

The Dissociation Pressure of a Solid Under Inert Gas Pressure

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only in nature but presumably also in frequency.

Now in the mustard oils there appears to be a characteristic frequency around 1070 cm^{-1} , about half of the $\text{C}\equiv\text{N}$ frequency which in this case is approximately 2150 cm^{-1} . This appears as a strong Raman line in the ethyl and isobutyl compounds and as an intense infrared band in the methyl and ethyl derivatives. The Raman line was not reported for allyl mustard oil but the spectrum appears to have been very weak and incompletely developed. Unfortunately infrared data on this region are also lacking. The Raman

line was also apparently missing in phenyl and *p*-tolyl mustard oils but in the former a strong infrared band was found at about 1070 cm^{-1} and in the latter no data are available. In methyl and ethyl thiocyanate, which show no splitting of the $\text{C}\equiv\text{N}$ line, the 1070 cm^{-1} Raman line is missing.

It seems rather probable that this frequency which is characteristic of the mustard oils is to be attributed to a C-N vibration. Owing to the asymmetry of the $\text{C}-\text{N}\equiv\text{C}-\text{S}$ group it is permitted to appear in both infrared and Raman spectra.

The Dissociation Pressure of a Solid Under Inert Gas Pressure¹

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(Received November 30, 1936)

The mole fraction of ammonia in equilibrium with barium chloride octamine at 32°C and at various pressures of helium, argon and nitrogen has been determined. At every pressure, the mole fraction is greater than that expected by a simple application of the Poynting relation. An equation has been derived for the chemical potential of a component of a gaseous mixture in terms of the total pressure, the mole fraction, and the second virial

coefficients. This equation has been tested and shown to give fair agreement between calculated and observed values. One advantage is the fact that it can be used to calculate the mole fraction of the component of a gas mixture which arises from the dissociation of a solid with which the mixture is in equilibrium. It is also shown how these measurements might be used to calculate the second virial coefficients of gaseous mixtures.

INTRODUCTION

FOR the calculation of equilibria in systems containing one component in two phases, that is, in both the gaseous and solid states, it is necessary to know the vapor pressure of that component over the solid. The way in which the vapor pressure changes with the total pressure is also of great importance. It is well known that increasing the pressure on a solid increases its vapor pressure and that from thermodynamic formulae we may get a quantitative measure of this increase.

At constant temperature, the change of the Gibbs free energy of a system with a change in pressure is given by the relation

$$(\partial G/\partial P)_T = V. \quad (1)$$

¹ This article is based upon the dissertation submitted to the Faculty of Philosophy of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

When mixtures are to be discussed it is much more convenient to use the chemical potential or partial molal free energy as a measure of the state of any component. The chemical potential of the component *i* is defined as

$$\mu_i = (\partial F/\partial n_i)_{T, V, n_k} = (\partial G/\partial n_i)_{T, P, n_k} \quad (2)$$

and the change of μ_i with pressure is given by

$$(\partial \mu_i/\partial P)_T = \bar{v}_i, \quad (3)$$

where \bar{v}_i is the partial molal volume of the component *i*. The condition that the same substance be in equilibrium between two phases at the same temperature but at different pressures is

$$d\mu_i^1 = d\mu_i^2, \quad \text{or} \quad \bar{v}_i^1 dP^1 = \bar{v}_i^2 dP^2, \quad (4)$$

where superscripts refer to the phase and subscripts refer to the component. This relation was first derived by Poynting² for the case of a pure substance in two phases, in which case the

² Poynting, *Phil. Mag.* (5) **12**, 32 (1881).

chemical potentials become the molal free energies of each phase and the partial molal volumes are the molal volumes.

The effect of pressure on the vapor pressure of liquids has been studied by several investigators.³⁻⁶ In all cases the experimental increase in vapor pressure was greatly in excess of that calculated by a simple application of Poynting's equation in the integrated form, assuming that the volume of the liquid phase remains constant and using total volume in place of partial molal volume for the gas phase. For example, Bartlett⁴ found a fourfold increase above the calculated value for water compressed by nitrogen at 1000 atmospheres. Van Laar⁷ using Bartlett's data demonstrated that his complex equation of state for gas mixtures in equilibrium with a condensed phase was able to predict the effect of a compressed gas upon the vapor pressure of water.

TABLE I.

P	X_2	PX_2	$\log PX_2$
A. WITH HELIUM			
3.809	1.000	3.809	.58081
3.810	1.000	3.810	.58092
12.711	.3023	3.882	.58900
13.363	.2907	3.884	.58930
37.94	.1046	3.969	.59863
42.52	.0937	3.984	.60032
52.07	.0775	4.035	.60584
57.47	.0704	4.046	.60703
B. WITH ARGON			
12.807	.3165	4.053	.60778
34.12	.1250	4.265	.62992
41.26	.1086	4.481	.65137
54.17	.0840	4.550	.65801
54.77	.0832	4.558	.65877
C. WITH NITROGEN			
33.70	.1238	4.172	.62034
34.12	.1234	4.213	.62459
D. WITH HYDROGEN			
22.36	.1745	3.901	.5912

³ Larson and Black, *J. Am. Chem. Soc.* **47**, 1015 (1925).

⁴ Bartlett, *J. Am. Chem. Soc.* **49**, 65 (1927).

⁵ Pollitzer and Strebel, *Zeits. f. physik. Chemie* **110**, 768 (1924).

⁶ Saddington and Krase, *J. Am. Chem. Soc.* **56**, 353 (1934).

⁷ J. J. Van Laar, *Zeits. f. physik. Chemie* **A145**, 207 (1929).

Because of the complexity of the treatment necessary for the calculation of the vapor pressure of solutions, a much simpler case is that of a dissociating solid. McHaffie⁸ studied the system sodium sulfate-sodium sulfate decahydrate-water vapor under air pressure up to 100 atmospheres. He obtained negative as well as positive deviations from the calculated values. Braune and Strassman⁹ determined the vapor pressure of iodine in carbon dioxide with total pressures as high as fifty atmospheres. The system used in this investigation was barium chloride-barium chloride octamine-ammonia, which has been the subject of two previous studies.^{10, 11} Lurie and Gillespie,¹⁰ working at 45°C, used nitrogen as the compressing gas and covered the pressure range from the vapor pressure of the pure ammine to a total pressure of sixty atmospheres. Field¹¹ used both mechanical and inert gas pressure, hydrogen being the compressing gas in the majority of his

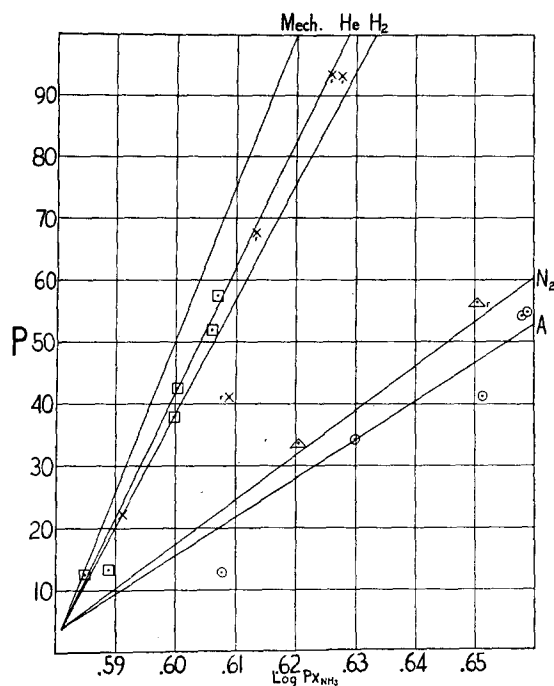


FIG. 1. Results with helium—□; results with argon—○; results with nitrogen—△; Field's nitrogen results—△_F; result with hydrogen—×; Field's hydrogen results—×_F.

⁸ McHaffie, *Phil. Mag.* (7) **1**, 561 (1926).

⁹ Braune and Strassman, *Zeits. f. physik. Chemie* **A143**, 225 (1929).

¹⁰ Lurie and Gillespie, *J. Am. Chem. Soc.* **49**, 1146 (1927).

¹¹ T. E. Field, *J. Am. Chem. Soc.* **56**, 2535 (1934).

measurements. He also made several measurements with nitrogen. Inasmuch as the magnitude of the discrepancy between the observed vapor pressures and those calculated by Ponyting's equation depends upon the nature of the compressing gas, it was thought that measurements using several other gases as the compressing agent might prove to be of interest. The two monatomic gases, helium and argon, were used with pressures ranging from the vapor pressure of the pure ammine up to a total pressure of 58 atmospheres.

EXPERIMENTAL

The anhydrous barium chloride was made by heating the C.P. dihydrate, crushing the resulting mass and reheating over a low gas flame. Ammonia was taken from a tank of the anhydrous liquid. The various compressing gases were used as obtained from commercial sources.

The method and apparatus is fully described by Field.¹¹ The only change made in the design of the apparatus was in the construction of the high pressure manometers. Instead of using a tube made from two capillaries of different bore, two small bulbs were blown near the top of the manometers. When carefully made, they withstood the highest pressure reached. Besides helium and argon, hydrogen and nitrogen were used in the preliminary experiments. The entire apparatus was enclosed in an air thermostat held at $32^\circ\text{C} \pm .05$.

RESULTS

The results are given in Table I, where P is the total pressure in atmospheres, X_2 is the mole fraction of ammonia and PX_2 is the Dalton partial pressure of ammonia.

These results are plotted in Fig. 1 along with those of Field for hydrogen and nitrogen. The curves drawn are those given by the method of least squares. The curve labeled mechanical is taken from Field's measurements with mechanical pressure.

DISCUSSION

The curves in Fig. 1 show that the Dalton partial pressure does not reproduce the true state of affairs in gas mixtures. This is to be expected

since Dalton's law applies only to perfect gases. The quantities to be compared are the chemical potential of ammonia in the gas mixture at a total pressure P and the chemical potential of pure ammonia at a pressure given by the ammine when under the mechanical pressure P . Before calculating the chemical potential of a component of a gas mixture, an expression for the free energy of that mixture must first be obtained. Statistical mechanics gives for the Helmholtz free energy,

$$F = \sum_i n_i F_i^0(T) + \sum_i n_i RT \log n_i/V - NRT \sum_{ik} \frac{B_{ik} n_i n_k}{\sigma_{ik} V}, \quad (5)$$

where n_i is the number of moles of component i , $F_i^0(T)$ is the part of the free energy of component i which depends only on the temperature and is the free energy of that component in the pure state at unit value of n/V . V is the volume, σ_{ik} is a symmetry number which is unity except when $i=k$, in which case it is equal to two, and B_{ik} is given by,

$$B_{ik} = \int_0^\infty (e^{-U_{ik}/kT} - 1) 4\pi r^2 dr. \quad (6)$$

This equation is taken from Guggenheim.¹² Here U_{ik} is the potential energy between the pair of molecules i and k as a function of r , the distance between them. A derivation and discussion for the case of a single gas is given in Slater and Frank.¹³ The calculation of the B_{ik} 's will be given later.

From Eq. (5) and the definition of the chemical potential as given in the introduction, we get,

$$\mu_i = F_i^0(T) + RT + RT \log n_i/V - NRT \sum_k B_{ik} n_k/V. \quad (7)$$

This can be written as

$$(\mu_i - \mu_i^0)/RT = \log n_i/V - N \sum_k B_{ik} n_k/V, \quad (8)$$

where $\mu_i^0 = F_i^0(T) + RT$, and is a function of the

¹² Guggenheim, *Modern Thermodynamics* (Methuen Co., London), pp. 73.

¹³ Slater and Frank, *Introduction to Theoretical Physics* (McGraw-Hill Book Co., N. Y.), pp. 462.

TABLE II.

GAS	b cc mole	a cc ² atmos. mole	E erg molecule	B_1 cc mole	B_2 cc mole	B_{12} cc mole
Argon	32.19	1.345×10^6	2.7014×10^{-14}	0.711×10^{-22}		1.915×10^{-22}
Helium	23.70	.0341	3.875	-0.737		-0.527
Nitrogen	39.13	1.390	2.7082	0.540		1.854
Hydrogen	26.61	.244	2.3074	-0.556		00.275
Ammonia	37.07	4.170	1.7946		4.272×10^{-22}	

temperature alone. This equation gives the chemical potential in terms of the concentration of the gases. However, in the experiments, the measured quantities were the total pressure and the mole fractions of the components, and therefore the chemical potential must be expressed in terms of those quantities. Using Eq. (5) again, we can get an expression relating total pressure and the composition, i.e.,

$$P = -(\partial F / \partial V)_{T, n} = \sum n_i RT / V - NRT \sum_{ik} \frac{B_{ik} n_i n_k}{\sigma_{ik} V^2}. \quad (9)$$

Since this is a two component system, there is also the condition

$$n_1 / V = (X_1 / X_2)(n_2 / V), \quad (10)$$

where subscript 1 refers to the inert gas and the subscript 2 to the ammonia. Combining (9) and (10) and solving for (n_2 / V) gives

$$n_2 / V = PX_2 / RT(1 + DPX_2^2 / (RT)^2 + \dots), \quad (11)$$

where

$$D = RT[(X_1 / X_2)^2 NB_1 / 2 + NB_2 / 2 + NB_{12}(X_1 / X_2)]. \quad (12)$$

Use of higher terms in the expansion would be unjustified since only the second virial coefficient was taken in (9).

Putting this value for n_2 / V into Eq. (8) we get

$$M = (u_2 - u_2^0) / RT = \log PX_2 / RT + P / RT[(NB_1 / 2 - NB_{12} + NB_2 / 2) \times (1 - X_2)^2 - NB_2 / 2]. \quad (13)$$

In order to use this relation it is necessary to get values for the B 's by evaluating the integral of

Eq. (6). To do this two assumptions have to be made: first, that the attractive part of U_{ik} is small compared to kT , and second, that the repulsive part varies so rapidly with r that it can be considered zero if r is greater than r_0 and infinite if r is less than r_0 . The integral then becomes

$$B_{ik} = -4\pi r_0^3 / 3 + 1/kT \int_{r_0}^{\infty} 4\pi r^2 U_{ik} dr, \quad (14)$$

the exponential being expanded in a power series and terms after the first dropped. London and Eisenschitz¹⁴ have shown that U_{ik} is approximately of the form

$$U_{ik} = 3/2(1/r^6)\alpha_i \alpha_k \Delta E_i \Delta E_k / (\Delta E_i + \Delta E_k), \quad (15)$$

where the α 's are the polarizabilities of the molecules i and k , and ΔE_i and ΔE_k are approximately their ionization potentials. Substituting into Eq. (14) and integrating gives

$$B_{ik} = -4\pi r_0^3 / 3 + 4\pi / 3kT A_{ik} / r_0^3, \quad (16)$$

where $A_{ik} = 3/2\alpha_i \alpha_k \Delta E_i \Delta E_k / (\Delta E_i + \Delta E_k)$. (17)

Returning now to Eq. (9) for the pressure of a gas mixture, we see that for a pure gas it can be put into the form

$$PV / RT = 1 - NB / 2V. \quad (18)$$

Comparing this with Eq. (16) we see that $NB/2$ can be written as

$$NB = -b + a / RT, \quad (19)$$

where $b = 2\pi N r_0^3 / 3$; $a = 2\pi N^2 A / 3r_0^3$. (20)

The two quantities a and b may be identified with the constants in van der Waals' equation of

¹⁴ London and Eisenschitz, Zeits. f. Physik **60**, 491 (1930).

state for gases. Thus we have a means of calculating the radii of the molecules of a gas and the forces between those molecules.

This result may be used in the following manner to calculate approximately the B for a pair of unlike molecules, assuming that for the distance between their centers at a collision we may take the sum of their individual radii. The individual radii are calculated from van der Waals' b constant. This result is then used with the a constant to get a value of A for the pure gas. These constants were taken from Landolt-Börnstein.¹⁵ In the case of a perfect gas Eq. (17) reduces to $A = 3/2\alpha^2\Delta E/2$. Values for the polarizability can be obtained from this by substituting in it the values of A just found and the values of ΔE from the dispersion formula of the gas. These values of the α 's and the ΔE 's can then be used in Eq. (17) to obtain the A 's between unlike molecules. From these values of the A_{ik} 's and the sum of the individual radii, we can calculate the B_{ik} 's using Eq. (16).

In Table II are tabulated the values of van der Waals' a and b used, the values of ΔE used, and the values of B_1 , B_2 and B_{12} calculated therefrom.

TABLE III.

P	M	$M - M_{\text{mech}}$	X_2 OBS.	X_2 CAL.
A. WITH HELIUM				
12.711	-8.8148	-0.0112	.3023	.3056
13.363	-8.8042	-0.0012	.2907	.2917
37.94	-8.7786	+0.0019	.1046	.1044
42.52	-8.7734	+0.0026	.0937	.0934
42.62	-8.7861	-0.0103	.0922	.0932
52.07	-8.7575	+0.0096	.0775	.0767
57.47	-8.7545	+0.0075	.0704	.0697
B. WITH ARGON				
12.81	-8.7880	+0.0155	.3165	.3115
34.12	-8.8190	-0.0352	.1250	.1295
41.26	-8.7974	-0.0203	.1086	.1109
54.17	-8.8310	-0.0658	.0840	.0897
54.77	-8.8322	-0.0676	.0832	.0890
C. WITH NITROGEN				
33.70	-8.8407	-0.0566	.1238	.1297
34.12	-8.8334	-0.0496	.1234	.1290
56.68	-8.8560	-0.0932	.0793	.0869
55.97	-8.8516	-0.0881	.0804	.0877

¹⁵ Landolt-Börnstein, *Tabellen*, HwI (Springer, Berlin), pp. 253.

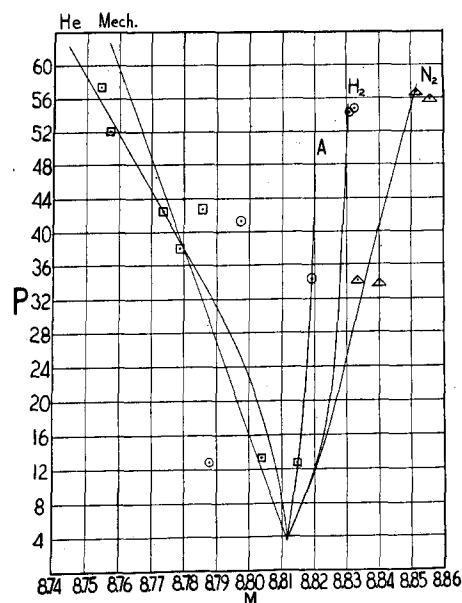


FIG. 2. Helium—□; argon—○; nitrogen—△.

From the experimental results and the values of the B 's given in Table II, the values of the function $M = (\mu_2 - \mu_2^0)/RT$ have been calculated. Eq. (13) has also been used to predict the mole fraction of ammonia in the gas mixture at a total pressure P , the M used being that of pure ammonia at a pressure of the ammine under mechanical pressure P . These values are given in Table III.

These values of M have been plotted in Fig. 2 along with the curve for the value of the function M at a mechanical pressure P . The curves given in Fig. 2 for the various gases were obtained by making calculations of M from points on the curves of Fig. 1.

The agreement between the mechanical pressure curve and the curve for helium is quite good, the deviation being about 0.1 percent. This would mean a discrepancy of about 1 percent in the dissociation pressure of the ammine under mechanical pressure. For the other three gases the deviations are large and from them one would get a dissociation pressure less than the normal vapor pressure of the ammine. The calculation of the mole fraction of ammonia present gives in general a larger value than that observed. The greatest deviation

TABLE IV.

MIXTURE	B_{12} THEO.	B_{12} OBS.
Argon Ammonia	1.915×10^{-22}	1.379×10^{-22}
Nitrogen Ammonia	1.854	1.076
Hydrogen Ammonia	0.275	-0.347

is with nitrogen at 56 atmospheres, where it is 9 percent.

The reverse calculation has been carried out. That is, the values for the constant B_{12} which would give agreement between the respective gas pressure and mechanical pressure curves were calculated. They are given in Table IV as B_{12} obs. If it is assumed that the values of A_{12} are correct and that the blame might be laid to the fact that one cannot add the individual radii of unlike molecules to get the collision diameter between them, one finds that a small increase in the collision diameter for unlike molecules will account for the discrepancy. For argon ammonia, the collision diameter must be increased by 4.3 percent. For nitrogen ammonia, the increase calculated is 0.198×10^{-8} cm, or 5.6 percent. The collision diameter for the calculation of B_{12} for hydrogen ammonia mixtures has to be altered the largest amount, an increase of 8.5 percent being necessary. The reason that such a small change in the collision diameter has such a large effect on the value of B_{12} is due to the fact that B_{12} is given by the difference of two terms, one of which is directly proportional to the cube of the collision diameter and the other inversely proportional to the cube of the diameter.

As a check on the results obtained here for nitrogen ammonia mixtures and on the application of the method of calculation, the experi-

TABLE V.

P	M	$M - M_{\text{mech}}$	X_2 OBS.	X_2 CAL.	%
7.123	-8.2415	0.0000	1.000	1.000	
10.133	-8.2514	-0.0125	.7040	.7062	+0.3
11.716	-8.2080	+0.0295	.6393	.6204	-2.9
13.272	-8.2103	+0.0258	.5655	.5734	-1.4
23.695	-8.1902	+0.0381	.3313	.3186	-3.8
32.818	-8.1740	+0.0470	.2478	.2360	-4.8
47.912	-8.1762	+0.0331	.1743	.1682	-3.5
60.864	-8.1244	+0.0747	.1484	.1372	-7.5

mental results of Lurie and Gillespie¹⁰ have been used in a similar calculation using the observed value of B_{12} . The results of these calculations are given in Table V, where P is the total experimental gas pressure at which Lurie and Gillespie measured the equilibrium mole fraction X_2 obs. M is the characteristic function of ammonia over the ammine under the experimental conditions, calculated from Lurie and Gillespie's mole fractions and using our B_{12} . $M - M_{\text{mech}}$ is the difference between the calculated characteristic function and that of pure ammonia over the ammine under the mechanical pressure P . Finally X_2 cal. (which should be identical with X_2 obs.) is the mole fraction of the ammonia one would expect with a total gas pressure P . The agreement between the calculated and the true values is quite good considering the approximations which have to be made.

Acknowledgment.—The author wishes to thank Professor J. C. W. Frazer for his continued advice and encouragement, also, Dr. J. H. Frazer and Dr. J. E. Mayer for their assistance with the theoretical problem. Special thanks are due to Dr. T. E. Field who kindly lent the pressure block around which the apparatus was built.