[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Effect of Pressure upon the Dissociation of a Solid

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Part I. The Effect of a Piston Pressure upon the Vapor Pressure

Introduction

The geologist often uses a qualitative knowledge of the effects of pressure upon a system to explain fundamental phenomena. For example, the formation of glaciers and sedimentary rocks is clearly a result of pressure and it is significant that carbonate rocks are never found under the hydrostatic head of the deepest parts of the ocean. Thermodynamics can give a quantitative expression for the effect. At constant temperature the free energy of a substance changes with pressure according to the equation

$$(\partial F/\partial P)_T = V$$

For two phases of the same substance at the same temperature but different pressures, the condition for equilibrium is that

$$\mathrm{d}F_1 = \mathrm{d}F_2 \text{ or } V_1\mathrm{d}P_1 = V_2\mathrm{d}P_2$$

which shows that to maintain equilibrium the two changes of pressure must be inversely proportional to the two molal volumes. This relation was first derived by Poynting[3] from consideration of a cyclic process. He found experimentally that by compressing marble chips in water by a piston, the water being free to move through a porous sand base, the marble could be obtained as a stone-like mass although similar pressure upon both the water and the marble produced no change. These are just the conditions that one gets in the formation of sedimentary rocks.

Since Poynting's equation is based upon simple straightforward thermodynamics, chemists have not hesitated to use it and for fifty years it has remained without quantitative experimental demonstration. In connection with the second part of this work a knowledge of the partial molal volume of ammonia in a barium chloride-barium chloride octammine mixture was desired and it was decided to use Poynting's equation to calculate that value. The experimental measurements are the first actual demonstration of the effect of a piston pressure upon vapor pressure.

Determination of Partial Molal Volume

Hüttig and Martin[4] reported that barium chloride formed only the octammine when exposed to ammonia, and Lurie and Gillespie[5] that they found no evidence of any other ammine when nitrogen was added up to a pressure of 60 atmospheres, so the vapor pressure of ammonia from the ammine is independent of the composition of the solid phases as long as some barium chloride is always present. For the utilization of Poynting's equation the necessary data then, besides an equation of state of ammonia which is already known, are the vapor pressures at various piston pressures. This requires an experimental set-up which will allow compression of the solid phases by a known piston pressure without compressing the dissociating ammonia which is however confined so that the resulting increase in vapor pressure can be measured.

These conditions are not easily realized, but after trial of several designs an apparatus was evolved which would give reversible and reproducible results. It is essential that the applied pressure be transmitted throughout the salt and that the ammonia dissociating be in contact with both the compressed salt and the compressed amine. Compressed gas was used as the most convenient and most readily measured pressure, a pure piston effect being obtained by separating it from the salt by a rubber membrane cut from an automobile inner tube and covered by a 5-cm. layer of mercury and a 60 cm. layer of oil to prevent diffusion of the gas through it.[6] The anhydrous barium chloride was mixed with about four times its volume of flake graphite and compressed by the membrane in a 4-mm. layer over two crossed disks of fine woven stainless steel filter cloth in the bottom of a steel bomb.

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[3] Poynting, *Phil. Mag.*, [5] **12**, 232 (1881).

[4] Hüttig and Martin, *Z. anorg. allgem. Chem.*, **125**, 269 (1922).

[5] Lurie and Gillespie, THIS JOURNAL, **49**, 1146 (1927).

[6] Mercury alone failed to prevent diffusion presumably because it did not wet the sides of the steel cylinder, for addition of oil above it did effectively stop diffusion. The mercury was still needed to separate the oil and rubber. Incidentally the limitation of mercury as a seal was strikingly illustrated at one time when ammonia was left overnight condensed above mercury in the two arms of a 5-mm. glass U-tube manometer. When allowed to evaporate off it was found that the liquid had penetrated 15 cm. downward between the mercury and the glass where upon release of pressure it broke the mercury column into numerous slugs. The mercury levels had not moved either during the condensation or evaporation.

The powder was not forced through the gauze which therefore acted as a semi-permeable membrane for the ammonia, the addition of which is described below, which easily found its way between the interstices of the cloth over the entire area of the disk which was 6.4 cm. in diameter and communicated through a small hole with the vapor pressure manometer. The volume of the vapor phase part of the system was kept small so that only a slight dissociation of the ammine would be required to build up pressure, thus ensuring the presence of both solid phases in the surface in contact with the ammonia. The experiment consisted simply in determining after equilibrium the vapor pressure corresponding to various piston pressures.

Experimental

The anhydrous barium chloride was made by heating, grinding and reheating the c. p. dihydrate over a low gas flame. Ammonia was taken from a commercial cylinder of the anhydrous liquid without purification since by formation of the ammine and later partial dissociation during the experiment the barium chloride itself acts as an excellent purifier. Through manipulation of appropriate valves the vapor phase system was evacuated and flushed several times with ammonia and the ammine first formed to saturation and then partially dissociated. It was then compressed by nitrogen above the membrane to various pressures as read on a glass capillary nitrogen-filled manometer of the same type as that to be described in detail in Part II but no corrections for the volume of the menisci were applied here since its useful precision of 1% could be obtained without them. The corresponding increase in vapor pressure was read on a differential manometer in the form of a mercury-filled glass U-tube placed in series with another steel bomb containing the ammine under its own vapor pressure, thus permitting readings to one millimeter. The normal vapor pressure was determined in a separate experiment with an open tube mercury manometer, equilibrium being approached from both sides. The apparatus was immersed in a water thermostat at 32.6° while the manometers were at room temperature in a constant temperature room thermostated at 27°. By alternately increasing and decreasing the nitrogen pressure the vapor pressure was correspondingly too low or too high thus giving approach of the equilibrium from both sides. The vapor pressure ceased to change after 24 hours.

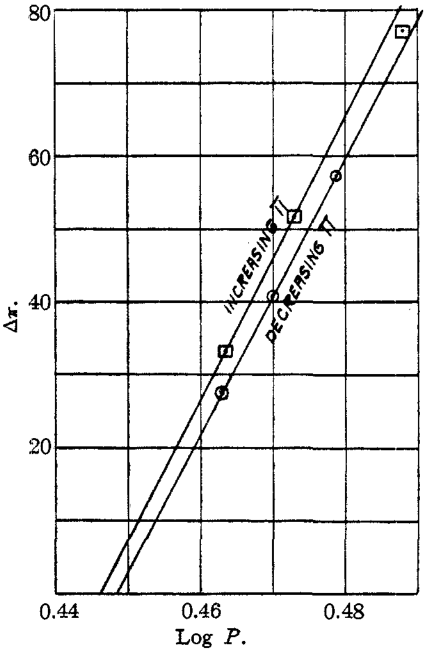

Fig. 1.

Results

By separate experiment the normal vapor pressure was determined as 2.855 meters of ice-cold mercury. The results for one run are given in Table I, also in meters of mercury. The last column gives the direction of change in the mechanical pressure.

TABLE I

Δp	p	Log p	π	$\Delta\pi$	π
0.210	3.065	0.4864	80.1	77.0	Inc.
.146	3.001	.4773	60.1	57.1	Dec.
.084	2.939	.4682	43.7	40.8	Dec.
.108	2.963	.4717	54.5	51.5	Inc.
.038	2.893	.4613	30.2	27.3	Dec.
.041	2.896	.4618	36.3	33.4	Inc.

To obtain the theoretical results it is necessary to integrate Poynting's equation. The Bureau of Standards[7] gives an equation of state for ammonia of v in terms of p. When $v\,dp$ was integrated between the close limits here involved, it was found that all terms in p after the first were negligible, giving

$$\int v_2\,dp_2 = 44005 \log p/p_0$$

where v is in cc. and p in meters for one mole. Considering the left-hand side of Poynting's equation, if the partial molal volume of the ammonia in the condensed phases does not change with pressure, its integration gives

$$\int v_1\,d\pi = v_1\,(\pi - p_0)$$

If this assumption is correct a straight line will be obtained when $(\pi - p_0)$ is plotted against the log of the ammonia pressure and the slope of that line will be $44{,}005/v_1$. A graph of the experimental data is shown in Fig. 1. The points determined with increasing and with decreasing piston pressure fall on two separate straight lines, the hysteresis being slight. The slope with increasing pressure gives a value for v_1 of 23.7 cc. and with decreasing pressure 23.5 cc.

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(7) Bureau of Standards Scientific Paper 501.

The fact that the extrapolated lines do not cut the axis of zero increase of pressure at the log of the normal vapor pressure shows that after initial compression there is a pressure gradient of about fifteen meters through the solid layer. This displaces the line downward on the pressure axis but does not alter its slope. If the pressure gradient were a significant function of pressure it would produce curvature in the line. In the absence of any significant curvature we may conclude that the partial molal volume of ammonia in the solids is not a function of pressure in the limits used here and has a value of 23.6 cc. at 32.6°.

Gillespie and Gerry[8] by determining the density and composition of various mixtures of barium chloride and the octammine at 25° under its own dissociation pressure determined the partial molal volume of ammonia to be 21.53 cc.

Part II. Effect of an Inert Gas upon the Dissociation of a Solid

Introduction

To the chemist the chief usefulness of the Poynting equation has been in the prediction of the effect of pressure by an inert gas upon vapor pressure. The vapor pressure in the presence of an inert gas may be defined as the pressure which at equilibrium would be exerted on a membrane separating the system from the pure inert gas to which alone it is permeable. If both the inert gas and the vapor were ideal gases the vapor pressure would be the Dalton partial pressure, that is, the vapor mole fraction–total pressure product. Lurie and Gillespie[5] have shown that the Dalton law necessarily implies obedience to Boyle's and Avogadro's laws and therefore that we can expect some error with actual gases. On the other hand, if we assume that the effect of the inert gas upon the activity of the solid or liquid is purely a pressure phenomenon, the vapor pressure can be calculated accurately from the Poynting equation. Since the chemist is often interested in calculating the vapor mole fraction, several experimental investigations of the relation between the Dalton partial pressure and the Poynting pressure have been made. Pollitzer and Strebel[9] have measured the mole fraction of water in air, hydrogen and carbon dioxide up to 200 atm. Larson and Black[10] have investigated the technically very important system hydrogen–nitrogen–liquid ammonia up to 1,000 atmos. McHaffie[11] has investigated the dissociation of sodium sulfate decahydrate under 100 atm. of air pressure. Bartlett[12] has measured the mole fraction of water vapor in compressed hydrogen, nitrogen and the three to one mixture up to 1,000 atm. Lurie and Gillespie[5] have determined the mole fraction of ammonia over barium chloride octammine when compressed by nitrogen up to 60 atm.

With the exception of the results of McHaffie which are quite anomalous, in every case the mole fraction–total pressure product was markedly greater than the quantity calculated from Poynting's equation upon the assumption of a pure pressure effect. Bartlett[11] found for example that the Dalton partial pressure was four times greater than the Poynting pressure for water compressed by nitrogen at 1,000 atm. and also that nitrogen holds 44% more water vapor than hydrogen. Saddington and Krase[13] made both gaseous and liquid phase analyses of the nitrogen–water system up to 300 atm. and 240° and found the divergence between the two quantities greater at the higher temperatures.

Various explanations have been offered such as association of the vapor under the influence of the inert gas, or the "solubility" of the vapor in the inert gas, or the necessity of using activities instead of partial pressures, or the effect of the attractive forces of the inert gas upon the molecules of the vapor. Van Laar[14] recently has pointed out that the liquid phase must be considered as a solution of the inert gas in the liquid, and on this basis and by using van der Waals equations for both phases he showed that an approximate four-fold increase in Dalton partial pressure of water vapor as found by Bartlett[12] was to be expected.

Since the solubility of the inert gas is a function of pressure, and the partial molal volume of the liquid may also be changing in an unknown manner, it is obvious that as the first step toward a quantitative treatment experimental data are desirable on a system less complicated, of proved equilibrium, and of known or independently determinable partial molal volume. It is our purpose to present here such results with a simple system.

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[8] Gillespie and Gerry, THIS JOURNAL, **53**, 3962 (1931).

[9] Pollitzer and Strebel, *Z. physik Chem.*, **110**, 768 (1924).

[10] Larson and Black, THIS JOURNAL, **47**, 1015 (1925).

[11] McHaffie, *Phil. Mag.*, [7] **1**, 561 (1926).

[12] Bartlett, THIS JOURNAL, **49**, 65 (1927).

[13] Saddington and Krase, THIS JOURNAL, **56**, 353 (1934).

[14] Van Laar, *Z. physik Chem.*, **145**, 207 (1929).

The System

If the activity is responsible for the divergence, the simplest system will use as a compressing gas one already above its Boyle point so that deviations from a perfect gas are uniform. Hydrogen is such a gas at room temperature. To avoid the uncertainties of solubility, the simplest system will use a dissociating solid, in which case solubility is presumably negligible. McHaffie[11] used sodium sulfate decahydrate but the partial pressure of water is so small and determination therefore so difficult that the system does not recommend itself aside from the fact that the anomaly of the results hints at a metastable equilibrium.

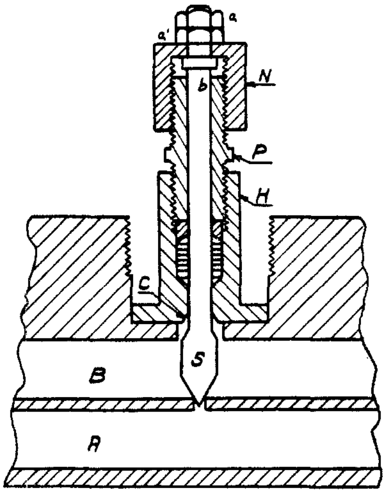

Fig. 2.

Many salts form amines which yield a considerable vapor pressure of ammonia which is of course a gas readily determined experimentally in mixture with an inert gas. Most of these salts form more than one ammine, which would necessitate an analysis of the solid phases if used. Search of the literature however revealed a report by Hüttig and Martin[4] that barium chloride formed only the octammine, with a dissociation pressure of over 2500 mm. at room temperature. They also reported that the equilibrium with the ammine was obtained rather slowly which is a disadvantage. Nevertheless the octammine was selected as the most ideal solid and the choice proved doubly fortunate when it was later discovered that Lurie and Gillespie[5] in an investigation of the thermodynamic properties of gaseous mixtures had already determined the Dalton partial pressure of ammonia over barium chloride octammine when compressed by nitrogen up to 60 atm. Use of this system thus made possible a comparison with results with another gas.

Compression by Inert Gas

In experiments with gases it is required to prove that equilibrium exists, to analyze a portion of the gas phase at equilibrium, and to measure the total pressure accurately. To prove the existence of a true equilibrium it was decided to approach it from both sides. This was done by admitting the hydrogen in one case to the ammine and in the other case by admitting a hydrogen–ammonia mixture, in which the ammonia pressure was greater than the equilibrium pressure, to the anhydrous barium chloride.

The usual procedure for analysis of the gas phase is to blow off a small sample for analysis so quickly that its composition does not have time to change. Preliminary experiments showed, however, that the ammine is so sensitive to partial pressure changes that this method was not feasible. It was accordingly decided to so arrange the gas space that after equilibrium part of it could be isolated without change of pressure from all contact with the solid. This also made check analyses possible. The system consists essentially of two parallel chambers in a brass block separated by only a 3.2 mm. wall through which a 3.2 mm. hole allowed diffusion of gases when the valve in Fig. 2 was opened or isolated them in one chamber from contact with the ammine in the other chamber when the valve was closed. As can be seen from the diagram the valve is absolutely tight to both chambers when open and packing is not exposed to the pressure except during the few moments required to close it in isolating the gas sample chamber. Such a valve may prove useful in other researches. Diffusion of the gases at 150 atm. was still fast compared to the attainment of chemical equilibrium.

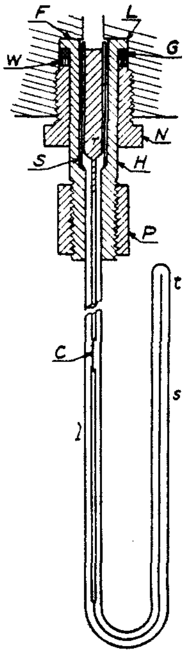

Fig. 3.

The pressure was read on specially designed closed-end nitrogen-filled glass capillary manometers. Since many have felt the need for a simple but accurate manometer it is illustrated in Fig. 3. Closed-end manometers suffer the disadvantage that the length of the gas column is halved every time the pressure is doubled and soon becomes too short for accurate measurement. Its range can be increased by trapping off a larger volume of gas but if bulbs are blown for this purpose the glass will not stand the pressure. Our manometer obtains the same result by utilization of two capillaries of different bore. The smaller capillary is one-half the diameter of the larger and thus the length of the nitrogen column is four times as long when compressed into the smaller tube. The smaller tube is carefully calibrated but the larger is not and at the point where the seal is made is narrowed down to prevent any weakening. A mercury thread is sealed in the end at *t* so that the nitrogen column is contained between two mercury menisci which can be read on a cathetometer. The mercury reservoir *r* is of such diameter that it falls only slightly under pressure, thus avoiding any dead space where diffusion would be slow. The glass was sealed into the steel holder with de Khotinsky cement. By screwing up the nut *P* on the unscrewed nut *N* the manometer can be pulled from its socket. Of course correction was made for the mercury head, and the volume of the menisci, and for the deviation of nitrogen from a perfect gas. The latter correction was made from a graph constructed from values calculated by the Beattie–Bridgeman[15] equation of state for nitrogen. Such a manometer is quite accurate to the highest pressure of commercial gas cylinders. Since the manometer is not read until the mercury enters the calibrated capillary it was standardized at about five meters against a single tube manometer which in turn was standardized at one meter against a mercury U-tube and barometer. It has a precision of 0.1%.

Experimental

Parallel experiments were run at about the same pressure, one starting from above and one from below the equilibrium vapor pressure. The mole fraction of ammonia was determined by withdrawing at atmospheric pressure a 250-cc. sample from the isolated sample chamber into a fixed volume over mercury, reading with the cathetometer the pressure on an attached barometer, absorbing the ammonia in concentrated sulfuric acid, and after replacing in the original volume reading the pressure of the hydrogen remaining. The ammonia was considered as a perfect gas since its greatest partial pressure was only 6 cm. Duplicate or triplicate analyses were made checking to 0.3%. Existence of true equilibrium was shown when the parallel experiments gave the same Dalton partial pressure of ammonia, which occurred at the end of seven or eight days. The entire apparatus was enclosed in an air thermostat at 31.85 ± 0.05°.

Results

The results with the hydrogen are given in Table II, π is the total pressure in meters and X_1 the mole fraction of ammonia. The last column gives the direction of approach of the equilibrium. The normal vapor pressure was read on the single tube closed end manometers against which the high pressure manometers were standardized.

TABLE II

π	X_1	πX_1	$\log \pi X_1$	From
2.840	1.00000	2.840	0.4533	Below
2.846	1.00000	2.846	.4542	Above
31.173	0.09912	2.976	.4736	Below
51.406	.06075	3.123	.4946	Below
70.860	.04548	3.223	.5082	Below
71.048	.04521	3.212	.5068	Above
93.935	.03571	3.364	.5269	Below
115.28	.03040	3.504	.5446	Below
115.42	.03050	3.520	.5466	Above
With Nitrogen				
43.074	.07931	3.416	.5335	Below
43.543	.08042	3.422	.5342	Above

If we plot $(\pi - p_0)$ against the log of the Dalton partial pressure as in Fig. 4, we obtain a straight line but of quite different slope from that of the Poynting equation.

It can be seen that in the presence of a partial pressure of 40 meters of nitrogen the Dalton partial pressure of ammonia is 573 mm. greater than the normal vapor pressure while with an equal pressure of hydrogen it is only 230 mm. greater. In terms of divergence from the Poynting pressure, the Dalton partial pressure in the nitrogen is 429 mm. higher and in hydrogen only 83 mm. higher.

The effect of temperature can be shown by comparing the value with nitrogen at 31.85° with the results of Lurie and Gillespie[5] at 45° with the same system. Extrapolation of their data reveals for 40 meters partial pressure of nitrogen, a Dalton partial pressure of ammonia 1,240 mm. higher than the 5,658 mm. Poynting pressure or a 21.9% divergence while from our

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(15) Beattie and Bridgeman, *Z. Physik*, **62**, 95 (1930).

data the divergence is 429/2987 or 14.3%. It is to be noted that the chief effect of the temperature increase is to increase the mole fraction of the ammonia because of the greater dissociation pressure.

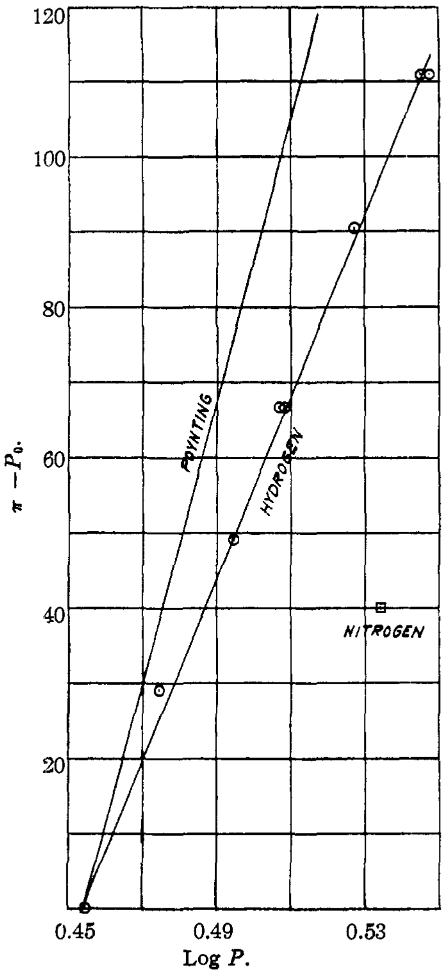

Fig. 4.

Poynting's equation can be directly derived from thermodynamics by equating at equilibrium the chemical potentials of the vapor and condensed phases. Alternatively we can write at constant temperature

$$V_1 d\pi = d(RT \ln a)$$

which gives upon integration, if the normal vapor pressure is taken as standard state

$$V_1(\pi - p_0) = RT \ln a = RT \ln fp/p_0$$

where f is the relative activity coefficient and can be calculated as a function of the partial pressure of the inert gas. It was in this manner that McHaffie[11] expressed his data. The results thus calculated with our system are given in Table III.

TABLE III

$(\pi - p_0)$	28.333	48.566	68.020	91.095	112.44
f	1.033	0.966	0.959	0.945	0.928

It can be seen from these figures that the Dalton partial pressure is 7% higher than the activity at the highest pressure.

Summary

The effect upon the dissociation pressure of barium chloride octammine of piston pressures up to 105 atm. has been determined and from the Poynting equation a partial molal volume of ammonia in the solid phases of 23.6 cc. was calculated.

The mole fraction of ammonia in equilibrium with the octammine at 31.85° and at various pressures of hydrogen up to 150 atm. has been determined by approaching the equilibrium from both sides.

At every pressure the mole fraction–total pressure product is greater than the pressure calculated from the Poynting equation on the assumption that the inert gas has only a pressure effect on the activities of the solids, and the divergence is greater the higher the pressure.

One determination with nitrogen at 56.5 atm. has been made and compared with Lurie and Gillespie's value at 45°, greater divergence between the Dalton partial pressure and the Poynting pressure being found at the higher temperature (and higher mole fraction of ammonia).

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