

parison with the electron for which such effects according to Mott and Sauter do not appear until the second Born approximation. However, a certain similarity which the Dirac-Proca equations bear to the Maxwell equations and the vectorial character of the wave functions (as compared to the spinor character for $s = \frac{1}{2}$) may render our result more plausible.

The effect is of the fourth order in v/c for

$$k^4/K^2e^2 = \beta^4/(1 - \beta^2)$$

and is most pronounced at right angles to the direction of the incident particles.

The evaluation of the second approximation (34) and a closer discussion of the matrix element $(\mathbf{k} | V | \mathbf{k}_0)$ will be given in a later paper.

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The Vapor Pressure of Isotopes

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It is shown here that if all degrees of freedom in a vapor are nearly classical and if there is no association, the vapor pressure of the lighter isotope is always higher. If only the external degrees of freedom are nearly classical and the internal ones are in the lowest state, the coupling of purely harmonic vibrations has either no influence or tends probably to a further increase of the excess vapor pressure of the light isotope. Anharmonicity and the change in the van der Waals forces probably account for those cases in which the heavier isotope has the higher vapor pressure.

I. INTRODUCTION

THE difference in the physical and chemical equilibrium conditions for isotopes is a pure quantum phenomenon.¹ Classical theory would give no effects of the difference in mass. This latter only affects the statistical distribution of momenta.² In classical theory, however, the integration over the momenta is independent of the integration over the coordinates and influences the different states (e.g., vapor and liquid) in the same manner. Therefore it does not modify the equilibrium between two states. This suggests a systematic investigation of the isotope effect in different temperature regions.

II. LOW TEMPERATURES

At low temperatures the differences are most conspicuous. The adequate method which is in

¹ We exclude cases in which gravity or centrifugal forces are of importance.

² The very small differences in potential energies for different isotopes shall be neglected except at the end of the paper.

general use starts from the condition at absolute zero. The greatest effect in this region is due to the difference in zero point energy of the motion of the molecule as a whole in the field of its neighbors. Since the operator of the kinetic energy is positive definite the lowest quantum level of the lighter isotope will always be higher than that of the heavier isotope. As a consequence the lighter molecule will have a smaller heat of evaporation and therefore a greater vapor pressure.³ The difference of entropy of translation and possibly rotation in the vapor state works in the opposite direction but has less importance in the low temperature region. All this has frequently been the subject of discussions.

III. HIGH TEMPERATURES

As mentioned before, there are no differences between isotopes at temperatures so high that

³ A possible exception might occur if one has association in the vapor phase connected with a very high intermolecular vibrational frequency.

classical treatment is justified. At temperatures not quite as high, the differences are due to small deviations from classical theory. It seems therefore to us that an expansion in powers of \hbar (i.e., Planck's constant divided by 2π) in which the first term is given by classical theory is more appropriate than the method usually applied, which starts from considerations of the behavior near absolute zero. In fact if the latter method is applied the small differences in vapor pressure at high temperature result from cancelation of much bigger terms.

Expansions of the partition function in terms of \hbar have been developed by Bloch⁴ and by Wigner.⁵ According to Wigner the first quantum correction is proportional to \hbar^2 , the coefficient of \hbar being zero.⁶ In classical theory the partition function is given by

$$Z_{cl} = \int d\Omega \exp(-\epsilon/kT), \quad (1)$$

where $d\Omega$ signifies the volume element of the complete phase space and the energy ϵ is expressed in the form

$$\epsilon = \frac{1}{2} \sum_i p_i^2/m_i + V(x). \quad (2)$$

Here the p_i are the momenta, m_i the masses and V the potential energy, depending on all the coordinates x but not the momenta p or masses m . According to Wigner, $\exp(-\epsilon/kT)$ has to be replaced in first approximation of the quantum correction by

$$\exp(-\epsilon/kT) \left\{ 1 + \frac{\hbar^2}{8(kT)^2} g_2 \right\}, \quad (3)$$

where

$$g_2 = \sum_i \frac{1}{m_i} \left[-\frac{\partial^2 V}{\partial x_i^2} + \frac{1}{3kT} \left(\frac{\partial V}{\partial x_i} \right)^2 \right] + \sum_i \sum_j \frac{1}{3kT} \frac{p_i p_j}{m_i m_j} \frac{\partial^2 V}{\partial x_i \partial x_j}. \quad (4)$$

⁴ F. Bloch, *Zeits. f. Physik* **74**, 295 (1932).

⁵ E. Wigner, *Phys. Rev.* **40**, 749 (1932). J. G. Kirkwood, *Phys. Rev.* **44**, 31 (1933).

⁶ For the special case of the harmonic oscillator, this is a well-known fact.

Therefore

$$Z = Z_{cl} + \frac{1}{8} \left(\frac{\hbar}{kT} \right)^2 \int dx \exp \left(-\frac{V}{kT} \right) \times \int dp g_2 \exp \left(-\frac{1}{kT} \sum \frac{p^2}{2m} \right), \quad (5)$$

where dx, dp stand for the products of all dx_i, dp_i . It must be emphasized that in Wigner's method, the integrations over the p 's and x 's can be performed independently of each other, in spite of the fact that p and x cannot have definite values simultaneously in quantum theory.

We write

$$Z_{cl} = Z_{cl}' Z_{cl}''$$

where Z_{cl}' is the contribution from the kinetic, Z_{cl}'' that from the potential terms. Integrating over the momenta and performing a partial integration over the first terms of g_2 , we get from (5)

$$Z = Z_{cl}' \left\{ Z_{cl}'' - \frac{1}{24} \left(\frac{\hbar}{kT} \right)^2 \times \left[\frac{1}{kT} \int dx \left(\exp -\frac{V}{kT} \right) \sum_i \frac{1}{m_i} \left(\frac{\partial V}{\partial x_i} \right)^2 + \text{surface terms} \right] \right\}. \quad (6)$$

The surface terms, resulting from the partial integration may be omitted, if we consider closed systems for which V becomes infinite at the boundary.

Therefore the partition function can be written

$$Z = Z_{cl}' \left\{ 1 - \frac{\hbar^2}{24(kT)^3} \left\langle \sum_i \frac{1}{m_i} \left(\frac{\partial V}{\partial x_i} \right)^2 \right\rangle_{av} \right\}, \quad (7)$$

where $\sum_i (1/m_i) (\partial V/\partial x_i)^2$ has to be averaged over the classical probability distribution in configuration space.

Part of the integration we have carried out has also been discussed by Kirkwood.⁵ In comparing our expression with his formula (21) we can neglect his second term since it vanishes at high temperatures in an exponential manner.

The factor T^{-3} in the correction term of (7) represents the actual temperature dependence only if

$$\left\langle \sum_i \frac{1}{m_i} \left(\frac{\partial V}{\partial x_i} \right)^2 \right\rangle_{Av}$$

is independent of the temperature. That is not the case if the atoms remain in the neighborhood of equilibrium positions, since under those conditions $(\partial V/\partial x)^2$ increases with T . With the help of a partial integration one can transform (7) into

$$Z = Z_{cl} \left\{ 1 - \frac{\hbar^2}{24(kT)^2} \left\langle \sum_i \frac{1}{m_i} \frac{\partial^2 V}{\partial x_i^2} \right\rangle_{Av} \right\}. \quad (7')$$

This formula applied to the harmonic oscillator yields the well-known result

$$Z = Z_{cl} \left\{ 1 - \frac{1}{24} \left(\frac{\hbar\omega}{kT} \right)^2 \right\}. \quad (7'')$$

It can be seen from (7), that the quantum correction always diminishes the partition function and its absolute value increases with the mean square value of the forces and diminishing mass of the particles concerned. Thus, if we compare the liquid and vapor state, the quantum correction will be in general greater for the liquid on account of the stronger forces and the difference between gas and liquid is greater for the lighter isotope. Therefore the lighter isotope will have the higher vapor pressure. This has of course been known under the assumption of quasi-elastic forces, but has now been proved to be generally valid. It follows from our formulae that for rare gases the vapor pressure of the light isotope will be higher at sufficiently high temperatures. For molecules the equations deduced now can be applied only if all degrees of freedom behave classically. In such cases however the problem of comparing vapor pressures is frequently complicated by the fact that dissociation takes place. It is interesting to note that under the conditions which we are here discussing the dissociation into atoms will be always stronger for the lighter isotope. If one considers, therefore, the total vapor pressure of a molecule, dissociation into atoms can only cause a further relative increase of the vapor pressure of the lighter

isotope. About the dissociation into radicals no general statements can be made.

IV. INTERMEDIATE TEMPERATURES

In most liquids made up of molecules, the external degrees of freedom (i.e., the motion of a molecule as a whole in the field of its neighbors) behave in an almost classical way at temperatures where the internal degrees of freedom are still in the lowest state. Then considerations similar to those of the preceding section show that the influence of the external degrees of freedom will again be so as to increase the vapor pressure of the light isotope more than that of the heavy one above the classical value.

Nevertheless, a higher vapor pressure has been observed in many cases for the heavier isotope, e.g.,⁷ in C_6D_6 compared to C_6H_6 . This must be due to the influence of the internal vibrations, overcompensating the effect of the external degrees of freedom. Two ways have been proposed to explain this influence. The first explanation proceeds in the following manner.⁸ It is well known that the frequencies of the internal vibrations are somewhat different in the gaseous and the liquid state. This difference will cause a difference in the heat of evaporation of the two isotopes. If, as is frequently observed in infra-red and Raman spectra, the frequency is lower in the liquid, the result would be a higher heat of evaporation and a lower vapor pressure of the lighter isotope. The second explanation⁹ makes use of the different value of the van der Waals forces for the isotopes, which has its origin in the small difference of the polarizabilities and molecular volumes of the isotopes, which have been found experimentally.

With regard to the first explanation, one must keep in mind that the optically determined frequencies cannot be used directly to calculate average heats of evaporation. For the sake of simplicity we shall replace the liquid by a crystal.

⁷ C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.* 915 (1936).

⁸ The effect in question has been pointed out by B. Topley and H. Eyring, *J. Chem. Phys.* 2, 217 (1934). It has been used as an explanation by F. G. Brickwedde, Symposium on Recent Adv. in Physical Chemistry, A. A. S., Indianapolis, 1937.

⁹ C. R. Bailey and B. Topley, *J. Chem. Soc.* 921 (1936).

For a fundamental frequency to be observed in the infra-red or Raman spectrum, neighboring molecules must vibrate practically in the same phase. This however is only one vibration among many others which have arbitrary values of the phase differences. These vibrations will have different frequencies; the optically observed frequency is probably either at the upper or the lower end of the frequency band. Thus the mean value of the frequencies in the condensed state which is the one to be used to determine effective zero-point energies, may differ considerably from the observed infra-red or Raman frequency.

In order to evaluate therefore the change of zero-point energy of the internal vibrations, it is necessary to consider theoretically the effect of the coupling of neighboring molecules. We shall discuss here only the sign of the change to be expected. It shall be assumed that all forces including those arising from neighboring molecules are harmonic. In view of the small changes expected we will be justified in applying perturbation theory and restricting ourselves to perturbations of the first order. In doing so, it will be sufficient to consider diagonal terms in the secular determinant, that is to consider the effect on the normal vibrations of one molecule, when it moves in the field of the neighboring molecules which are considered at rest.¹⁰ Now the forces in the condensed state tend to hold the molecules in equilibrium configurations and therefore it is probable that the perturbing potential exerted on an atom by a neighboring molecule will have positive second derivatives. It is therefore to be expected that the mean value of the frequencies, and therefore the

effective zero-point energy, will be higher in the condensed state and give rise to an additional excess of the vapor pressure of the light isotope. This last statement however is not to be considered as proved rigorously. It should be mentioned in particular, that according to Bauer and Magat¹¹ the anharmonicity of the internal vibrations and long range interactions (Coulomb forces) between atoms of different molecules may combine to cause an effective lowering of frequencies in the condensed state.

The second proposed explanation we have mentioned, i.e., the change of the van der Waals forces, seems to us to be the probable reason for the higher vapor pressure of the heavier isotope, whenever such an effect is observed for non-associated vapors. It can be seen from Bailey and Topley's paper⁹ that the change in dispersion forces for benzene as calculated from the measured mole fractions and mole volumes would give rise to a greater difference in vapor pressure than has been observed. It is probable that the correct value would be obtained if the other phenomena discussed above could be taken into account and subtracted from the effect of the van der Waals forces.

The general explanation of the difference in van der Waals forces can be given by considering the difference of polarizabilities and dipole moments which are obtained by averaging over the zero-point vibrations of the internal degrees of freedom. As long as the vibration is strictly harmonic and the dipole moment and polarizability are strictly linear functions of all atomic displacements, the same mean values will be found for the two isotopes. However as soon as mechanical or electrical anharmonicities appear, a difference of the mean values and consequently of the van der Waals forces will be obtained, the sign of which depends on the specific properties of the molecules concerned.

¹⁰ If we want to calculate the first-order perturbation for each mode of crystal vibration, those nondiagonal terms should also be considered, for which row and column belong to the same value of the unperturbed frequency. If however only mean values are wanted, one has to be concerned only with the *sum* of diagonal terms. Thus the Lorentz-Lorenz force will cause the splitting of an internal vibration into a band without affecting the mean value in the first order (see R. H. Lyddane and K. F. Herzfeld, Phys. Rev. **54**, 846 (1938)).

¹¹E. Bauer and M. Magat, J. de Phys. **9**, 319 (1938).