87	18·45	20·80	26·00	33·90	39·10	49·30	56·20	63·20
Δpmm ...	1	−1	0	−3·3	0	8·9	2·0	3·0	1·0	−9·0

$FeCl_2$,1/0NH_3.

t	253·0°	261·0°	271·0°	276·0°	285·5°	292·0°
p, cm. ...	4·07	6·00	8·75	10·60	15·85	19·75
Δpmm. ...	0	0·6	0	−1·6	0	−2·6

$FeCl_2$,1/0ND_3.

253·0°	261·0°	271·0°	276·0°	292·0°
3·68	5·37	8·23	9·95	18·65
0	−0·6	1·0	−0·7	−1·0

$NiCl_2$,6/2NH_3.

t	99·6°	105·5°	110·0°	118·6°	153·9°	158·0°	159·5°	164·7°	172·7°
p, cm. ...	3·26	4·37	5·65	8·73	43·5	51·72	54·0	66·45	92·90
Δpmm. ...	0	−0·2	−0·2	0	9·0	0	0	−3·5	8·0

$NiCl_2$,6/2ND_3.

99·60°	110·0°	118·6°	158·0°	164·7°	172·7°
2·86	4·99	7·75	46·35	61·40	85·30
0	0	2·0	−2·0	−5·0	3·0

$NiCl_2$,2/1NH_3.

t	230·0°	247·7°	263·5°	265·5°	270·0°	280·0°	285·0°	288·0°
p, cm. ...	6·90	13·20	23·40	24·62	27·80	39·50	46·40	50·20
Δpmm. ...	0	0	4·0	0	−6·0	1·0	4·0	0

$NiCl_2$,2/1ND_3.

t	230·0°	247·7°	263·5°	265·5°	270·0°	280·0°	285·0°	288·0°
p, cm. ...	6·46	12·70	22·15	23·62	26·50	38·10	43·90	48·60
Δpmm. ...	0	0	3·0	2·0	−5·0	4·0	0	0

$MnCl_2$,6/2NH_3.

t	48·50°	60·50°	66·00°	72·50°	80·50°	82·00°	86·10°
p, cm. ...	10·74	20·40	27·75	37·85	56·30	61·60	73·40
Δpmm. ...	0·6	−1·0	1·0	−2·0	−3·0	6·0	0

$MnCl_2$,6/2ND_3.

48·50°	60·50°	66·00°	82·00°	86·10°
9·10	17·87	24·40	55·65	67·95
0	0	0	0	4·5

$MnCl_2$,2/1NH_3.

t	180:2°	192·0°	197·0°	206·5°	211·5°	222·5°	231·5°	243·5°
p, cm. ...	8·25	12·92	15·64	22·51	27·33	40·20	53·70	77·74
Δpmm. ...	0·5	−1·0	−1·6	1·1	0	0	1·0	1·4

$MnCl_2$,2/1ND_3.

t	180·2°	192·0°	197·0°	206·5°	211·5°	222·5°	231·5°	243·5°
p, cm. ...	7·50	11·89	14·70	20·50	25·25	37·50	51·10	74·50
Δpmm. ...	0	−0·8	0	−2·0	1·0	0	0	2·0

LiCl,4/3NH_3.

t	0·0°	5·30°	10·00°	14·10°
p, cm. ...	38·90	51·50	67·70	80·01
Δpmm. ...	−1·0	2·5	−1·0	2·0

LiCl,4/3ND_3.

0·0°	5·30°	10·00°	14·10°
32·20	43·05	56·00	70·00
0	−2·5	0	0

LiCl,3/2NH_3.

t	20·10°	26·80°	30·10°	40·40°	45·80°	49·90°	54·10°
p, cm. ...	8·23	12·60	15·45	28·20	37·80	47·03	58·67
Δpmm. ...	0	0	0	2·0	0	0	0

LiCl,3/2ND_3.

25·10°	30·10°	39·90°	40·40°	50·20°	53·50°	59·30°
10·24	13·70	24·80	25·10	43·20	60·10	71·50
2·0	−0·2	0	3·0	−1·5	0	−6·0

LiCl,2/0NH_3.

t	41·10°	51·20°	66·10°	66·70°	73·40°	87·10°
p, cm. ...	6·94	12·50	26·90	27·90	38·00	71·50
Δpmm. ...	−0·4	0·8	0	2·0	−1·0	0

LiCl,2/0ND_3.

40·00°	50·60°	57·80°	66·70°	80·40°	90·20°
5·65	10·70	15·65	24·80	48·10	74·20
−1·0	3·0	0	0	0	−5·0

LiBr,5/4NH_3.

t	−41·0°	−37·7°	−32·9°	−30·9°	−28·5°	−25·7°	−23·9°	−21·3°	−20·7°
p, cm. ...	12·90	16·90	24·16	28·51	34·01	41·17	47·80	50·10	56·12
Δpmm ...	0	0·7	−2·8	0	0	−2·5	2·5	−3·0	5·0

LiBr,5/4ND_3.

t	−37·8°	−35·5°	−34·7°	−30·1°	−27·5°	−27·4°	−26·2°	−25·2°	−24·3°	−21·80°	−19·8°
p, cm. ...	14·00	17·40	18·57	26·65	32·46	33·00	36·40	38·80	42·0	49·60	58·39
Δpmm. ...	−1·0	1·0	0	0	−2·0	0	1·0	0	1·0	−5·0	0

LiBr,4/3NH_3.

t	18·30°	18·77°	21·10°	21·25°	24·15°	24·85°	28·10°	35·10°	45·40°	55·06°	56·40°	60·40°
p, cm. ...	7·80	8·27	9·41	9·50	11·18	11·65	13·90	20·02	35·57	52·13	56·02	66·05
Δpmm. ...	−0·5	0	0	−0·7	0	0	0	0	0	0	6·0	−1·5

LiBr,4/3ND_3.

t	21·10°	24·85°	30·20°	37·10°	48·30°	60·40°
p, cm. ...	8·10	10·00	13·58	19·70	34·50	60·35
Δpmm. ...	0	−2·0	0	1·0	0	0

LiBr,3/2NH_3.

t	47·60°	54·70°	60·40°	64·90°	69·20°	72·50°
p, cm. ...	7·80	11·70	16·02	20·25	26·05	30·55
Δpmm. ...	0·7	−0·6	−0·8	0	0	0

LiBr,3/2ND_3.

47·60°	54·70°	60·40°	64·90°	69·20°	72·50°
7·10	10·90	15·25	19·54	24·70	29·42
0	0	0·5	1·4	0	−2·0

LiBr,2/1NH_3.

t	42·30°	50·20°	56·50°	60·50°	68·40°	72·00°	74·10°	76·20°	80·00°	81·60°	84·60°	95·00°	99·60°	105·5°
p, cm. ...	5·95	9·02	12·60	15·35	22·45	26·45	28·90	32·15	36·25	38·08	41·43	55·20	62·20	73·50
Δpmm. ...	−0·1	−0·6	4·0	0	1·0	0	−1·0	1·0	0	0	0	0	2·0	4·0

LiBr,2/1ND_3.

t	42·30°	50·20°	56·50°	60·50°	68·40°	72·00°	74·10°	76·20°	80·00°	81·60°	84·60°	95·00°	99·60°	105·5°
p, cm. ...	5·30	8·04	11·00	13·75	20·00	23·80	26·15	29·05	33·42	35·08	38·47	55·20	59·10	72·50
Δpmm. ...	0·5	0	0	1·5	0	−1·0	−0·6	0	−0·8	0	0	0	2·0	0

TABLE II.—(*Continued.*)

LiBr,1/0NH$_3$.

t	78·60°	92·10°	101·6°	103·9°	111·5°	120·0°	122·6°	123·9°	125·8°	131·6°
p, cm. ...	3·15	6·28	9·90	11·21	15·85	23·10	25·80	27·50	29·30	38·00
Δ*p*mm. ...	5·0	0	−1·0	0·3	0	0	2·0	0	0	0

LiBr,1/0ND$_3$.

t	78·60°	92·10°	101·6°	103·9°	120·0°	122·6°	123·9°	125·8°	131·6°
p, cm. ...	2·88	5·82	9·30	10·45	21·70	24·30	25·75	27·92	35·70
Δ*p*mm. ...	0·6	0	0	3·5	0	2·0	−1·5	1·2	0

LiI,5/4NH$_3$.

t	−46·5°	−40·6°	−36·4°	−36·2°	−31·7°	−29·6°	−26·5°	−23·0°	−18·4°
p, cm. ...	7·56	12·13	16·73	17·02	23·68	28·05	35·00	46·30	61·50
Δ*p*mm. ...	0·6	1·1	0	−2·0	−3·1	0	0	0	0

LiI,5/4ND$_3$.

t	−41·5°	−35·6°	−33·0°	−25·5°	−21·8°	−18·0°
p, cm. ...	9·70	15·80	19·20	33·60	43·80	57·20
Δ*p*mm. ...	2·0	1·0	0	0	−2·0	0

LiI,4/3NH$_3$.

t	32·3°	47·0°	51·9°	56·1°	65·1°	73·4°	74·4°	79·1°	81·4°	87·0°	91·4°
p, cm. ...	2·12	4·90	6·40	7·94	12·40	18·35	19·65	25·75	28·50	41·65	54·00
Δ*p*mm. ...	−0·1	0	0·6	0	−0·5	−1·0	0	−2·5	0	0	3·0

LiI,4/3ND$_3$.

t	38·4°	47·0°	56·1°	58·1°	58·4°	62·6°	71·4°	74·4°	81·4°	87·0°	91·4°
p, cm. ...	2·62	4·34	7·08	7·95	8·12	10·02	15·65	18·30	26·30	39·00	51·90
Δ*p*mm. ...	0	0	−0·7	0·5	0	0	−0·5	0·6	0	−2·8	4·0

LiI,3/2NH$_3$.

t	46·6°	55·4°	58·4°	62·6°	67·7°	72·0°	75·3°	73·7°	80·8°	87·6°	92·3°
p, cm. ...	4·30	6·88	8·00	10·02	12·95	15·65	16·95	17·55	20·90	25·22	29·00
Δ*p*mm. ...	0	−0·4	0	0·2	1·0	−1·3	−0·6	0	0·6	−2·5	0

LiI,3/2ND$_3$.

t	46·6°	55·4°	58·4°	62·6°	67·7°	72·0°	73·7°	75·3°	80·8°	87·6°	92·3°
p, cm. ...	3·91	6·36	7·45	9·36	12·16	14·85	16·20	16·70	19·80	24·5	28·3
Δ*p*mm. ...	0	−0·2	0	0·4	1·1	0	−0·8	0	−1·0	−0·5	1·2

LiI,2/1NH$_3$.

t	85·0°	90·8°	94·9°	96·9°	100·2°	101·4°	103·1°	104·4°	105·4°	108·6°	120·5°
p, cm. ...	3·14	4·18	4·97	5·50	6·35	6·80	7·72	8·50	9·24	12·10	27·30
Δ*p*mm. ...	0	0·4	−0·4	0·3	0	0	0·1	−0·9	0·9	0	0

LiI,2/1ND$_3$.

t	85·0°	90·8°	94·9°	96·9°	100·2°	101·4°	103·1°	104·4°	105·4°	108·6°	120·5°
p, cm. ...	2·82	3·76	4·54	5·06	5·90	6·27	7·12	7·82	8·50	11·16	22·90
Δ*p*mm. ...	0	0·2	−0·2	0·4	0	0	1·2	0·4	−0·7	0	0

NaI,4·5/0NH$_3$ (Liquid ammine).

t	0·0°	2·0°	3·3°	4·0°	6·0°	8·0°	9·1°	10·7°	14·3°	20·0°	30·6°	35·9°
p, cm. ...	12·35	14·12	15·40	15·90	17·80	19·75	20·90	22·70	27·10	35·30	55·88	69·30
Δ*p*mm. ...	−0·5	0·7	0·7	0	0	−0·3	0	0	0	1·0	0	0

NaI,4·5/0ND$_3$ (Liquid ammine).

t	0·0°	2·0°	3·3°	4·0°	6·0°	7·1°	8·0°	9·1°	10·4°	11·45°	14·0°	20·0°	26·6°	32·1°	36·3°	39·55°
p, cm. ...	11·45	12·95	13·80	14·60	16·60	17·46	18·20	19·40	20·70	21·80	24·75	32·75	44·00	55·60	65·20	74·90
Δ*p*mm. ...	1·0	1·0	−1·0	−0·3	−0·5	−1·0	0	0	0	0	1·0	1·0	0	2·0	0	−0·3

NaI,4·5/0NH$_3$ (Solid ammine).

t	−33·3°	−29·9°	−28·7°	−23·8°	−20·8°	−19·4°	−14·5°	−11·3°
p, cm. ...	1·14	1·52	1·65	2·51	3·14	3·45	4·88	6·00
Δ*p*mm. ...	0	−0·3	−0·2	1·0	1·0	0	−2·0	0

NaI,4·5/0ND$_3$ (Solid ammine).

t	−31·8°	−29·5°	−24·6°	−20·6°	−16·9°	−12·8°	−8·1°	−6·3°
p, cm. ...	1·12	1·35	2·04	2·77	3·66	4·89	6·68	7·52
Δ*p*mm. ...	0	0	0·6	0	0	0	−1·0	−1·0

Calcium Ammine.—Some measurements on the dissociation pressures of the ammines of metallic calcium (Moissan, *Compt. rend.*, 1898, **127**, 685) made by Biltz and Hüttig (*Z. anorg. Chem.*, 1920, **114**, 241) were in excellent agreement with earlier ones of Kraus (*J. Amer. Chem. Soc.*, 1908, **30**, 653). Both agree that only a hexammine is formed (Moissan states that it is a tetrammine) and that this decomposes to pure metal, the equilibrium being reached instantaneously. The results were found by Biltz and Hüttig to be reproducible and not to be affected by an irreversible side reaction $Ca(NH_3)_6 = Ca(NH_2)_2 + 4NH_3 + H_2$, which Kraus found to be appreciable only at 40°. Biltz and Hüttig, by extrapolation to zero, claim to have eliminated the effect of this side reaction, and give an example of a pressure–time curve at 0° which shows only a very slight linear increase of pressure after a number of hours.

We made a number of measurements with various specimens of calcium, and in every case found that the side reaction was so rapid that equilibrium pressures of the hexammine dissociation could not be measured. As an example, we give some results found with redistilled calcium of 99·9% purity at 0°, which showed a smaller effect of the side reaction than less pure metal:

Time, mins.	1	1·5	2	3	3·5	4	5	6	8	10	15	21
p, cm.	1·80	2·20	2·40	2·70	2·85	3·00	3·30	3·50	4·01	4·48	5·60	6·85

The linear increase of pressure between 2 and 21 mins. extrapolated to 1·90 cm. at zero time. Six series of measurements gave identical results. Several series of measurements were made at 5°, one of which is as follows:

Time, mins.	0·5	1	2	4	6	8	10	15
p, cm.	2·0	2·65	3·5	4·55	5·58	6·4	7·25	9·16

These results, which were reproducible, extrapolated to 2·6 cm. at zero time. Results at 10° were more difficult to extrapolate but a value of about 4 cm. was estimated. Above 10° no useful results could be obtained.

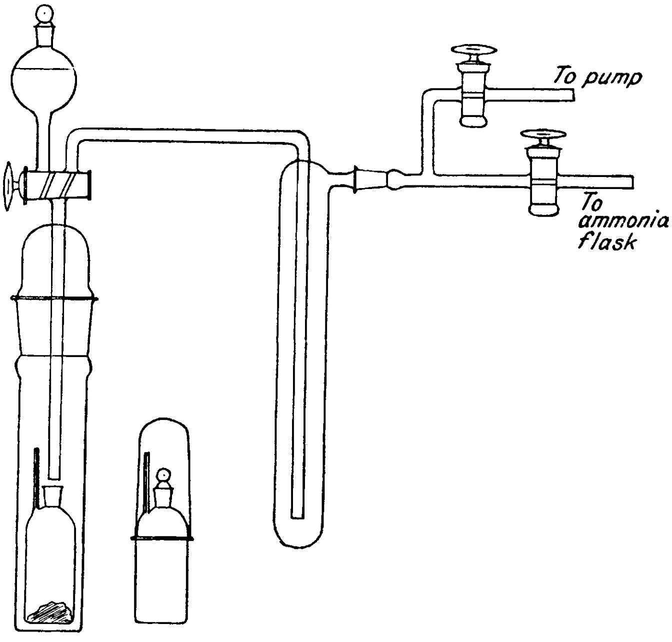
Even with the purest metal, the side reaction forming calcium amide was still 60—100 times faster than was found by Biltz and Hüttig. Further experiments with this system were not made.

Barium Chloride Ammine.—Barium chloride forms only an octammine, the dissociation pressures of which were measured by Hüttig and Martin (*loc. cit.*) below 0°, and by Gillespie and Lurie (*loc. cit.*) in the range 0—50°. Barium chloride dihydrate gives anomalous results for dissociation pressures (Partington, J., 1911, **99**, 466), and we find that for the ammine also, in contradiction to the experiments named, anomalous results are obtained. About 1 g. of recrystallised barium chloride, dehydrated at 150°, rapidly formed a compound with ammonia at 30°, the solid swelling to many times its original volume. The excess of ammonia was removed, and a little gas taken off before the pressure measurements were begun. Both the above pairs of workers obtained a pressure of 50·0 cm. at 0°, although Hüttig and Martin remark that in one of the four experiments made equilibrium was reached much more slowly and the final pressure at 0° was only 41·0 cm. We found that equilibrium was reached extremely slowly. After 24 hours, with pressure increasing, the final pressure was in several cases 40·2—40·4 cm., and with pressure decreasing, 40·8—42 cm. With a second sample of barium chloride 40·35 cm. was reached after 36 hours. A third sample was left in contact with a large excess of liquid ammonia, and the ammine partly recrystallised from this giving a hard cake of material. A much slower rate of pressure increase was found, the pressure after 4 days reaching a constant value of 39·2 cm. at 0°. In view of the peculiar behaviour of this system, experiments on it were discontinued.

Density Measurements.—A determination of the molecular volumes of the ammines and deuterammines of a typical salt gave results parallel to those found by Bell (*loc. cit.*) for several hydrates and deuterates. Ubbelohde (*loc. cit.*) has suggested that the smaller heat of dissociation of the deuterate should accompany a smaller lattice spacing. We have measured the densities of $NiCl_2,6NH_3$ and $NiCl_2,6ND_3$.

FIG. 10.

Density Apparatus.



Previous accurate work on the densities of ammines is not very extensive and is mainly confined to compounds relatively stable at ordinary temperatures, such as the hexammines of the halides of bivalent manganese, iron, and nickel (Biltz and Birk, *Z. anorg. Chem.*, 1923, **127**, 34; Clarke and Buckner, *J. Amer. Chem. Soc.*, 1922, **44**, 230; Wyckoff, *ibid.*, p. 1239). Gillespie and Gerry (*ibid.*, 1931, **53**, 3962) dealt with the unstable octammines of calcium and barium.

A small sample (0·4—0·8 g.) of anhydrous nickel chloride was transferred to a previously tared weighing bottle, which was reweighed and placed inside the apparatus shown in Fig. 10, which was then evacuated. The tap and joint were greased with soft and with hard vacuum grease, respectively. The apparatus was filled with ammonia at about 1·5 atm. With the bottle cooled to 0°, absorption of 5 mols. of ammonia took place very rapidly, but above this composition it became slow and it was very difficult to exceed 5·8 mols. of ammonia per mol. of the chloride. By cooling the solid in carbon dioxide–alcohol, the hexammine could be reached. The composition of the solid was determined by reweighing.

The solid was transferred to the accurately weighed density bottle, which was reweighed and placed in the apparatus, the tap and joint of which were now free from grease, and this was pumped out for 5 mins. The bottle was removed, wiped, and reweighed, and usually showed a small loss in weight due to removal of adsorbed ammonia or air. The process was repeated until the weight was constant, and after a short final evacuation purified kerosene was added through the three-way tap until the solid was covered. The bottle was removed and filled with the liquid, the stopper firmly replaced, and the whole weighed after 30 mins. in a thermostat at 25·00°.

The composition of the solid as determined by synthesis was not exact, since evacuation altered it appreciably; hence, after the final weighing the contents of the density bottle were washed into excess of N-hydrochloric acid and titrated with N/10-alkali with bromothymol-blue, the end-point not being obscured by the pale green nickel ion. The results are given below, V_m being the molecular volume. Extrapolation gave the molecular volume of $NiCl_2,6NH_3$ as 156·52 c.c. (d = 1·4808). The density of the pure anhydrous salt was found to be 3·5426, and the molecular volume of ammonia in the hexammine is thus 19·99 c.c. per mol. In the solid of lowest ammonia content ($4·574NH_3$) the average molecular volume is 19·39. Wyckoff (*loc. cit.*), with large crystals of hexammine and a flotation method, found the density to be 1·5206, and as calculated from X-ray analysis, 1·49.

$NiCl_2,xNH_3$.			$NiCl_2,xNH_3$.			$NiCl_2,xND_3$.		
x.	d.	V_m.	x.	d.	V_m.	x.	d.	V_m.
5·966	1·4838	155·81	5·516	1·5320	146·05	6·950	1·6111	155·12
5·779	1·5029	151·75	5·507	1·5311	145·88	5·654	1·6356	148·38
5·693	1·5158	149·82	4·674	1·6380	127·22	5·338	1·6675	141·75
						4·782	1·7460	129·13

Extrapolation gives the density of the hexadeuterammine as 1·5960 and the molecular volume as 156·40 c.c., which is only 0·08% lower than that of the ammine. This small difference is comparable with that found for various hydrates and deuterates by Bell (*loc. cit.*), *e.g.*, $SrCl_2$, $6H_2O$, $6D_2O$, −0·4%; $CoCl_2$, $6H_2O$, $6D_2O$, nil.

The graph of molecular volume against composition was in each case a perfectly straight line, which enabled the molecular volumes of the hexammines to be determined very accurately.

Heats of Dissociation.—In Fig. 11, the ratio p_{ND_3}/p_{NH_3} for a selection of systems is plotted against $10^6/T$, and it is seen that for the range of systems a continuous line can be drawn through the points, the ordinate of which approaches unity with increasing temperature. The points for calcium chloride lie on a second line below the first. The gradual approach to equality with rise of temperature is to be expected from the similar results found with the vapour pressures of water and deuterium oxide.

The dissociation pressure measurements can all be represented with sufficient accuracy by the equation $\log p = A/T + B$, where A and B are constant for each system. The thermodynamic treatment, with approximations fully discussed by Scheffer (*loc. cit.*), shows that this may be written as $\log_{10} p = q/4·576T + B$, where q is the heat of dissociation absorbed per mole of NH_3 or ND_3. Although q is given by the slope of the linear graph of $\log p$ against $1/T$, a tabulation of the deviations of each point from the line enabled the final value to be improved by the method of least squares. The values of q and B found are given in Table III, in which the values of B refer to cm. of mercury as the pressure unit.

FIG. 11.

Relation between p_{NH_3}/p_{ND_3} and Temperature.

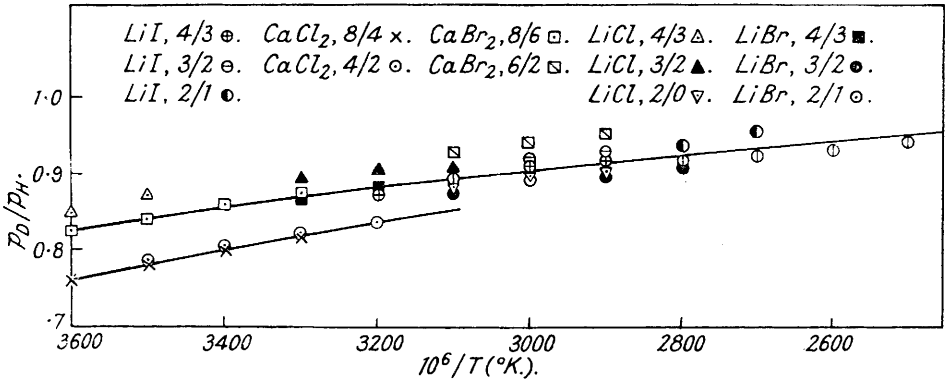


TABLE III.

System.	q, g.-cals.	$-A$.	B.
$CaCl_2$,8/4NH_3	10,950	2303	9·79
$CaCl_2$,8/4ND_3	11,630	2542	10·21
$CaCl_2$,4/2NH_3	11,160	2440	9·65
$CaCl_2$,4/2ND_3	11,780	2575	10·01
$CaBr_2$,8/6NH_3	10,920	2387	9·85
$CaBr_2$,8/6ND_3	11,310	2472	10·07
$CaBr_2$,6/2NH_3	11,950	2612	9·04
$CaBr_2$,6/2ND_3	12,200	2667	9·07
$CaBr_2$,2/1NH_3	15,550	3398	8·67
$CaBr_2$,2/1ND_3	15,920	3486	8·82
$CaBr_2$,1/0NH_3	17,950	3924	9·10
$CaBr_2$,1/0ND_3	18,400	4022	9·25
$BaBr_2$,8/4NH_3	9,860	2155	8·85
$BaBr_2$,8/4ND_3	10,200	2230	9·08
$BaBr_2$,4/2NH_3	10,190	2228	7·99
$BaBr_2$,4/2ND_3	10,530	2303	8·21
$BaBr_2$,2/1NH_3	12,530	2739	10·12
$BaBr_2$,2/1ND_3	12,790	2810	10·32
$FeCl_2$,6/2NH_3	12,430	2719	8·895
$FeCl_2$,6/2ND_3	12,840	2805	9·154
$FeCl_2$,2/1NH_3	19,380	4236	9·57
$FeCl_2$,2/1ND_3	19,630	4291	9·64
$FeCl_2$,1/0NH_3	24,300	5312	10·71
$FeCl_2$,1/0ND_3	24,450	5345	10·73
$NiCl_2$,6/2NH_3	15,320	3285	9·33
$NiCl_2$,6/2ND_3	15,030	3349	9·43
$NiCl_2$,2/1NH_3	19,180	4194	9·18
$NiCl_2$,2/1ND_3	19,360	4232	9·22
$MnCl_2$,6/2NH_3	11,700	2557	8·981
$MnCl_2$,6/2ND_3	12,230	2673	9·267
$MnCl_2$,2/1NH_3	16,750	3661	8·98
$MnCl_2$,2/1ND_3	17,010	3718	9·08
LiCl,4/3NH_3	8,006	1750	7·994
LiCl,4/3ND_3	8,620	1884	8·404
LiCl,3/2NH_3	10,960	2395	9·09
LiCl,3/2ND_3	11,230	2454	9·23
LiCl,2/0NH_3	11,350	2481	8·543
LiCl,2/0ND_3	11,580	2531	8·843
LiBr,5/4NH_3	8,693	1900	9·453
LiBr,5/4ND_3	9,150	2000	9·66
LiBr,4/3NH_3	9,705	2123	8·19
LiBr,4/3ND_3	10,000	2186	8·34
LiBr,3/2NH_3	11,980	2618	9·06
LiBr,3/2ND_3	12,560	2745	9·41
LiBr,2/1NH_3	10,760	2352	8·24
LiBr,2/1ND_3	11,140	2435	8·44
LiBr,1/0NH_3	13,300	2907	8·76
LiBr,1/0ND_3	13,500	2951	8·85
LiI,5/4NH_3	8,648	1890	9·212
LiI,5/4ND_3	8,898	1945	9·382
LiI,4/3NH_3	11,100	2426	8·268
LiI,4/3ND_3	11,540	2518	8·504
LiI,3/2NH_3	11,200	2448	8·292
LiI,3/2ND_3	11,610	2538	8·529
LiI,2/1NH_3	12,430	2717	8·08
LiI,2/1ND_3	12,770	2792	8·25
NaI,4·5/0NH_3	9,400	2055	8·46
NaI,4·5/0ND_3	9,690	2118	8·82
$CuSO_4$,5/4NH_3	14,250	3115	10·47
$CuSO_4$,5/4ND_3	15,090	3298	10·91
$CuSO_4$,4/2NH_3	15,270	3338	9·58
$CuSO_4$,4/2ND_3	15,930	3482	9·85
$CuSO_4$,2/1NH_3	19,380	4181	9·25
$CuSO_4$,2/1ND_3	19,610	4289	9·41

The difference between the heats of dissociation for the solid and partly liquid systems containing lithium halides are equal to the latent heats of fusion L per mole of one or other of the solids, in some cases the higher and in others the lower ammine or deuterammine, as explained above. In the following table the solid system is denoted by s and the solid–liquid by $s.l.$ Except for sodium iodide, L is greater for the ammonia system.

	LiBr,2/1NH_3.	LiBr,2/1ND_3.	LiI,4/3NH_3.	LiI,4/3ND_3.
q_s.	10,760	11,140	11,100	11,540
$q_{s.l.}$	7,077	7,731	14,970	15,130
L	3,683	3,409	3,870	3,590

	NaI,4/5NH_3.	NaI,4/5ND_3.	LiI,3/2NH_3.	LiI,3/2ND_3.
q_s.	9,400	9,690	11,200	11,610
$q_{s.l.}$	7,730	7,836	7,595	7,925
L	1,670	1,854	3,826	3,625

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