THE VAPOR PRESSURE CONSTANT OF AMMONIA, THE ENTROPY OF CRYSTALLINE AMMONIA, AND THE REACTION $N_2+3H_2 \rightleftarrows 2NH_3$

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Abstract

§**1.** It is shown by statistical quantum mechanics that the vapor pressure constant of an ammonia molecule whose principal moments of inertia are A, A, and C is

$$i = \log \frac{64\pi^5 m^{3/2} k^4 A C^{1/2}}{h^6} + \sum_r D_r \log \frac{G_r}{{}_r\omega_0}$$

at ordinary temperatures; where m is the mass, k is Boltzmann's constant, h is Planck's constant, and the D_r's are the gram molecular fractions of the two varieties; and where the G_r's and ${}_r\omega_0$'s are constants.

§**2.** The *rotational partition functions* of ammonia molecules of both varieties are evaluated, and G_1 and G_2 are found to be equal to 4/3.

§**3** and §**4.** The spherical oscillatory motion of ammonia molecules in crystal lattices is investigated by quantum mechanics, and ${}_1\omega_0$ and ${}_2\omega_0$ are shown to be equal to 4; if the spins of the hydrogen nuclei are taken into consideration but the spin of the nitrogen nucleus neglected, which is permissible.

§**5.** With the values $A=2.79\times10^{-40}$ and $B=5.47\times10^{-40}$ CGS units, we find that the vapor pressure constant of ammonia, for common logarithms and atmospheres, is -1.55. This agrees with the experimental result given by Eucken, -1.50 ± 0.04.

§**6** and §**7.** When the reaction $N_2+3H_2 \rightleftarrows 2NH_3$ proceeds to the left between the crystalline phases at the absolute zero, there is an increase in entropy of (9/4) R log 3 E.U.

§**8.** The value of the constant I' in the equation for the equilibrium constant in the above homogeneous gas reaction is found in accordance with the previous sections to be equal to -7.17; which agrees fairly well with Eucken's experimental value -7.04 ± 0.10.

Introduction

In recent papers which appeared elsewhere,[1,2,3,4] the author has studied the vapor pressures of hydrogen, of chlorine, and of hydrogen chloride. The work was an extension of that of R. H. Fowler,[5] who first investigated, theoretically, the vapor pressure of hydrogen made up of the two non-combining varieties para-hydrogen and ortho-hydrogen.

It may be shown by using the first and second laws of thermodynamics that the vapor pressure p of a substance is given by the expression

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[1] T. E. Sterne, Proc. Roy. Soc. **A130**, 367 (1931).

[2] T. E. Sterne, Proc. Roy. Soc. **A130**, 551 (1931).

[3] T. E. Sterne, Proc. Roy. Soc. **A131**, 339 (1931).

[4] T. E. Sterne, Proc. Roy. Soc. **A133**, 303 (1931).

[5] R. H. Fowler, Proc. Roy. Soc. **A118**, 52 (1928).

$$\log p = -\frac{\Lambda_0}{RT} + \frac{(C_p)_0}{R}\log T + \int_0^T \frac{dT'}{RT'^2}\int_0^{T'}[(C_p)_1 - (C_p)_{\text{sol}}]dT'' + i.$$

Here Λ_0 is the work which must be done to evaporate one gram molecule of the substance at the absolute zero; R is the gas constant; $(C_p)_0$ is the constant and $(C_p)_1$ is the variable part of the specific heat per gram molecule of the vapor at constant pressure; and $(C_p)_{\text{sol}}$ is the specific heat at constant pressure of the condensed phase. i is a constant called the vapor pressure constant of the substance, and since its value depends upon the choice which is made of $(C_p)_0$, the latter should be specified whenever one states the value of i. At ordinary temperatures, for monatomic gases, $(C_p)_0=5R/2$; for diatomic gases it is $7R/2$, and for non-linear polyatomic gases $(C_p)_0=4R$.

The theoretical values for the vapor pressure constants of monatomic vapors are also well understood (see, for instance, Fowler's *Statistical Mechanics*, Chap. VII) that nothing more will be said about them here. In an article which is expected to appear shortly in *The Reviews of Modern Physics* by Fowler and the author, it is shown that the vapor pressure constant at ordinary temperatures of any diatomic vapor at all should be given by the expression

$$i = \sum_r D_r i_r \tag{1}$$

where

$$i_r = \log\frac{(2\pi m_r)^{3/2}k^{7/2}8\pi^2 I_r}{h^5} + \log\frac{G_r}{{}_r\omega_0}\cdot$$

Here D_r is the gram molecular fraction of the molecules of the r'th species present; m_r is the mass of a molecule of the r'th species; k is Boltzmann's constant; h is Plank's constant; I_r is the moment of inertia of a molecule of the r'th species; G_r is the constant factor which appears before $8\pi^2 I_r kT/h^2$ in the rotational partition function for the r'th species; and ${}_r\omega_0$ is the number of linearly independent wave functions capable of representing a molecule of the r'th species when it is in its lowest quantum state in the crystalline phase at the absolute zero. This equation is quite general; it can be used to find the vapor pressure constant of a substance with a diatomic vapor even if the structural units in the crystalline phase are not the same molecules as those that exist in the gas, but are groups of molecules, or separate atoms, or even atomic ions and electrons. All that one needs to do is always to interpret ${}_r\omega_0$ as being equal to C^{1/P_r}, where C is the number of linearly independent wave functions which can represent the crystal of the r'th species, containing in all $2P_r$ atomic nuclei, at the absolute zero. It is shown in the article by Fowler and the author, referred to above, that there is in general a satisfactory agreement between the observed diatomic vapor pressure constants and those calculated by the use of Eq. (1).

It would be interesting to extend these methods, so as to apply them to polyatomic vapors. The simplest type of polyatomic molecule from the point of view of our methods of investigation would be the type for which the three moments of inertia A, B, and C about the principal axes were all equal; the next simpler type would be that for which two of these moments of inertia, A and B say, were equal with C differing from A and B. The vibration-rotation spectra of both ammonia[6,7] and methane have been rather completely analysed. Since methane molecules are of the former type, while ammonia molecules are of the latter type, it might be supposed that it would be simpler to commence the study of polyatomic vapors by considering methane. The non-combining groups of terms, however, are simpler in the case of ammonia than they are in the case of methane; for there are fewer possible nuclear and vibrational arrangements in the case of ammonia; and we shall therefore proceed in this paper to discuss ammonia first in some detail, in order to make it clear in just what fashion the vapor pressure constant arises in statistical mechanics, in the case of polyatomic vapors. We shall consider the vapor pressure of methane in a subsequent paper.

§1. THE VAPOR PRESSURE OF AMMONIA

The ammonia molecule NH_3 very probably consists of a regular pyramid with the nitrogen nucleus at the vertex. There are two varieties of ammonia molecules, which should retain their separate identity over fairly long periods at ordinary and low temperatures. The first variety is characterized by wave functions which are completely symmetrical $S(3)$ in the spins of the three hydrogen nuclei, so that the part of a wave function depending upon the spins of those nuclei does not change its sign when any two of them are interchanged. The second variety of ammonia molecules is characterised by wave functions partly symmetrical $S(2+1)$ and by wave functions partly antisymmetrical $A(2+1)$ in the spins of the hydrogen nuclei. Following Dennison,[8] we say that there are 4 spin wave functions for the first variety with the symmetry characters α, and 2 degenerate spin wave functions for the second variety with the symmetry character (γ, δ) each. At ordinary temperatures, or after cooling from ordinary temperatures, the two varieties of molecule should exist in equal numbers, so that $D_1 = D_2 = 1/2$.

We suppose that the reader is familiar with the methods of enumerating wave functions described in chapters II, IV, V, and XXI of Fowler's *Statistical Mechanics*, and in the author's papers.[1,3] Consider an assembly containing in all X_1 molecules of the first variety, and X_2 molecules of the second variety. Let there be numbers P_1 and P_2 of the two varieties in the crystalline phase, and N_1 and N_2 in the vapor phase. Let the crystalline partition function for normal modes of oscillation of the molecules as a whole in the crystal lattice be in the form $[\kappa(z)]^{P_1+P_2}$. Then the normal modes of oscillation contribute to the total number of linearly independent wave functions capable of representing the entire assembly a factor equal to the coefficient of z^Q in $[\kappa(z)]^{P_1+P_2}$, if the total energy of these modes is Q. Let a partition function for a molecule of the r'th variety for rotations or spherical oscillations in the

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[6] Barker, Phys. Rev. **33**, 684 (1929).

[7] Badger and Cartwright, Phys. Rev. **33**, 692 (1929).

[8] Dennison, Rev. of Mod. Phys. **3**, 280 (1931).

crystalline phase be $f_r(z)$. Then these motions, if their total energy is S, contribute to the total number of wave functions a factor equal to the coefficient of z^S in $f_1(z)^{P_1}f_2(z)^{P_2}(P_1+P_2)!/P_1!P_2!$. Thus the whole crystal, if its energy is U, contributes a factor equal to the coefficient of $x_1^{P_1}x_2^{P_2}z^U$ in

$$1/\{1-\kappa(z)[x_1f_1(z)+x_2f_2(z)]\}.$$

We may use the classical approximation, with sufficient accuracy, to the correct Einstein-Bose statistics for the vapor. The vapor, if its total energy is F, contributes to the total number of linearly independent wave functions capable of representing the entire assembly a factor equal to the coefficient of $x_1^{N_1}x_2^{N_2}z^F$ in

$$\exp\,[x_1F_1(z)+x_2F_2(z)]$$

where $F_1(z)$ and $F_2(z)$ are the partition functions for the two varieties of gas molecules. We have of course that $N_1+P_1=X_1$, and $N_2+P_2=X_2$. Accordingly the entire assembly, if its total energy is E, and if we allow all possible partitions of the molecules between the different phases, can be represented by a total number of linearly independent wave functions equal to the coefficient of $x_1^{X_1}x_2^{X_2}z^E$ in

$$\frac{e^{x_1F_1(z)+x_2F_2(z)}}{1-\kappa(z)[x_1f_1(z)+x_2f_2(z)]},$$

and hence this number is given by

$$W=\left(\frac{1}{2\pi i}\right)^3\int\!\!\int\!\!\int\frac{dx_1dx_2dze^{x_1F_1(z)+x_2F_2(z)}}{x_1^{X_1+1}x_2^{X_2+1}z^{E+1}\{1-\kappa(z)[x_1f_1(z)+x_2f_2(z)]\}}\cdot \tag{1.1}$$

We find by the usual methods that the mean values

$$\overline{N}_r=\xi_rF_r(\theta) \tag{1.2}$$

and

$$\overline{P}_r=\frac{\xi_rf_r(\theta)\kappa(\theta)}{1-\kappa(\theta)[\xi_1f_1(\theta)+\xi_2f_2(\theta)]}. \tag{1.3}$$

Here the parameters ξ_1, ξ_2, and θ $(=e^{-1/kT})$ corresponding to the thermodynamic partial potentials and to the temperature, respectively, are determined by the unique position of the saddle point of the integrand of W, given by the vanishing of its three partial differential coefficients. If $\overline{P}_1+\overline{P}_2$ is large, then we have very nearly

$$\kappa(\theta)[\xi_1f_1(\theta)+\xi_2f_2(\theta)]\sim 1.$$

If, further, nearly all of the molecules are in the crystal, then we have, very nearly,

$$\overline{P}_1:\overline{P}_2=D_1:D_2.$$

It follows from these equations that

$$\overline{N}_r=D_rF_r(\theta)/\kappa(\theta)f_r(\theta). \tag{1.4}$$

Making use of the relation $pV=\overline{N}kT$ where p is the pressure, it follows that the vapor pressure

$$p = \sum_{1,2} D_r p_r \tag{1.5}$$

where

$$p_r = F_r(\theta)kT/Vf_r(\theta)\kappa(\theta); \tag{1.6}$$

which is not the partial pressure of the r'th species, but is the vapor pressure of a crystal made up wholly of the r'th sort of molecule. We take as the zero of energy the state when all the molecules are in their lowest quantum states, in the lattice at the absolute zero and at zero pressure. We suppose the partition functions $f_r(\theta)$ to be of the form

$$f_r(\theta) = \sum_j {}_r\omega_j \theta^{{}_r\epsilon_j}$$

where ${}_r\omega_j$ is the number of linearly independent wave functions capable of representing the j'th eigenstate of a molecule of the r'th species in the crystal, and ${}_r\epsilon_j$ is the energy of the state. We denote by C_r the specific heat per gram molecule at constant pressure of a crystal made up wholly of the r'th sort of molecules. Then we may readily show[9] that

$$\int_0^T \frac{dT'}{RT'^2}\int_0^{T'} C_r dT'' = \log K(T)f_r(T) - \log {}_r\omega_0.$$

Here R is the gas constant per gram molecule. It follows from this last relation and (1.6) if we neglect all but the lowest vibrational levels of the gas molecules, that

$$\begin{aligned}\log p_r = {} & -\frac{\chi}{kT} + 4\log T - \int_0^T \frac{dT'}{RT'^2}\int_0^{T'} C_r dT'' \\ & + \log \frac{(2\pi m_r)^{3/2}k^4 16(2)^{1/2}\pi^{7/2}AC^{1/2}}{h^6} + \log \frac{G_r}{{}_r\omega_0}\end{aligned} \tag{1.7}$$

very nearly. Here G_r is a number which appears as a factor in front of $16(2)^{1/2}\pi^{7/2}AC^{1/2}(kT)^{3/2}/h^3$ in the rotational partition function for a gas molecule of the r'th sort, when nuclear spins are taken account of. We shall show how this form results for the rotational partition function, and how G_r may be found, in the next section. The quantity χ, which we have taken to be the same for all five sorts of molecules (the differences are trivial) is the work which must be done on a molecule in the crystal, in a state of zero energy defined above, in order to put it in a state of rest, in its lowest quantum state, at infinity.

We can show[9] that

$$\log p = \log (D_1p_1 + D_2p_2) = D_1 \log p_1 + D_2 \log p_2 \tag{1.8}$$

very nearly. Further, we can show by using the complete crystalline partition

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[9] Sterne, Proc. Roy. Soc. **131,** 348 (1931).

function that if C_{sol} is the specific heat at constant pressure of the mixed crystal made up of both varieties of ammonia, then

$$C_{\mathrm{sol}} = D_1C_1 + D_2C_2.$$

Hence, from Eqs. (1.7), (1.8), and (1.9), we obtain

$$\log p = -\frac{\chi}{kT} + 4\log T - \int_0^T \frac{dT'}{RT'^2}\int_0^{T'} C_{\mathrm{sol}}dT'' + i \tag{1.91}$$

where

$$i = \log\frac{64\pi^5 m^{3/2}k^4AC^{1/2}}{h^6} + \sum_{1,2} D_r \log\frac{G_r}{{}_r\omega_0}\cdot \tag{1.92}$$

The quantity i is just the vapor pressure constant of ammonia; when, as should be done at ordinary temperatures, the constant part of the specific heat at constant pressure of the vapor is assigned the value $4R$ per gram molecule. We have neglected the vibrational levels other than the lowest in the gas molecules, but by adding to the right-hand member of Eq. (8) a term

$$\int_0^T \frac{dT'}{RT'^2}\int_0^{T'} (C_p)_1 dT''$$

where $(C_p)_1$ is the "vibrational", or variable, part of the specific heat at constant pressure of the vapor we may take account of the vibrations; and no change need be made in the value of i.

§2. THE ROTATIONAL PARTITION FUNCTIONS OF FREE AMMONIA MOLECULES

Two of the moments of inertia of ammonia molecules, A and B, are equal; the third moment of inertia about the axis of figure, C, differs from these. The energy levels are given by[10]

$$W = \frac{h^2}{8\pi^2}\left[\frac{1}{A}j(j+1) + \left(\frac{1}{C} - \frac{1}{A}\right)K^2\right], \tag{2.0}$$

where j and K take on positive integral values. The weights of the levels appear to be given correctly by Villars.[11] For each value of j, K can take on the values $0, 1, 2, 3, \cdots, j$. When K is 0, there are $4(2j+1)$ linearly independent wave functions for ammonia molecules of the first variety; when K is divisible by 3 there are $8(2j+1)$ linearly independent wave functions for this variety; and for all other values of K the weights for the first variety of ammonia molecules are zero. For ammonia molecules of the second variety, there are $4(2j+1)$ linearly independent wave functions when K is neither 0 nor divisible by 3. For $K=0$, or a multiple of 3, the weights for ammonia molecules of the second variety are zero. We have of course only considered those complete

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[10] Dennison, reference 8.

[11] Villars, Phys. Rev. **38**, 1552 (1931); Table II.

wave functions which are antisymmetrical in the hydrogen nuclei, in accordance with the Pauli exclusion principle. Let us calculate the partition functions[12] given by the energy levels (2.0) when we use these statistical weights. Let us denote the rotational partition function for the first variety of ammonia molecule by R_1, and that for the second variety by R_2. Then we have by the definition of partition functions generally, the above rules for weights, and Eq. (2.0),

$$R_1 = 4\sum_{j=0}^{\infty}(2j+1)e^{-(\sigma/A)j(j+1)} + 8\sum_{n=1}^{\infty}e^{-\sigma(1/C-1/A)9n^2}\sum_{j=3n}^{\infty}(2j+1)e^{-(\sigma/A)j(j+1)} \tag{2.1}$$

and

$$R_2 = 4\sum_{n=0}^{\infty}e^{-\sigma(1/C-1/A)(1+3n)^2}\sum_{j=1+3n}^{\infty}(2j+1)e^{-(\sigma/A)j(j+1)} + 4\sum_{n=0}^{\infty}e^{-\sigma(1/C-1/A)(2+3n)^2}\sum_{j=2+3n}^{\infty}(2j+1)e^{-(\sigma/A)j(j+1)}, \tag{2.2}$$

where $\sigma = h^2/8\pi^2kT$. We wish to evaluate these sums for the case of ordinary and high temperatures, for which both σ/A and σ/C are small. C is of the same order of magnitude as A, but larger. To evaluate these sums approximately, and at the same time obtain some idea of the order of magnitude of the errors in the resulting approximate expressions, we proceed thus.

To evaluate the first sum, we make use of the following relations:

$$\sum_{l}^{\infty}(2j+1)e^{-(\sigma/A)j(j+1)} = \frac{A}{\sigma}e^{-(\sigma/A)l(l+1)} + O\left(\left(\frac{A}{\sigma}\right)^{1/2}\right) \quad \text{if } l < \left(\frac{A}{2\sigma}\right)^{1/2} - \tfrac{1}{2} \tag{2.3}$$

and

$$\sum_{l}^{\infty}(2j+1)e^{-(\sigma/A)j(j+1)} = \frac{A}{\sigma}e^{-(\sigma/A)l(l+1)} + O[(2l+1)e^{-(\sigma/A)l(l+1)}] \quad \text{if } l \geqq \left(\frac{A}{2\sigma}\right)^{1/2} - \tfrac{1}{2}. \tag{2.4}$$

To show this we have only to compare the series with the corresponding integral

$$\int_{l}^{\infty}(2j+1)e^{-(\sigma/A)j(j+1)}dj.$$

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[12] These partition functions seem to be calculated incorrectly by Villars, reference 11. The expressions (19) and (20) in his article, which differ from those derived here by the author, do not have the correct limiting forms at high temperatures. It is for this reason that the calculations in the text above are given in considerable detail.

It is easy to show, if necessary by breaking up the sum and the integral into two parts at the maximum of the integrand which is then monotonic in each part, that they differ at most by a term of the order of the largest term occurring in the series. We have, also,

$$\sum_1^\infty e^{-\sigma(1/C-1/A)9n^2-3n(3n+1)\sigma/A} = \tfrac{1}{3}\left(\frac{C}{\sigma}\right)^{1/2} e^{\sigma C/4A^2}\int_{3(\sigma/C)^{1/2}+(\sigma C)^{1/2}/2A}^{\infty} e^{-x^2}dx + O(1);$$

which is true since the series is one made up of decreasing positive terms; so that the integral differs at most from the series by the first term of the series which is of the order of unity. Hence

$$\sum_1^\infty e^{-\sigma(1/C-1/A)9n^2-3n(3n+1)\sigma/A}$$
$$= \tfrac{1}{3}\left(\frac{C}{\sigma}\right)^{1/2}\left[1+O\left(\frac{\sigma C}{A^2}\right)\right]\left[\tfrac{1}{2}\pi^{1/2}+O\left(\frac{\sigma}{C}\right)^{1/2}+O\left(\frac{\sigma C}{A^2}\right)^{1/2}\right]+O(1). \tag{2.5}$$

We have, too, that the series of increasing terms

$$\sum_1^{n_0} e^{-\sigma(1/C-1/A)9n^2} = O((AC/\sigma(C-A))^{1/2}) \tag{2.6}$$

where

$$n_0 \sim \tfrac{1}{3}(A/2\sigma)^{1/2}$$

and that the series

$$\sum_{n_0}^\infty e^{-\sigma(1/C-1/A)9n^2}(6n+1)e^{-(\sigma/A)3n(3n+1)} = O(C/\sigma). \tag{2.7}$$

Substituting Eqs. (2.3), (2.4), (2.5), (2.6), and (2.7) in Eq. (2.1) we find for R_1, if we remember that A and C are of the same order or magnitude,

$$R_1 = \frac{4}{3}(\pi)^{1/2}\frac{AC^{1/2}}{\sigma^{3/2}}\{1+0[(\sigma/A)^{1/2}] + \text{terms of higher order in } (\sigma/A)\}. \tag{2.8}$$

In similar fashion we can show that

$$R_2 = \frac{4}{3}(\pi)^{1/2}\frac{AC^{1/2}}{\sigma^{3/2}}\{1+0[(\sigma/A)^{1/2}] + \text{terms of higher order in } [\sigma/A)\}. \tag{2.9}$$

It is conceivable that methods similar to those used by Mulholland[13] and Sutherland[14] could be used instead of ours to derive these results, and to give in addition, exactly, the higher terms in the asymptotic expansions; but for the present we must be content with our results, which give what should be the correct limiting forms at high temperatures

$$R_1 \sim \frac{4}{3}\,\frac{16(2)^{1/2}\pi^{7/2}AC^{1/2}k^{3/2}T^{3/2}}{h^3} \tag{2.91}$$

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[13] Mulholland, Proc. Camb. Phil. Soc. **24**, 280 (1928).

[14] Sutherland, Proc. Camb. Phil. Soc. **26**, 402 (1930).

and

$$R_2 \sim \frac{4}{3}\,\frac{16(2)^{1/2}\pi^{7/2}AC^{1/2}k^{3/2}T^{3/2}}{h^3}. \qquad (2.92)$$

These limiting values are in precisely the same form as the rotational partition function given by Fowler[15] when $A=B$, except for the numerical factor 4/3 which was introduced by the symmetry properties of the wave functions. Fowler probably derived his expression from the older quantum mechanics; for the notion of a "symmetry factor" such as the σ which appears in Fowler's equation, a notion which was in use at the time when he wrote his book, has since been replaced by the notion of non-combining sets of terms obeying the Pauli exclusion principle.

From Eqs. (2.91) and (2.92) we see that G_1 and G_2 for ammonia are both 4/3; and further, since the ratio at ordinary or high temperatures between R_1 and R_2 is unity, we see that both sorts of ammonia molecules are present in equal numbers in ammonia gas which has rested for a long time at ordinary or high temperatures.

We must now determine the values of ${}_1\omega_0$ and ${}_2\omega_0$.

§3. The Spherical Oscillatory Motion of Ammonia Molecules in Crystalline Ammonia

If we make a calculation for crystalline ammonia similar to that made for the case of chlorine by the writer,[3] it appears that at the absolute zero ammonia molecules should "oscillate", rather than "rotate", about orientations of minimum potential energy in the crystal lattice. From the low temperature thermal measurements of Eucken and Karwat[16] the specific heat of the crystalline phase appears to be 5 calories per gram molecule at a temperature of about 76°K; from which one may deduce that $h\nu_0/k$ is equal to about 230°K; and if one takes the moment of inertia in this calculation to be equal to about 3×10^{-40} CGS units, one finds V_0 to be equal to approximately 3.7×10^{-14} ergs. Taking the combined heat of transition and fusion as 1426 calories per gram molecule, we find that V_0 is equal to about 20×10^{-14} ergs. In neither case should rotation occur until temperatures of the order of 500°K have been reached. The methods of considering the motion of the molecules of ammonia, used above, were developed by Pauling[17] and the author[2] to apply to diatomic molecules, but the considerations of later portions of this section will make it obvious that the same methods may be used to investigate roughly the behavior of polyatomic molecules as well. We may therefore study the spherical oscillatory motion of a molecule of ammonia in the crystal lattice, with a fair assurance that this is the type of motion approximated to by molecules of ammonia in the crystalline lattice at very low temperatures.

We may treat the problem by a perturbation method. We take the origin,

[15] Fowler, "Statistical Mechanics", p. 146, Eq. (442).

[16] Eucken and Karwat, Zeits. f. phys. Chem. **112,** 478 (1924).

[17] L. Pauling, Phys. Rev. **36,** 430 (1930).

0, at the mass center of the molecule; and fixed orthogonal axes OX, OY, OZ such that the orientation of minimum potential energy for the ammonia molecule corresponds to the presence of a nitrogen nucleus at the point $(0, 0, a)$; and of hydrogen nuclei at the points $(-2b(3)^{1/2}/3, 0, -c)$, $(b(3)^{1/2}/3, -b, -c)$, and $(b(3)^{1/2}/3, b, -c)$. We have of course that $3c=sa$, where s is the ratio of the mass of a nitrogen nucleus to that of a hydrogen nucleus (we neglect the trivial mass of the electrons). Let us investigate the forms of the potential and kinetic energies of the molecule, regarded as rigid, for small displacements of the molecule from this orientation of minimum potential energy. We may specify the displacement by the small rotations x, y, and z of the molecule about the axes OX, OY, and OZ respectively. Let the moments of inertia of the molecule about these axes, when it is in its orientation of minimum potential energy, be A, A, and C respectively; the moments of inertia about the axes OX and OY of course being equal. Then the kinetic energy of the motion relative to the center of mass will be, very nearly, for small displacements,

$$T = \frac{A}{2}(\dot{x}^2 + \dot{y}^2) + \frac{C}{2}\dot{z}^2,$$

or in terms of the angular momenta p_x, p_y, and p_z,

$$T = \frac{1}{2A}(p_x^2 + p_y^2) + \frac{1}{2C}p_z^2.$$

We may regard the potential energy V of the molecule, for small displacements from the orientation of minimum potential energy, to be capable of expression in the form $\mathbf{A}(q_1^2+q_2^2+q_3^2)+\mathbf{B}q_4^2$ plus higher powers in the q's. Here $\mathbf{A}$ and $\mathbf{B}$ are constants; and q_1, q_2, and q_3 are the distances of the three hydrogen nuclei, and q_4 the distance of the nitrogen nucleus, from the respective positions of the nuclei when the molecule is in its position of minimum potential energy. In terms of the small rotations, this expression becomes

$$V = \mathbf{A}[(2b^2 + 3c^2)(x^2 + y^2) + 4b^2z^2] + a^2\mathbf{B}(x^2 + y^2)$$
$$+ \text{ terms of higher order in the } x\text{'s, } y\text{'s, and } z\text{'s,}$$

so that the Hamiltonian

$$H = \frac{1}{2A}(p_x^2 + p_y^2) + \frac{1}{2C}p_z^2 + [\mathbf{A}(2b^2 + 3c^2) + \mathbf{B}a^2][x^2 + y^2]$$
$$+ 4\mathbf{A}b^2z^2 + \text{ terms of higher order in the } x\text{'s, } y\text{'s, and } z\text{'s.}$$

Consider now the plane passing through the vertex of the pyramidal molecule, parallel to the base, when the molecule is in its orientation of minimum potential energy. Take a set of axes $O'X'$, $O'Y'$ in this plane, with the origin at the vertex of the pyramid, and parallel to the axes OX, OY respectively. Denote the coordinates relative to these new axes of the projection P' upon the invariable plane of the vertex of the displaced pyramid by ξ and η;

so that $\xi = ay$ and $\eta = -ax$, very nearly. Imagine a lamina, of mass A/a^2, and whose center of mass is P', to move in the invariable plane; and let its moment of inertia about an axis through P' normal to the invariable plane be C. Let the angular displacement of this lamina from its orientation $\theta = O$ in the plane be denoted by θ, and let $\theta = z$. Then the position of the lamina is completely specified by the coordinates ξ, η, θ; and these coordinates also serve to specify the position of the molecule. And finally, if the lamina moves in a field of force of potential energy

$$V = \frac{A}{a^2}\left[(\eta^2 + \xi^2)(2b^2 + 3c^2) + 4a^2b^2\theta^2\right] + \boldsymbol{B}\left[\xi^2 + \eta^2\right]$$

then we may regard the exact motion of the molecule as being completely specified by the motion of the lamina, when the latter is suitably perturbed. The unperturbed motion of the lamina is given by the Hamiltonian

$$H' = \frac{a^2}{2A}(p_\xi{}^2 + p_\eta{}^2) + \frac{1}{2C}\left[\boldsymbol{B} + \frac{A}{a^2}(2b^2 + 3c^2)\right]\left[\xi^2 + \eta^2\right] + 4Ab^2\theta^2.$$

The perturbation terms, given by $H - H'$, are all small for small displacements of the molecule from its orientation of minimum potential energy.

Let us consider the unperturbed motion of the lamina. The Hamiltonian H' is separable in the coordinates ξ, η, and θ. The wave functions of the unperturbed system can therefore be expressed in the form

$$\Psi = \psi_{n_1}(\xi)\psi_{n_2}(\eta)\psi_{n_3}(\theta)$$

where the ψ's are the usual wave functions for the linear harmonic oscillator; and the energy levels of the unperturbed system are given by the expression

$$E = h\nu_0(n_1 + \tfrac{1}{2}) + h\nu_0(n_2 + \tfrac{1}{2}) + h\nu_3(n_3 + \tfrac{1}{2}), \tag{3.0}$$

where the n's may have any positive integral values, including zero. Here h is Planck's constant;

$$\nu_0 = (2\left[A(2b^2 + 3c^2) + \boldsymbol{B}a^2\right]/A)^{1/2}/2\pi,$$

and

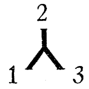
$$\nu_3 = b(8A/C)^{1/2}/2\pi.$$

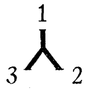
We thus see that the lowest energy level of the molecule, for spherical oscillations, is obtained by setting all of the n's in Eq. (3.0) equal to zero; and further that this energy level can be represented by only a single linearly independent wave function. When we take account of the perturbation terms in the Hamiltonian, the lowest energy level retains its nondegenerate character but is perhaps somewhat displaced. The higher levels corresponding to values of n_1 and n_2 greater than zero will be displaced also, but may in addition be separated; since they are degenerate. It is easy to see that these displacements and separations must be very small. For in the case of "oscillation" the wave functions will be trivially small except for values of ξ, η, and θ very nearly equal to zero; and for these small values of the variables the perturbation terms are very small. Accordingly the energy levels when the perturbation terms are taken account of are not appreciably different in this case of oscillation from the values given by Eq. (3.0), and we shall not undertake to give here an accurate analysis of the amounts of the changes in energy caused by the perturbation terms in the Hamiltonian.

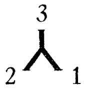
An inspection of the potential energy functions which we have used here, and a comparison of them with such expressions as $V_0\,(1-3\cos\theta)$ shows that the methods of Pauling and the author, employed in the beginning of this section to find out whether ammonia molecules were rotating or oscillating in the crystalline phase at very low temperatures, may be used for this purpose; although the methods were developed originally only so as to be applicable to the motions of diatomic molecules.

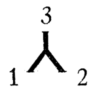
§4. THE VALUES OF $_1\omega_0$ AND OF $_2\omega_0$

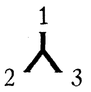
Since the spin of the nitrogen nucleus contributes the same factor to both numerator and denominator of $G_r/{}_r\omega_0$, we may neglect it in these calculations. Consider now the motion of the ammonia molecule when it is in the state of spherical oscillation for which n_1, n_2, and n_3 are all equal to zero, in which all the normal modes of nuclear oscillation are in their lowest quantum states, and in which the molecule is in its lowest electronic state. We must take account of the spins of the hydrogen nuclei. The wave functions in these spins alone are eight in number; there are 4 spin wave functions of symmetry character α and 2 wave functions of symmetry character (γ, δ) each. To find the number of wave functions for the spherical and nuclear oscillations with the various symmetry characters we may consider all of the different sorts of oscillations together. In the lowest state of oscillation there are then six linearly independent wave functions when symmetry properties are neglected altogether; we may denote these six linearly independent vibrational wave functions by the following six diagrams:

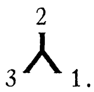












Here the numbers denote the hydrogen nuclei, and the lines indicate the directions in which the hydrogen nuclei must lie, in the base of the pyramidal molecule, if the molecule is to be in its position of minimum potential energy. Thus the upper left figure in the diagram denotes that wave function for which there is a considerable probability of finding the three atoms close to the positions indicated in the figure by the numbers, with but a very small probability of finding them in the positions indicated in the figure below it, for instance.

We have made the plausible assumption that there is only one position and not two positions for the nitrogen nucleus, when the molecule is in its orientation of minimum potential energy. When we take linear combinations of the above wave functions, we find that there are two wave functions with the symmetry character (γ, δ) each, one with the character α, and one with the character β (antisymmetrical in all three hydrogen nuclei). There are still six linearly independent wave functions, as there should be. If the molecule had been free to rotate instead of being in a field of force in a crystal, we should have found but two linearly independent wave functions instead of six, for the vibrations.

Taking account of both spins and vibrations, we wish to find the number of linearly independent complete wave functions, antisymmetrical in the hydrogen nuclei, and capable of representing the ammonia molecule in its lowest vibrational state in the crystal lattice. It follows from the above enumerations and the rules for combining the factors of the complete wave functions given by Dennison,[8] that there are eight of these linearly independent complete wave functions with the symmetry character β in the hydrogen nuclei; and of these 4 represent ammonia molecules of the first variety and 4 represent ammonia molecules of the second variety. We have thus found that ${}_1\omega_0 = {}_2\omega_0 = 4$.

§5. THE VAPOR PRESSURE CONSTANT OF AMMONIA

From §2 and §4 we find that the second term in the right hand member of Eq. (1.92) is equal to log 1/3. We can now calculate i', the vapor pressure constant when pressures are expressed in atmospheres and logarithms are taken to the base 10, by the use of Eq. (1.92). With sufficient accuracy, we take the molecular weight of ammonia to be 17. Following Giauque, Blue, and Overstreet[18] we take $A = B = 2.79 \times 10^{-40}$ CGS units, and $C = 5.47 \times 10^{-40}$ CGS units. We find that the vapor pressure constant of ammonia at ordinary temperatures should be

$$i' = -1.55.$$

This is in satisfactory agreement with the experimental result given by Eucken[19], $i' = -1.50 \pm .04$.

§6. THE ENTROPY OF CRYSTALLINE AMMONIA AT THE ABSOLUTE ZERO OF TEMPERATURE

Taking account of the nuclear spin ($h/2\pi$) of nitrogen, the number of linearly independent wave functions which can represent a gram molecule of crystalline ammonia at the absolute zero[20] if the molecules oscillate in the crystalline phase is

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[18] Giauque, Blue, and Overstreet, Phys. Rev. **38**, 196 (1931), who take these values from the work of Badger and Cartwright, Phys. Rev. **33**, 692 (1929), and from the Raman spectral study of Dickinson, Dillon, and Rosetti, Phys. Rev. **34**, 582 (1929).

[19] Eucken, Phys. Zeits. **31**, 361 (1930).

[20] To understand the sense in which the writer uses the expression "entropy at the absolute zero" the reader is referred to the footnote in the author's paper on the vapor pressure constant

$$C = 12^{N/2}12^{N/2}N!/(N/2)!(N/2)!$$

and thus the entropy of a gram molecule of crystalline ammonia at the absolute zero, if we use Stirling's asymptotic expression for factorials and neglect trivial terms, is by the principles of statistical mechanics

$$S_0 = k \log C = R \log 24;$$

where N is the number of molecules in a gram molecule, and where R is the gas constant.

§7. THE CHANGE OF ENTROPY ACCOMPANYING THE REACTION $N_2+3H_2 \rightleftarrows 2NH_3$ BETWEEN THE CRYSTALLINE PHASES AT THE ABSOLUTE ZERO

The entropy of a gram molecule of crystalline ammonia at the absolute zero has just been calculated; the entropy of a gram molecule of hydrogen[1] is $R \log 4 + \frac{3}{4}R \log 3$, and the entropy of a gram molecule of nitrogen calculated in the same fashion is $2R \log 3$. Accordingly, when a gram molecule of nitrogen in the crystalline phase at the absolute zero reacts with three gram molecules of hydrogen at the absolute zero in the crystalline phase and yields two gram molecules of ammonia in the crystalline phase at the absolute zero, the decrease in entropy is $(9/4)\, R \log 3$.

§8. THE CONSTANT IN THE EQUATION FOR THE EQUILIBRIUM CONSTANT

If K_p is the equilibrium constant in a homogeneous gas reaction, then[21]

$$\log K_p = \log \{\textstyle\prod_t p_t^{q_t}\} = -\frac{(Q_p)_0}{RT} + \frac{1}{R} \sum_t q_t (C_p^t)_0 \log T + \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} \sum_t q_t (C_p^t)_1 dT'' + I.$$

In this equation q_t is the number of gram molecules of the t'th species reacting, with a negative sign for those that disappear when the reaction takes place, and p_t is the partial pressure of the t'th species. $(Q_p)_0$ is the work which must be done to make the reaction go in this sense at constant pressure at the absolute zero, and $(C_p^t)_0$ and $(C_p^t)_1$ are the constant and variable parts of the specific heat at constant pressure of the t'th species. I is a constant of integration which is not to be confused in this section with the use of I, in previous sections, to denote moments of inertia. Then it is shown in the article which should appear shortly in the *Reviews of Modern Physics* by Fowler and the author that

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of chlorine, reference 3, on page 352 of that paper; to §4 in the author's paper on the vapors of hydrogen and hydrogen chloride, reference 4; and to the article which should appear shortly in the Reviews of Modern Physics by R. H. Fowler and the author.

[21] R. H. Fowler, "Statistical Mechanics", §7.2.

$$I' = \sum_t q_t i_t' + \frac{1}{R \log 10} \Delta S_0$$

if atmospheres and common logarithms are used; where ΔS_0 is the change in entropy when the reaction proceeds forwards at the absolute zero between the crystalline phases, and where the i''s are the chemical constants which we have investigated in this and other papers.

We have shown that for the reaction $N_2+3H_2-2NH_3$, ΔS_0 is equal to 9/4 R log 3; and the theoretical i''s are for ammonia -1.55; for nitrogen (this will be shown in the article by Fowler and the author referred to above) -0.18; and for hydrogen[1] -3.72. Accordingly we should have for this reaction

$$I' = -7.17.$$

The value given by Eucken,[22] found experimentally, is $I' = -7.04 \pm .10$; which is in fairly satisfactory agreement with our predicted result.

The author wishes to express his appreciation for the interest taken in his work by Professors E. C. Kemble and J. C. Slater. He also wishes to thank the National Research Council for a grant which enabled these investigations to be carried out.

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[22] Eucken, Phys. Zeits. **30**, 818 (1929).