A DISTRIBUTION METHOD FOR THE DETERMINATION OF THE DISSOCIATION PRESSURES OF SALT AMMONIATES

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The difficulties attending the measurement of the dissociation pressures of hydrates by static and dynamic methods have been discussed by various investigators.[1] The same difficulties are encountered in measuring the dissociation pressures of ammoniates by similar methods. It seemed, therefore, worth while to investigate the possibilities of an indirect method, analogous to the one first suggested by Linebarger and since employed by others.[1a,2] This method consists of shaking the dissociating hydrates with an inert solvent in which the solid phases are practically insoluble until equilibrium is reached. The concentration of water in the solvent is then determined and from the previously determined relation between the water content of the liquid and the vapor pressure of water in equilibrium with it the dissociation pressures of the hydrate are calculated.

Chloroform was chosen as the solvent since it combines high solvent power for ammonia with very slight solvent power toward inorganic salts and their ammoniates. The salt chosen for the investigation was zinc chloride, since it forms a well-defined series of ammoniates whose properties are quite well known and the magnitudes of their dissociation pressures lend themselves to ready measurement.

The solubility of ammonia gas in chloroform at several pressures at 25° was measured since the values are required in calculating the dissociation pressures and no direct measurements appear in the literature. Biltz and Messerknecht[3] measured, by the usual static methods, the pressures of ammonia gas in equilibrium with solid ammoniates of zinc chloride of different compositions. Since they made no measurements at 25°, which was decided on as a desirable temperature for this work, static measurements on this system have been made for comparison with those by the indirect method.

Possible advantages of the proposed method over the static method are: (1) attainment of equilibrium in a shorter time due to the shaking up of the materials; (2) the measurements unlike those by the static method should be independent of the presence of adsorbed or combined gases other than ammonia. To investigate the last question some measure-

[1] (a) R. E. Wilson, THIS JOURNAL, **43**, 704 (1921); (b) W. C. Schumb, *ibid.*, **45**, 342 (1923).

[2] Linebarger, *Z. physik. Chem.*, **13**, 500 (1894); Foote and Scholes, THIS JOURNAL, **33**, 1309 (1911); Noyes and Westbrook, *ibid.*, **43**, 726 (1921).

[3] Biltz and Messerknecht, *Z. anorg. allgem. Chem.*, **129**, 161 (1923).

ments both static and by the indirect method have been made on a hy-. drated ammoniate, $ZnCl_2\cdot 4NH_3\cdot H_2O$, prepared in aqueous solution; (3) an additional advantage, of particular value where only one or two measurements are desired, is that the indirect method does not require the construction of any special apparatus such as manometers, McLeod gage, etc., required by the static method.

Solubility of Ammonia in Chloroform

The chloroform used in the measurements was prepared from U. S. P. chloroform. This material contains from five to seven tenths of one per cent. by weight of alcohol, which is the principal impurity. The alcohol may be removed readily by shaking with concentrated sulfuric acid or allowing it to stand over anhydrous zinc chloride. After removing the alcohol, the chloroform was washed with water and allowed to stand over anhydrous potassium carbonate for two days to dry it. Pure chloroform decomposes, or is oxidized readily, on standing even in a dark glass bottle. A white precipitate appears on the addition of ammonia gas to the contaminated product. No consistent values for the solubility could be obtained with this material. For this reason it was considered desirable to have a small amount of alcohol present as recommended by Baskerville and Hamor.[4] The measurements reported were made on chloroform to which one tenth of one per cent. of alcohol had been added. It is essential that the alcohol content be known as experiments with chloroform containing varying amounts of alcohol showed that the addition of one per cent. of alcohol increases the solubility of ammonia in chloroform by about twenty per cent.

The solubilities were measured by determining the ammonia content of chloroform solutions and of the vapor phases in equilibrium with them. The apparatus used is shown in Fig. 1. The upper bulb is of about one liter volume and the lower one 50 cc. In making the measurements about 25 cc. of a saturated chloroform–ammonia solution was poured into the apparatus, which was then placed in a thermostat at 25° with the upper and lower stopcocks closed and the middle one open. After standing awhile to reach the temperature of the thermostat, the bulbs were inverted several times, allowing the liquid to flow back and forth between the two compartments, to ensure uniform distribution of the ammonia throughout the gaseous phase. The apparatus was then allowed to stand upright in the thermostat for a half hour to ensure complete draining of the liquid into the smaller bulb.

Fig. 1.

The connecting stopcock was then closed and the apparatus removed from the thermostat. The ammonia in the upper bulb of known volume was then determined by allowing an excess of standardized sulfuric acid to flow in to neutralize all the ammonia and the excess acid determined
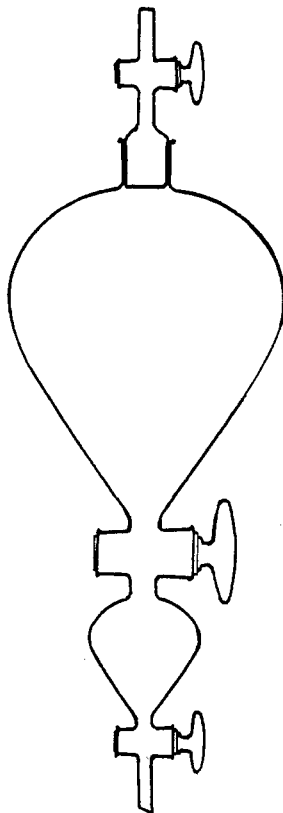
[4] Baskerville and Hamor, *J. Ind. Eng. Chem.*, 4, 364 (1912).

by titration. The ammonia content of the liquid was determined by allowing it to flow out into excess acid and the excess determined by titration, without removing the chloroform, using methyl orange as the indicator. The volume of the liquid was calculated from its weight and known density.

Table I gives the results obtained using a series of solutions of varying concentration, produced by diluting the original saturated solution, C_1 is the concentration of ammonia in the liquid phase in moles per liter of solution, C_2 the concentration of ammonia in the vapor phase, $R = C_1/C_2$ is the distribution ratio, and p is the partial pressure of ammonia, in millimeters of mercury, calculated from C_2 assuming Dalton's law to hold in the gaseous phase and neglecting the deviations of ammonia gas from the perfect gas law. The decomposition pressures calculated on this basis will be in error to the amounts neglected here, but they are probably not great for decomposition pressures well below one atmosphere. It is seen that the distribution ratio R increases as the concentrations decrease but apparently approaches a constant value 52.0 $\pm$ 0.3, within the limits of experimental error, at lower concentrations.

TABLE I

SOLUBILITY OF AMMONIA IN CHLOROFORM AT 25°

C_1	C_2	R	p	C_1	C_2	R	p
1.105	0.0244	45.2	453.5	0.246	0.00474	51.9	88.1
0.851	.0175	48.7	325.4	.1157	.002215	52.3	41.2
.661	.0132	50.1	245.4	.0888	.001716	51.8	31.9
.423	.00814	52.0	151.3	.0393	.000756	52.0	14.0
.392	.00749	52.3	139.2				

The specific gravity of the chloroform used was determined at 25°, using a pycnometer, as 1.480 $\pm$ 0.002. The specific gravity of the solutions required in calculating the concentrations does not differ greatly from that of the pure solvent. The specific gravity of a solution containing 1.315 moles of ammonia per liter was found to be 1.450 and the small corrections required were obtained by assuming a linear relation between the specific gravity and ammonia concentration.

Pressure Measurements on the System $ZnCl_2$–NH_3.—Since the object of these measurements was to compare the results obtained by the static and indirect methods, "C. P." anhydrous zinc chloride was used without further purification.

In making the static measurements a weighed amount of the anhydrous zinc chloride was placed in a small glass-stoppered flask and ammonia gas passed in while the flask was kept cool until no further gain in weight was observed. Approximately six moles of ammonia per mole of zinc chloride are absorbed in this way. The flask was then placed in the thermostat and connected through a ground glass joint to a mercury manometer and vacuum pump. After pumping off ammonia, which was

absorbed in concentrated sulfuric acid, from the solid for a short time the tube leading to the pump was closed and the flask allowed to stand until the manometer indicated that equilibrium was reached. The other side of the manometer was connected to the pump and the thoroughness of evacuation of this arm checked by a McLeod gage. After making a pressure reading the flask was detached and weighed. The composition of the solid could then be calculated. By pumping off more ammonia and repeating the above procedure a series of pressure measurements for solid ammoniates of different composition was obtained.

The pressures found and the composition of the corresponding ammoniates are given in Table II.

TABLE II

DECOMPOSITION PRESSURES OF ZINC CHLORIDE AMMONIATES BY THE STATIC METHOD

No.	p, mm.	moles NH_3/moles $ZnCl_2$	No.	p, mm.	moles NH_3/moles $ZnCl_2$
1	122.5	5.85	9	17.8	3.60
2	121.0	5.65	10	17.7	3.40
3	118.3	5.40	11	17.2	2.62
4	118.3	4.95	12	17.2	2.21
5	116.5	4.40	13	16.0	2.05
6	114.5	4.05	14	11.5	1.90
7	17.5	3.95	15	6.0	1.88
8	17.8	3.87	16	1.2	1.82

A similar series of measurements was made by the indirect method. The procedure followed consisted of first making up a zinc ammoniate of known composition by adding ammonia gas to a known weight of solid anhydrous zinc chloride and weighing the product. Equilibrium was secured by adding a measured volume of chloroform to the solid in a glass-stoppered Erlenmeyer flask, placing in the thermostat at 25° and shaking at frequent intervals for one to two hours. Experiment showed that this time was sufficient. A sample of the liquid in the flask was then forced through a filter into a 25-cc. pipet by means of air pressure and the ammonia content determined by titrating with sulfuric acid of suitable strength. The equilibrium pressure was then calculated by means of the previously determined relation between the ammonia content of the solutions and the partial pressures of ammonia in equilibrium with them. The composition of the remaining solid was calculated by subtracting the weight of ammonia extracted by the several additions of chloroform from the amount present at the start. This calculation is not as exact as that possible in the static method through direct weighing of the solid since a small but unknown amount (probably not more than 2% of that extracted) of ammonia was lost in the vapor phase on each addition of fresh chloroform to the solid.

The results obtained from a series of measurements are given in Table III.

TABLE III

DECOMPOSITION PRESSURES OF ZINC CHLORIDE AMMONIATES AT 25° BY THE INDIRECT
METHOD

No.	Concn. of NH₃ in liquid, moles/liter	p, mm. calcd.	Moles NH₃/moles ZnCl₂	No.	Concn. of NH₃ in liquid, moles/liter	p, mm. (calcd.)	Moles NH₃/moles ZnCl₂
1	0.338	121.0	5.25	10	0.0504	18.0	4.01
2	.331	118.5	5.09	11	.0479	17.2	3.03
3	.321	115.0	4.92	12	.0476	17.1	2.89
4	.325	116.3	4.74	13	.0462	16.6	2.74
5	.331	118.5	4.57	14	.0475	17.1	2.69
6	.324	116.0	4.40	15	.0421	15.2	2.45
7	.312	111.5	4.23	16	.0402	14.9	2.30
8	.274	97.3	4.02	17	.0180	6.6	2.07
9	.180	63.9	4.02				

Determination No. 10 in Table III is the mean of six consecutive de-
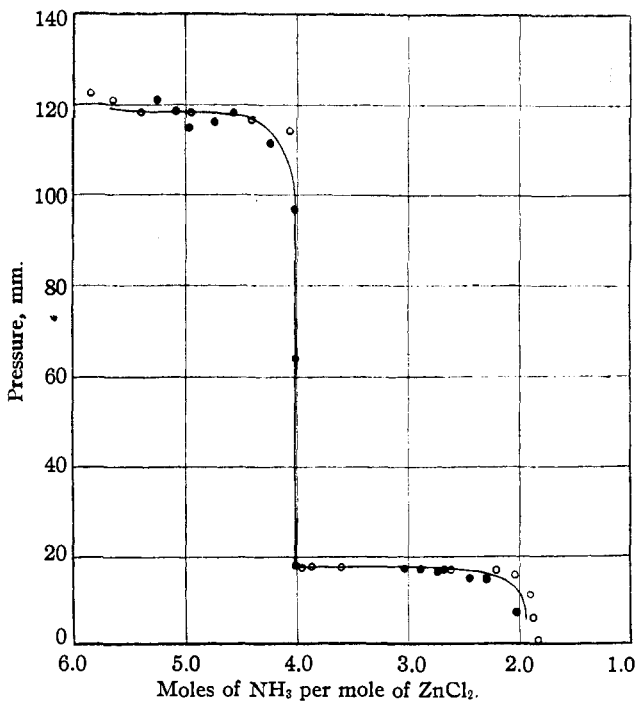terminations none of the values varying from the mean by more than one

Fig. 2.—Dissociation pressures of zinc chloride ammoniates:
O, static; ●, indirect.

millimeter. Since the amount of ammonia extracted at the lower pressure
is small, the composition of the solid did not change much during these
determinations. For the following values another sample of ammoniate
of smaller weight was used.

For ready comparison of the results obtained by the two methods the pressures and corresponding compositions have been plotted in Fig. 2. Inspection of the figure shows that the results obtained by the two methods are in good agreement and indicate an equilibrium pressure for the reaction $ZnCl_2 \cdot 6NH_3 \rightleftharpoons ZnCl_2 \cdot 4NH_3 + 2NH_3$ of about 118 mm. at 25° and for the reaction $ZnCl_2 \cdot 4NH_3 \rightleftharpoons ZnCl_2 \cdot 2NH_3 + 2NH_3$ a pressure of approximately 17.5 mm.

Time Required to Reach Equilibrium.—In many cases, especially at low pressures, the time required in reaching equilibrium by the static method is many hours. Since in the indirect method the sample can be continuously shaken, it was thought that it might be possible to reach equilibrium in a shorter time. The time required by the two methods was compared in the following manner. After pumping off ammonia for several minutes from a sample of a solid ammoniate on which several pressure measurements had already been made with the apparatus previously described, the stopcock to the pump was closed and the pressure in the manometer read at intervals. The values are recorded in Table IV. The composition of the ammoniate at this point was $ZnCl_2 \cdot 3.75NH_3$.

TABLE IV		TABLE V	
TIME REQUIRED TO REACH EQUILIBRIUM BY THE STATIC METHOD		TIME REQUIRED TO REACH EQUILIBRIUM BY THE INDIRECT METHOD	
Time	p, mm.	Time of rotation	p, mm.
20 minutes	11.5	15 minutes	16.65
45 minutes	13.0	30 minutes	17.00
2 hrs., 45 minutes	15.5	45 minutes	17.45
3 hrs., 45 minutes	15.6	60 minutes	17.61
5 hrs., 15 minutes	15.8	90 minutes	17.42
7 hrs., 45 minutes	15.9		
24 hrs.	17.7		
28 hrs.	17.7		

It may be seen that more than eight hours was required to reach equilibrium. Indirect measurements were then made on the same sample; it was removed to a glass-stoppered bottle, chloroform added, and rotated in the thermostat for fifteen minutes. The chloroform was then removed and its ammonia content found. Fresh chloroform was then added and the rotation continued for a longer time. Table V gives the pressures found for different times of rotation.

These values indicate that equilibrium was reached in less than one hour of rotation.

Effect of Gases Other than Ammonia.—The values obtained by the indirect method should, unlike the static method, be independent of the presence of other gases, either adsorbed or combined, except for the amounts which their presence may affect the solubility of ammonia in chloroform. Measurements were made on a hydrated ammoniate, pre-

pared in aqueous solution, to test this question. This product was pre-
pared according to the method of Divers[5] by adding solid zinc chloride
to 14 N ammonium hydroxide, the solution being kept cool and fresh
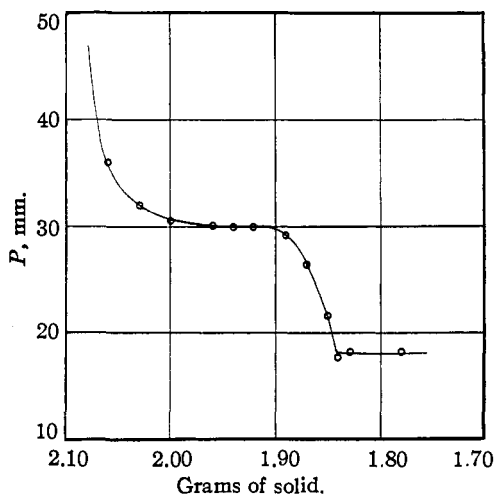additions of solid made until the solution was nearly saturated. Am-
monia gas was then passed
through the solution until a
considerable amount of solid
appeared. This was redis-
solved by warming and when
the solution was cooled well-
defined crystals appeared.
The liquid was drained from
the crystals and they were
washed with alcohol and ether.
Part of the crystals were then
used for the static measure-
ments and the rest for the in-
direct measurements.

Table VI gives the pressure
measurements recorded by the
manometer as the solid decom-
posed. Since the composition
of the solid was unknown the weight of the sample remaining is given so
the decomposition may be shown graphically. This is done in Fig. 3.

Fig. 3.—Dissociation pressures of hydrated
ammoniates.

TABLE VI

DISSOCIATION PRESSURES OF A HYDRATED ZINC CHLORIDE AMMONIATE BY THE STATIC
METHOD

No.	p, mm.	Solid, g.	No.	p, mm.	Solid, g.
1	167	2.19	8	30.0	1.92
2	68.5	2.09	9	29.1	1.89
3	36.0	2.06	10	26.5	1.87
4	32.0	2.03	11	21.7	1.85
5	30.5	2.00	12	17.6	1.84
6	30.1	1.96	13	18.2	1.83
7	30.0	1.94	14	18.2	1.78

Several extractions were made with chloroform for the hydrated am-
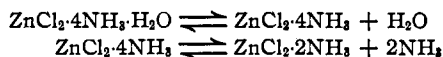moniate. The values obtained are given in Table VII.

TABLE VII

DECOMPOSITION PRESSURES OF A HYDRATED ZINC CHLORIDE AMMONIATE BY THE
INDIRECT METHOD

No.	1	2	3	4	5	6	7
p, mm.	23.3	20.6	19.6	19.2	18.7	18.6	18.7

[5] Divers, *Chem. News*, 18, 13 (1868).

Figure 3 shows that by the static method a well-defined region of constant pressure, about 30 mm., exists as the decomposition progresses. This does not appear in Fig. 2 as the unhydrated ammoniate is decomposed.

This apparently monovariant system may be explained by assuming decomposition to proceed according to the equations

$$ZnCl_2 \cdot 4NH_3 \cdot H_2O \rightleftharpoons ZnCl_2 \cdot 4NH_3 + H_2O$$
$$ZnCl_2 \cdot 4NH_3 \rightleftharpoons ZnCl_2 \cdot 2NH_3 + 2NH_3$$

and the 30 mm. pressure to be the sum of the ammonia and water vapor partial pressures. It may also be noted that in the last points the pressure has fallen to the normal value for the decomposition of the unhydrated $ZnCl_2 \cdot 4NH_3$, approximately 18 mm. This apparently corresponds to the disappearance of the hydrated ammoniate. Table VII shows that by the indirect method the values fall off at once to a value in good agreement with the dissociation pressure of the anhydrous $ZnCl_2 \cdot 4NH_3$. The value is slightly high, however, perhaps due to an increase in the solubility of ammonia in the chloroform caused by the presence of water or alcohol from the solid. It seems reasonable, therefore, to attribute the difference between 30 mm. and 18 mm., or approximately 12 mm., to the partial pressure of water vapor produced by decomposition of the hydrated ammoniate.

Divers gives the formula $ZnCl_2 \cdot 5NH_3 \cdot H_2O$ to the product obtained by the method described. The fact that the ammonia pressure measured by the indirect method is in good agreement with that of $ZnCl_2 \cdot 4NH_3$ and not a much higher value seems good evidence that the formula $ZnCl_2 \cdot 4NH_3 \cdot H_2O$ as given by other investigators for the compound prepared by similar methods is more likely.[6]

Summary

1. An indirect method for the measurement of the dissociation pressures of ammoniates analogous to that of Linebarger for hydrates has been developed.

2. Dissociation pressures of salt ammoniates in good agreement with those obtained by the static method may be obtained by shaking the solid ammoniates with chloroform and determining the ammonia content of the chloroform solution obtained.

3. The solubility of ammonia in chloroform at 25° has been measured.

4. Measurements on a hydrated ammoniate indicate that a dissociation pressure of ammonia can be measured by the indirect method in the presence of another volatile dissociation product.

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[6] Thomas, *Ber.*, **20**, 743 (1887); Kane, *Ann. chim. phys.*, [2] **72**, 290 (1839).