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Vapor Pressures of Isotopic Molecules*

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The question of the differences in vapor pressures of isotopic molecules is, in fact, the oldest experimental and theoretical problem in the chemistry of isotopes. It was recognized from the outset by Lindemann and then Stern that the difference in vapor pressure was a result of the difference in heats of vaporization which resulted from the quantum mechanical zero point energy. Although a significant body of experimental data has accumulated since the discovery of the difference in vapor pressures of the neon isotopes by Keesom and van Dijk, no quantitative correlations between theoretical calculations and experimental data were made up until the time of the International Conference in Amsterdam in 1957. Marked progress has taken place in the last five years, both with respect to refinement of experiment and the development of theory.

The major theoretical advance has been the development of a theory which explicitly takes into account the role of molecular structure. The theory leads to particularly simple results for small quantum effects, i.e. $\epsilon/kT < 2\pi$, or for small changes in large quantum effects. Under these conditions, the vapor pressure

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depends upon the mass of the atom which is isotopically substituted and the potential field in which the atom finds itself. If, on the other hand, some of the motions have large quantum effects and others small quantum effects, then the mass dependence is also a function of the masses of the other atoms in the molecule. In the latter case, the temperature dependence is also complex and one frequently encounters the cross over phenomenon. The theory shows that the molal volume is a second order effect, but that gas imperfection plays a significant role particularly with respect to deviations from Raoult's Law.

After a discussion of the general theory, a number of specific different types of structural effects will be considered and compared with experimental results. First there is the effect of nearest neighbor number, which is conveniently studied by comparison of the vapor pressure ratio $\text{Ne}^{20}/\text{Ne}^{22}$ in the solid and liquid at the triple point. We next consider the case of coupling of molecular translation with other types of motion, which in part explains the difference in vapor pressures of HT and D_2 . The role of molecular rotation, per se, is rather uniquely studied in the series of isotopic molecules $^{14}_{\text{N}}\text{N}^{16}_{\text{O}}$, $^{14}_{\text{N}}\text{N}^{15}_{\text{N}}\text{O}$, $^{15}_{\text{N}}\text{N}^{16}_{\text{O}}$, $^{14}_{\text{N}}\text{N}^{14}_{\text{N}}\text{O}$. Specific chemical interaction, such as the formation of dimers, leads to large vapor pressure differences. These are readily accounted for by the theory and detailed calculations for the isotopic NO molecules show quantitative agreement with experiment. An introduction will be given to the theory of quantum effects of higher order.

INTRODUCTION

A discussion of the state of our knowledge of the vapor pressures of isotopic molecules is a particularly appropriate topic to open this meeting on the physical chemistry of isotopes. Historically, this is the first difference in physical or chemical property that was studied.⁽¹⁾ Although the process may appear to be a simple one, experiment has shown it to be one of the most complex of all the properties for which isotope effects have been investigated. There are a large number of small effects, which add up to the final difference in vapor pressure. Many of these effects have opposing signs and the final difference in vapor pressure may be a small fraction of that of one of the contributing factors. Yet when a full explanation is achieved, and this has now been carried through for a number of significantly different types of systems, we obtain information which will enrich our understanding of isotope effects in chemical exchange equilibria, ion exchange, chromatography, thermal diffusion, chemical kinetics, ion diffusion, etc. In fact it covers almost the entire spectrum of subjects under discussion at the present symposium. Further, the study of isotope effects on vapor pressure has enlarged our understanding of the theory of the interaction of molecular systems and the associated quantum effects. We may expect more information from future studies.

A ZERO POINT ENERGY EFFECT

It was recognized from the outset by Lindemann⁽¹⁾ (the late Lord (Herwell)) that a difference in vapor pressure of isotopic molecules was to be associated with the zero point vibrational energy. Consider

a molecule bound in a liquid or solid by a potential of the form given in Fig. 1. At the absolute zero the molecules are in the ground states, which differ for the light and heavy molecules. The heats of vaporization will differ by the zero point energy difference, $\delta \epsilon_0$. This simple consideration leads one to expect a difference in vapor pressures of the form

$$\ln P'/P = \delta_{AH}/RT \quad (1)$$

In actuality no systems can be described by this elementary approach. If we commence the study of isotope effects on vapor pressure by considering systems in order of their normal boiling points, we must immediately take cognizance of whether the system obeys Fermi-Dirac or Bose-Einstein statistics. This has been found to have a profound effect on the properties of ^3He and ^4He . The study of these two interesting substances is a unique and fascinating one in itself. The considerations involved will not be generally applicable to other systems, for which quantized Boltzmann statistics will suffice. We shall, therefore, omit further consideration of the ^3He - ^4He problem and refer the reader to the large literature on this subject. (2)

For the case of systems obeying Boltzmann statistics, equation (1) fails for two reasons: (1) at any temperature at which the system has a measurable vapor pressure it is essential to consider the excited states; in fact it is just from these states that the vaporization takes place; (2) it is necessary to consider not only the intermolecular potential, but all forces acting on the individual atoms in the molecule in the condensed and gaseous states.

We shall consider first the effect of the higher excited states

for atomic systems. We assume that the Born-Oppenheimer approximation is a good description of the electronic energy states of this system. In this approximation the potential energy of the system is independent of the nuclear mass. For such a system, Lindemann showed that a solid, with a harmonic Debye lattice frequency distribution, in equilibrium with an ideal gas leads to a $1/T^2$ dependence to the vapor pressure ratio. The result found was

$$\ln P'/P = \frac{3}{40 T^2} (\Theta'^2 - \Theta^2) + \dots \quad (2)$$

where Θ' and Θ are the Debye characteristic temperatures for the light and heavy atoms which have vapor pressures P' and P respectively. Some twenty years later Herzfeld and Teller⁽³⁾ showed that the same type of temperature dependence could be obtained for any arbitrary frequency distribution through the use of Wigner's formulation of the quantum mechanical partition function in terms of the classical distribution in configuration space. One obtains quantum corrections ordered in powers of $(\hbar/kT)^{2n}$. More recently Mayer and Band⁽⁴⁾ have given a reformulation of Wigner's theorem which permits its extension to systems of many particles with significant quantum effects. One obtains to order $n=1$

$$\ln Q_{q.m.} = \ln Q_{cl} - \frac{1}{24} (\hbar/kT)^2 \sum_i^{3N} \left\langle \frac{1}{m_i} \frac{\partial^2 V}{\partial x_i^2} \right\rangle \quad (3)$$

where $Q_{q.m.}$ and Q_{cl} are respectively the quantum mechanical and classical partition functions. From eq. (3) it follows for a liquid or solid in equilibrium with an ideal monatomic gas

$$\ln P'/P = \frac{1}{24} (\hbar/kT)^2 \left(\frac{1}{m'} - \frac{1}{m} \right) \left\langle \frac{\partial^2 V}{\partial x^2} \right\rangle \quad (4)$$

Quite analogous to this development is the de Boer method⁽⁵⁾ which develops quantum deviations from the law of corresponding states in terms of the parameter $\Lambda^* = h/\sigma(m\epsilon)^{1/2}$, where σ is the range of the intermolecular force and ϵ is the depth of the intermolecular potential.

For the real gas, which obeys an equation of state of the form

$$PV/RT = 1 + B_0P + C_0P^2 \quad (5)$$

one obtains⁽⁶⁾ after taking cognizance of the fact that at equilibrium the Gibbs free energies and not the Helmholtz free energies of the two phases are equal

$$\begin{aligned} \ln P'/P = & \frac{1}{24} (h/kT)^2 \left(\frac{1}{m'} - \frac{1}{m} \right) \left\langle \frac{\partial^2 V}{\partial x^2} \right\rangle + (RT)^{-1} (P'v' - PV) \\ & - (B_0P + 1/2 C_0P^2)' + (B_0P + 1/2 C_0P^2) \end{aligned} \quad (6)$$

A test of this development can be made with the data of Keesom and Hantjes⁽⁷⁾ on the vapor pressures of the neon isotopes, ^{20}Ne and ^{22}Ne . The comparison is shown in Fig. 2. The solid line through the origin is drawn in accord with eq. (2) and the Θ for neon, 63° , is taken from heat capacity measurements. We note that the data for the solid give a finite intercept at infinite temperature. More extensive calculations by Johns,⁽⁸⁾ who used an anharmonic Einstein model, failed to remove the discrepancy. It was necessary for Johns to assume a difference in the potential for the two neon isotopes in order to reconcile his calculations with the Leiden data. The discrepancy is actually worse than that calculated by Johns, for in fact the lattice distance in solid neon is 4.429 \AA ⁽⁹⁾ rather than the values 4.539 – 4.581 \AA derived by Johns by minimizing his free energy

function with respect to the lattice distance. The discrepancy has been shown to be a result of the inadequacy of the Leiden data for a test of this theory and the extension of the theory to include higher order quantum corrections.

The results of the recent investigation of the neon isotopes by Bigeleisen and Roth⁽¹⁰⁾ are given in Fig. 3. The quantity plotted is not $\ln P_{\text{Ne}20}/P_{\text{Ne}22}$ but rather $\ln f_c = \ln [Q(^{22}\text{Ne})/Q(^{20}\text{Ne})]_{\text{q.m.}} / [Q(^{22}\text{Ne})/Q(^{20}\text{Ne})]_{\text{cl}}$, which has direct theoretical significance. The partition function ratio is related to the vapor pressure ratio in the general case by the equation⁽⁶⁾

$$\ln P'/P = \ln s/s' f_c - \ln s/s' f_g + (RT)^{-1} (P'V' - PV) - (B_0 P + 1/2 C_0 P^2) + (B_0 P + 1/2 C_0 P^2) \quad (7)$$

where $s/s' f_g$ is the well known reduced partition function ratio for the ideal gas introduced by Bigeleisen and Mayer.⁽¹¹⁾ For a monatomic solid with a harmonic potential^(6,10)

$$\ln f_c = \sum_j (-1)^{j+1} \frac{3B_{2j-1} (h/kT)^{2j}}{2j(2j)!} [1 - (m'/m)^j] \mu_{2j}^* \quad (8)$$

$$[h \nu_{\text{max}}^* / kT < 2\pi]$$

where μ_{2j}^* is the $2j$ 'th moment of the lattice vibration

$$N^{-1} \sum_{i=1}^{3N} \nu_i^{2j} = 3\mu_{2j}^* \quad (9)$$

For the Debye distribution, one has the well known relation

$$\mu_{2j}^* = [3(k_B/h)^{2j}] / (2j + 3) \quad (10)$$

It is apparent that there is curvature in a plot of $\ln f_c$ vs. $1/T^2$ due to the higher order quantum corrections. The extrapolation to the

origin is facilitated by the use of the Debye distribution and a Debye Θ of 74.6°K gives an excellent fit of the data. The discrepancy between this value of Θ and the one derived from heat capacity measurements, 66.7°K, ⁽¹²⁾ has been shown to be a consequence of the anharmonicity of the lattice vibrations. The behavior of the liquid between the melting point and the normal boiling point can be described by the change in the coordination number of the solid, 12, to 8.8 nearest neighbors in the liquid. The nearest neighbor distance in the liquid differs by a negligible amount from the lattice distance in the solid. This leads to a characteristic temperature of 63°K for the liquid, which is in excellent agreement with the experimental data.

The contribution of the gas imperfection to the vapor pressure ratio can be tested experimentally. For a solution of isotopes with a negligible volume change on mixing

$$\ln P'/P = (\ln \alpha) [1 - P(B-V/RT)] \quad (11)$$

$$\text{where } \alpha = (N'/N)_{\text{gas}} / (N'/N)_{\text{liquid}} \quad (12)$$

Thus comparing eqs. (7) and (11)

$$\ln \alpha = \ln f_c - \ln f_g \quad (13)$$

The fractionation experiment gives directly the difference between the partition function ratio in the condensed phase and the ideal gas. The physical interpretation of the difference between the solution experiment and the experiment with the pure phases is the following. In the solution experiment both isotopes are present in the gas phase at the same density. In the approximation that the virial coefficients are the same, any effect of the gas density cancels and the system

behaves as though an ideal gas mixture were in equilibrium with the condensed phase. In the case of the pure components, the equilibrium vapor pressure of a liquid is greater than that which would be obtained for the hypothetical ideal gas. This is due to the attractive forces in the gas. In Fig. 4 we give a comparison of $\ln P_{20\text{Ne}}/P_{22\text{Ne}}$ from measurements on pure phases and from solution equilibration.⁽¹³⁾ The agreement is excellent. Further confirmations of the theory are given in the communication to this symposium by Boato.⁽¹⁴⁾

The present theory has been applied to the isotopes of argon by Boato and co-workers, who have in addition made an evaluation of the role of the anharmonic effects.⁽¹⁴⁾ The agreement between theory and experiment is excellent. We may thus conclude that the difference in vapor pressures of the isotopes of the rare gases can be quantitatively described within the Born-Oppenheimer approximation by straightforward quantum statistics.

MOLECULAR SYSTEMS

It has been known for a long time that the description given above for atomic systems is grossly inadequate even in a qualitative way to describe the difference in vapor pressures of isotopic polyatomic molecules. In the case of hydrocarbons, deuterium substitution for protium usually leads to a higher rather than a lower vapor pressure. In such systems the sign of the vapor pressure difference depends on the temperature and the behavior is known as the cross over phenomenon. Numerous examples are available to show that for isotopic systems the vapor pressure does not depend on the molecular weight but rather must be correlated with the structure of the molecule and its interaction with other molecules in the condensed phase.

Typical structural effects are the vapor pressures of the methanes $^{12}\text{CH}_3\text{D} > ^{12}\text{CH}_4 > ^{13}\text{CH}_4$. In a homologous series the rule of the mean is obeyed, e.g. $P_{\text{HD}} \approx (P_{\text{H}_2} P_{\text{D}_2})^{1/2}$. Successive isotopic substitution, e.g. H, D, T, leads to a very much faster leveling off with increasing mass than that to be expected from simple considerations of spherical molecules. Thus the ratio of ratios $(P_{\text{H}_2\text{O}}/P_{\text{HTO}})/(P_{\text{H}_2\text{O}}/P_{\text{HDO}})$ has been found to be 1.37 rather than 1.90 to be expected from masses 18, 19 and 20. (15) These findings can be readily understood if one builds a theory which takes cognizance of the molecular structure. In addition to the contribution of the translation (molecular weight effect) to the vapor pressure, one must consider the molecular rotation and the mutual interaction of these modes as well as their coupling with the molecular vibrations. In a formal way this is inherent in eq. (7). The problem then becomes the evaluation of $\ln s/s' f_c$ for a molecular system.

In the harmonic approximation

$$\ln s/s' f_c = N^{-1} \left\{ \frac{hc}{2kT} \sum_{i=1}^{3nN} (\nu_i' - \nu_i) + \sum_{i=1}^{3nN} \ln \frac{u_i [1 - \exp(-u_i')]}{u_i' [1 - \exp(-u_i)]} \right\} \quad (14)$$

The vapor pressure equation then becomes

$$\begin{aligned} \ln P'/P = N^{-1} \left\{ \frac{hc}{2kT} \sum_{i=1}^{3nN} (\nu_i' - \nu_i)_c - (\nu_i' - \nu_i)_g \right. \\ \left. + \sum_{i=1}^{3nN} \ln(u_i/u_i')_c (u_i'/u_i)_g \left[\frac{1 - \exp(-u_i')}{1 - \exp(-u_i)} \right]_c \left[\frac{1 - \exp(-u_i)}{1 - \exp(-u_i')} \right]_g \right\} \quad (15) \\ - G(\sigma, \sigma')_g + (RT)^{-1} (P'V' - PV) - (B_0 P + \frac{1}{2} C_0 P^2)' + (B_0 P + \frac{1}{2} C_0 P^2) \end{aligned}$$

where $G(\sigma, \sigma')_g$ is a correction for non classical rotation of the molecule in the gas phase. If the internal vibrations are not much different in

the condensed phase from the gaseous state and if the quantum levels associated with the translation and rotation in the condensed phase have energies not more than $2\pi kT$, then

$$\ln P^*/P = \frac{1}{24N} \left(\frac{h}{kT}\right)^2 \sum_{i=1}^{3nN} (\mu_i' - \mu_i) (a_{ii} - b_{ii}) + \dots \quad (16)$$

The summation in eq. (16) runs over all atoms in the condensed phase. The reciprocal masses μ' and μ are atomic masses and the Cartesian force constants a_{ii} and b_{ii} are the restoring forces when the i 'th atom is displaced from its equilibrium position in the condensed and gas phases respectively. Up to order $(h/kT)^2$ the harmonic approximation is not necessary for the derivation of eq. (16). The derivation proceeds directly from the Mayer-Band theorem.⁽¹⁶⁾ Under the conditions where eq. (16) is applicable (these are discussed in detail along with its derivation⁶) one obtains directly the rule of the mean. The relative behavior of different isotopes of the same element is uniquely given by the atomic masses and in the case of H, D, T the ratio

$$\frac{\ln a (H/T)}{\ln a (H/D)} = 1.33$$

is in excellent agreement with the aforementioned experiments of Avinur and Nir. One sees directly that the vapor pressures of $^{12}\text{CH}_3\text{D}$ and $^{13}\text{CH}_4$ can never be equal, except by some fortuitous circumstance. A difference arises in eq. (16) between these molecules both from the $(\mu' - \mu)$ term and the force term $(a_{ii} - b_{ii})$, which are both different for the carbon and hydrogen atoms. Even for a molecule where $(a_{ii} - b_{ii})$ is the same for different atoms, the vapor pressure does not depend on the molecular weight. One is led to predict differences in vapor

pressures between HT and D_2 . We point out that eq. (16) is not applicable to such light molecules at such low temperatures. Nevertheless, in a qualitative way we are led to expect a difference due to the fact that in this approximation the vapor pressure depends on the reciprocal atomic masses. From a molecular point of view, a difference is to be expected as a consequence of the perturbation of the translation and internal vibration by the rotation in the liquid. Such a difference has been found experimentally.⁽¹⁷⁾ A theoretical treatment which considers only the translation-rotation has been given by Babloyantz⁽¹⁸⁾ and extended by Friedmann.⁽¹⁹⁾ A more general treatment within the framework of perturbation theory is given in the paper presented at this symposium by Wolfsberg.⁽²⁰⁾ His calculations show the rotation-vibration interaction to be significant.

The detailed description of the normal modes and their perturbation from various types of interaction is unnecessary for substances with small quantum effects. It is only necessary to know the change in the mean force between the condensed and gaseous state. When the quantum effects associated either with the translation or rotation or the shifts in the internal vibrations are large, then eq. (16) is no longer applicable. In the latter case

$$\ln P^*/P = \sum_{j=1}^{\infty} (-1)^{j+1} \frac{B_{2j-1} (h/kT)^{2j} 6(\mu_{2j}^* - \mu_{2j})}{2j(2j)!} + \ln \left(\frac{\omega_g^*}{\omega_g} \right) \quad (17)$$

$$+ (RT)^{-1} (P^*V^* - PV) - (B_0P + \frac{1}{2} C_0P^2)^* + (B_0P + \frac{1}{2} C_0P^2) - G(\sigma, \sigma')_g$$

where μ_{2j}^* and μ_{2j} are the vibrational moments associated with the translation and rotation and

$$\ln \mathcal{D}' = N^{-1} \sum^{3N(n-2)} \left\{ (hc/2kT) (\nu_{ic}^g - \nu_{ig}^g) + \ln \frac{u_{ig}^g [1 - \exp(-u_{ic}^g)]}{u_{ic}^g [1 - \exp(-u_{ig}^g)]} \right\} \quad (18)$$

The summation in eq. (18) runs over the internal vibrations of the molecule. In the first approximation eq. (17) reduces to one of the form

$$\ln P'/P = \frac{A}{T^2} - \frac{B}{T} \quad (19)$$

The T^{-2} term is associated with translation and rotation; the T^{-1} term with shifts in the zero point energies of the internal vibrations on condensation. We have already pointed out that one contribution to these shifts arises from the coupling of the vibrations with the translation and rotation. A more usual effect arises from the van der Waals's forces. This has been discussed by Bauer and Magat⁽²¹⁾ and more recently by Baertschi and Kuhn⁽²²⁾ and by Wolfberg.⁽²⁰⁾ Equation (19) directly predicts the cross over phenomenon. At low temperatures the A/T^2 term predominates and the light isotope has the higher vapor pressure. At high temperatures the B/T term becomes greater than the A/T^2 term and the heavy isotope has the higher vapor pressure. At still higher temperatures eq. (17) goes over to eq. (16), the light isotope again has the higher vapor pressure and then finally at still higher temperatures the vapor pressure difference vanishes.

The cross over phenomenon has been discussed at times in terms of the difference in molar volumes of the isotopes. The difference in molar volumes is per se not an additional effect to be considered. It is associated with the zero point energy difference of the isotopic molecules and the anharmonicity of the intermolecular force. A quantitative correlation between the molar volume difference and vapor

pressure ratio has been established.⁽⁶⁾ In Fig. 5 we give a correlation of the experimental data on the isotopic liquid hydrogens with the theory.

The number of molecular systems in which isotope vapor pressure differences have been studied is large. Very few studies have been subjected to theoretical analysis and we shall deal with those systems where a quantitative theoretical analysis has been carried through. Three systems have now been analyzed in complete detail: the NO system,⁽²³⁾ the N₂O system,⁽²⁴⁾ and the ethylene system.⁽²⁵⁾ In the present paper we shall give a summary of the behavior of the nitrogen oxides. A discussion of the ethylene system is given elsewhere in this symposium.⁽²⁵⁾ To these we may add the calculation of the van der Waals shift in liquid CCl₄ and the resulting vapor pressure difference for ¹²C-¹³C and ³⁵Cl-³⁷Cl in this molecule.⁽²⁰⁾

The isotopic N₂O molecules afford a simple and direct method for the study of the effect of hindered rotation in the liquid on the vapor pressure. By single isotopic substitution one can study ¹⁴N¹⁴N¹⁶O, ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, and ¹⁴N¹⁴N¹⁸O. The study of all of these species by the method of column distillation has been carried through by Bigeleisen and Ribnikar⁽²⁴⁾ subsequent to the Raleigh distillation experiments of Kuhn, Narten and Thürkauf.⁽²⁶⁾ The latter workers measured the ¹⁴N¹⁴N¹⁶O/¹⁴N¹⁴N¹⁸O and ¹⁴N/¹⁵N fractionation factors. Simultaneously with the experiments of Bigeleisen and Ribnikar, Clusius and Schleich⁽²⁷⁾ measured the vapor pressure difference between ¹⁴N¹⁴N¹⁶O and ¹⁵N¹⁴N¹⁶O. The experimental results of all these workers by different methods are in good agreement with

one another, within the limits of the experimental errors. The elementary separation factor, $\ln P'/P$, is of the order $1-2 \times 10^{-3}$ and the agreement is 10% of the separation factor.

A summary of the relative and absolute separation factors is given in Tables I and II. The relative separation factors are rather simply calculated in this particular case. N_2O is a linear molecule which condenses into the solid random end for end.⁽²⁸⁾ The intermolecular forces acting on the end nitrogen atom and the oxygen atom are therefore nearly identical. The center of gravity of the molecule is within a few parts in 10^5 at the central nitrogen atom.⁽²⁹⁾ Inasmuch as the molecule has a very small dipole moment and polarizability, it is reasonable to assume that the internal vibrations are not much perturbed on condensation. These facts and the last assumption lead to the relation

$$(a_{ii} - b_{ii})_O = (a_{ii} - b_{ii})_{END\ N}$$

From eq. (16) we can now write

$$\frac{\epsilon(^{14}N^{14}N^{16}O / ^{14}N^{14}N^{18}O)}{\epsilon(^{14}N^{14}N^{16}O / ^{15}N^{14}N^{16}O)} = \frac{\mu_{16} - \mu_{18}}{\mu_{14} - \mu_{15}} = \frac{\frac{1}{16} - \frac{1}{18}}{\frac{1}{14} - \frac{1}{13}} = 1.46$$

The ratio $[\epsilon(^{14}N^{14}N^{16}O / ^{15}N^{14}N^{16}O)] / [\epsilon(^{14}N^{14}N^{16}O / ^{14}N^{15}N^{16}O)]$ requires some knowledge about the force field and the frequency distribution for the translational and rotational modes. We assume an isotropic force, an Einstein distribution for the rotation and both Einstein and Debye distributions for the translation. The ratios to be calculated are the coefficients of the $(h/kT)^2$ term in eq. (17).

We find

	Einstein Translation	Debye Translation
$\frac{\epsilon(^{14}\text{N}^{14}\text{N}^{16}\text{O}/^{15}\text{N}^{14}\text{N}^{16}\text{O})}{\epsilon(^{14}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}^{15}\text{N}^{16}\text{O})}$	$\frac{5}{3}$	$\frac{\frac{2}{34} + \frac{3}{40}}{\frac{3}{40}} = 2.11$

The agreement between theory and experiment is rather good. It is a direct confirmation of hindered rotation in the liquid through the use of isotopic substitution in non-equivalent positions. The absolute elementary separation parameters are calculated through the above theoretical ratios and the theoretical calculation of $\epsilon(^{14}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}^{15}\text{N}^{16}\text{O})$, which is directly given by the translational contribution. One finds ⁽²⁴⁾ $\epsilon(^{14}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}^{15}\text{N}^{16}\text{O}) = 8.2 \times 10^{-4}$. This forms the basis quantity for the calculation of the theoretical separation factors given in Table II. The agreement between theory and experiment is all that could be desired.

We now consider the case of a polyatomic molecule which has strong association in the liquid phase. In the case of NO definite dimers exist, which are negligibly dissociated in the liquid but completely dissociated in the gas phase. ⁽³⁰⁾ The vapor pressures of all the three ^{15}N and ^{18}O substituted NO molecules have been studied as a function of temperature by Clusius and co-workers. ⁽³¹⁾ A summary of their experimental observations is given in Table III. We note that a rather large effect has been found and empirically the system obeys the rule of the mean,

$$\ln\left(\frac{P_{^{14}\text{N}^{14}\text{N}^{16}\text{O}}}{P_{^{15}\text{N}^{14}\text{N}^{16}\text{O}}}\right) = \ln\left(\frac{P_{^{14}\text{N}^{14}\text{N}^{16}\text{O}}}{P_{^{14}\text{N}^{15}\text{N}^{16}\text{O}}}\right) + \ln\left(\frac{P_{^{14}\text{N}^{14}\text{N}^{16}\text{O}}}{P_{^{14}\text{N}^{14}\text{N}^{18}\text{O}}}\right), \text{ etc.}$$

This is just the behavior to be expected if the system has small quantum effects and/or small perturbations of the large quantum effects. A very good criterion for this description is given in the published

theory of the vapor pressures of the isotopic nitric oxide molecules. (23)

If the system obeys eq. (16), then by straightforward classical thermodynamics

$$\Delta(\Delta H)_T \text{ vap} = -2RT \ln(P'/P)_T \quad (20)$$

A comparison between the "experimental" values and the ones calculated from eq. (20) is given in Table IV. This definitely establishes the effect as a small quantum effect, $1/T^2$ dependence, with no $1/T$ nor temperature independent terms in the vapor pressure ratio. As such, we may proceed to apply eq. (16) directly.

Liquid NO has random dimers. In the dimer, displacement of oxygen along or perpendicular to valence bonds is equivalent to displacement of nitrogen. Thus if one neglects interactions across the ring $(a_{11}-b_{11})_O = (a_{11}-b_{11})_N$, just as in the case of N_2O . This naturally predicts the $(^{18}O/^{16}O) \wedge (^{15}N/^{14}N)$ isotope effects in the vapor pressure and related quantities to be 1.46. These are compared with experiment in Table V. The contribution of the dimerization process to the difference in vapor pressure has been calculated to be 0.021 for $\ln(P_{14N16O}/P_{15N16O})$ at 115°K. We now make a new estimate for the contribution of the dimers. Following the procedure given in our discussion for N_2O , we calculate the translation and rotation to contribute 6×10^{-3} for a Debye translation. If a different frequency spectrum is used, then a new characteristic temperature needs to be defined and the result will be the same. This new calculation of the translation-rotation contribution leads to the theoretical value of $\ln(P_{14N16O}/P_{15N16O}) = 0.027$ at 115°K (previously we had calculated 0.025). The result is in good agreement with experiment. The

calculation is further confirmed by recent experiments of Clusius, Schleich, Piesbergen, and Varde.⁽³²⁾ By comparison of the ^{15}N fractionation in a dilute solution of NO in CH_4 with the vapor pressure ratio of the pure liquid, they set a lower limit of 0.018 for the contribution of the dimerization process to the logarithm of the vapor pressure ratio at 111°K .

SUMMARY

It is apparent that major progress has been made both in the experimental and theoretical study of the vapor pressures of isotopic molecules in the last five years. Vapor pressure measurements are being made in different laboratories by different methods which agree with one another within a few hundredths of one percent. The theory has advanced to the point where a large body of experimental data can be systematized and understood. Quantitative calculations have been carried out which verify the mass, temperature, and potential energy dependence aspects of the theory. An old subject has been revived by advances in modern experimental and theoretical methods and is now useful for the study of quantum effects and structural effects in liquids and solids.

ACKNOWLEDGMENT

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Table I. Relative elementary separation parameters for the isotopic N_2O molecules. (25)

$$\epsilon_j = \ln \left[\frac{({}^{14}N_2{}^{16}O/N_2O)_j \text{ vapor}}{({}^{14}N_2{}^{16}O/N_2O)_j \text{ liquid}} \right]$$

Isotopic Species	Experimental	Theoretical
$\epsilon_{\substack{14\ 14\ 18 \\ N\ N\ O}} / \epsilon_{\substack{15\ 14\ 16 \\ N\ N\ O}}$	1.38 ± 0.07	1.46
$\epsilon_{\substack{15\ 14\ 16 \\ N\ N\ O}} / \epsilon_{\substack{14\ 15\ 16 \\ N\ N\ O}}$	2.10 ± 0.10	1.67 Einstein 2.11 Debye

Table II. Absolute elementary separation parameters for the isotopic
 N_2O molecules at 184°K

Isotopic species	Raleigh distillation ⁽²⁶⁾	Mercury manometry pure species ⁽²⁷⁾	Column distillation ⁽²⁴⁾	Theory
$^{14}_N^{14}_N^{16}_O / ^{14}_N^{14}_N^{18}_O$	$18 \pm 5 \times 10^{-4}$		$22 \pm 2 \times 10^{-4}$	25×10^{-4}
$^{14}_N^{14}_N^{16}_O / ^{15}_N^{14}_N^{16}_O$		$19.8 \pm 1 \times 10^{-4}$	$16.2 \pm 2.8 \times 10^{-4}$	17×10^{-4}
$^{14}_N^{14}_N^{16}_O / ^{14}_N^{15}_N^{16}_O$			$7.8 \pm 1.4 \times 10^{-4}$	8×10^{-4}
[$^{14}_N^{14}_N^{16}_O /$ $(^{15}_N^{14}_N^{16}_O + ^{14}_N^{15}_N^{16}_O)$]	$11.6 \pm 0.6 \times 10^{-4}$		$12 \pm 2 \times 10^{-4}$	13×10^{-4}

Table III. Properties of isotopic NO molecules

	$^{15}\text{N}^{16}\text{O}$	$^{14}\text{N}^{18}\text{O}$	$^{15}\text{N}^{18}\text{O}$
$\ln P(^{14}\text{N}^{16}\text{O})/P(^x\text{N}^y\text{O})$ at 115°K	0.0295	0.0406	0.0701
δ Triple Point ($^x\text{N}^y\text{O} - ^{14}\text{N}^{16}\text{O}$)	0.099°K	0.139°K	0.223°K
δ Boiling Point ($^x\text{N}^y\text{O} - ^{14}\text{N}^{16}\text{O}$)	0.228°K	0.313°K	0.528°K
δ Heat of Vaporization ($^x\text{N}^y\text{O} - ^{14}\text{N}^{16}\text{O}$) in cal mole ⁻¹	14.1	20.4	33.5

Table IV. Calculated and experimental differences in heat of vaporization of NO molecules (cal mole⁻¹)

	$^{15}\text{N}^{16}\text{O}$	$^{14}\text{N}^{18}\text{O}$	$^{15}\text{N}^{18}\text{O}$
"Experimental"	14.1	20.4	33.5
Calculated (eq. 20)	13.5	18.7	32.3

Table V. Relative ^{18}O and ^{15}N isotope effects in the vapor pressure of NO

	Experimental	Theoretical
$\frac{\ln (P_{^{14}\text{N}^{16}\text{O}}/P_{^{14}\text{N}^{18}\text{O}})}{\ln (P_{^{14}\text{N}^{16}\text{O}}/P_{^{15}\text{N}^{16}\text{O}})}$	1.38	1.46
$\frac{\delta \Delta H(^{14}\text{N}^{18}\text{O}-^{14}\text{N}^{16}\text{O})}{\delta \Delta H(^{15}\text{N}^{16}\text{O}-^{14}\text{N}^{16}\text{O})}$	1.45	1.46
$\frac{\delta T_{\text{tr}}(^{14}\text{N}^{18}\text{O}-^{14}\text{N}^{16}\text{O})}{\delta T_{\text{tr}}(^{15}\text{N}^{16}\text{O}-^{14}\text{N}^{16}\text{O})}$	1.40	1.46

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Fig. 2. Vapor pressure ratio $^{20}\text{Ne}/^{22}\text{Ne}$ (data of Keenan and Haantjes). Upper line through data on solid neon, lower line liquid neon.

BNL Neg. 1-326-60

Fig. 3. Partition function ratio for the neon isotopes in the solid and liquid derived from vapor pressure measurements.

BNL Neg. 1-325-60

Fig. 4. Comparison of manometric vapor pressure measurements θ with solution equilibria for the neon isotopes

BNL Neg. 9-92-60

Fig. 5. Correlation of molal volumes of the liquid hydrogens with vapor pressure. (The apparent finite intercept at $\log (P_{\text{H}_2}/P_{\text{X}_2}) = 0$ is of course fictitious. See the original literature⁽⁶⁾ for the meaning of the intercept.)

BNL Neg. 8-215-60

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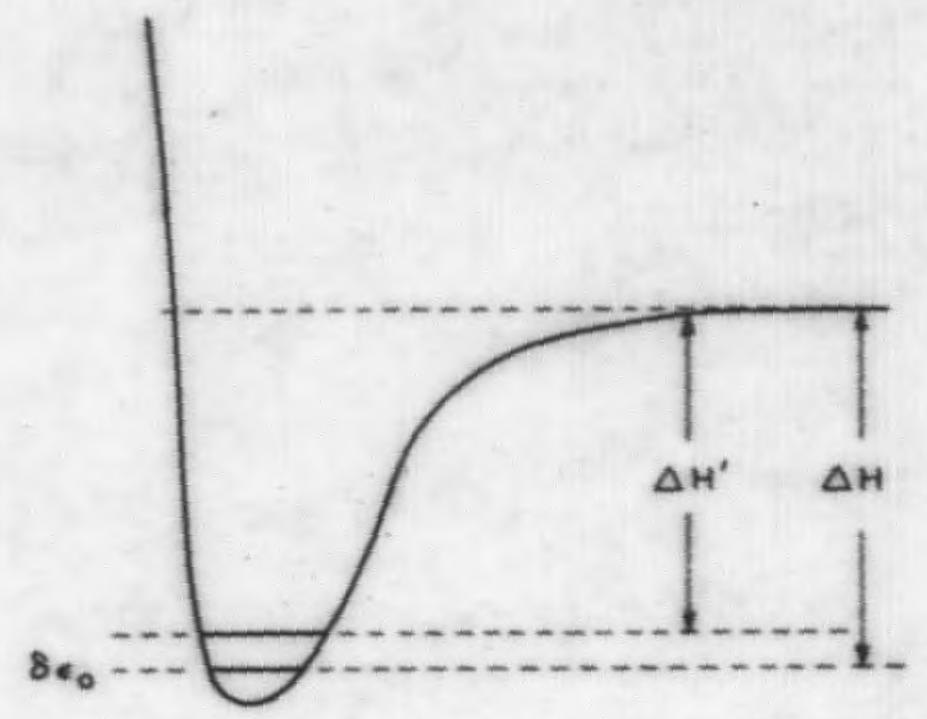
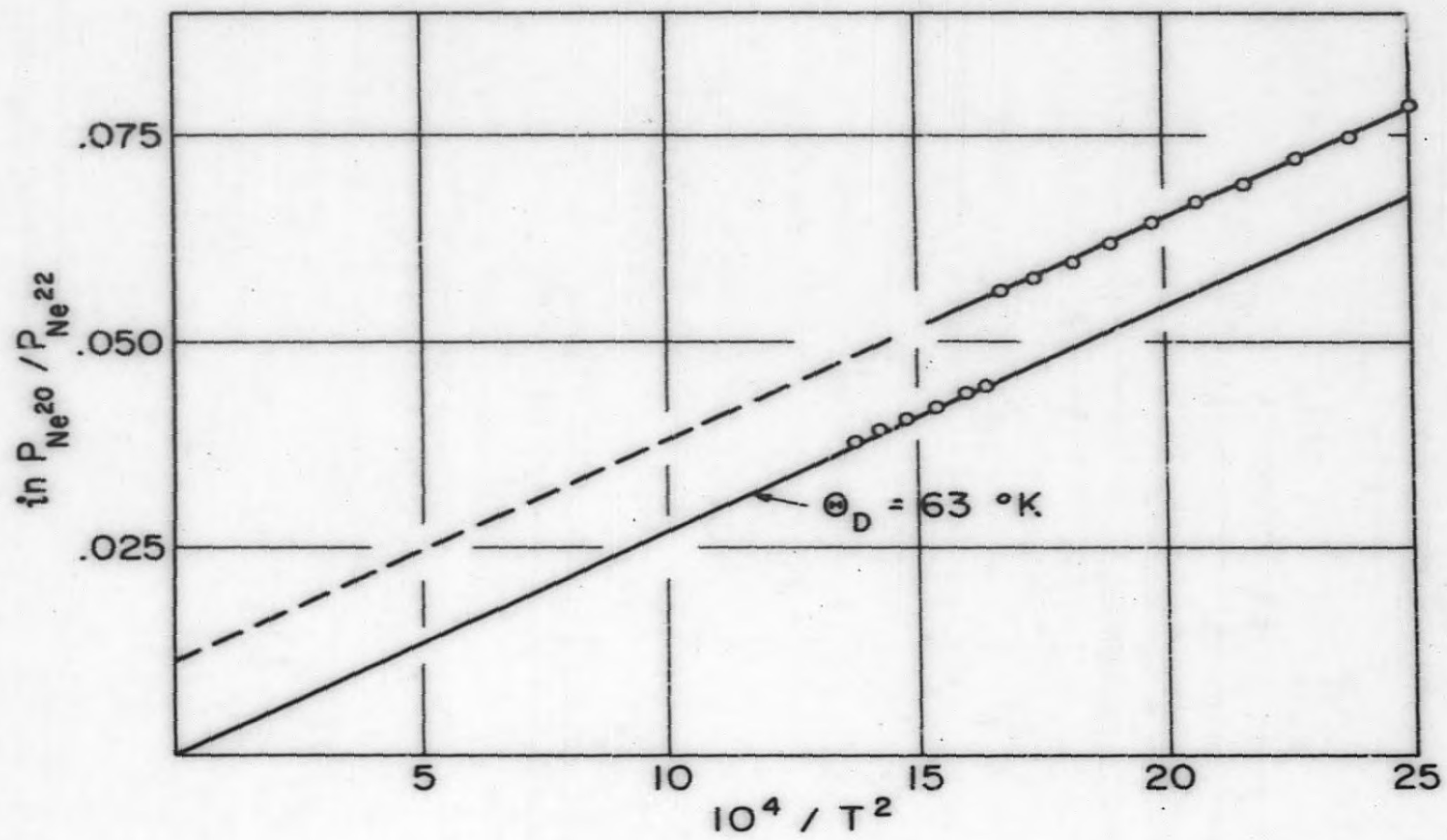
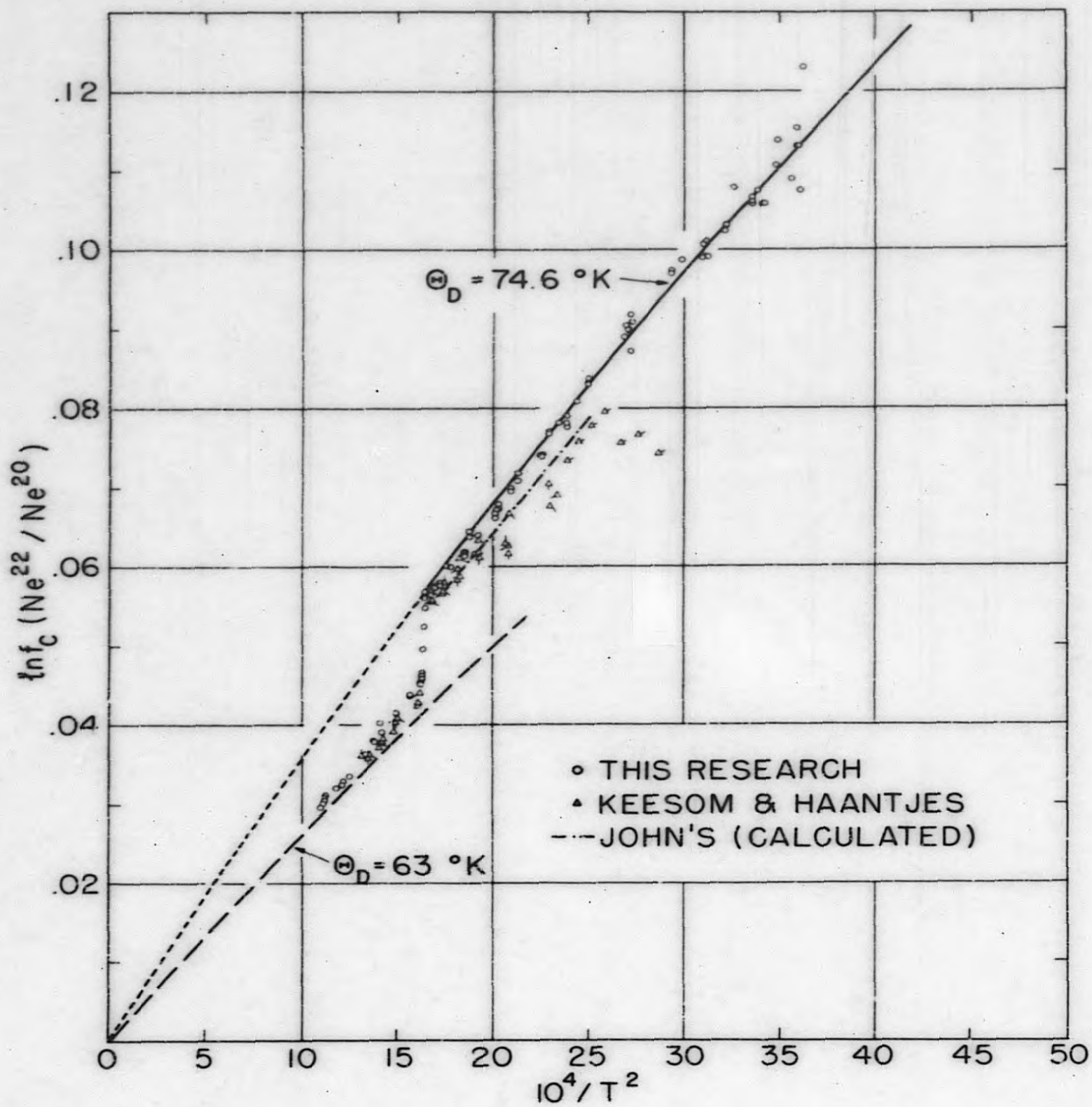


FIG 1
J. BILKLEISEN

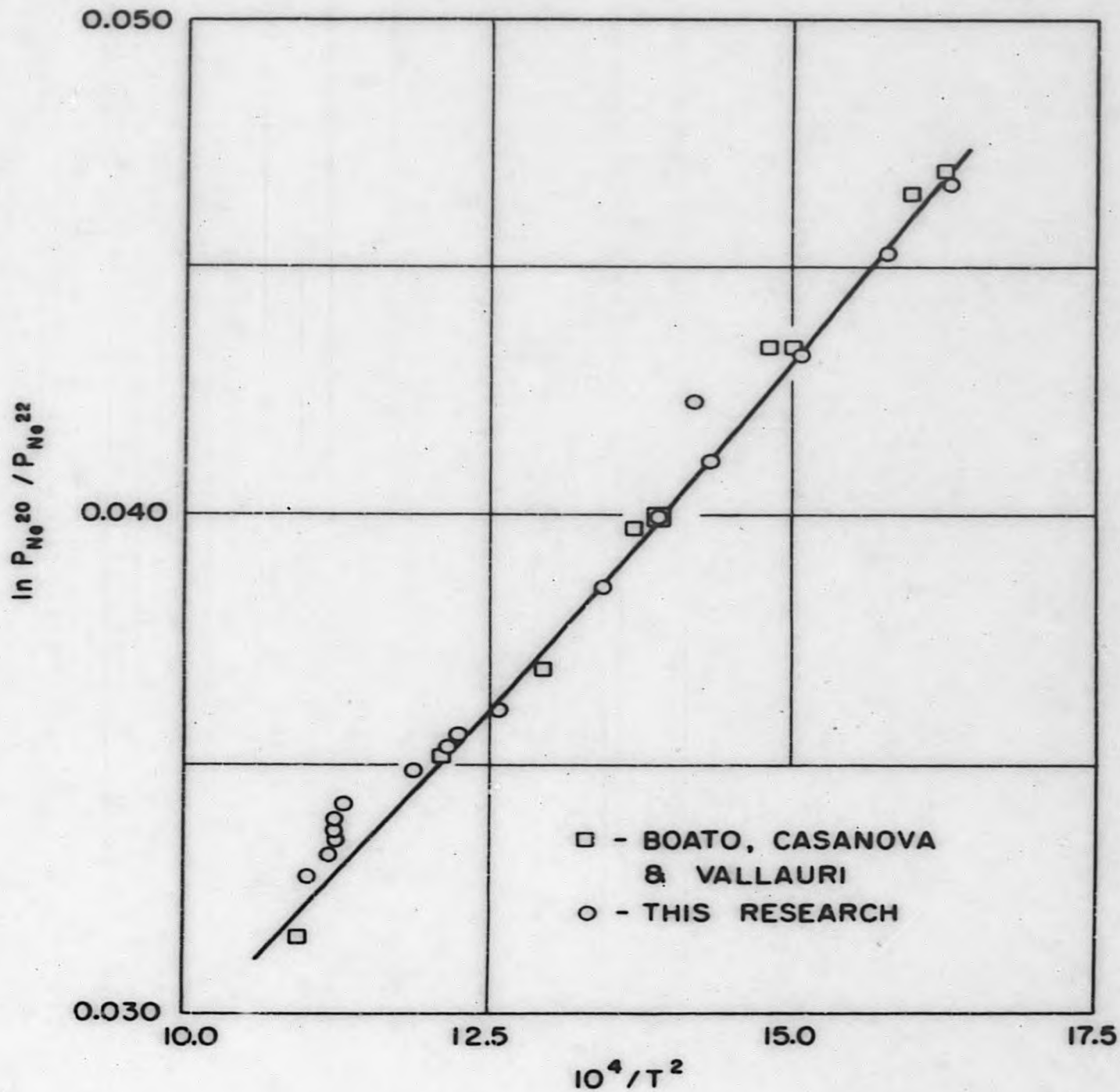
7-527-62



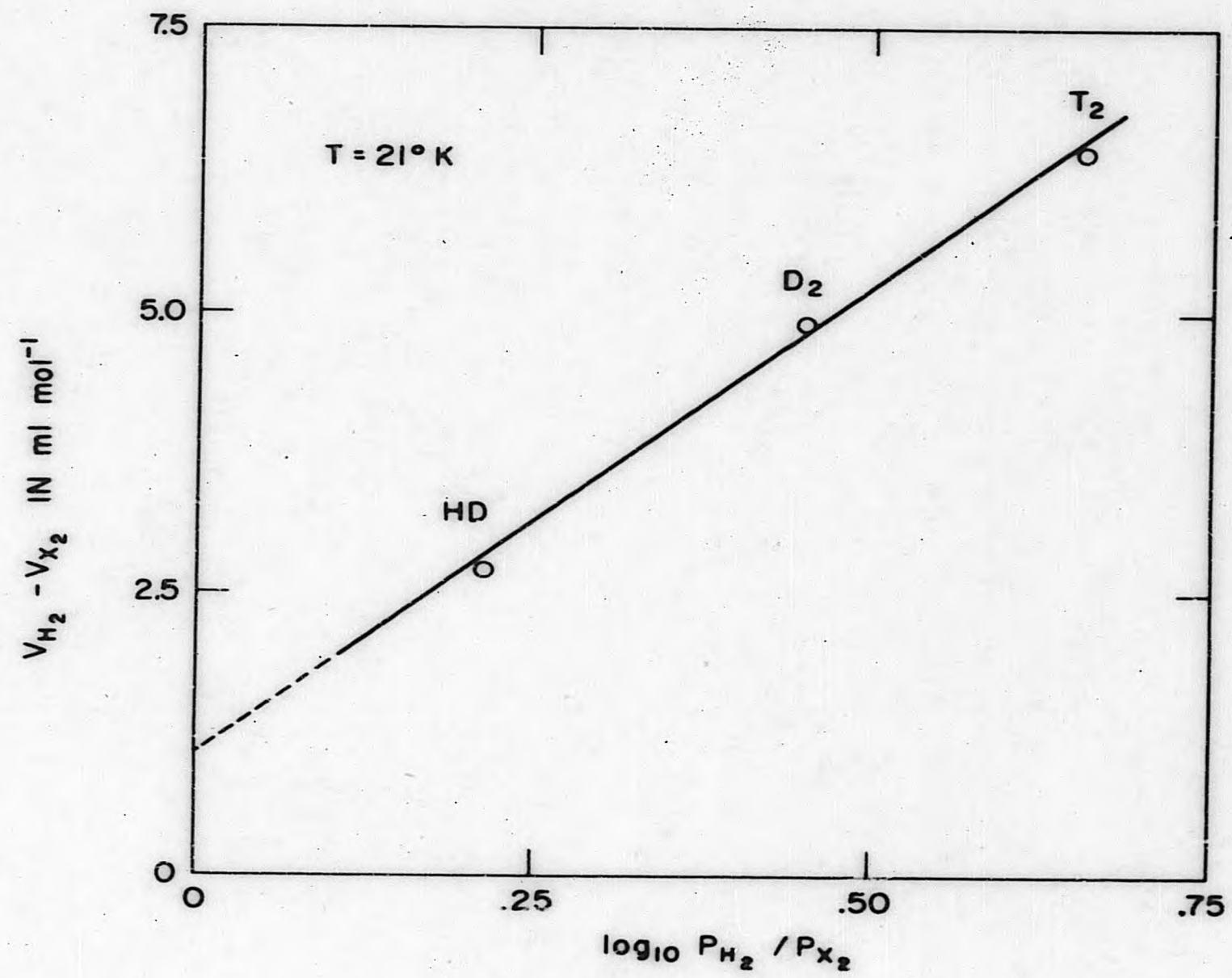
BNL NEG.#1-326-60, FIG. 2[#]



BNL NEG. #1-325-60. FIG. #3



BNL NEG. #9-92-60. FIG. 4



END

BNL NEG. # 8-215-60 FIG. # 5