5. The heat of neutralization of citric acid and the acid citrate has been measured. The values found are much less than for strong acids. The temperature coefficient of the heat of neutralization of these acids is decidedly smaller than for inorganic acids and, indeed, in one case, is of opposite sign. These results are discussed.

BRYN MAWR, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE VAPOR PRESSURE AND VAPOR DENSITY OF INTENSIVELY DRIED AMMONIUM CHLORIDE[1]

BY WORTH H. RODEBUSH AND JOHN C. MICHALEK

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The anomalous behavior of intensively dried ammonium chloride was first reported in the literature by Baker,[2] who found that the vapor density as determined by a Victor Meyer method indicated no dissociation into ammonia and hydrogen chloride. Baker's work was repeated by Gutmann,[3] who obtained results indicating complete dissociation. Baker[4] again repeated his measurements and remained convinced that the vapor density of intensively dried ammonium corresponds to no dissociation. Two determinations of vapor density were made upon dried ammonium chloride by Johnson[5] with contradictory results. Smith, Eastlack and Scatchard[6] report that Smith and Lombard found no dissociation for dry ammonium chloride vapor but these results have not been published. Most investigators have found the vapor of moist ammonium chloride to be completely dissociated, but here again there is lack of complete agreement and Smith and Lombard[7] in an extensive investigation found only partial dissociation for undried ammonium halides.

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[1] This manuscript was prepared for publication some months ago but publication has been delayed because of the appearance of a preliminary report by A. Smits [*Rec. trav. chim.*, **46**, 445 (1927)] of a similar series of experiments, with results differing from those here reported. A note was published by the authors [*Proc. Nat. Acad.*, **14**, 131 (1928)] commenting on the discrepancies between the two series of experiments. Since a detailed report of Smits' experiments has not appeared, it seemed advisable to submit the manuscript for publication as originally prepared. Meanwhile a paper has appeared by Braune and Knoke [*Z. physik. Chem.*, **135**, 49 (1928)] reporting measurements on undried ammonium chloride which are in substantial agreement with those described in this paper.

[2] Baker, *J. Chem. Soc.*, **65**, 611 (1894).

[3] Gutmann, *Ann.*, **299**, 267 (1898).

[4] Baker, *J. Chem. Soc.*, **73**, 422 (1898).

[5] Johnson, *Z. physik. Chem.*, **61**, 458 (1908).

[6] Smith, Eastlack and Scatchard, THIS JOURNAL, **41**, 1961 (1919).

[7] Smith and Lombard, *ibid.*, **37**, 48 (1915). These authors give references to previous determinations.

Several determinations[8] have been made upon the vapor pressure of undried ammonium chloride, of which the work of Smith and Calvert is probably the best. Johnson, however, made measurements on both dried and undried specimens of ammonium chloride. His measurements were made with a spiral glass manometer under conditions which did not ensure high accuracy, but they indicated that the vapor pressures of the dried and undried forms were identical. This last result has appeared to many as very surprising indeed and the theoretical implications have been discussed at some length by Abegg[9] and Wegscheider.[10]

If the vapor pressures of the dried and undried forms are the same and the vapor of the one is dissociated while the vapor of the other is not, we have a situation very difficult to explain, for there must exist an equilibrium between the dissociated and undissociated molecules in the vapor state and in turn between each of these and the solid. The removal of the last traces of moisture must be supposed to shift this equilibrium. The most probable way in which this could be imagined to come about would be for the removal of the last traces of moisture to increase the free energy of the solid and in addition prevent the establishment of the dissociation equilibrium. This is not necessarily a thermodynamic impossibility, since the removal of traces of moisture might conceivably involve large energy changes, but it is certainly contrary to experience. Results so surprising as these cannot be accepted without ample experimental confirmation and it appeared to the authors that it would be worth while to redetermine the vapor pressures and vapor density of ammonium chloride in various stages of dryness.

Experimental

Method of Drying.—The term "intensively dried" used in this paper is, of course, relative. In his work on liquids, Baker[11] used materials which had been dried for several years. In the case of ammonium chloride, however, all authors who observed abnormal behavior have obtained this result after drying for a period of a few days to a few weeks. The following general procedure was used in the preparation of what we designate as "intensively dried" material.

The apparatus of pyrex glass was baked out for eight to ten hours at 400–500°. During this outgassing process it was connected to the drying pump system and the highest possible vacuum maintained. Attached to the apparatus by a tube which projected outside the furnace was a bulb containing the sample of ammonium chloride

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[8] Smith and Menzies, This Journal, **32**, 1448 (1910); Smith and Calvert, *ibid.*, **36**, 1363 (1914); Johnson, *Z. physik. Chem.*, **65**, 38 (1909); Ramsay and Young, *Phil. Trans. Roy. Soc.*, **177**, 71 (1886); Horstman, *Ber.*, **2**, 137 (1869).

[9] Abegg, *Z. physik. Chem.*, **61**, 455 (1908).

[10] Wegscheider, *Z. anorg. allgem. Chem.*, **103**, 207 (1918).

[11] Baker, *J. Chem. Soc.*, **121**, 2555 (1922).

which was to be introduced. When the apparatus was cool this sample was introduced by repeated sublimations until it was spread in a thin layer over the inside of the apparatus. A high vacuum was maintained during this process so that the salt as introduced was free from all but minute traces of moisture. The temperature of the apparatus was then raised to the highest point (60–70°) which could be maintained without driving the salt out of the apparatus and the pumping out process was continued for five to ten days. The pump and drying-tube system merit a detailed description. The apparatus containing the salt to be dried was connected to a mercury vapor diffusion pump of special design and high capacity. Beyond this pump was a drying tube containing phosphorus pentoxide which had been introduced by distillation in a current of oxygen. Beyond this drying tube was an ordinary diffusion pump, another phosphorus pentoxide tube and then a high-vacuum type of oil pump. Liquid-air traps were used whenever their use appeared advantageous. It must be recognized, however, that a liquid-air trap in a line has the same effect on the passage of water vapor as a very narrow constriction.

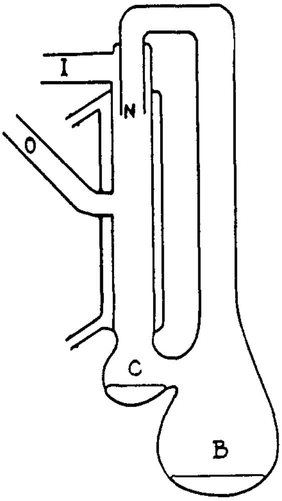

Fig. 1.

The "superpump" was designed by one of the authors to take care of a defect in the ordinary diffusion pump that has been pointed out by Molthan.[12]

In the ordinary type of diffusion pump the mercury is condensed against a cold surface and runs back into the reservoir whence it is reëvaporated and goes around the circuit again. Any substance, *e. g.*, water, which the pump is removing from the vessel to be evacuated will be to a slight extent dissolved in and adsorbed on the surface of the condensing drops of mercury. This establishes in the ascending column of mercury vapor a small but definite partial pressure of water vapor and the limit of exhaustion is reached when the partial pressure in the vessel to be evacuated has reached this value. The phosphorus pentoxide tube immediately beyond the pump would tend to overcome this difficulty but it was felt that the design of the pump could be materially improved and the model shown in Fig. 1 was devised. It is not possible to avoid the condensation against a cold surface but the drops of mercury flow down against a refluxing stream of hot mercury vapor, so that any volatile constituent should be distilled out before the mercury reaches the reservoir. For the construction of the difficult seal we are indebted to Dr. Phipps of this Laboratory. The pump functioned perfectly and showed a high capacity on test with a McLeod gage. No stopcocks or rubber connections were used between the apparatus containing the material to be dried and the diffusion pumps. The tube connecting the apparatus to the pump system was preheated thoroughly at the point where the final seal off was to be made. It is believed that drying under the above-described conditions of high vacuum and elevated temperature is far more rapid than with the ordinary technique that has been used by previous investigators.

Materials.—The ammonium chloride used was either Mallinckrodt's or Kahlbaum's reagent quality. It did not give tests for other halogens and left no residue on sublimation. It was always introduced into the apparatus by repeating sublimation. Upon prolonged heating the ammonium chloride took on a yellowish tinge but there was no evidence of appreciable decomposition. The phosphorus pentoxide was Mallinckrodt's reagent quality. It was purified by distillation in a current of oxygen.

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[12] Molthan, *Z. Physik*, **39**, 1 (1926).

The distillation of phosphorus pentoxide in pyrex glass was always a troublesome operation.

The Vapor Pressure of Moist and Dry Ammonium Chloride.—By far the most satisfactory apparatus for measuring vapor pressures of substances like ammonium chloride is the glass diaphragm manometer. We are indebted to Professor Farrington Daniels for his experience in the construction of this gage and the apparatus shown in Fig. 2 embodies his latest ideas in its construction. The side tube A contains the ammonium chloride and is kept cool while the rest of the apparatus is being baked out. When the ammonium chloride is introduced into the main part of the apparatus the side tube A is sealed off. Connection is made with the drying pumps through the Tube G. When vapor pressure determinations are to be made the Tube G is sealed off under a high vacuum and the apparatus is introduced into a fused nitrate bath to the level shown at I. The details of the gage have been described by Professor Daniels. It is only necessary to note one point. The zero point of the gage changes with the temperature and (possibly) with the lapse of time, so that it must be rechecked after each determination. The tube G projects above the bath and may be cooled by a blast of air. When this is done the ammonium chloride sublimes out of the bulb and condenses in the tip of G, giving practically zero pressure in the apparatus. When a determination is to be made a heating coil is slipped over the end of the tube and the salt is driven back into the main part of the apparatus. The nitrate bath was provided with a thermo-regulator and while measurements were being taken the temperature was held constant to 0.02°. Temperatures were registered by means of thermocouples calibrated against fixed points recommended by the U. S. Bureau of Standards and temperature control of the bath was maintained by an automatic regulator which was actuated through a contact galvanometer by a thermocouple. The pressures on the outside of the diaphragm were measured by a mercury U-tube manometer. The vacuum above the mercury on the high side of this manometer was maintained by a mercury vapor pump. The heights of the mercury columns were measured with a cathetometer and repeated readings taken during a period of some hours usually checked to a few hundredths of a millimeter. The height of the mercury column was corrected to 0°. For the determinations on the moist salt the apparatus was sealed off from the pumps as soon as a good vacuum was obtained. The dry material was prepared by holding the apparatus at 60° for four days with the pumps operating continuously. A liquid-air trap was put into operation sometime before sealing off to remove mercury vapor.

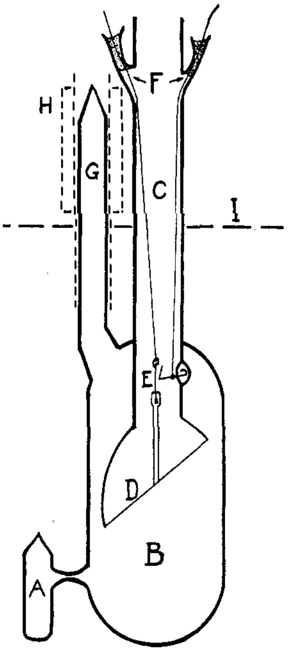

Fig. 2.

The data obtained are shown in Table I and the graph in Fig. 3. The figures given are in each case the means of several observations. The data obtained from the dried sample are indicated by asterisks. The results are in as good agreement as could be expected with the results of Johnson and Smith and Calvert, in view of the uncertainty in their measurements especially as regards temperature. The figures in Col. 4 are calculated from the equation $\log p = -(4402.1/T) + 10.1070$.

Table I

Vapor Pressure of Ammonium Chloride

	Temp., °K.	Obs. press., mm.	Log p (obs.)	Log p (calcd.)
1	557.0	159.63	2.2031	2.2030
2	546.1	111.19	2.0461	2.0460
3	523.2	49.47	1.6940	1.6940
4	507.1	26.46	1.4226	1.4260
5*	533.7	73.17	1.8643	1.8590
6*	532.6	69.76	1.8436	1.8400
7*	532.3	62.87	1.7984	1.8400
8*	529.9	63.63	1.8037	1.8010
9	532.5	69.31	1.8408	1.8410
10	471.3	5.93	1.7733	1.7660
11	501.3	21.68	1.3361	1.3250

The deviation is of the order of 1% except in the case of No. 7 and here there is reason to believe that the gage was not functioning properly. In

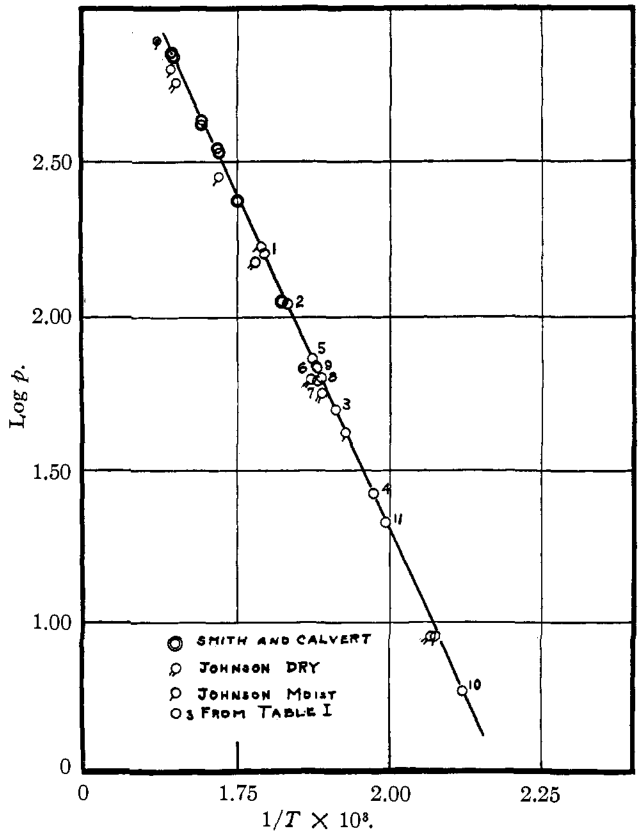

Fig. 3.

view of Johnson's results and ours there is no ground for believing that drying affects the vapor pressure of the salt. One effect of drying was unmistakable, however. This was the slowing up of the rate of evaporation and condensation. When the bulb contained moist salt and the Tube G was cooled the pressure fell very rapidly so that ten minutes would suffice for the pressure to fall to a value of a few mm., which corresponds to the transition temperature 184.3°, where the pressure would remain constant for some time. With the dried salt several hours would be required for all of the ammonium chloride to sublime out of the bulb and condense in the tube. So far as rate of evaporation and condensation were concerned the salt scarcely seemed to be volatile at all. This behavior would tend to confirm the reports that are to be found in the literature to the effect that gaseous ammonia and hydrogen chloride will not react when intensively dried. Another point requires comment. The heat of sublimation *per mole of vapor* as calculated from the vapor pressure equation above the transition point is 20,139. The heat of dissociation of solid ammonium chloride as measured calorimetrically is 41,900 Cal. per mole at 18°.[13] Allowing for a heat of transition of 970 Cal.,[14] but neglecting the difference in heat capacities of the solid and vapor, this gives a heat of sublimation above the transition point of 20,465 Cal. per *mole of vapor* for the completely dissociated salt. This figure is in such close agreement with the heat of sublimation obtained above from the vapor pressure equation that it is evidence in favor of complete dissociation for the vapor under all conditions. If the dissociation is not complete, then this agreement can only occur provided the heat of sublimation to the undissociated molecule be almost exactly half the heat of dissociation of the solid.

Vapor Density of Ammonium Chloride.—As was mentioned in the introduction to this paper, the experimental results on the vapor density of dried ammonium chloride which are given in the literature are not convincing. The methods which have been used are for the most part modifications of the Victor Meyer or Dumas methods. Neither of these methods is adapted for use in a determination where moisture is to be excluded or upon a substance which volatilizes slowly. The method of Knudsen[15] for the determination of vapor pressure by the rate of diffusion through an orifice is equally applicable to vapor density when the vapor pressure is known. This method has been used in this Laboratory for the determination of vapor pressures with success,[16] the only particular precaution necessary being that the surface of substance exposed be at least 100 times

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[13] Thomsen, "Thermochemistry," Longmans, Green and Company, New York, 1908.

[14] Bridgman, *Proc. Am. Acad.*, **52**, 89 (1916).

[15] Knudsen, *Ann. Physik*, **29**, 179 (1909).

[16] Rodebush and DeVries, This Journal, **47**, 2488 (1925); DeVries with Rodebush, *ibid.*, **49**, 656 (1927).

the area of the orifice in order that the pressure of vapor in front of the orifice be kept at saturation. Such a method would seem to be ideal from the standpoint of intensive drying, since the solid salt will be subject to a continuous drying action during a run and successive runs should show a progressive drying effect, if such exists, in the apparent molecular weight. The apparatus is shown in Fig. 4.

The orifice was made by grinding away a tip drawn in the end of a pyrex tube. The edges of the orifice were very thin and the opening was nearly round. A large number of measurements of the diameter of the opening in different directions were made under a microscope with a step micrometer eyepiece. The diameter varied by only a small amount in different directions so that the area of the opening could be calculated with satisfactory accuracy. The orifice tube was sealed into the Bulb C, which was about 6 cm. in diameter. The ammonium chloride was introduced either directly or by sublimation from the side Tube B. The Bulb C was immersed in an oil-bath thermostat and a tube furnace was placed around the tube leading from the orifice to prevent premature condensation of the salt. During a run the ammonium chloride was condensed in the U-shaped bend T, which was surrounded by liquid air. The end of the tube was connected to the cascade of diffusion pumps and drying tubes.

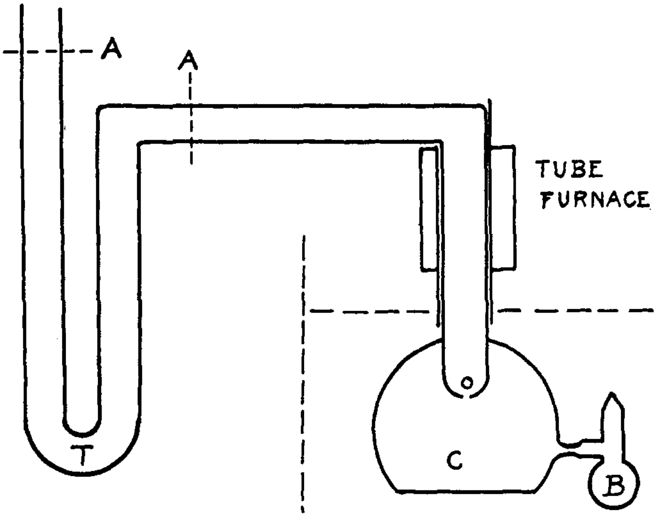

Fig. 4.

The temperature control was of the same accuracy as in the vapor pressure experiments and the same precautions were taken in the preliminary outgassing of the apparatus. In order to obtain a pressure low enough so that the simple kinetic theory could be applied to the process of effusion, it was necessary to work at temperatures below 100°. The pressures at these temperatures were calculated by means of the vapor-pressure equation, taking account of the heat of transition at 184.3 which has been determined by Bridgman[17] to be 970 cal. per mole. In making this calculation the vapor was assumed to be undissociated. The equation for rate of diffusion is

$$w = pat\sqrt{\frac{M}{2\pi RT}}$$

where w is the weight diffusing, p is the pressure in dynes, a is the area of the orifice, t is the time, M is the molecular weight, R is the gas constant in c. g. s. units and T is the absolute temperature. In case the vapor is not dissociated, this equation may be used directly to solve for the molecular weight. If the ammonium chloride is completely dissociated into ammonia and hydrogen chloride, it is easy to show that an apparent molecular weight will be obtained which is slightly different from the average for the two gases.

The preliminary drying was carried out in the manner previously described. When the apparatus was ready to begin a run it was brought to the desired temperature and the trap was immersed in liquid air. The time was noted with an accurate watch. The runs were of several hours duration. At the end of a run the trap was cut out of the apparatus at A, A, (Fig. 4) and the ammonium chloride was determined by precipitation of the chloride with silver nitrate. It was feared that the ammonia and hydrogen chloride might condense separately and escape on warming, so in several instances the trap was sealed off before the liquid air was removed, but no difference was noted in the results.

Results.—The results are shown in Table II. Except for No. 13, which is included for sake of completeness since the temperature got out of control during the overnight run, the results are uniformly low. Only one result is even high enough to correspond to complete dissociation. Since the surface of ammonium chloride exposed in the flask was more than 1000 times the area of the orifice, we are forced to conclude that a pronounced drying effect is obtained as soon as a vacuum is established, which slows up the rate of evaporation so that the pressure below the orifice falls below the saturation pressure. Even when moist ammonium chloride was introduced and the run started immediately the results obtained were low. When a preliminary pumping with the drying tubes was carried out, the results obtained were much lower still. If in extrapolating the vapor pressure to this temperature we had assumed complete dissociation, we should have obtained a higher pressure and consequently a still lower result would have been calculated for the apparent molecular weight. No conclusion may be drawn from these experiments as to the vapor density but the effect of drying on the rate of evaporation which was noticed in the vapor pressure

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[17] Bridgman, *Proc. Am. Acad.*, **52**, 89 (1916).

measurements is here confirmed in a positive manner. It must be noted that this slow rate of evaporation must be reckoned with in any method for the determination of vapor density.

TABLE II

MOLECULAR WEIGHT BY DIFFUSION METHOD

Run no.	Wt. diff., g.	Time, sec.	Temp., °K.	Press. mm. of Hg	Area of orifice, cm.²	Mol. wt.	Remarks
4	0.1152	30960	369.33	0.0122	0.0218	21.2	No drying
5	.0985	35250	365.63	.00916	....	20.9	....
7	.0877	31260	365.42	.00910	....	21.5	....
10	.0932	38280	365.20	.00902	....	16.4	....
11	.0689	21600	365.42	.00910	....	27.7	....
12	.0837	31980	365.42	.00910	....	18.7	....
13	.1064	44100	358.86	.00521	....	47.6	Temp. out of control
14	.0202	24750	358.86	.00521	....	5.48	Dried with P_2O_5
15	.0154	29040	358.86	.00521	....	2.3	....
16	.0039	12840	358.86	.00521	....	0.76	....
17	.0178	21270	358.86	.00521	....	5.7	No drying
18	.0197	27000	358.86	.00521	....	4.37	....
19	.0278	44640	358.86	.00521	....	3.28	Dried with P_2O_5
20	.0122	17940	358.86	.00521	0.0149	8.1	No drying
21	.0119	15240	358.86	.00521	....	10.7	....
22	.0307	33260	358.86	.00521	....	14.9	....
23	.0131	16320	358.86	.00521	....	11.3	....

Vapor Density by the Microbalance

The determination of vapor density by means of the buoyancy effect upon a thin-walled bulb has been developed to a high degree of precision by Stock.[18] A microbalance patterned after the design of Stock was constructed of quartz (see Fig. 5). The balance was enclosed in a tube which was maintained at a temperature constant to 1° by a surrounding furnace which was regulated by automatic thermostatic control. The balance case was connected by a tube to a bulb which was surrounded by a second furnace with an independent automatic temperature control. When solid

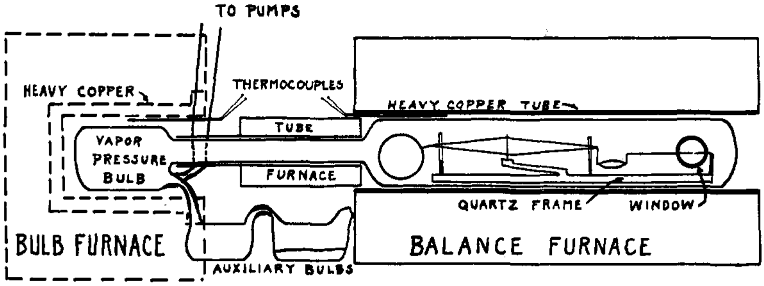

Fig. 5.

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[18] Stock and Siecke, *Ber.*, **57**, 562 (1924).

ammonium chloride was placed in the bulb any desired pressure could be maintained in the balance case by varying the temperature of the bulb and hence the vapor pressure. This furnace could be held at a temperature constant to 0.1° for long periods.

Mode of Operation.—The apparatus was outgassed for ten hours at 480–500° under a high vacuum. The apparatus was then cooled and dried air introduced for the purpose of calibrating the balance. From the pressure and temperature the density necessary to bring the balance to the zero point was calculated by the gas laws. The data for the calibration are given in Table III. The two sets of figures given represent the extreme values of a series of determinations. A displacement of the pointer of 0.2 mm. corresponds to a change in density of about 0.001 g. per liter, and while it was possible to bring the pointer within 0.2 mm. of the zero position, accidental factors due to the high temperature and complicated apparatus caused a variation of an amount indicated by the figures in Table III. The temperature coefficient of the balance is negligible.

After the air had been removed, ammonium chloride was introduced into the vapor-pressure bulb and dried for ten days with the pump system operating continuously. The bulb containing the ammonium chloride was maintained at 60° and the rest of the apparatus at 300–400° during the drying operation.

A liquid-air trap was put into operation in the last twenty hours of drying. The apparatus was then sealed off according to the usual technique and the furnace brought to such temperatures that the density of the ammonium chloride vapor in the balance case was just sufficient to bring the balance to the zero point. The temperatures and corresponding vapor pressures for a series of observations are given in Table IV. In the fourth column are the apparent molecular weights as calculated by the gas laws from the pressures and temperatures. It will be seen that apparent molecular weights correspond to complete dissociation.

In order to be sure that complete equilibrium had been established between the vapor and solid, the apparatus was held at constant temperature

TABLE III

CALIBRATION OF MICROBALANCE WITH AIR

Pressure, mm.	170	177		
Temp., °K.	587.8	588.8		
Calcd. *d*, g./l.	0.1346	0.1400	Av.	0.1373

TABLE IV

VAPOR DENSITY OF AMMONIUM CHLORIDE

Vapor pressure bulb, °K.	561.2	562.7	562.1	562.7	
Vapor pressure	183.6	192.3	188.8	192.3	
Balance case temp., °K.	593.3	596.9	598.0	588.0	
Apparent mol. wt.	27.7	26.6	27.1	26.2	Av. 26.9

for twenty-four hours. When the temperature of the vapor-pressure bulb was changed by 1°, more than an hour was required for the resulting change in the microbalance pointer, showing again the effect of drying on the rate of establishment of equilibrium between vapor and solid.

Conclusions

It is impossible, of course, to assert positively that the ammonium chloride was sufficiently dried to produce the results reported by Baker and co-workers. It appears to the authors, however, that under the high vacuum and elevated temperature used in these experiments a few days' drying should be equal to several weeks by the methods used by previous workers in the field. The remarkable lag in the evaporation and condensation of the ammonium chloride observed in every case where the salt was dried would appear to be a satisfactory criterion of intensive drying. This slow vaporization would account for the high results obtained by Baker in his use of the Victor Meyer and Dumas methods, just as it caused low results in the effusion method as described in this paper. It must be remembered that Gutmann was not able to reproduce the work of Baker and that Johnson's results were contradictory. Smith and Lombard's results on the vapor density of the moist salt indicating incomplete dissociation are believed by the authors to be due to experimental error. In their determinations they distilled the salt into a bulb at constant temperature and the bulb was sealed off when filled with the saturated vapor. It seems likely that an excess of ammonium chloride was introduced into the bulb either by absorption on the glass surface or by mechanical convection. Smith argued that the vapor should be at the saturation pressure in order to show abnormal vapor density, but from the standpoint of thermodynamics there is nothing unique about the saturated vapor. In our experiments the temperature of the balance case was maintained 20–30° above the temperature of the vapor pressure bulb in order to avoid the adsorption of ammonium chloride on the microbalance. Since the largest area of surface was offered by the float bulb, adsorption would cause low results for the density. The temperature difference we believe would prevent any appreciable adsorption. On the other hand, if the dissociation is nearly complete at this temperature an extraordinary temperature coefficient would be required for any considerable reduction in the percentage dissociation at a temperature 25° lower. As has been pointed out earlier the hypothetical value for the heat of dissociation in the vapor phase is 20,000 Cal., which gives only a small temperature coefficient.

Summary

The vapor pressure of ammonium chloride is unaffected by intensive drying. This result confirms the work of previous investigators.

The rate of vaporization and condensation is affected to a remarkable degree by the state of dryness.

Ammonium chloride which has been dried for ten days at 60° in a high vacuum appears to be completely dissociated in the vapor state.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

SONIC STUDIES OF THE PHYSICAL PROPERTIES OF LIQUIDS. I. THE SONIC INTERFEROMETER. THE VELOCITY OF SOUND IN SOME ORGANIC LIQUIDS AND THEIR COMPRESSIBILITIES[1]

BY EGBERT B. FREYER[2] WITH J. C. HUBBARD AND DONALD H. ANDREWS

RECEIVED OCTOBER 27, 1928 PUBLISHED MARCH 6, 1929

A number of investigators[3] have studied the velocity of sound in liquids at audible frequencies but the methods are beset with so many difficulties and involve the use of such large quantities of liquids that few results of adequate precision for thermodynamic treatment have been obtained. More recently[4] the field of high frequency sound production using piezoelectric crystals has been entered, and Hubbard and Loomis[5] have developed a method which has yielded very accurate values for the velocity of sound in liquids. The investigation recorded here was conducted according to their method and is a part of the general program of thermodynamic research on organic compounds now being undertaken at this Laboratory. The sonic interferometer has been further developed with especial reference to temperature control, the prevention of evaporation of the liquid being studied and of contamination by water vapor from the air.

Apparatus and Method

The electrical equipment is shown in Figs. 1, 2 and 3. When the circuit Y is tuned by means of the condenser (15), a heterodyne is produced between the two oscillating circuits. When the note is made to coincide in pitch with that produced by the tuning fork, the crystal in the interferometer is known to be vibrating with the same frequency

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[1] This paper was presented in part at the Swampscott meeting of the American Chemical Society in September, 1928.

[2] From the dissertation submitted by Egbert B. Freyer in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Schmidt, *Wiener Ber.*, (IIa) **114**, 945 (1905); Dörsing, "Inaug. Diss.," Bonn, 1907; *Ann. Physik*, [4] **25**, 227 (1908); Busse, *ibid.*, **75**, 657 (1924); Pooler, *Phys. Rev.*, **31**, 157 (1928) (abstract).

[4] Boyle, *Trans. Roy. Soc. Canada*, **17**, 141 (1923); 159, 191, 197 (1925); 79 (1927); Langevin, British Patent Spec. N. S. 457, No. 145,691 (1920).

[5] Hubbard and Loomis, *Nature*, **120**, 189 (1927); *Phys. Rev.*, **31**, 158 (1928); *Phil Mag.*, VII, **5**, 1177 (1928).