Condensed Phase Isotope Effects (Especially Vapor Pressure Isotope Effects)§

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I. Introduction

A. General Remarks

Chemists have long been aware that the electronic structure of atoms and molecules is essentially independent of the isotopic distribution of nuclear mass (that is to within the limits established by the Born–Oppenheimer approximation). This may be expressed with the statement that, for a given electronic state, a properly calculated potential energy (PE) surface is isotope independent. At the same time, we are also aware that a reasonably complete description of any process of chemical interest involves formulation of the equations of motion on a PE surface describing that process. An isotope dependence may arise here because the kinetic energy part of the expression *is* mass dependent. Although properly calculated potential energy parameters are isotope independent, kinetic energy parameters are not. It follows that in many problems of interest where the kinetic energy parameters are known in terms of the molecular structure, one can often deduce information concerning the nature of the PE surface from experimental data on isotope effects. An excellent example of the application of this approach is found in current methods used to interpret the large body of information now available on kinetic isotope effects. The field has recently been reviewed by Collins and Bowman.[1] Many studies have resulted in useful information such as the assignment of reaction coordinates, transition state geometry, etc. In a similar spirit we note that the focus of the present review on condensed phase isotope effects is with a view toward gaining information concerning the potential energy surfaces used to describe condensed phases. Thus condensed phase isotope effect studies are partly made for the purpose of enhancing

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the understanding of the nature of intermolecular forces and of the motions of molecules in condensed phases.

A number of different properties will be of interest; these include most importantly the vapor pressure isotope effect (VPIE) (because it has been the most thoroughly investigated), but we will also consider isotope effects on condensed phase molar volumes, on heats of solution, on solubilities, on surface tension, etc. The field of condensed phase isotope effects has not recently been reviewed but some earlier discussions are of interest. The most important of these is the book by Rabinovich[2] which comprehensively discusses the experimental work through the early 1960's. Also Bigeleisen,[3,4] Höpfner,[5] Van Hook,[6] and Wolfsberg[7] have treated certain parts of the field, while Arnett and McKelvey[8] and more recently Friedman and Krishnan[9] have collected a good part of the material on thermodynamics of aqueous solvent isotope effects. A number of collections of papers from symposia have appeared under the editorships of London[10] (separation methods), Kistemaker, Bigeleisen, and Nier[11] (1957 Amsterdam Symposium), and Craig, Miller, and Wasserburg.[12] The proceedings of a 1963 symposium have been collected in Vol. 60 of the *Journal de chimie de Physique et de Physico-chimie Biologique,*[13] and reports are available from the International Symposia on the Peaceful Uses of Atomic Energy.[14]

In the present article we shall focus attention on systems which can be treated with Boltzman statistics and therefore will specifically exclude topics such as ^3He–^4He effects, isotope effects on normal conducting–super-conducting phase transitions, etc. Secondly, we do not intend to make a detailed review of isotope effects in condensed hydrogen and will content ourselves simply with offering references to leading articles. Neither do we intend to treat the literature of gas chromatography in any detail.

II. Theoretical Background: Especially the Vapor Pressure Isotope Effect

A number of review articles (Clusius,[15] Johns,[16] Rabinovich,[17] Bigeleisen,[3,18] Boato and Casanova,[19] Van Hook,[6] Wolfsberg,[7] Höpfner[5]) and two books (Rozen[20] and Rabinovich[2]) have appeared on the topic of the vapor pressure isotope effect (VPIE). In the present chapter the theory of the VPIE will be discussed in an historical context but without aiming at bibliographical completeness.

A. Early Theories

1. Lindemann, 1919

The effect of isotopic substitution on vapor pressure is an old problem, the first theoretical calculations were carried out more than 50 years ago by Lindemann.[21,22] He started from an equation derived from the theory for a monoatomic Debye solid.

$$\ln P = -\frac{\lambda_0}{RT} + \int_0^T \frac{dT}{RT^2}\int_0^T (C_p - c_p)dT + i \qquad (1)$$

In eq 1 P is the vapor pressure, λ_0 is the latent heat at absolute zero, C_p and c_p are the heat capacities of gas and solid, respectively, and i is a constant. Over a very wide temperature range $C_p' = C_p$, and therefore the logarithmic ratio of the isotopic vapor pressures is

$$\ln \frac{P'}{P} = \int_0^T \frac{dT}{RT^2}\int_0^T (c_p - c_p')dT + (i' - i) - \frac{\lambda_0' - \lambda_0}{RT} \qquad (2)$$

The primes designate isotopic substitution. The difference in atomic heats at constant pressure can be approximated by the difference at constant volume. Using the Debye frequency distribution and recalling that $(i' - i) = (3/2) \ln m'/m$ and $\theta'/\theta = (m/m')^{1/2}$ ($\theta = h\nu_m/k$, ν_m is Debye limiting frequency, m is the atomic weight, $m > m'$), Lindemann obtained for higher temperatures the expression

$$\ln \frac{P'}{P} = \frac{3}{40}\left(\frac{\theta}{T}\right)^2\left(1 - \frac{m^1}{m}\right) + \ldots \qquad (3)$$

A point of interest is that if the then controversial zero-point energy did not exist, another term, *i.e.*, $-(9/8)(\theta/T)(1 - \sqrt{m'/m})$ should arise in eq 3; it was therefore suggested that experimental investigation of the VPIE could be a powerful tool in settling the question of existence of the zero-point energy. Similar calculations had been carried out by Otto Stern before 1914, but those were not published.[23] In 1931 Keesom and van Dijk,[23] while observing the behavior of neon in a rectifying column just above the triple point, found that ^{20}Ne is more volatile than ^{22}Ne. This was considered to be a proof of the existence of the zero-point energy.

2. Other Early Theories

In 1934 Scott, Brickwedde, Urey, and Wahl[24] formulated a statistical thermodynamic interpretation of the difference between the vapor pressures of solid H_2 and D_2. In the absence of experimental data, they incorrectly assumed that there was no change in the rotational and internal vibrational energies of the molecules on the phase transition from the gas to the solid state. Even so, they were careful to point out that the VPIE can be affected by a change in the energies of rotation and internal vibration on condensation, by the anharmonicity of the vibrations, and by the possible isotope effect on the heat of vaporization of the vibrationless solid to the motionless gas at absolute zero.

In the same year Topley and Eyring[25] obtained an expression for the H–D VPIE of water in a simplified statistical thermodynamic calculation. In the calculation the internal vibrations were described as harmonic oscillators, the shifts on condensation were accounted for, and each liquid phase molecule was assigned three external quasi-oscillations. The authors made various assumptions concerning overall molecular motion (*i.e.*, free rotation, hindered rotation, etc.) and by comparing the calculation with the then available results[26] concluded (erroneously) that rotation is nearly free in liquid water. The measured values of the vapor pressure of ND_3[27] were cited as additional evidence of almost free rotation. In this paper[25] it was also suggested that the inverse isotope effect observed in the CH_3COOH–CH_3COOD system[28] is caused by the hindered motion of the molecules in the liquid phase. Two years later Bailey and Topley[29] attempted to interpret experimental data on the VPIE of the C_6H_6–C_6D_6 system which had been obtained by Ingold, Raisin, and Wilson.[30] The observed effect is inverse ($P > P'$ or $P_D > P_H$) and this was the point of interest. The partition functions employed in the statistical analysis were factored in the usual way into contributions from internal vibration, and hindered translation and rotation in the condensed phase. The shifts in the internal vibrational frequencies on condensation, which are responsible for the inverse isotope effect, could be only approximated because of the lack of experimental data. The authors considered the isotope effects observed on the polarizability and the molar volume of benzene. They suggested that the intermolecular van der Waals forces are not identical for the isotopic molecules, and that this explains why C_6D_6 is more volatile than C_6H_6. In spite of the fact that a precise quantitative description of the experimental data was not possible, this semiquantitative treatment of the VPIE of benzene called attention to several factors which may contribute to the VPIE, such as the zero-point energy shift of internal vibrations on phase change, the isotope effect on polarizability, etc.

3. Herzfeld and Teller

In 1938 Herzfeld and Teller[31] published an important paper on the VPIE. These authors showed that at low temperatures (in the neighborhood of absolute zero) the lighter molecule has a lower heat of evaporation and therefore has the higher vapor pressure. The determining factor in this temperature range is the isotopic zero-point energy differences associated with the external degrees of freedom. In this, the low temperature approximation, the lighter isotope necessarily has the higher energy because it lies higher in the well defined by the attractive potential (Figure 1). At very high temperatures, on the other hand, a classical treatment is justified and there is then no difference between the vapor pressures, but in the intermediate ranges which are commonly encountered care must be taken to properly account for the excitation into higher quantum levels. This is now approached in a number of different ways, but Herzfeld and Teller themselves developed the VPIE in terms of an expansion of the deviation from the classical expression (the method of quantum corrections). Their method is therefore limited to "almost classical" systems and hence may be designated the "high temperature approximation." It was developed by applying the Wigner quantum correction[32] to the Boltzmann distribution, thereby obtaining an expression for the quantum mechanical partition function of the condensed phase in terms of the classical partition function and a correction term. In first order

$$Z = Z_{cl}\left[1 - \frac{\hbar^2}{24(kT)^2}\left\langle \sum_i \frac{1}{m_i}\frac{\partial^2 V}{\partial x_i^2}\right\rangle\right] \qquad (4)$$

where Z and Z_{cl} are the partition function and the classical partition function, respectively, V is the potential energy (a function of all the coordinates, x), and m stands for the masses. The brackets indicate an average over the classical probability distribution in the configuration space. Because of stronger van der Waals forces the quantum correction is generally larger in the condensed phase than in the vapor phase and the difference between the condensed and vapor phase is larger for the lighter isotopic molecules (Figure 1). It follows from this that the lighter isotope exhibits the higher vapor pressure. The inverse isotope effect often observed for molecules with structure can be explained in two ways: first, there may be a shift of the internal frequencies on transition from gas to condensed phase, the frequencies are generally lower in the latter, and this could result in a larger heat of evaporation and a lower vapor pressure for the lighter isotopic molecule. An alternative explanation[29] was expressed in terms of the isotope effect on the van der Waals forces due to the observed small differences in the polarizability and the molal volume of the isotopic molecules.

B. de Boer's Method

1. Quantum Theory of Corresponding States

A semiempirical method of calculation has been developed by de Boer[33-35] in terms of his quantum theory of corresponding states and successfully applied to the calculation of the thermodynamic properties of ^{3}He.[36] In the corresponding states formulation the thermodynamic quantities, temperature (T), volume (V), and pressure (P) are expressed in "reduced units" ϵ/k, $N\sigma^3$, and ϵ/σ^3 derived from the well depth, ϵ, and size parameter, σ, of the spherically symmetric Lennard-Jones (6-12) potential.

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (5)$$

In eq 5, r is the distance between molecular centers. The reduced variables are denoted by an asterisk, $T^* = kT/\epsilon$, $V^* = V/N\sigma^3$, and $P^* = P\sigma^3/\epsilon$. According to the law of corresponding states, the reduced equation of state is a universal relation $P^* = f(V^*,T^*)$. In order to calculate quantum corrections de Boer introduced the parameter $\Lambda^* = \Lambda/\sigma = h/\sigma(m\epsilon)^{1/2}$, where Λ represents the de Broglie wavelength of the relative motion of two particles with intermolecular energy ϵ, and m is the particle mass. The reduced equation of state now may be written $P^* = f(V^*,T^*,\Lambda^*)$, but the exact form of the function, $f(V^*,T^*,\Lambda^*)$, is not generally known. In the application of the theory a semiempirical method was used to calculate the vapor pressures. In this method values of P^* for substances with known vapor pressures were plotted against Λ^* at constant V^* and T^*. The value of P^* for the molecule in question can be found graphically from the known value of Λ^* as exemplified in Figure 2. In this fashion de Boer predicted the vapor pressure and the boiling point of ^{3}He by correlating P^* and Λ^* for the inert gases. The value of the vapor pressures as measured 1 year later, agreed with the prediction within the limits of the experimental error.[37]

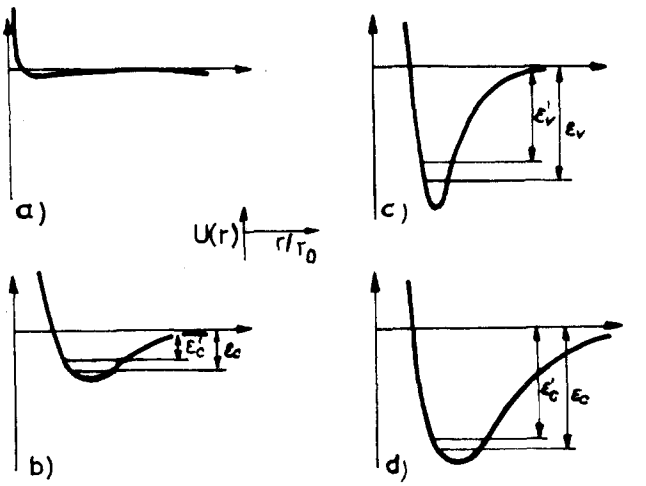

Figure 1. Potential energy diagrams: (a) external translation (gas phase); (b) external translation (condensed phase); (c) internal vibration (gas phase); (d) internal vibration (condensed phase). In (a), r_0 denotes the average intermolecular distance in the gas phase; in (b), r_0 denotes the value of the intermolecular distance evaluated at the minimum; and in (c) and (d), r_0 denotes the value of the coordinate describing the molecular distortion evaluated at the minimum. Notice for the external motions the zero point energy change on condensation, $(E_c' - E_c) - (E_v' - E_v) > 0$, because $E_v' \simeq E_v \simeq = 0$, but for the internal motions it may be positive, negative, or zero depending on the effect of the intermolecular forces on the specific motion under consideration.

2. Hydrogen Isotopes

While the application of the de Boer method to inert gases yields good results, the results obtained for the hydrogen isotopes are in serious disagreement with the experimental data (see, *e.g.*, the values predicted by Hammel[38] for D_2 and T_2 as compared with the experimental data[39,40]). The reason[40] is attributed to the fact that the intermolecular potential of hydrogen isotopes is orientation dependent, that of the inert gases is not, and therefore a direct comparison is not possible. If one assumes that the orientation effects are the same for all the isotopic forms of a molecule, it follows[40] that the properties of the isotopic molecules can vary only with molecular mass. In this case, plots of the boiling points, triple points, and critical constants of the isotopic hydrogens against $1/M^{1/2}$ should yield straight lines. For example, the vapor pressures of HT and D_2 molecules are predicted as equal. This prediction was in agreement with the early data of Libby and Barter.[41] More recent experiments, however, show that the vapor pressure of HT is definitely greater than that of

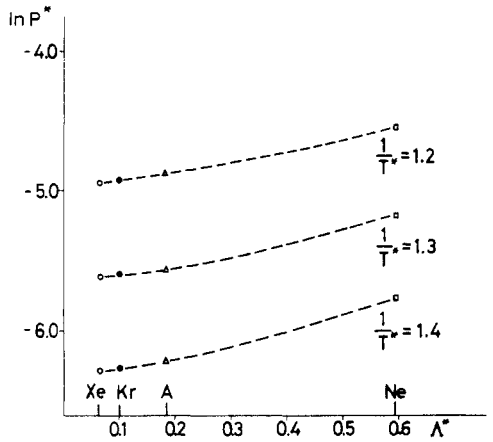

Figure 2. The reduced vapor pressure (P^*) as a function of the parameter Λ^* for monatomic substances.

D_2[42,43] and suggest that any theory of VPIE must take molecular structure into account as well as molecular weight.

C. Translational–Rotational Coupling: Hydrogen Continued

1. Perturbation Calculations

Belgian workers beginning around 1959[44,45] considered that the deviations from the theory of corresponding states for the hydrogen isotopes might be due either to a slight change of the intermolecular forces with isotopic substitution (*vide infra*) or to quantum rotational corrections. The rotational correction itself varies as the moment of inertia so that if one considers two isotopic molecules, A and B ($I_A < I_B$, but $M_A = M_B$), the vapor pressure of A will be found higher than B. An additional correction to those molecules where the center of mass does not coincide with the geometric center (for example HD and HT) is necessary. These molecules show a rotational–translational coupling which is not found in homonuclear molecules where the two centers coincide. This effect, which cannot appear in a classical calculation, was treated *via* a perturbation method by Babloyantz.[45] She demonstrated that it is the predominant effect for the isotopic hydrogens.

In the calculations the author considered a system of N mutually interacting diatomic molecules. Let A and B be two isotopic molecules with equal molecular masses. A is homonuclear and B heteronuclear (*e.g.*, A = D_2, B = HT). It is assumed that the intermolecular potential is the same for an A pair as for a B pair. The potential may be expressed in terms of the distance between the geometric centers ("centers of interaction") and two angles which express the relative orientation of the molecules. In this system the H_ith term of the Hamiltonian ($\mathcal{H} = \sum_{i=1}^{N} H_i + V$) can be written

$$H_i = H_i^0 + \alpha H_i^{(1)} + \alpha^2 H_i^{(2)} \qquad (6)$$

where V is the potential energy, $\alpha = (d/2)[(M_1 - M_2)/(M_1 + M_2)]$ (d is the intermolecular distance and M_1, M_2 are atomic masses), and $\alpha H_i^{(1)}$ and $\alpha^2 H_i^{(2)}$ are taken to be the perturbation terms. $H^{(1)}$ and $H^{(2)}$ are of complicated algebraic form. The unperturbed problem with $H^0 = \sum_i H_i^0 + V^0$ (V^0 is angle independent) corresponds to homonuclear molecules, in this case $\alpha = 0$.

The perturbation calculation showed in a quite general way that the lowest energy level of an assembly of heteronuclear molecules is higher than that of an assembly of homonuclear molecules. The application to hydrogen was carried out using both a smoothed potential cell model and an harmonic oscillator cell model, and assuming that near the absolute zero the VPIE can be written as

$$\ln \frac{P_A}{P_B} = \frac{e_A - e_B}{T} \qquad (7)$$

where $e_A - e_B$ is the difference between the energies of vaporization of the two isotopes. The values deduced for the ratio P_{HT}/P_{D_2} are in qualitative agreement with experiment.

Bigeleisen[46,47] carried out calculations of partition function ratios for isotopic liquid hydrogens under the assumption of free rotation in the liquid. He found a discrepancy between the results and the Babloyantz calculation of the absolute zero-point energy difference between HT and D_2. He points out that Babloyantz neglected significant entropy effects. It can also be shown that there is a large anharmonic correction to the thermodynamic properties of condensed hydrogen. The interaction between rotational and translational motions was also discussed in detail by Wolfsberg.[48] Meckstroth and White[49] recently applied the approach of Babloyantz in a calculation on σ–ρ D_2 liquid and solids. Byrns and Mazo[50] and earlier Prigogine[51,52] treated H_2–D_2 solutions, especially in regard to nonideality.

Simple model calculations cannot be expected to give quantitative descriptions of experimental results. Nevertheless those described above show that for heteronuclear molecules the fact that the center of force does not coincide with the center of gravity leads to a perturbation of the translational energy states and to an increase in the lattice zero-point energy as compared with that of the homonuclear molecule. This appears to be a sound qualitative explanation of the experimental results.

2. Friedmann's Approach, 1962

An expression for the partition function of a system of interacting rigid linear rotators was derived by Friedmann[53] in the approximation of small quantum corrections. He assumed that the interaction potential of the system depends only on the positions of the centers of interaction of the N molecules (the "centers of interaction" are taken as the centers of electrical charge in the molecule) which in the case of a heteronuclear diatomic molecule does not coincide with the center of mass. The two centers can be related. For a diatomic one obtains

$$a = \left| \frac{R}{2} \frac{m_h - m_1}{M} - d \right| \qquad (8)$$

where a is the distance between the center of interaction and the center of mass, $(R/2)[(m_h - m_1)/M]$ is the distance between the midpoint of the molecule and its center of mass, R is the internuclear distance, m_h is the mass of the heavier and m_1 that of the lighter atom, d is the distance between the midpoint of a molecule and its center of interaction, and M is the molecular mass. If the atoms of the diatomic molecule belong to the same element (*e.g.*, HT, D_2), d is zero and then $a = (R/2)[(m_h - m_1)/M]$.

By standard methods Friedmann obtained an expression for the configurational part of the partition function, Q_N

$$Q_N = Q_{NCl}\left[1 - \frac{\beta^3 \hbar^2 N}{24 M_{eff}} \langle F^2 \rangle\right] \qquad (9)$$

where Q_{NCl} is the classical configuration integral, $\langle F^2 \rangle$ is the mean square force exerted on one molecule by all others, and

$$\frac{1}{M_{eff}} = \frac{1}{M}\left(1 + \frac{2}{3}\frac{Ma^2}{I}\right) \qquad (10)$$

Equation 9 is identical with that obtained for atoms[31] except that the total mass M has been replaced by an "effective mass" which takes the distribution of the total molecular

mass over the constituent atoms of the molecule into account. If the condensed and vapor phases are in equilibrium, the free energy per molecule is the same in both phases, so the VPIE can be expressed

$$\ln\frac{P_1}{P_2} = \frac{\beta^3\hbar^2}{24}\langle F^2\rangle\left[\frac{1}{(M_{\text{eff}})_1} - \frac{1}{(M_{\text{eff}})_2}\right] \qquad (11)$$

If $a = 0$ then $(M_{\text{eff}})_1 = M_1$ and $(M_{\text{eff}})_2 = M_2$, and eq 11 transforms to the equation derived by Landau and Lifshits.[54]

With the use of eq 11, the relative vapor pressures of three isotopic molecules may be expressed as

$$R = \frac{\ln\frac{P_2}{P_3}}{\ln\frac{P_1}{P_3}} = \frac{\frac{1}{(M_{\text{eff}})_2} - \frac{1}{(M_{\text{eff}})_3}}{\frac{1}{(M_{\text{eff}})_1} - \frac{1}{(M_{\text{eff}})_3}} \qquad (12)$$

R is independent of the temperature. For the isotopic nitrogens $(\ln P_{^{14}N^{15}N}/P_{^{15}N_2})/(\ln P_{^{14}N_2}/P_{^{15}N_2}) = 0.494 \pm 0.002$ as measured in the liquid phase between 64 and 77°K.[55,56] The theoretical value is 0.495. For the N_2 molecule d was taken as zero. This is not the case for CO where d was found to be about 0.1 Å toward the carbon atom.[57]

The prediction that R be independent of temperature is supported by the available experimental VPIE data for CO[58] and NO.[59] The model is not applicable to the liquid hydrogen because it does not satisfy the conditions under which the first quantum correction is applicable.[46,60] Later this theory was generalized[61] to the case of nonlinear molecules, but no actual calculations of VPIE have been yet carried out for such complicated molecules. Gordon[57] has described a refined approach to this kind of model and applied it in an analysis of the data for CO (section II.G.3).

D. More Complicated Molecules: Isotope Effects on van der Waals Forces and the VPIE

The material discussed in sections II.B and II.C has focused on the correlation between the VPIE and the difference in the mean square forces and torques on the molecule in the two phases. In an alternate terminology we would say that it has concentrated on the translational and rotational contributions to the partition function. In a complete analysis it is clear that we must also consider the effect of the intermolecular forces on the other motions characterizing the molecule (*i.e.*, on the internal modes). In complicated molecules these later effects can predominate and can even lead to inverse isotope effects. The effects which the intermolecular or van der Waals forces have on the internal motions of the molecule, and consequently on the vapor pressure and the VPIE, have been variously described in terms of vibrational isotope effects, intermolecular force isotope effects, etc. Each of these approaches will be discussed below and the equivalence of the two points of view demonstrated.

1. Baertschi and Kuhn

Baertschi and Kuhn advanced an explanation of their studies of heavy atom isotope effects.[62-64] They observed that the substitution of ^{13}C for ^{12}C in the molecules $CHCl_3$, CCl_4, CH_3OH, and C_6H_6 increased the volatility (inverse isotope effect), whereas the substitution of ^{37}Cl for ^{35}Cl in $CHCl_3$ and CCl_4, and of ^{18}O for ^{16}O in methanol, decreased the vapor pressure. The normal effect could be easily rationalized in terms of the zero-point energies of the molecules vibrating as a whole in the solid or liquid lattice; if the van der Waals attraction and the molecular size were the same for both species, then the vibration frequency of the lighter isotope would be higher, thus leading to a normal effect. However, to understand the inverse isotope effect (*i.e.*, $^{13}CCl_4 > {}^{12}CCl_4$), it is necessary to also consider the effect of dispersion forces on the internal vibrational modes. The theory can be formulated by considering two molecules, 1 and 2, at a distance d from each other. The dispersion interaction between them is given according to London, as

$$E = -\frac{3}{2}\frac{h}{d^6}\sum_{i,k}\alpha_{1,i}\alpha_{2,k}\frac{\nu_{1,i}\nu_{2,k}}{\nu_{1,i}+\nu_{2,k}} \qquad (13)$$

where $\nu_{1,i}$ and $\nu_{2,k}$ are the frequencies of the various absorption bands and $\alpha_{1,i}$ and $\alpha_{2,k}$ are the corresponding polarizability components of the molecules 1 and 2. The authors assumed that the absorption frequencies in the visible and ultraviolet regions and the corresponding polarizabilities were the same for both isotopic species. Even so, the contribution from infrared frequencies, which must be also taken into account if the isotopically labeled atoms take part in the corresponding vibrations, is generally smaller for the heavy isotope. Therefore, they conclude that the van der Waals dispersion force is weaker for it. (The infrared polarizabilities are assumed to be isotope independent.) The contribution to the VPIE from this "infrared effect" $((\ln P'/P)_{IR})$ could be approximately predicted and the results of some such calculations are shown in Table I. Bradley[65] had earlier discussed certain aspects of this kind of approach, but not in specific terms.

2. Wolfsberg, 1963

Several years later Wolfsberg,[48] in an excellent paper, reinvestigated the problem of the isotope effect on the dispersion interaction. He employed second-order perturbation theory and arrived at an expression like that of Baertschi and Kuhn by a different route. In terms of the Born–Oppenheimer approximation the electronic energy of the interacting system may be calculated in order to find the potential energy surface on which the nuclear motions (vibrations) take place. Force constants can be evaluated from the second derivatives of the potential differentiated with respect to the various nuclear displacements. The perturbation expansion demonstrated that the description of the VPIE in terms of an isotope effect on the van der Waals interaction forces is equivalent to the description in terms of a change in the vibrational energy of the molecules in the condensed phase as compared to the gas. This is to say that it may be described in terms of perturbations (on phase change) in a set of isotope independent vibrational force constants. The result is an important one. It enables the construction of a methodology to correlate VPIE measurements with spectroscopic frequency shift data (*vide infra*). The intramolecular modes generally red-shift on condensation owing to the dispersion forces, and this contributes in the direction of an inverse isotope effect. Gordon[57] and Whalley[66-68] have also discussed the equivalence of these alternate points of view.

E. Calculations on Molecules with Structure: Various Approaches Since 1950

1. Johns, 1958

In calculating the VPIE of isotopic CO and methane molecules, Johns[58] started from the integrated form of the Clausius–Clapeyron equation and applied the following common assumptions:[22,69] (1) the difference between the specific heats of different isotopic species is the same at constant pressure as at constant volume; (2) the specific heat in the solid state can be represented by a Debye-type function; (3) the vibrational frequencies of the isotopic species, and hence their characteristic Debye temperatures, are inversely proportional to the square roots of their masses; (4) the potential energies of the different isotopic species are identical. In the case of polyatomic molecules Johns postulated in addition

TABLE I. "Infrared Contributions" to the VPIE and Their Comparison with Experimental Results

Substance	Ln $(P'/P)_{IR}$[63,64]	Ln $(P'/P)_{IR}$[48]	Ln $(P'/P)_{exptl}$	Ref
$^{10}BF_3$–$^{11}BF_3$	-1.2×10^{-2}		-0.8×10^{-2}	228, 232
$^{10}BCl_3$–$^{11}BCl_3$	-6×10^{-3}		-3×10^{-3}	235
C_6H_6–C_6D_6	-3.5×10^{-2}		-2.4×10^{-2}	323
$^{12}C_6H_6$–$^{13}C_6H_6$	-3×10^{-3}		-1.8×10^{-3}	64
$^{12}CS_2$–$^{13}CS_2$	-1.6×10^{-3}		-1×10^{-3}	64, 246
$^{12}CCl_4$–$^{13}CCl_4$	-2.7×10^{-3}	-2.1×10^{-3} -2.5×10^{-3}	-2.03×10^{-3}	64
$C^{35}Cl_4$–$C^{37}Cl_4$	$\sim -4 \times 10^{-5}$	-3×10^{-5} -7×10^{-6}	$\sim +10^{-4}$	64

TABLE II. Comparison of Values for the VPIE Calculated by Devyatykh[70] (Eq 15) with Experiment

System	Temp of triple point, °C	Ln (P'/P) Calcd	Ln (P'/P) Exptl	Ref
$^{12}CH_4$–$^{13}CH_4$	90.7	0.0072	0.0059	58
CH_4–CD_4	90.7	−0.0042	−0.0129	262
$H_2{}^{16}O$–$H_2{}^{18}O$	273.16	0.012	0.0116	75
H_2O–D_2O	273.16	0.166	0.241	75
^{12}CO–^{13}CO	68.1	0.012	0.011	58
$C^{16}O$–$C^{18}O$	68.1	0.016	0.009	58
NH_3–ND_3	195.4	0.237	0.285	193
NH_3–NT_3	195.4	0.296	0.569	72[a]

[a] There are no experimental data available. The value for P_{NH_3}/P_{NT_3} was obtained by using the relationship $(P_{NH_3}P_{NT_3})^{1/2} = P_{ND_3}$.

that the heat capacity is the sum of Debye and Einstein terms, and that the rotational frequencies, hence the characteristic Einstein temperatures, are inversely proportional to the square roots of the moments of inertia of the molecules. With these assumptions he obtained the expression

$$\ln\frac{P'}{P} = -\frac{E'-E}{RT} + \frac{1}{T^2}\left\{\frac{3}{40}\theta_D'^2\left(1-\frac{M'}{M}\right) + \sum_{n_E}\frac{1}{24}\theta_E'^2\left(1-\frac{I'}{I}\right)\right\} \quad (14)$$

where E is the binding energy of the molecules, θ_D is characteristic Debye temperature, n_E is the number of possible rotational and torsional degrees of freedom, θ_E is the corresponding characteristic Einstein temperature, and M and I are the masses and moments of inertia of molecules, respectively. In the calculation $E' = E$ was assumed. The predicted values, ln P'/P, were too low for the α-solid form of the $^{12}C^{16}O$–$^{13}C^{16}O$ system, too high for $^{12}C^{16}O$–$^{12}C^{18}O$, and again low for $^{12}CH_4$–$^{13}CH_4$.

2. Devyatykh

Devyatykh[70] derived an equation for the VPIE of crystalline materials. He expressed the chemical potentials in terms corresponding to various degrees of freedom in the vapor and solid phases. After introducing approximations, he obtained

$$\ln\frac{P'}{P} = \frac{3}{2}\ln\frac{M'}{M} + \frac{9}{8}\frac{\theta'-\theta}{T} - \left[F\left(\frac{\theta'}{T}\right) - F\left(\frac{\theta}{T}\right)\right] + \ln\left(\frac{A'B'C'}{ABC}\right)^{1/2} + \frac{\mu_R{}' - \mu_R}{RT} - \frac{h}{2kT}\sum(\Delta\nu_i' - \Delta\nu_i) \quad (15)$$

M is the molecular mass, θ is the characteristic Debye temperature, F is the Debye function for free energy, A, B, and C are principal moments of inertia, μ_R is the chemical potential corresponding to the rotation or libration of the molecule in the solid phase, and $\Delta\nu_i$ is the frequency shift of the ith vibration on condensation. The predictions for the VPIE of CH_4, H_2O, CO, and NH_3[70–72] obtained by eq 15 are shown in Table II along with the corresponding experimental data.

3. Rabinovich, 1962

An interpretation of the VPIE was suggested by Rabinovich[2,17] which qualitatively explains some experimental results. By equating the free energy of the liquid and the vapor he obtained

$$\ln\frac{P'}{P} = \frac{1}{RT}[(E_0' - E_0) - (U_d' - U_d) - (U_0' - U_0) - (U_p' - U_p) - (U'_{ass} - U_{ass})] + \frac{1}{R}[(S^{\circ\prime} - S^\circ)_v - (S^{\circ\prime} - S^\circ)_l] \quad (16)$$

where E_0 is the zero-point energy of the quasi-oscillations of the molecules in the liquid phase, U_d, U_o, U_p, and U_{ass} are the dispersion, orientation, polarization, and association energies, respectively, and S° is the entropy at $P = 1$. The effect on the VPIE of each term in eq 16 was thoroughly discussed. Equation 16 is not suitable for the quantitative description of the temperature dependence of the VPIE, although calculations for the system CH_3OD–CH_3OH and H_2O–D_2O[73] at 25° have been carried out with results which are in reasonable agreement with the measured values: CH_3OH–CH_3OD: ln $(P'/P)_{obsd} = 0.0573$,[74] ln $(P'/P)_{calcd} = 0.0672$. H_2O–D_2O: ln $(P'/P)_{obsd} = 0.1450$,[75] ln $(P'/P)_{calcd} = 0.113$.

4. Kiss, Matus, and Opauszky

Kiss, Matus and Opauszky[76] compared the VPIE of compounds subject to isotopic substitutions of the same nature (*e.g.*, CH_3–/CD_3–) as a function of the reduced temperature. At a given reduced temperature they empirically correlated the VPIE's with the reciprocal square root of the molecular weight. Since this type of comparison does not have any sound theoretical basis, it is difficult to interpret the rules inferred from the observations.

F. Bigeleisen's Theory, 1961

1. Formulation of the VPIE Equation[77]

In 1961 the previous theoretical work on the VPIE was briefly reviewed by Bigeleisen, and in that same paper he formulated a new approach in terms of the reduced partition function ratios[78] (RPFR) of condensed and ideal gas-phase molecules. In the condensed phase the Gibbs free energy (G_c) is given as

$$G_c = -kT\ln Q + PV \quad (17)$$

where Q is the partition function for an assembly of N molecules. By defining an average molecular partition function ($\bar{Q}$) of the form

$$\bar{Q} = Q^{1/N} \quad (18)$$

the condensed phase free energy can be written as

TABLE III. Values of the Correction Terms to the VPIE (Eq 25) for Some Selected Systems

System	Temp, °C	P', Torr	Ln P'/P	$B_0(P'-P)+\frac{1}{2}C_0(P'^2-P^2)+\ldots$	$(1/RT)\cdot(P'V'-PV)$	$(1/RT)\int_v^{v'}P'dV$	Ref
				Per cent correction			
CD_4-CH_4	−175	209	−0.0202		0.05		316
	−161	781	−0.0287	~1	0.3		
C_6D_6-C_6H_6	20	74.9	−0.0274	<1	0.03	0.03	323
	70	553	−0.0249	3	0.2	0.02	
	160	5580	−0.0174	13	2.5	0.3	
C_6D_{12}-C_6H_{12}	20	77.0	−0.0874	<1	0.05	0.001	323
	60	390.0	−0.0727	2	0.2	0.002	
p-$C_6H_4DCH_3$-$C_6H_5CH_3$	20	12.38	−0.0081	<1	0.01	0.003	323
	70	204.0	−0.0058	2	0.2	0.06	
	145	1880	−0.0029	8	0.3	0.07	
C_2H_5OD-C_2H_5OH	51	224	0.0383	2	0.06	0.003	74
	120	3220	0.0045	12	<0.5		
D_2S-H_2S	−78	284.2	0.0153	0.9	0.06	0.02	409
	3	17 atm	−0.0143	16	5.3	1.3	

$$G_c = -RT \ln \bar{Q} + PV \quad (19)$$

Introducing the virial expression to describe the equation of state for the gas

$$PV = RT(1 + B_0P + C_0P^2 + \ldots) \quad (20)$$

(B_0 and C_0 are gas phase virial coefficients), the Gibbs free energy (G_v) for the real gas is

$$G_v/RT = \ln P + \frac{3}{2}\ln M + \frac{5}{2}\ln T - \ln Q_{int} + \left(B_0P + \frac{1}{2}C_0P^2\right) + K_{ST} \quad (21)$$

M is the molecular weight, Q_{int} comprises the rotational and vibrational partition functions, K_{ST} is the Sackur-Tetrode constant. From the equilibrium condition, $G_c = G_v$, it follows that

$$\ln P = \ln\frac{Q_{int}M^{3/2}}{\bar{Q}} + \frac{PV}{RT} + \frac{5}{2}\ln T - \left(K_{ST} + B_0P + \frac{1}{2}C_0P^2\right) \quad (22)$$

and the vapor pressure ratio for a pair of isotopic molecules (P and P') at the temperature T is

$$\ln\frac{P'}{P} = \ln\frac{Q_{int}M'^{3/2}\bar{Q}}{Q_{int}M^{3/2}\bar{Q}'} + (RT)^{-1}(P'V' - PV) - \left(B_0P + \frac{1}{2}C_0P^2\right)' + \left(B_0P + \frac{1}{2}C_0P^2\right) \quad (23)$$

The primes conventionally refer to the lighter isotope and V and V' refer to the condensed phase molar volumes. Using the reduced partition function ratio for isotopic molecules as defined by Bigeleisen and Mayer[78]

$$\frac{s}{s'}f = \frac{s}{s'}\frac{Q}{Q'}\prod_{i=1}^{n}\left(\frac{m_i'}{m_i}\right)^{3/2} = \left(\frac{Q}{Q'}\right)_{qm}\Big/\left(\frac{Q}{Q'}\right)_{cl} \quad (24)$$

(the product runs over the n atoms in the molecule, m_i is the mass of the ith atom, qm and cl denote the quantum mechanical and classical partition functions). Comparing the two isotopic systems at the same molal volume, eq 23 becomes

$$\ln\frac{P'}{P} = \left(\ln\frac{s}{s'}f_c - \ln\frac{s}{s'}f_g\right) + (RT)^{-1}(P'V' - PV) - \left(B_0P + \frac{1}{2}C_0P^2\right)' + \left(B_0P + \frac{1}{2}C_0P^2\right) - (RT)^{-1}\int_v^{v'}P'\,dV \quad (25)$$

2. Relationship between P'/P, α, and the RPFR

The first term in eq 25, $\ln(s/s')f_c - \ln(s/s')f_g$, represents the differences in quantum effects for the condensed and gaseous states. The correction terms $(RT)^{-1}(P'V' - PV)$ and $(B_0P + \frac{1}{2}C_0P^2)' - (B_0P + \frac{1}{2}C_0P^2)$ account for the effect on the VPIE from the difference between the Helmholtz and Gibbs free energies of the condensed phase, and from the gas imperfection. The $(RT)^{-1}\int_v^{v'}P'dV$ term arises from the difference in the condensed phase molar volumes of the isotopic molecules. Values of these correction terms for some isotopic systems are shown in Table III.

For most calculations eq 25 can be simplified if $\ln P'/P$ is small, *i.e.*, $\ln(P'/P) \simeq (P' - P)/P$. Assuming $B_0' = B_0$, $V' = V$, and neglecting $(RT)^{-1}\int_v^{v'}P'dV$ and terms of order C_0P^2, then

$$\ln\frac{f_c}{f_g} = \ln\frac{P'}{P}\left[1 + P\left(B_0 - \frac{V}{RT}\right)\right] \quad (26)$$

Equations 25 and 26 refer to measurements on separated isotopes. It is also important to develop the relationship between the RPFR and measured separation factors, α, which refer to the single stage isotopic enrichment (on distillation) for a dilute nonideal solution. These relations have also been derived by Bigeleisen.[46] For the case of infinite dilution

$$\ln\alpha = \ln\left(\frac{N'}{N}\right)_{vap}\Big/\left(\frac{N'}{N}\right)_{liq} = \ln\frac{f_c}{f_g} - \frac{(V' - V)^2}{2\beta'V'RT} \quad (27)$$

β is the isothermal compressibility and V is the molal volume of the condensed phase. The second term is generally quite small and is often neglected, thus accounting for the common idea that RPFR's are directly measured in distillation experiments. Quite recently the isotope effect on the molar volume of the gas has also been considered, and an expression somewhat different from eq 27 was obtained.[79]

The point of concern in this section has been to indicate that either separated isotope data or data on single or multistage fractionation can be used to obtain experimental values of RPFR's. In either case, at low to moderate pressure, the corrections to the raw data are small and readily evaluated.

3. Calculations of the RPFR

a. The Stern-Van Hook-Wolfsberg Model[48,80]

In 1963 these authors presented a methodology for the calculation of the VPIE from input data which includes com-

plete force fields for the gaseous and condensed phases. The force fields may be obtained from spectroscopic measurements in the two phases. The calculations are presented in the harmonic approximation although a generalization to anharmonic force fields would appear to be possible. In the gas phase the partition functions for translation and rotation are evaluated in the classical approximation and no vibrational–rotational interaction is assumed. The RPFR for the gas phase is then

$$\frac{s}{s'}f_g = \frac{Q_{\text{vibrqm}}}{Q'_{\text{vibrqm}}} \Big/ \frac{Q_{\text{vibrcl}}}{Q'_{\text{vibrcl}}} = \prod_{i=1}^{3n-6} \frac{u_i}{u_i'} \frac{\exp(-u_i/2)/(1-\exp(-u_i))}{\exp(-u_i'/2)/(1-\exp(-u_i'))} \quad (28)$$

where Q_{vibrqm} is the quantum mechanical vibration partition function

$$Q_{\text{vibrqm}} = \prod_{i=1}^{3n-6} \frac{\exp(-u_i/2)}{1-\exp(-u_i)} \quad (29)$$

Q_{vibrcl} is the classical vibration partition function

$$Q_{\text{vibrcl}} = \prod_{i=1}^{3n-6} \frac{1}{u_i} \quad (30)$$

and $u_i = hc\nu_i/kT$, ν_i is the ith normal mode harmonic frequency in cm^{-1}. At low rotational temperatures a correction for nonclassical rotation may be necessary. Formulas for this purpose for different rotor types have been summarized.[81]

In order to evaluate f_c the authors chose a simplified cell model which assumed an average condensed phase molecule with $3n$ degrees of freedom. The $3n - 6$ vibrational modes were treated in a fashion analogous to that used in the gas phase, and the remaining six external degrees of freedom corresponding to gas phase translations and rotations were assumed to be subject to harmonic restoring force. Then eq 31 and 32 apply.

$$\frac{s}{s'}f_c = \prod_{i=1}^{3n} \left[\frac{u_i}{u_i'} \frac{\exp(-u_i/2)/(1-\exp(-u_i))}{\exp(-u_i'/2)/(1-\exp(-u_i'))} \right] \quad (31)$$

$$\frac{f_c}{f_g} = \prod_{\text{int freq}}^{3n-6} \left[\frac{(u_i/u_i')_c}{(u_i/u_i')_g} \frac{\exp((u_i'-u_i)_c/2)}{\exp((u_i'-u_i)_g/2)} \right] \times \left[\frac{(1-\exp(-u_i')_c/(1-\exp(-u_i)_c)}{(1-\exp(-u_i')_g)/(1-\exp(-u_i)_g)} \right] \prod_{\text{ext}}^{6} \frac{u}{u'} \times \left[\exp\left(\frac{u'-u}{2}\right) \right] \left[\frac{1-\exp(-u')}{1-\exp(-u)} \right] \quad (32)$$

b. Computer Calculations

In order to evaluate f_c/f_g in the framework of the SVHW model $3n - 6$ gas and $3n$ condensed phase frequencies are required. The authors particularly caution against the procedure of selecting experimental gas and liquid frequencies for the different isotopes to substitute directly into eq 32. This is because the accumulated experimental error on the frequencies is such that it may result in an unreasonably large error on the predicted value for the VPIE's. Rather it is suggested that to minimize error in the calculated RPFR's, one should first construct a common, best fit force field (F matrix) for each phase. This force field should reproduce the spectroscopic frequencies to within experimental error as a minimum requirement. It is taken as isotope independent (*vide infra*) and used to compute a consistent set of frequencies for the different isotopic isomers in the different phases. These frequencies are then substituted into eq 32.

The details of the calculational problem are described in terms of F and G matrices.[82] In eq 33 V and T are the potential energy and kinetic energy, respectively; s_i and p_i stand for internal coordinates and conjugate momenta. The f_{ij} are force constants (the elements of the isotope independent F matrix) and the g_{ij} are the elements of the isotope dependent Wilson G matrix. The isotope dependence of the normal frequencies arises through the isotope dependence of the G matrix which can be calculated from the geometry of the molecule and the atomic masses.

$$2V = \sum f_{ij}s_is_j \qquad 2T = \sum g_{ij}p_ip_j \quad (33)$$

The frequencies are obtained by solving the eigenvalue problem for the FG matrix.[82] Note that in general both the F and the G matrices contain terms coupling internal with external, as well as internal with internal and external with external modes. These depend on the symmetry of the specific molecule as well as its mass, moment of inertia, etc. The inclusion of these terms form the mechanism by which rotational–vibrational, rotational–translational, etc., coupling effects are incorporated into the problem.

A problem arises in the condensed phase when one proceeds in normal fashion to describe the potential energy in terms of $3n - 6$ internal and 6 external coordinates. This is because the external coordinates as conventionally defined by the Eckart conditions[82] depend by definition on the isotopic masses. This would result in an artificial mass dependence in the F matrix. The problem was reconciled by suggesting that an external coordinate system based on just one isotopic molecule should be used for all isotopic isomers. Since the same set of coordinates is used throughout, regardless of isotopic substitution, the force constant matrix is mass independent for both internal and external modes. This is a distinguishing feature of the SVHW model.

The actual calculations are conveniently carried out by digital computer techniques. A number of programs have been written to calculate the RPFR[83,84] from a starting point which includes the molecular geometry, atomic masses, and force constants as input data. The machine calculation of isotope effects has become a routine procedure in many laboratories. It is to be emphasized that eq 32 takes explicit account of the details of molecular structure in that the frequencies which enter it must be calculated by a proper dynamical analysis of the molecules.

4. Approximate Methods: The AB Equation[3,77]

a. Derivation

A detailed calculation of the RPFR without the aid of a digital computer is impossibly tedious. It is consequently advantageous to have available an approximate relation for cases when there is not enough input information to define the complete problem, or when a quick albeit inexact result is desired. The approximate equations sometimes have the further advantage that they allow considerably more physical insight into the problem at hand than do the very detailed, but also very complicated, complete calculations.

The most common approximation applied to the VPIE makes use of the fact that very often the $3n$ molecular frequencies happen to fall neatly into two groups; the first group contains the high frequencies, $u_i = hc\nu_i/kT \gg 1$, and may be treated in the low-temperature (zero-point energy) approximation because the excitation factors for these frequencies all approach unity. The second group contains only low frequencies and is treated in the high-temperature approximation. In the derivation one can use the expansion of

ln $(s/s')f$ in even powers of u[85] for the high-temperature group

$$\ln \frac{s}{s'} f = \sum_i \sum_j^{\infty} (-1)^{j+1} \frac{B_{2j-1} \delta u_i^{2j}}{(2j)(2j)!} \quad (u_i' < 2\pi) \quad (34)$$

where $\delta u_i^{2j} = u_i'^{2j} - u_i^{2j}$ and B's are the Bernoulli numbers ($B_1 = 1/6$, $B_3 = 1/30$, $B_5 = 1/42$, etc.). The assumption is often made that the low-frequency group contains the external gas-phase frequencies (assigned zero value) together with corresponding condensed phase values, while the high-frequency group contains only internal modes. By proper reorganization of eq 32 and using only the first term of the Bernoulli expansion, one obtains

$$\ln \frac{f_c}{f_g} = \frac{1}{24}\left(\frac{hc}{kT}\right)^2 \left[\sum^{ext} (\nu_i'^2 - \nu_i^2)\right] - \frac{1}{2}\frac{hc}{kT}\left[\left(\sum^{int} \nu_{ig}' - \sum^{int} \nu_{ic}'\right) - \left(\sum^{int} \nu_{ig} - \sum^{int} \nu_{ic}\right)\right] \quad (35)$$

Thus

$$\ln \frac{P'}{P} \approx \ln \frac{f_c}{f_g} = \frac{A}{T^2} - \frac{B}{T} \quad (36)$$

with

$$A = \frac{1}{24}\left(\frac{hc}{k}\right)^2 \left[\sum^{ext} (\nu_i'^2 - \nu_i^2)\right] \quad (37)$$

$$B = \frac{1}{2}\frac{hc}{k}\left[\left(\sum^{int} \nu_{ig}' - \sum^{int} \nu_{ic}'\right) - \left(\sum^{int} \nu_{ig} - \sum^{int} \nu_{ic}\right)\right] \quad (38)$$

The A term is associated with the first-order quantum correction for the external modes (see eq 4 and ref 32); the hindered translations may be taken as the average Debye frequency (if the Debye ν_{max} frequency is used, the coefficient $1/24$ will be replaced by $1/30$) and the librational frequencies assume an Einstein distribution. The A term is always positive and predicts a normal VPIE. The B term is the contribution due to the changes in zero-point energies of the large internal frequencies on condensation. An increase in force constants for the internal degrees of freedom on condensation will lead in the direction of a normal isotope effect, while a decrease will tend to an inverse isotope effect. Notice that the A and B terms display different temperature dependencies. At low enough temperatures the A/T^2 term must predominate and the *IE* will be normal and fall off proportional to T^{-2}. At intermediate temperatures the B term, which may be positive, negative, or zero, can dominate and account for a crossover to an inverse isotope effect. As the temperature is raised further the contribution of both terms dies out and ln (RPFR) approaches zero as T^{-2}. It can be shown that[77]

$$\ln \frac{P'}{P} \cong \frac{1}{24N}\left(\frac{\hbar}{kT}\right)^2 \sum_{i=1}^{3nN}\left(\frac{1}{m_i'} - \frac{1}{m_i}\right)(a_{ii} - b_{ii}) + O\left(\frac{h^4}{T^4}\right) \quad (39)$$

where a_{ii} and b_{ii} are the Cartesian force constants for the ith atom in the condensed and gaseous phases, respectively. This equation is valid if $u_i'_{max} < 2\pi$ and leads to the rule of the geometric mean[86] in the vapor pressure. The validity of eq 39 can be extended to lower temperatures by applying various series expansions which are not subject to the above convergence restriction. Such approaches have been treated in considerable detail by Bigeleisen and coworkers,[87-90] Jancso and coworkers,[91] and Vojta.[92]

It is to be noted that temperature dependencies predicted by eq 32 or 36 are made with the assumption of temperature-independent force constants. In actual liquids we expect small temperature dependencies in the effective force constants because of anharmonicities, lattice expansion, etc. Also there is a distinct possibility of more complicated temperature dependencies within the context of eq 32 (for example, multiple crossovers, apparent temperature independence over broad ranges, etc.). These and related points have been discussed in detail by Stern, Spindel, and Monse.[93,94]

b. Application to Rare Gases

In the case of rare gases the only degrees of freedom are translational, and the RPFR can be written[77]

$$\ln f_c = \sum_{j=1}^{\infty} (-1)^{j+1} \frac{3B_{2j-1}}{2j(2j)!}\left(\frac{h}{kT}\right)^2 \left[1 - \left(\frac{m'}{m}\right)^j\right] \mu_{2j}' \quad (40)$$

where μ_{2j}' is the $2j$th moment of the frequency distribution. For the Debye distribution

$$\mu_{2j}' = \frac{3(k\theta_D'/h)^{2j}}{2j+3} \quad (41)$$

θ_D' is the Debye characteristic temperature. The value of θ_D' or μ_{2j}' can also be determined from the heat capacity measurement of such systems, and the two methods should give the same value for θ_D' or μ_{2j}'.

c. Anharmonicity

Although our discussion to now has been in terms of the harmonic approximation, we must indicate that real frequencies should be described as slightly anharmonic oscillators, commonly approximated with an effective harmonic force field. For the low lattice frequencies, in particular, anharmonicity must be important and can arise from two causes: first, from the anharmonic curvature in the potential and, second, as a result of the expansion of the lattice on warming (see also section II.G.1.a.ii.). The internal phase frequency shifts in the liquid must also be density (and thus temperature) dependent. In first approximation, the contribution of all these effects is often lumped together by introducing a temperature independent constant into eq 36

$$\ln \frac{P'}{P} \approx \ln \frac{f_c}{f_g} = \frac{A}{T^2} - \frac{B}{T} + C \quad (42)$$

Alternatively the effect can be treated in the context of equations of the type eq 32 by introducing the temperature dependency into the effective force constants.

Although few, if any, detailed calculations of the VPIE have been made using detailed anharmonic partition functions, it is to be hoped that some will soon be attempted. Such calculations have been reported for a number of important isotopic exchange vapor phase equilibria.[95,96] Wolfsberg[97,98] and Hulston[99] have recently cleared up an apparent difficulty in the application of the anharmonic theory to the calculation of isotope effects. It was associated with a (previously neglected) isotope-dependent but term-independent factor, G_0, which appears in the expression for the energy of the anharmonic oscillator as developed through perturbation theory. The failure to include G_0 in early anharmonic calculations led to rather large calculational errors. Fortunately the proper calculation gives results which are in good agreement with those found *via* the harmonic approximation, at least for those systems which have been investigated. The result is comforting because almost all calculations in every field of isotope effects have customarily employed the harmonic approximation.

G. Other Recent Approaches

1. *Monatomic Solids in the High-Temperature Approximation*

a. Boato and Coworkers[19,100,101]

Boato and coworkers started from the Mayer and Band reformulation[102] of Wigner's theorem[32] on the quantum correction for thermodynamic equilibrium which is expressed in terms of a power series in $(\hbar/kT)^{2j}$ and obtained an expression similar to eq 39.

$$\ln \alpha = \ln \left(\frac{N'}{N}\right)_A \Big/ \ln \left(\frac{N'}{N}\right)_B = \frac{\hbar^2}{24k^2T^2}\left[\frac{1}{m'} - \frac{1}{m}\right](\langle \nabla^2 \boldsymbol{U}\rangle_B - \langle \nabla^2 \boldsymbol{U}\rangle_A) \quad (43)$$

The subscripts A and B refer to the different phases, and $\langle \nabla^2 \boldsymbol{U}\rangle$ is the force constant averaged over classical configuration space, the mean value of the Laplacian of the intermolecular potential.

When considering solid–vapor equilibria, $\langle \nabla^2 \boldsymbol{U}\rangle$ is nearly zero in the vapor, and practically independent of temperature in the solid. Therefore, in a first approximation ln α depends linearly on T^{-2}; however, a careful analysis of experimental results shows a small deviation and demonstrates that a corrective negative term proportional to $1/T$ must be added. The necessity of the correction term was also shown theoretically.

b. Anharmonicity

The anharmonic Einstein model introduced by Henkel[103] has been used by Johns[104] and Casanova, Fieschi, and Terzi[105] to evaluate the vapor pressure ratio for the common isotopes of neon and argon. These calculations demonstrated that for specific models anharmonic effects may be appreciable. Klein[106] later elaborated and showed that if one writes the crystal potential energy in expanded form

$$U = U_0 + \phi_2 + \phi_3 + \phi_4 \quad (44)$$

where $U_0 + \phi_2$ is the potential energy in the harmonic approximation, and ϕ_3 and ϕ_4 are the anharmonic corrections of the third and fourth order, then the vibrational anharmonicity caused by ϕ_4 gives an additional contribution to the VPIE which can be represented by an effective shift in the normal mode frequencies. There is no corresponding effect from ϕ_3. The thermal expansion of the solid also gives rise to a frequency shift and the lattice vacancies may contribute, but the latter effect should be small. Numerical calculations for the VPIE of ^{36}Ar and ^{40}Ar showed a near cancellation of the effects of thermal expansion and vibrational anharmonicity. Unfortunately, the anharmonic contribution deduced from perturbation theory for Ar at 80°K was found to be nearly as large as the harmonic part. This questions the applicability of the conventional formulation of the lattice dynamical perturbation theory to the system.[107]

2. *Liquid–Vapor Equilibrium for Monatomics*

a. Radial Distribution Function and the VPIE

In the treatment of liquid–vapor equilibrium it is convenient to introduce the radial distribution function g(r). Following Oppenheim and Friedman[108] one can write

$$\langle \nabla^2 U\rangle = 4\pi\zeta \int_0^\infty g(r)\frac{d}{dr}\left[r^2\frac{du(r)}{dr}\right]dr \quad (45)$$

where ζ is the mean number density, $u(r)$ the two-body potential (three and many body forces are neglected), and U is the potential energy obtained from the pair summation.

$$U = \sum_{i>j}\sum u(r_{ij}). \quad (46)$$

Equation 45 and eq 43 can be used[109,110] to compare values of $\langle \nabla^2 U\rangle$ obtained from VPIE measurements with those evaluated from a Lennard-Jones (12-6) or other potential together with radial distribution functions derived in different ways.

b. Rowlinson's Correlation

A comparison of $\langle \nabla^2 U\rangle$ values with other experimental data has been made possible with a correlation established by Rowlinson.[111] He defined the virial function v(r), its derivative w(r), and the macroscopic equivalents $\boldsymbol{V}$ and $\boldsymbol{W}$ by

$$v(r) = r\frac{du}{dr},\ w(r) = r\frac{dv}{dr} \quad (47)$$

$$\boldsymbol{U} = \sum_{i<j}\sum u_{ij},\ \boldsymbol{V} = -\frac{1}{3}\sum_{i<j}\sum v_{ij},\ \boldsymbol{W} = \frac{1}{9}\sum_{i<j}\sum w_{ij} \quad (48)$$

The mean values of $\boldsymbol{U}$ and $\boldsymbol{V}$ in a classical fluid are

$$\langle \boldsymbol{U}\rangle = U,\ \langle \boldsymbol{V}\rangle = pV - NkT \quad (49)$$

where U is the configurational energy. $\langle \boldsymbol{W}\rangle$ is generally inaccessible experimentally, but a simple relationship holds between $\langle \boldsymbol{W}\rangle$ and $\langle \nabla^2 \boldsymbol{U}\rangle$

$$\langle \nabla^2 \boldsymbol{U}\rangle = 6N^{-1}R^{-2}(3\langle \boldsymbol{W}\rangle - \langle \boldsymbol{V}\rangle) \quad (50)$$

It can be shown that R is very close to the molecular diameter (σ) and can be replaced by it. The following properties of $\boldsymbol{W}$ are important:[110] (i) $\langle \boldsymbol{W}\rangle$ cannot be less than a certain minimum value which can be calculated from experimental data on the configurational heat capacity and the thermal pressure coefficient ($\gamma_v = (\partial P/\partial T)_v$).[112] The value of $\langle \boldsymbol{W}\rangle$ obtained from the VPIE measurements through eq 43, 49, and 50 can then be used to check the consistency between α and the thermodynamic properties. (ii) If a specific form is assumed for the potential, then $\langle \boldsymbol{W}\rangle$ can be expressed in terms of the parameters defining the potential and the thermodynamic properties of the liquid. For the Lennard-Jones (n-m) potential one obtains

$$\langle \boldsymbol{W}\rangle = -\frac{nm}{9}\langle \boldsymbol{U}\rangle + \frac{n+m}{3}\langle \boldsymbol{V}\rangle \quad (51)$$

In this fashion values for α over the whole liquid range can be calculated. Comparison with experimental results comprises a test of the form of the potential.[109]

In an application of the above formulas, Rowlinson[113] used the isotopic separation factor between liquid and vapor argon to test Kihara's intermolecular potential and concluded from the results that a sum of true pair potentials is an incomplete representation of $\boldsymbol{U}$ at high densities.

c. Many-Body Forces

The effect of many-body forces was considered by Present and Chen.[114,115] These are of two kinds: (i) the modification of g(r) by the many-body interactions (this effect may be taken into account through the use of experimental g(r) data), (ii) extra terms in eq 45 which combine the n-body interaction potential with the n-body correlation function. The authors used the superposition approximation to express the triplet correlation function in terms of the experimental g(r) functions and with the triple-dipole potential estimated the three-body nonadditivity effect for argon. The resulting value of $\langle \nabla^2 \boldsymbol{U}_3\rangle$ amounted to about 1% of the experimental value of $\langle \nabla^2 \boldsymbol{U}\rangle_{liq}$ at 84.4°K as obtained from VPIE measurements,[116,117] and therefore the triple-dipole nonadditivity effect appears to be insignificant.

3. *Diatomic Systems*

a. Gordon, 1966

According to Gordon[57] four different terms contribute sig-

TABLE IV. Predicted VPIE and Changes in Mean-Squared Torques of the Isotopes of Liquid CO at 77°K[57]

Isotope	$(P - P')V/RT$	$[\langle(O'U)^2\rangle - \langle(OU)^2\rangle]/\langle(OU)^2\rangle$, %
$^{12}C^{16}O$	0[a]	0
$^{12}C^{17}O$	0.00285	3.7
$^{12}C^{18}O$	0.0056[a]	7.5
$^{13}C^{16}O$	0.0076[a]	−4.5
$^{13}C^{17}O$	0.0107	−1.1
$^{13}C^{18}O$	0.01325	2.3
$^{14}C^{16}O$	0.0147	−8.1
$^{14}C^{17}O$	0.0199	−5.1
$^{14}C^{18}O$	0.0202	−2.1

[a] Measured values.[55,120]

nificantly to the VPIE: (i) the mean squared force $\langle(\nabla U)^2\rangle$ on a molecule in the condensed phase (contribution from translations), (ii) the mean-squared torque about the center of mass (defined by $\langle(OU/kT)^2\rangle$, where O is the gradient operator with respect to angles of rotation about the principal axis of inertia, U is the intermolecular potential energy), (iii) the change in the mean-squared torque when the position of the center of mass is changed by isotopic substitution, and (iv) the mean change in intermolecular potential due to isotopic substitution (*i.e.*, the intramolecular frequency shifts). Both the mean-square torque and the mean-frequency shift on condensation may be derived by moment analysis of the band shapes of infrared or vibrational Raman spectra.[118] Therefore by combining VPIE and spectroscopic data on the same system it is possible to obtain separate values for the mean-square force and mean-square torque on a molecule in the condensed phase. The two are quantitative measures of the translational and rotational freedom of molecules in the condensed phase. Gordon proceeded to estimate the position of the center of force (defined as the point about which the mean-square torque is a minimum) for CO in condensed phases by combining the VPIE data of $^{13}C^{16}O$ and $^{12}C^{18}O$ with infrared and Raman data. The mean-square torque and force so derived for liquid and solid CO were used to predict vapor pressure differences for other isotopic CO molecules where data are not yet available. The results are shown in Table IV.

b. Friedmann and Kimel

Friedmann and Kimel[119] about the same time also evaluated mean-square torques on solid and liquid CO from experimental VPIE data,[58,120] but the values obtained were much smaller than those found by Gordon from the third and fourth moments of infrared spectra. One reason for the discrepancy may be that the authors' assumption of a spherically symmetric force field is not justified for CO.

4. Significant Structure Theory and the VPIE

a. Grosh, Jhon, Ree and Eyring

Grosh, Jhon, Ree, and Eyring[121] have interpreted the vapor pressure differences of isotopic liquids in terms of the significant structure theory of Eyring and coworkers. According to this theory[122,123] the liquid is made up of solidlike molecules and holes. A hole is assumed to confer gaslike properties on neighboring molecules. In the liquid there are $N(V_l - V_s)/V_l$ molecules with gaslike degrees of freedom and NV_s/V_l molecules with solidlike degrees of freedom. V_s and V_l are the molal volumes of the solid and liquid, respectively. The partition function is given by

$$f_l = [f_s(1 + n_h e^{-\epsilon_0/kT})]^{NV_s/V_l} f_g^{N(V_l - V_s)/V_l} \qquad (52)$$

TABLE V. Comparison of Observed Values of VPIE with Those Calculated by the Significant Structure Theory

System	Temp, °K	Ln $(P'/P)_{exptl}$	Ln $(P'/P)_{calcd}$[121]	Ref (exptl)
H_2O–D_2O	293.15	0.1552	0.1445	75
	313.15	0.1183	0.1023	
	353.15	0.0692	0.0504	
NH_3–ND_3	213.15	0.1772	0.1235	193
	229.15	0.1423	0.1104	
C_6H_{12}–C_6D_{12}	293.16	−0.0874	−0.0874	323
	313.16	−0.0789	−0.0786	
	333.16	−0.0727	−0.0711	
C_6H_6–C_6D_6	298.15	−0.0273	−0.0152	323
	328.15	−0.0259	−0.0186	
	373.15	−0.0230	−0.0154	
	423.15	−0.0180	−0.0307	
CH_4–CD_4	90.68	−0.0131	0.0724	262
	99.67	−0.0216	−0.0275	
	111.67	−0.0286	0.0126	
SiH_4–SiD_4	103.2	0.0642	0.0472	334
	113.2	0.0321	0.0107	
	123.2	0.0106	−0.0043	
	133.2	−0.0027	−0.0095	
	143.2	−0.0096	−0.0097	
	153.2	−0.0112	−0.0078	
	163.2	−0.0086	−0.0056	

where f_s and f_g are the partition functions for the solid and gaslike degrees of freedom, respectively. The factor $(1 + n_h e^{-\epsilon_0/kT})$ takes into account the positional degeneracy for the solidlike degrees of freedom; n_h and ϵ_0 can be evaluated from the properties of solid and the liquid volume at the melting point. It is assumed that the solidlike molecules can be taken to be an assembly of polyatomic molecules in an Einstein lattice. Calculations were carried out for the vapor pressure differences of various isotope compounds: H_2O–D_2O, H_2–D_2, NH_3–ND_3, C_6H_6–C_6D_6, C_6H_{12}–C_6D_{12}, $^{14}N_2$–$^{15}N_2$, CH_4–CD_4, and SiH_4–SiD_4. Deviations between the calculated and observed values are quite large in many cases (Table V). Further simplifications of the calculations on the methane, nitrogen, and ammonia effects have been made by Devyatykh, Mikheev, and Stepanov.[124a]

b. VPIE near the Triple Point

Jeevanandam[124b] has discussed the large discontinuity in the VPIE observed near the triple point with an application of Bigeleisen's theory to the significant structure theory of liquids. He points out that the equation

$$\ln \alpha_{liq} = \left(\frac{V_s}{V_l}\right) \ln \alpha_{solid} \qquad (53)$$

is adequate to explain the change in the vapor pressure ratios of ^{36}Ar–^{40}Ar, ^{20}Ne–^{22}Ne, $^{12}C^{16}O$–$^{13}C^{16}O$, $^{12}C^{16}O$–$^{12}C^{18}O$, and $^{12}CH_4$–$^{13}CH_4$ systems. In the case of systems exhibiting the crossover phenomenon (for example, the deuterated methanes), in addition to the above simple volume effect the difference in the rotational contribution to the ratio of the RPFR's between the liquid and solid states must also be taken into account. The outline of a similar approach to quantum phenomena on melting (but not in the context of significant structure theory) had been earlier presented by Toda.[125]

III. Experimental Methods: Principally for the VPIE

A. Measurement of the VPIE

Vapor pressure isotope effects are normally expressed in

terms of logarithm of the pressure ratio, ln (P'/P). P' and P stand for the pressures of the lighter and heavier isotopic species at a given temperature. The VPIE is labeled as normal if ln $(P'/P) > 0$, inverse if ln $(P'/P) < 0$. The temperature at which ln $(P'/P) = 0$ is called the crossover temperature. Several techniques have been developed for the experimental determination of VPIE. Their limitations and advantages are compared in ref 126–128.

In principle it is possible to evaluate the VPIE if one measures the temperature dependence of the vapor pressure of each of the two species individually. This method has been replaced in common practice by more reliable techniques because the strong temperature dependence of the vapor pressures requires that the two vapor pressure measurements be performed at precisely the same temperature. Much more accurate data can be obtained if the measurement is performed simultaneously on the two pure species or on mixtures of known isotopic composition and the pressures compared differentially. Kesom and Haantjes[129] were the first to use a differential manometer to assess the difference between the vapor pressures of isotopes. Various types of mercury, oil, or the more sensitive membrane[130–132] and differential capacitance[133,134] manometers have been employed for such measurements. If mercury manometers are used, the measured values of the pressure must be corrected for the capillary depression of mercury, the temperature of the mercury columns (to 0°), and the local variation of gravity. Care must be taken to work with material of high purity and to keep the two species at exactly the same temperatures. For instance, in order to determine a pressure difference of 1% to 1% accuracy at 100°K, the temperature difference between the two samples must be less than 10^{-3}°K. A cryostat suitable for measurements from 2 to 300°K was described by Bigeleisen, *et al.*,[135] and an apparatus for those between −20 and 100°C by Pupezin, *et al.*[136]

Another approach is *via* the group of distillation techniques. Their chief advantage over manometric procedures is that only one sample of known isotopic composition (and that often the natural composition) is sufficient for the evaluation of the isotope effects. Moreover, the purity of the samples is less important than in differential measurements. The separation factor (α) for the equilibrium between a condensed phase and its saturated vapor is given by the ratio of concentration ratios

$$\alpha = \left(\frac{N'}{N}\right)_{vap} \Big/ \left(\frac{N'}{N}\right)_{liq} \tag{54}$$

N' and N are the mole fractions of the light and heavy isotopic molecules. The separation factor is related to the vapor pressures of the pure isotopic molecules

$$\ln \alpha + \frac{(V' - V)^2}{2\beta VRT} = \ln \frac{P'}{P}\left[1 + \frac{P(B - V)}{RT}\right] \tag{55}$$

where B is the second virial coefficient of the gas, β is the isothermal compressibility, and V is the molar volume of the condensed phase (see section II.F.2). This equation can be used to compare experimental data obtained by differential vapor pressure measurement and distillation experiments.

The separation factor, α, can be evaluated by isotope analysis of the two phases in equilibrium (see, *e.g.*, ref 137). Since the separation factor is usually not much different from unity, the method is limited by the accuracy of the isotope analysis. At the now achievable accuracy of isotope analysis, reliable values of α can be best obtained by multiplication of the elementary separation process. One multiplying method is that of Rayleigh distillation. In this case a mixture of two components, the quantity and isotope concentration of which are m_0 and N_0, respectively, is evaporated under equilibrium conditions until just enough residue for isotope analysis remains.[138] The initial values m_0 and N_0 and the residual values m_r and N_r can be then used to evaluate α by the formula

$$N_0/N_r = (m_0/m_r)^{\alpha - 1} \tag{56}$$

provided N_0 and thus N_r are much less than 1. Although the elementary effect is not multiplied by a large factor on Rayleigh distillation, the method has been frequently used because of its easy implementation. The chief drawback of the technique is the often poor agreement found between manometric and Rayleigh distillation data (for example, compare ref 141, 233, and 226 on $^{10}BF_3$ and $^{11}BF_3$). Some authors have attributed these differences to difficulties in maintaining equilibrium conditions of the evaporation during the Rayleigh distillation.[139,142] However, it was shown[127,143] that the dependence of α on the distillation rate is smaller than the difference between the two types of experiment. In any event one good objection to the Rayleigh distillation method is that in this technique the contributions to experimental error are quite difficult to assess. Therefore it should be chosen only if no other method is conveniently available.[212] Equation 56 has been extended to systems with a larger number of isotopic isomers (*e.g.*, H_2O, D_2O, HDO).[144]

A large multiplication of the elementary separation can be achieved with distillation columns. The behavior of isotopic molecules on distillation columns has been extensively studied.[20,145–150] A low-temperature distillation apparatus has been described by Bigeleisen and Ribnikar;[151] Johns[16] has given a review of distillation technique as applied to isotope separation. If N_b and N_t stand for the isotope concentrations at the bottom and the top of the distillation column, respectively, α can be calculated by making use of the Fenske equation

$$\frac{N_t}{1 - N_t} = \frac{N_b}{1 - N_b}\alpha^{n_\infty} \tag{57}$$

where n_∞ is the number of theoretical plates for infinite reflux[126] at equilibrium. However, the number of theoretical plates is difficult to evaluate as it depends not only on the properties of the column and the experimental conditions but also on the nature of the distilled material. Nevertheless, if we determine the relative separation of two isotopic species of the same molecule (*e.g.*, CH_3D–CH_4, $^{13}CH_4$–$^{12}CH_4$) during the distillation of a dilute solution, and if the VPIE of one isotopic species is known from other experiments, it is possible to obtain the elementary separation parameter for the other isotope. Here it is reasonably assumed that in a given distillation the number of effective theoretical plates is the same for all isotopic species.

Under special experimental conditions, the separation factor can be calculated from the behavior of the column when removing distillate.[126,150,152,153] Under these conditions the equations describing the operation of the column are simplified; thus, for example, Kuhn, Narten, and Thürkauf[128,154] found that for $(\alpha - 1) \ll 1$, $R < n_\infty/4$, and $(\alpha - 1)R \ll 1$

$$\alpha - 1 = \frac{1}{R}\ln\left[\frac{N_t}{1 - N_t}\frac{1 - N_b}{N_b}\right] \tag{58}$$

where R is the reflux ratio. It follows from the above conditions that N_t can be only a few per cent higher than N_b, and consequently the accuracy of the α determination is limited by that of the isotope analysis.[126] Alternatively, the separation parameter may be evaluated from the kinetic behavior of the column observed both in the initial stage of the distillation and at a point close to steady-state.[151,153]

In principle it is possible to evaluate the difference between

TABLE VI. Vapor Pressure Isotope Effects of the Rare Gases

Isotopes	Ref (date)	Phase[i]	Temp range, °C	Method[j]	Reported as	Range of ln R = ln P'/P
Neon						
^{20}Ne–^{22}Ne	23 (31)	l	−248.4	D	$P' > P$	
^{20}Ne–^{22}Ne	129 (35)	s	−253.15 to −248.65	DP	Table (10 points)	0.0787_2 (−253.15)
						0.0563_7 (−248.65)
		l	−248.45 to −246.15	DP	Table (6); graph	0.04467 (−248.45)
						0.03788 (−246.15)
^{20}Ne–^{22}Ne	158 (60)	l	−248.35 to −234.57	D	Table (36); graph	0.0468 (−248.35)
	117 (61)					0.0156 (−234.57)
^{20}Ne–^{22}Ne	156 (60)	s[a]	−256.73 to −248.65	DP	Table (91)	0.123 (−256.73)
	157 (61)					0.0583 (−248.65)
		l	−248.40 to −243.04	DP	Table (28); graph	0.0467 (−248.40)
						0.0328 (−243.04)
^{20}Ne–^{22}Ne	159 (72)	l	−248.61 to −245.94	P	Ln $P_x = A + B/T + C \ln T + DT + ET^2$ [b]	
Argon						
^{36}Ar–^{40}Ar	163 (53)	l	∼−189 to ∼−188	D	Ln $R^k = 0.0045 - 0.0065$	0.0045–0.0065
^{36}Ar–^{40}Ar	137 (59)	l	−188.75 to −186.15	D	Table (15); graph	0.0067_8 (−188.75)
	117 (61)					0.0063 (−186.15)
^{36}Ar–^{40}Ar	158 (60)	l	−184.95 to −154.45	D	Table (23); graph	0.0060_2 (−184.95)
	117 (61)					0.0027 (−154.45)
^{36}Ar–^{40}Ar	164 (62)	s	−201.30 to −195.75	D[c]	Table (25)	0.0102_5 (−201.30)
						0.0087_0 (−195.75)
^{36}Ar–^{40}Ar	165 (63)	l	−189.33 to −185.85	DP	Log $R = 0.5455 - 3.62 \times 10^{-3}$	0.00665 (−189.33)
	166 (63)					0.00605 (−185.85)
^{36}Ar–^{40}Ar	116 (70)	s[d]	−210.33 to −189.40	DP	Table (133); graph	0.01420 (−210.33)
						0.00760 (−189.40)
		l	−189.34 to −171.73	DP	Table (90); graph	0.00656 (−189.34)
						0.00426 (−171.73)
^{36}Ar–^{40}Ar	79 (72)	l	−189 to −122.72	D	$T^2 \ln R^{+k} = 28.5689x^{1/3} +$ $78.7815x^{2/3} - 58.1351x$; [e] table (53)	0.00615^{+f} (−188.95) 0.00023^{+f} (−122.72)
Krypton						
Kr[g]	167 (41)	s	−196, −183, −161.5	DP	Table (3)	<0.013 (−196)
						∼0.0031 (−161.5)
^{82}Kr–^{86}Kr	168 (62)	l	−153.2	D	Ln $R = 0.00047$	0.00047 (−153.2)
	169 (61)					
^{80}Kr–^{84}Kr	170 (72)	s[h]	−178.75 to −157.38	DP	Table (165)	0.00205 (−178.75)
						0.00125 (−157.38)
		l	−157.36 to −143.26	DP	Table (115)	0.00098 (−157.36)
						0.00077 (−143.26)
Xenon						
Xe	167 (41)		0–760 mm	DP	$\Delta P < 0.02$ mm	
^{130}Xe–^{136}Xe	168 (62)	l	−108.1	D	Ln $R = 0.0001$	0.0001 (−108.1)

[a] There are seven experimental data between the triple points of ^{20}Ne and ^{22}Ne. [b] The numerical values of the constants for ^{20}Ne and ^{22}Ne are respectively: A = 1149.5978797, 14.696183722; B = −3771.2487076, −206.66156175; C = −748.94223010, −409.760220078; D = 29.231697944, 15.773017439; E = −0.19016757357; −0.10122094714. The constants of the equations yield the pressure in N/m². [c] Steady-flow method. [d] There are 83 experimental data between the triple points of ^{36}Ar and ^{40}Ar. [e] $x = (1 - T/150.7)$. [f] Values were obtained from Table I of ref 79. [g] The difference of the two samples in atomic weight units was equal to 1.74. [h] There are 28 experimental data between the triple points of ^{80}Kr and ^{84}Kr. [i] l = liquid/gas; s = solid/gas. [j] D = distillation; DP = differential pressure; P = pressure. [k] Ln R = ln P'/P; ln R^+ = ln α.

the volatilities of isotopic compounds from molecular distillation. In an ideal mixture of two components the separation factor for molecular distillation is given by the formula

$$\alpha_M = \frac{P'}{P}\sqrt{\frac{M}{M'}} \qquad (59)$$

where M' and M are the molecular weights of the isotopic molecules.[155] This equation holds only if the mean free path of the molecules is longer than the distance from the evaporation to the condensation site. The method can be adopted for the determination of VPIE only if $(P'/P) - 1$ is considerably greater than the absolute error of the α_M determination.

IV. Experimental Results and the Interpretation of Experimental Data on the VPIE

In the material which follows we make a selective and nonexhaustive review of pertinent data on the vapor pressure isotope effect and its theoretical interpretation by a variety of methods. We consider in order (a) rare gases, (b) other monatomic systems, (c) molecules not containing hydrogen, (d) hydrogenic but nonaqueous molecules. Isotope effects in aqueous systems are considered in section V. The discussion of other kinds of isotope effects such as those on molar volume, surface tension, etc., will for the most part be included in the present sections but in part postponed to section VI.

A. Rare Gases (See Table VI)

1. Helium

Helium isotope effects are not discussed in this review.

2. Neon

As early as 1931 by means of rectification of neon at −248.4° Keesom found that ^{20}Ne is more volatile than ^{22}Ne[23] (see also section II.A.1). The vapor pressure differences between samples of various isotopic composition have been measured by Keesom and Haantjes[129] and Bigeleisen and Roth[156,157] in both the solid and the liquid phase. The vapor pressure of ^{20}Ne and ^{22}Ne was calculated from the

measured vapor pressure differences and the isotopic compositions of the samples assuming Raoult's law. Direct measurements of the isotopic separation factor for liquid neon have been performed by Boato, *et al.*,[117,158] up to a total pressure of 12 atm using natural isotopic mixtures. Very careful determinations of the vapor pressures of naturally occurring neon and the pure isotopes (^{20}Ne and ^{22}Ne) have been made by Furukawa[159] between the triple and boiling points. The results of Keesom and Haantjes are systematically about 6% lower than the data of Bigeleisen and Roth, but the agreement between the latter and those of Boato, *et al.*, is excellent. Furukawa used the NBS-1955 provisional temperature scale[160] while Bigeleisen and Roth employed the temperature scale of Crommelin and Gibson,[161] and the differences between these two sets of results are largely due to differences in the temperature scale.

The triple point temperatures and pressures, specific heats, and heats of melting of ^{20}Ne and ^{22}Ne have been determined by Clusius, *et al.*[162]

3. Argon

During the distillation of natural argon, Clusius and Meyer[163] found that the vapor pressure of ^{36}Ar is higher by 0.45–0.65% than that of ^{40}Ar just above the triple point. Boato, *et al.*,[117,137,158,164] measured the liquid–vapor and solid–vapor isotopic separation factors by a dynamic "steady flow method." The vapor pressures of liquid argon isotopes were studied manometrically by Clusius, Schleich, and Vogelmann[165,166] over a narrow temperature range (4°) while more recently vapor pressure differences between normal and enriched (in ^{36}Ar) argon samples were determined by Lee, Fuks, and Bigeleisen[116] in the solid and liquid phase. Finally the isotope fractionation factor between liquid and vapor has been measured from the triple point to the critical temperature by Phillips, Linderstrom-Lang, and Bigeleisen.[79] The results are in agreement with those of Boato, *et al.*, within the limits of experimental error, but systematically lower by some 5% than the previous vapor pressure data of Lee, *et al.*[116] There is a significant discrepancy between the solid VPIE data[116] and those of Boato.[164] It is claimed that this indicates that the steady flow method does not achieve thermodynamic equilibrium.

4. Krypton

The vapor pressure difference between isotopic mixtures with an effective atomic weight difference of 1.74 units was determined by Groth and Harteck[167] between −196 and −161.5°. The results show that the "light" isotopic mixture has 0.3% higher vapor pressure than the "heavy" one. Grigor'ev[168,169] obtained a value of 0.047% for the ^{82}Kr–^{86}Kr isotope effect at the boiling point (−153.2°) using distillation. The vapor pressure difference between normal krypton and a sample containing 50% ^{80}Kr has been measured by Lee, Eshelman, and Bigeleisen[170] in the temperature range −179 to −143°. The results are given in terms of vapor pressure ratios and RPFR of ^{80}Kr and ^{84}Kr for the solid and liquid phase.

5. Xenon

Groth and Harteck[167] measured the vapor pressure difference between isotopic mixtures differing by 2.95 atomic weight units and found no difference within the precision of the measurements (0.02 mm) in the absolute pressure range of 0–760 mm. A difference of 0.01% in the vapor pressures of ^{130}Xe and ^{136}Xe at the boiling point (−153.2°) was obtained by Grigor'ev[168] using a distillation column. Clusius[168a] also reported measurements at the triple point.

6. Discussion (see also sections II.G.1 and II.G.2)

We limit the discussion in this section to only the most important conclusions.

i. The comparison of the results of calculations for the VPIE of Ar and Ne[104,105] based on the anharmonic Einstein model with those of experiment showed the failure of the Einstein model which completely ignores the vibrational coupling of the atoms. Both these calculations, and calculations based on conventional lattice dynamics with anharmonic terms in the crystal Hamiltonian,[106,171] showed that anharmonic contributions can be significant.

ii. It is interesting to compare the Debye temperatures obtained from VPIE data with those derived from heat capacity measurements (see also section II.F.4.b). From the ratio of the vapor pressures of solid ^{20}Ne and ^{22}Ne Bigeleisen and Roth[157] obtained θ_D = 74.6°K for ^{20}Ne, in bad agreement with the values, 66.2 and 65.2°K for ^{20}Ne and ^{22}Ne, obtained from heat capacity.[162] This large discrepancy was thought to be due to lattice anharmonicity and not to the assumption of a Debye frequency distribution and the neglect of higher order quantum corrections. However more recent specific heat measurements of Somoza and Fenichel[172] tend generally 6% higher than those of Clusius[162] and give θ_0 values of 74.5 ± 1.2°K and 71.7 ± 1.2°K for ^{20}Ne and ^{22}Ne, respectively, in excellent agreement with the value obtained by Bigeleisen and Roth. From the VPIE data on solid argon[164] Boato[101] derived a harmonic Debye θ of about 85°K after taking into account an anharmonic correction term. Bigeleisen, *et al.*,[116] deduced a value of 91.93°K from their VPIE results by taking proper account of both anharmonicity and second-order quantum corrections. Heat capacity data of solid argon in the temperature range 2.2–83.8°K give a Debye θ_0 of 93.3°K. The VPIE results on ^{84}Kr–^{80}Kr yield a Debye θ of 71.8°K,[170] in excellent agreement with the 71.7°K determined from heat capacity measurements.[173]

iii. Klein, Blizard, and Goldman[107] performed theoretical calculations on the VPIE of ^{20}Ne–^{22}Ne and ^{36}Ar–^{40}Ar isotopes. They employed an improved modification of Choquard's[174] reformulation of the Born theory[175,176] and used both 13-6 and 12-6 potentials of Lennard-Jones type. Comparison of the calculated and experimental results shows better correlation with the 13-6 potential. Calculations for the liquid–vapor equilibrium isotope effect of Ne and Ar isotopes were carried out by Fieschi and Terzi[177] in terms of cell models, but reasonable agreement with experiment was obtained only around the triple point.

iv. The mean value of the Laplacian of the positional energy in the liquid, $\langle \nabla^2 \boldsymbol{U} \rangle$, can be evaluated from data on isotope separation factors (eq 43) and compared with calculated values.[109,110] The limit on space does not permit a detailed discussion of the results of these calculations (ref 79, 109, 110, 113, 114, 116, 178), but they are summarized for argon isotopes in Table VII. Similar calculations of $\langle \nabla^2 \boldsymbol{U} \rangle$ for krypton isotopes using neutron scattering measurements showed the exp-6 potential to be superior to the Lennard-Jones 12-6 potential for liquid krypton.[170] The large discontinuity of the VPIE of rare gases near the triple point has been considered by Bigeleisen, *et al.*,[116,170] in terms of a corresponding states argument. In order to bring Ne, Ar, and Kr to the same reduced scale, they multiplied T^* by a scale factor, β (1.06, 1.0, and 0.928 for Ne, Ar, and Kr, respectively), and then plotted the reduced quantity $\beta^2 \langle \nabla^2 \boldsymbol{U}^* \rangle = \beta^2 \sigma^2 \langle \nabla^2 \boldsymbol{U} \rangle / \epsilon$ *vs.* βT^*. Excellent agreement was found between the calculated and experimental values. The ratio $\langle \nabla^2 \boldsymbol{U}^* \rangle_s / \langle \nabla^2 \boldsymbol{U}^* \rangle_l$ at the triple point is equal to 1.20 ± 0.01 for both Ne and Ar, which could be explained by a simple molar volume change at the triple point in terms of the significant structure theory of liquids (see section II.G.4.b).[124] Application of Rowlinson's cor-

TABLE VII. Comparison of the Experimental Values of $\langle \nabla^2 U \rangle$ with the Calculated Values for Argon Isotopes

Authors	Year	Radial distribution function g(r) obtained from[a]	Pair potential u(r) used[a]	Some of the conclusions
Casanova, Levi, Terzi[109]	1964	X-Ray diffraction, 1940, 1942, 1967 Neutron diffraction, 1957 Percus-Yevick theory, 1958 Hypernetted chain theory, 1962 Monte Carlo calculation, 1958	Lennard-Jones 12-6	Distribution functions obtained from Percus-Yevick theory and hypernetted chain theory or Monte Carlo calculations give a satisfactory temperature dependence. The 20% discrepancy between theory and experiment can be due both to g(r) and the L-J 12-6 potential.
Rowlinson[113]	1965		Kihara	A sum of true pair potentials is an incomplete representation of U at high densities.
Casanova, Levi[110]	1968	X-Ray diffraction, 1940, 1942 Neutron diffraction, 1957 Hypernetted chain theory, 1962 Percus-Yevick theory,1958 Molecular dynamics calculation by Nijboer and Rahman, 1966 by Verlet, 1967 Monte Carlo calculation, 1958	Lennard-Jones 12-6	g(r) obtained from molecular dynamics calculation of Verlet, 1967, gives the best results. L-J 12-6 potential appears to be compatible with experimental results on the isotopic separation factor.
Lee, Fuks, Bigeleisen[116]	1970	X-Ray diffraction, 1942, 1967 Neutron scattering, 1959 Molecular dynamics calculation by Verlet, 1967 by Rahman, 1964 Kirkwood, Buff, Green, 1949	Lennard-Jones 12-6	Good agreement with the molecular dynamics calculation of Verlet, 1967. The L-J 12-6 potential fits the liquid state data well, while for the solid the 13-6 potential is better.
Present, Chen[114]	1971	X-Ray diffraction, 1967 Neutron diffraction, 1965	Lennard-Jones 12-6 Exp-6 Kihara Kingston Barker-Pompe Dymond-Alder	Barker-Pompe, Kingston, exp-6 potentials give the best results. Values of $\langle \nabla^2 U \rangle$ obtained from isotopic distillation provide a test for the repulsive region of the intermolecular potential.
Phillips, Lindestrom-Lang, Bigeleisen[79]	1972	Exp(−$U(r)/T$) for the gas phase	Exp(18)-6 Klein-Hanley× Kihara Dymond-Alder Barker-Pompe Bobetic-Barker× Exp(14)-6 Lennard-Jones×	Barker potentials are probably the best potentials available for argon. $\langle \nabla^2 U \rangle / \zeta$ for the liquid phase has been calculated as a function of temperature from VPIE data and from calculated values of $\langle \nabla^2 U \rangle / \zeta$ for the gas phase involving the potentials marked with ×.
Mandel[178]	1972	Weeks-Chandler-Anderson perturbation theory 1971 for liquid phase Percus-Yevick theory, 1958, for gas phase	Lennard-Jones 12-6	Whereas at temperatures less than 115°K the results are 5% higher than those of 116, the agreement between 115 and 140°K is very good. The reason for this 5% discrepancy is probably due to the approximations in the W-C-A theory.

[a] For references see the original papers.

relation[111] (section II.G.2.b) to the isotope fractionation data of argon[79] indicates that R values larger than 3.57 Å must be employed in order to satisfy the Schwarz inequality, $\langle (U - \langle U \rangle)^2 \rangle \langle (V - \langle V \rangle)^2 \rangle - [\langle (U - \langle U \rangle)(V - \langle V \rangle) \rangle]^2 > 0$. A recent determination of σ from second virial coefficient data gives a value of 3.58 Å.[179] The theory of transport properties in simple liquids is often formulated in terms of $\langle \nabla^2 U \rangle$. Using values of $\langle \nabla^2 U \rangle$ derived from isotope effect measurements, one can calculate the transport properties (*e.g.*, self-diffusion constant) and compare the results obtained with the experimental values. This type of comparison[110,180,181] provides a test of validity of different expressions proposed for the calculation of transport properties.

B. Other Monatomic Materials (See Table VIII)

1. Lithium

The VPIE of $^6Li/^7Li$ was investigated at absolute pressures ranging from 0.28 to 8.2 mm by equilibrium distillation.[182] Within the precision of the measurements, the distillate composition was not different from the feed composition. (The maximum ratio observed was 1.002 ± 0.004.) From the results of molecular distillation experiments[155] at about 500°, $P_{^6Li}/P_{^7Li} = 1.009 \pm 0.02$; *i.e.*, within the precision of both experiments the vapor pressures of the lithium isotopes are the same.

2. Mercury

The changes in the isotopic composition of mercury when evaporated under various conditions were investigated[183] and upper limits for ln $(P_{^{198}Hg}/P_{^{204}Hg})$ have been determined: $-20° \approx 0.002$; $200° < 0.0008$.

C. Diatomic Molecules (Table VIII)

1. Hydrogen

Aspects of the isotope effects of H_2, D_2, etc., insofar as they pertain to the problem of translation-rotation coupling have been discussed in sections II.B and II.C. A detailed criti-

TABLE VIII. Some Nonhydrogenic VPIE's

System	Ref (date)	Type	Temp, °C	Method[a]	Values of VPIE, $R = P'/P$, and method of reporting	Values at the lowest and highest temp
Li						
^{6}Li–^{7}Li	155 (62)	l	490 to 550	MD	$R = 1.009 \pm 0.02$	0.009 ± 0.02
^{6}Li–^{7}Li	182 (58)	l	0.28–8.2 mm	D	Ln $R^+ \sim 0$	$\sim 0^+$
Hg						
^{198}Hg–^{204}Hg	183 (57)	l	−20, +200	R	Table (2)	≤ 0.002 (−20) ≤ 0.0008 (+200)
CO						
$^{12}C^{16}O$–$^{13}C^{16}O$	120 (62)	l	−194.1 to −165.1	D	Table (5); graph	0.0076^+ (−194.1) 0.0024^+ (−165.1)
$^{12}C^{16}O$–$^{13}C^{16}O$	58 (58)	l	−205 to −192	DP	Ln $R = 78.2/T^2 - 0.394/T$; graph	0.0111 (−205) 0.0070 (−192)
$^{12}C^{16}O$–$^{13}C^{16}O$	58 (58)	l	−211.6 to −204.9	DP	Ln $R = 82/T^2 - 0.36/T$; graph	0.0158 (−211.6) 0.0123 (−204.9)
$^{12}C^{16}O$–$^{13}C^{16}O$	58 (58)	s	−216 to −211.5	DP	Graph	0.0205 (−216) 0.018 (−211.5)
$^{12}C^{16}O$–$^{12}C^{18}O$	58 (58) 58a (53)	l	−204.2 to −196.2	DP	Ln $R = 58.5/T^2 - 0.304/T$; graph	0.0079 (−204.2) 0.0059 (−196.2)
		s	−211.6 to −204.9	DP	Ln $R = 63/T^2 - 0.31/T$; graph	0.0116 (−211.6) 0.0090 (−204.9)
$^{12}C^{16}O$–$^{13}C^{16}O$	185 (58)	l	−205 to −191	R	Ln $R = -0.00055 + 0.889/T$	0.0124 (−205) 0.0102 (−191)
$^{12}C^{16}O$–$^{12}C^{18}O$	185 (58)	l	−205 to −191	R	Ln $R = -0.0610 + 5.41/T$	0.0184 (−205) 0.0049 (−191)
$^{12}C^{16}O$–$^{13}C^{16}O$	184 (54)	l	−205 to −198	DP	Log $R = 1.2190/T + 0.018692 \log T - 0.047251$	0.0112_8 (−205) 0.0093_2 (−198)
$^{12}C^{16}O$–$^{13}C^{16}O$	187 (48) 188 (52)	l	−194.60	D	$R = 1.0085 \pm 0.0005$	0.0085 ± 0.0005
N_2						
$^{14}N_2$–$^{14}N^{15}N$	120 (62)	l	−195.1 to −165.1	D	Table (19); graph	0.0038^+ (−195.1) 0.0010^+ (−165.1)
$^{14}N_2$–$^{14}N^{15}N$	137 (59)	l	−202.5 to −195.9	D	Table (3); graph	0.0048^+ (−202.5) 0.0037^+ (−195.9)
$^{14}N_2$–$^{14}N^{15}N$	55 (58) 56 (58)	l	−210.01 to −195.83	DP	Log $R = 0.3985/T - 3.43 \times 10^{-3}$	0.00663 (−210.01) 0.00396 (−195.83)
$^{14}N_2$–$^{15}N_2$	55 (58) 56 (58)	l	−210.01 to −195.83	DP	Log $R = 0.7974/T - 6.91 \times 10^{-3}$	0.01317 (−210.01) 0.00783 (−195.83)
$^{14}N_2$–$^{15}N_2$	194 (58)	l	100–730 mm	DP	Graph; $P_{^{14}N_2} - P_{^{15}N_2} = 2P_{^{14}N_2} - P_{^{14}N^{15}N}$	
$^{14}N_2$–$^{15}N_2$	193 (42) 192 (41)	l	−209.94 to −198.54	DP	Log $R = 0.7230/T - 0.005822$	0.01256 (−209.04) 0.00891 (−198.54)
NO						
$^{14}N^{16}O$–$^{15}N^{16}O$	202 (61)	l	$\sim$−163.1 to $\sim$−155.1	Cr[a]	Log $R = 3.042/T - 13.53 \times 10^{-3}$	0.0325 (−163.15) 0.0282 (−155.15)
$^{14}N^{16}O$–$^{14}N^{18}O$	202 (61)	l	$\sim$−163.1 to $\sim$−155.1	Cr[a]	Log $R = 4.399/T - 20.42 \times 10^{-3}$	0.0451 (−163.15) 0.0388 (−155.15)
$^{14}N^{16}O$–$^{15}N^{18}O$	202 (61)	l	$\sim$−163.1 to $\sim$−155.1	Cr[a]	Log $R = 7.441/T - 33.95 \times 10^{-3}$	0.0776 (−163.15) 0.0670 (−155.15)
$^{14}N^{16}O$–$^{14}N^{17}O$	202 (61)	l	$\sim$−163.1 to $\sim$−155.1	Th[b]	Log $R = 2.200/T - 10.21 \times 10^{-3}$	0.0225 (−163.15) 0.0194 (−155.15)
$^{14}N^{16}O$–$^{15}N^{17}O$	202 (61)	l	$\sim$−163.1 to $\sim$−155.1	Th[c]	Log $R = 5.241/T - 23.74 \times 10^{-3}$	0.0550 (−163.15) 0.0476 (−155.15)
$^{14}N^{16}O$–$^{15}N^{16}O$	198 (59)	l	−152.1	R	Ln $R^+ = 0.020 \pm 0.002$	0.020^+ (−152.1)
$^{14}N^{16}O$–$^{15}N^{18}O$	59 (59)	l	−163.32 to −152.41	DP	Log $R = 7.3230/T - 32.93 \times 10^{-3}$	0.07769 (−163.32) 0.06383 (−152.41)
$^{14}N^{16}O$–$^{15}N^{16}O$	59 (59)	l	$\sim$−163 to $\sim$−153	Cr[d]	Log $R = 3.0902/T - 13.94 \times 10^{-3}$	0.03281 (−163.52) 0.02683 (−152.41)
$^{14}N^{16}O$–$^{14}N^{18}O$	59 (59)	l	−161.82 to −152.67	Cr[d]	Log $R = 4.4691/T - 21.04 \times 10^{-3}$	0.04398 (−161.82) 0.03696 (−152.67)
$^{14}N^{16}O$–$^{15}N^{16}O$	199 (59)	l	$\sim$−163 to $\sim$−153	DP	Log $R = 3.141/T - 14.39 \times 10^{-3}$	0.03276 (−163.32) 0.02677 (−152.41)
$^{14}N^{16}O$–$^{15}N^{16}O$	55 (58) 56 (58)	l	−162.18 to −152.72	DP	Log $R = 3.0230/T - 13.40 \times 10^{-3}$	0.03187 (−162.18) 0.02694 (−152.72)
$^{14}N^{16}O$–$^{14}N^{18}O$[e]	55 (58) 56 (58)	l	−161.82 to −152.67	DP	Log $R = 4.4684/T - 21.03 \times 10^{-3}$	0.0440 (−161.82) 0.03698 (−152.67)
$^{14}N^{16}O$–$^{15}N^{16}O$	197 (58)	l	−153.1	R	Ln $R^+ = 0.017$	0.017^+ (−153.1)
O_2						
$^{16}O_2$–$^{18}O_2$	210 (56)	l	−219.0 to −183.02	R	Ln $R = 0.849/T - 0.000451$	0.0152 (−219.0) 0.0090 (−183.02)

TABLE VIII *(Continued)*

System	Ref (date)	Type	Temp, °C	Method[a]	Values of VPIE, $R = P'/P$, and method of reporting	Values at the lowest and highest temp
$^{16}O_2$–$^{16}O^{18}O$	137 (59)	I	−188.65 to −182.94	D	Table (3); graph	0.0061$^+$ (−188.65) 0.0050$^+$ (−182.94)
$^{16}O_2$–$^{18}O^{16}O$	211 (56)	I	−210.05 to −199.1	DP	Ln $R = 75.380/T^2 - 0.096$	0.0127 (−210.05) 0.0091 (−199.1)
$^{16}O_2$–$^{18}O_2$	211 (56)	I	−210.05 to −199.1	Th[f]	Ln $R = 150.760/T^2 - 0.096$	0.0254 (−210.05) 0.0182 (−199.1)
$^{16}O_2$–$^{18}O^{16}O$	209 (44) in 212	I	−182.96	R	Ln $R = 0.0065 \pm 0.0009$	0.0065 (−182.96)
$^{16}O_2$–$^{18}O^{16}O$	187 (48), in 212	I	−199.35 to −183.05	R	Table (2)	0.0084 (−199.35) 0.0062 (−183.05)
$^{16}O_2$–$^{16}O^{18}O$	207, (34), in 212	I	−183.0	D[g]	Ln $R \cong 0.01$	0.01 (−183.0)
$^{16}O_2$–$^{16}O^{18}O$	208 (34)	I	−183.0	D[h]	Ln $R \cong 0.05$	0.05 (−183.0)
$^{16}O_2$–$^{18}O_2$	212 (61)[i]	I	−209.63 to −182.96	DP	Log $R = 57.285/T^2 - 0.145/T - 0.661 \times 10^{-3}$	0.02591 (−209.63) 0.01099 (−182.96)
$^{16}O_2$–$^{16}O^{18}O$	58 (58)	I	−208.15 to −183.95	DP	Ln $R = 70/T^2 - 0.285/T$	0.01218 (−208.15) 0.00560 (−183.95)
$^{16}O_2$–$^{16}O^{18}O$	120 (62)	I	−189.35 to −155.05	D	Table (14); graph	0.00633$^+$ (−189.35) 0.00210$^+$ (−155.05)
Cl_2						
$^{35}Cl_2$–$^{37}Cl_2$	215 (60)	I	−75.15 to −42.15	R	Ln $R = 1.7736/T - 0.00723$	0.00173 (−75.15) 0.00045 (−42.15)
$^{35}Cl^{37}Cl$–$^{37}Cl_2$	215 (60)	I	−75.15 to −42.15	R	Ln $R = 1.1392/T - 0.003896$	0.00186 (−75.15) 0.00104 (−42.15)
$^{35}Cl_2$–$^{35}Cl^{37}Cl$	214 (58)	I	−36	D	Ln $R = 0.0004$ to 0.0002	0.0003 (−36)
B compounds						
$^{10}B(OCH_3)_3$– $^{11}B(OCH_3)_3$	224 (61) 225 (60) 140 (62)	I	+56	R	Ln $R^+ = -0.0035 \pm 0.0005$	−0.0035$^+$ (56)
	224 (61) 225 (60) 140 (62)	I	+56	D	Ln $R^+ = -0.0028$	−0.0028$^+$ (56)
$^{10}B(OC_2H_5)_3$– $^{11}B(OC_2H_5)_3$	224 (61) 225 (60) 140 (62)	I	+56	R	Ln $R^+ = -0.0023 \pm 0.0008$	−0.0023$^+$ (56)
	224 (61) 225 (60) 140 (62)	I	+56	D	Ln $R^+ = -0.0017^+$	−0.0017$^+$ (56)
$^{10}B(OC_4H_9)_3$– $^{11}B(OC_4H_9)_3$	224 (61) 225 (60) 140 (62)	I	+128	D	Ln $R^+ = -0.0007^+$	−0.0007$^+$ (128)
$^{10}BF_3$–$^{11}BF_3$	229 (67)	I	−78	D	Ln $R^+ = -0.0057$	−0.0057 (−78)
$^{10}BF_3$–$^{11}BF_3$	233 (65)	I	−126.1 to −25.4	DP	Ln $R^+ = 128/(14250 - T^2)$ (−126.1 to −101.1°) Ln $R^+ = -4.52/T + 17.135 \times 10^{-3}$ Table (26)(−101.1 to −24.5°)	−0.0174$^+$ (−126.15) −0.0084$^+$ (−101.15) −0.0091$^+$ (−101.15) −0.0012$^+$ (−25.45)
$^{10}BF_3$–$^{11}BF_3$	230 (63)	I	−112	D	Ln $R^+ = -0.011 \pm 0.002$	−0.011 (−112)
$^{10}BF_3$–$^{11}BF_3$	141 (61)	I	−113.1 to −102.7	DP	Table (8)	−0.0101 (−113.1) −0.0084 (−102.7)
$^{10}BF_3$–$^{11}BF_3$	226 (60)	I	−115.9 to −104.6	R	Log $R^+ = 2.6796/T - 0.01903$	−0.0046 (−115.9) −0.0072 (−104.6)
$^{10}BF_3$–$^{11}BF_3$	231 (58)	I	−103	DP	Ln $R = -0.0091 \pm 0.0003 = -0.0082$	−0.0091 (−103) −0.0082 (−103)[j]
$^{10}BF_3$–$^{11}BF_3$	232 (58)	I	−103	DP	Ln $R = -0.0082$	−0.0082 (−103)
$^{10}BF_3$–$^{11}BF_3$	228 (58)	I	−100	D	Ln $R^+ = -0.0075 \pm 0.0005$	−0.0075 (−100)
$B^{35}Cl_3$–$B^{37}Cl_3$	227 (56)	I	23	D	Ln $R^+ = 0.004$	0.004$^+$ (23)
$^{10}BCl_3$–$^{11}BCl_3$	235 (56)	I	−85 to +12.7	R	Log $R^+ = 1.00757/T - 0.00483$	+0.0012$^+$ (−85) −0.0030$^+$ (+12.7)
$^{10}BCl_3$–$^{11}BCl_3$	227 (56)	I	+23	D	Ln $R^+ = -0.0043$	−0.0043 (23)
$^{10}BCl_3$–$^{11}BCl_3$	236 (52)	I	+13	D	Ln $R^+ = -0.0018 \pm 0.0002$	−0.0018$^+$ (13)
CO_2						
$^{12}C^{16}O_2$–$^{12}C^{16}O^{18}O$	242 (68)	I	−53 to +30	D	Table (11); graph	0.0013$^+$ (−53.15) 0.00006$^+$ (+30.15)
$^{12}C^{16}O_2$–$^{13}C^{16}O_2$	242 (68)	I	−53 to +30	D	Table (11); graph	−0.00044$^+$ (−53.15) −0.00014$^+$ (+30.15)
$Me_2{}^{14}NH + CO_2$– $Me_2{}^{15}NH + CO_2$	244 (62)	I	60	R	Ln $R^+ = 0.0136 \pm 0.0012$	0.0136$^+$ (60)

TABLE VIII *(Continued)*

System	Ref (date)	Type	Temp, °C	Method[a]	Values of VPIE, $R = P'/P$, and method of reporting	Values at the lowest and highest temp
$Me_2NH + {}^{12}CO_2$–$Me_2NH + {}^{13}CO_2$	244 (62)	I	60	R	Ln $R^+ = 0.0021 \pm 0.0006$	0.0021^+ (60)
$Me_2NH + C^{16}O_2$–$Me_2NH + C^{18}O_2$	244 (62)	I	60	R	Ln $R^+ = -0.0065 \pm 0.0009$	-0.0065^+ (60)
$Me_2NH + CO_2$–$Me_2ND + CO_2$	244 (62)	I	60.2	*k*	Ln $R = -0.090$	−0.090 (60.2)
$MeEtNH + CO_2$–$MeEtND + CO_2$	244 (62)	I	61.12	*k*	Ln $R = -0.082$	−0.082 (61.12)
$Et_2{}^{14}NH + CO_2$–$Et_2{}^{15}NH + CO_2$	244 (62) 245 (58)	I	62	R	Ln $R^+ = 0.0080 \pm 0.0012$	0.0080^+ (62)
$Et_2NH + {}^{12}CO_2$–$Et_2NH + {}^{13}CO_2$	244 (62) 245 (58)	I	62	R	Ln $R^+ = 0.0023 \pm 0.0006$	0.0023^+ (62)
$Et_2NH + C^{16}O_2$–$Et_2NH + C^{18}O_2$	244 (62) 245 (58)	I	62	R	Ln $R^+ = -0.0081 \pm 0.0009$	-0.0081^+ (62)
$Et_2NH + CO_2$–$Et_2ND + CO_2$	244 (62)	I	62.03	*k*	Ln $R = -0.070$	−0.070 (62.03)
$Et^{14}NH_2 + CO_2 + EtOH$–$Et^{15}NH_2 + CO_2 + EtOH$	244 (62)	I	74	R	Ln $R^+ = 0.0143 \pm 0.0012$	0.0143^+ (74)
$EtNH_2 + C^{16}O_2 + EtOH$–$EtNH_2 + C^{18}O_2 + EtOH$	244 (62)	I	74	R	Ln $R^+ = -0.0103 \pm 0.0009$	-0.0103^+ (74)
$EtNH_2 + {}^{12}CO_2 + EtOH$–$EtNH_2 + {}^{13}CO_2 + EtOH$	244 (62)	I	74	R	Ln $R^+ = 0.0000 \pm 0.0006^l$	0.000^+ (74)
$Bu^{14}NH_2 + CO_2 + EtOH$–$Bu^{15}NH_2 + CO_2 + EtOH$	244 (62)	I	91	R	Ln $R^+ = 0.0128 \pm 0.0012$	0.0128^+ (91)
$BuNH_2 + C^{16}O_2 + EtOH$–$BuNH_2 + C^{18}O_2 + EtOH$	244 (62)	I	91	R	Ln $R^+ = 0.0002 \pm 0.0009$	-0.0002^+ (91)
$BuNH_2 + {}^{12}CO_2 + EtOH$–$BuNH_2 + {}^{13}CO_2 + EtOH$	244 (62)	I	91	R	Ln $R^+ = 0.0006 \pm 0.0006^l$	0.0006^+ (91)
$CFCl_3$						
$^{12}CFCl_3$–$^{13}CFCl_3$	246 (65)	I	+23.7	D	Ln $R^+ = -0.0030$	-0.0030^+ (23.7)
CS_2						
$^{12}CS_2$–$^{12}CS_2$	246 (65)	I	+46.5	D	Ln $R^+ = -0.0010$	-0.0010^+ (46.5)
$^{12}CS_2$–$^{13}CS_2$	64 (58)	I	+46.5	D	Ln $R^+ = -0.001$	-0.001^+ (46.5)
$^{12}CS_2$–$^{13}CS_2$	247 (58)	I	*m*	D	Ln $R^+ < 0$	
CCl_4						
$^{12}CCl_4$–$^{13}CCl_4$	128 (61)	I	+35.0	D	Ln $R = -0.00191 \pm 0.00004$	−0.00191 (35.0)
$^{12}CCl_4$–$^{13}CCl_4$	128 (61)	I	+35.0	R	Ln $R = -0.00210$	−0.00210 (35.0)
$^{12}CCl_4$–$^{13}CCl_4$	64 (58)	I	+34.6	D	Ln $R = -0.00203$	−0.00203 (34.6)
$C^{35}Cl_4$–$C^{37}Cl_4$	64 (58)	I	+34.6	D	Ln $R = \sim 10^{-4}$	$\sim 10^{-4}$ (34.6)
$^{12}CCl_4$–$^{13}CCl_4$	62 (53)	I	+34.6	D	Ln $R = -0.0013$	−0.0013 (34.6)
$C^{35}Cl^{37}Cl_3$–$C^{37}Cl_4$	62 (53)	I	+34.6	D	Ln $R = +3 \times 10^{-5}$	0.00003 (34.6)
N_2O						
$^{14}N^{14}NO$–$^{15}N^{14}NO$	248 (61)	I	−90.89 to −88.57	DP	Ln $R = 0.00198 \pm 0.00010$	0.00198 (−90.89 to −88.57)
$^{14}N_2{}^{16}O$–$^{14}N_2{}^{18}O$	151 (61)	I	−89.1	D	Ln $R = 0.0022 \pm 0.0002$	0.0022 (−89.1)
$^{14}N_2{}^{16}O$–$^{14}N^{15}NO$–$^{15}N^{14}NO$	151 (61)	I	−89.1	D	Ln $R^n = 0.0012 \pm 0.0002$	0.0012 (−89.1)
$^{14}N_2O$–$^{14}N^{15}NO$	151 (61)	I	−89.1	D	Ln $R = 0.00078 \pm 0.00014$	0.00078 (−89.1)
$^{14}N_2O$–$^{15}N^{14}NO$	151 (61)	I	−89.1	D	Ln $R = 0.00162 \pm 0.00028$	0.00162 (−89.1)
$^{14}N^{14}NO$–$^{14}N^{15}NO$–$^{15}N^{14}NO$	198 (59)	I	−89.25	R	Ln $R^n = 0.00116 \pm 0.00003$	0.00116 (−89.25)
N_2O–$N_2{}^{18}O$	198 (59)	I	−89.25	R	Ln $R = 0.0018 \pm 0.0002$	0.0018 (−89.25)
NO_2						
$^{14}NO_2$–$^{15}NO_2$	198 (59)	I	+20.35	R	Ln $R = 0.00275 \pm 0.00003$	0.00275 (20.35)
$^{14}N_2O_4$–$^{15}N_2O_4$	250 (56)	I	+21	D	Ln $R^+ = 0.0038$	0.0038^+ (21)
$^{14}N_2O_4$–$^{15}N_2O_4$	250 (56)	I	+21	D[o]	Ln $R^+ = 0.0031 \pm 0.0015$	0.0031^+ (21)
$^{14}N_2O_4$–$^{15}N_2O_4$	250 (56)	I	+21	R	Ln $R^+ = 0.0042$	0.0042^+ (21)
SO_2						
$S^{16}O_2$–$S^{18}O_2$	251 (70)	I	−26	D	Ln $R^+ = 0.00058 \pm 0.00007$	0.00058^+ (−26)
$^{32}SO_2$–$^{34}SO_2$	251 (70)	I	−26	D	Ln $R^+ = 0.00019 \pm 0.00008$	0.00019^+ (−26)
$S^{16}O_2$–$S^{18}O_2$	253 (62)	I	−75.51 to −4.15	DP	Log $R = 0.568/T - 0.00175$ Table (14)	0.00258 (−75.51) 0.00083 (−4.15)
$^{32}SO_2$–$^{34}SO_2$	214 (58)	I	*m*	D	Ln $R \sim 0$	
$^{32}SO_2$–$^{34}SO_2$	252 (58)	I	−23; −35	R	Table (2)	$0.0020 \pm 0.0016^+$ (−23)[p] $0.0012 \pm 0.0005^+$ (−35)[p]
$SiCl_4$:SiH_4						
$^{28}SiCl_4$–$^{29}SiCl_4$–$^{30}SiCl_4$	255 (56)	I	+57	D	$P_{^{30}SiCl_4}, P_{^{29}SiCl_4} > P_{^{28}SiCl_4}$	
$^{28}SiH_4$–$^{29}SiH_4$	255a	I	−117	D	$R = 1.00035 \pm 0.00007$	0.00035 (−117)
$^{28}SiH_4$–$^{30}SiH_4$	255a	I	−117	D	$R = 1.00061 \pm 0.00010$	0.00061 (−117)
$TiCl_4$						
$^{46}TiCl_4$, $^{47}TiCl_4$ ...	256 (61)	I	*m*	D	$P_{^{46}TiCl_4} < P_{^{47}TiCl_4} < P_{^{49}TiCl_4} < P_{^{50}TiCl_4}$	

TABLE VIII *(Continued)*

System	Ref (date)	Type	Temp, °C	Method[a]	Values of VPIE, $R = P'/P$, and method of reporting	Values at the lowest and highest temp
$^{46}TiCl_4$–$^{50}TiCl_4$	256 (61)	1	+136.5	R	Ln R = −0.004 to −0.002	−0.004 to −0.002 (136.5)

[a] MD = molecular distillation; D = column distillation; R = Rayleigh distillation; DP = differential pressure; Th = theoretical calculation; Cr = critical evaluation of extant data. In R = ln P'/P (the prime refers to lighter isotope); ln R^+ = ln α. [b] Calculated using the relationship ln $P_{^{14}N^{16}O}/P_{^{14}N^{17}O} = {}^1/_2$ ln $P_{^{14}N^{16}O}/P_{^{14}N^{18}O}$. [c] Calculated using the relationship ln $P_{^{14}N^{16}O}/P_{^{15}N^{17}O}$ = ln $P_{^{14}N^{16}O}/P_{^{15}N^{18}O}$ − $^1/_2$ ln $P_{^{14}N^{16}O}/P_{^{14}N^{18}O}$. [d] From ref 55, 56, 199. [e] Measurements on NO–CH_4 system; see ref 205. [f] Calculated using the relationship ln $P_{^{16}O_2}/P_{^{18}O^{16}O} = {}^1/_2$ ln $P_{^{16}O_2}/P_{O^{18}_2}$. [g] Technical air distillation. [h] Technical oxygen distillation. [i] See also Errata, ref 213. [j] New measurements[232] gave this value, see footnote on 410 in ref 231. [k] Obtained from the measured boiling point difference between nondeuterated and deuterated molecule. [l] These values are probably in error and a value of 0.0022 was obtained for the $BuNH_2 + CO_2 + H_2O$ system from a column distillation experiment. [m] The temperature was not given in the paper. [n] In R = ln $2P_{^{14}N^{14}N^{16}O}/(P_{^{14}N^{15}N^{16}O} + P_{^{15}N^{14}N^{16}O})$. [o] Single-stage equilibrium. [p] These data were obtained from the Rayleigh distillation data on $^{32}S/^{35}S$ isotope effect by correcting for the mass difference between ^{34}S and ^{35}S. [q] From ref 55, 56, 59, 199.

que of hydrogen isotope effects is not within the scope of this review.

2. Carbon Monoxide

The effect of the ^{13}C isotopic substitution on the vapor pressure of the CO molecule has been investigated in the solid[58,58a] and liquid[58,58a,184] phases by differential manometry, and in the liquid by Rayleigh distillation[185,186] and ordinary distillation techniques.[120,187,188] The $^{12}C^{18}O/^{12}C^{16}O$ VPIE was determined over the solid phase by differential manometry[58] and in the liquid phase by manometry[58] and Rayleigh distillation.[185] Enrichment during distillation has been also studied.[189–191] In both solid and liquid up to the boiling point, Johns' results[58] seem to be the most reliable for both the ^{13}C and ^{18}O isotope effects. The most striking feature of the experimental results is that the vapor pressures do not follow the mass sequence of the isotopic CO molecules but fall in the order $^{12}C^{16}O > {}^{12}C^{18}O > {}^{13}C^{16}O$. Calculations for the VPIE of CO have been carried out by Devyatykh[70] (see section II.E.2), Johns[58] (section II.E.1), and Friedmann[53] (section II.C.2). The recent interpretations of Friedmann and Kimel[119] (section II.G.3.b) and especially of Gordon[57] (section II.G.3.a) were based on a combination of VPIE and spectroscopic data and made it possible among other things to obtain information about molecular motions in liquid and solid CO.

3. Nitrogen

The VPIE in N_2 was first studied by Kirshenbaum and Urey[192,193] who measured the vapor pressure difference between a sample of natural nitrogen and an equilibrium mixture of $^{15}N_2$, $^{14}N^{15}N$, and $^{14}N_2$, containing 34.6 at. % ^{15}N. They assumed that the rule of the geometric mean applies ($P_{^{14}N^{15}N}{}^2 = P_{^{14}N_2}P_{^{15}N_2}$). This was proven within experimental accuracy by Johns[194] who compared the vapor pressure of natural nitrogen with mixtures containing 60 and 90 at. % ^{15}N. Clusius and Schleich[55,56] compared the vapor pressure of almost pure $^{15}N_2$ and $^{14}N^{15}N$ with natural nitrogen between the melting and boiling points. The separation factors in the liquid–vapor equilibrium were measured from the melting point to about 12 atm by Boato, *et al.*[120,137] There is a systematic deviation of several per cent between their data and those of the other workers. The most reliable results between the melting and boiling point are those of Clusius.

Kirshenbaum[195] reported model calculations in 1942 for the VPIE of liquid $^{15}N_2/^{14}N_2$ system at the triple point. He employed various assumptions concerning the motions of molecules in the liquid phase but obtained poor results. The application of Friedmann's theory[53] (see section II.C.2) gives a constant value for $(\ln P_{^{14}N^{15}N}/P_{^{15}N_2})/(P_{^{14}N_2}/P_{^{15}N_2}) = 0.495$; the experimental value is 0.494 over the entire range of experimental temperatures. The 1% deviation from 0.5 indicates a small deviation from the rule of geometric mean. The significant structure theory calculations of Grosh, *et al.*[121] (see section II.G.4.a), show a 2 to 36% discrepancy with experiment. The authors assumed that both the solidlike and gaslike molecules rotate freely and therefore do not contribute to the vapor pressure ratio. In their opinion the isotopic vapor pressure differences are determined by the relative effects of heat of sublimation and molecular mass differences. It was demonstrated that the calculated values of various thermodynamic properties of nitrogen improve when hindered rotational partition functions are used in the solidlike part of the total partition function.[196] However, no isotope effect calculations have been carried out in detail using the assumption of hindered rotation.

4. Nitric Oxide

The effect of ^{15}N and ^{18}O isotopic substitution on the vapor pressure of $^{14}N^{16}O$ molecule has been investigated in detail by Kuhn and coworkers[197,198] and by Clusius and coworkers.[55,56,59] Differential vapor pressure measurements were used to determine the vapor pressure differences between $^{14}N^{16}O$ and $^{15}N^{16}O$, $^{14}N^{16}O$ or $^{14}N^{18}O$, and $^{14}N^{16}O$ and $^{15}N^{18}O$.[55,56,59] The separation factor for $^{14}N/^{15}N$ isotopic substitution obtained by Rayleigh distillation[197,198] is about 40% smaller than the value obtained by the differential measurements. The probable reason for this is that equilibrium between the bulk and the surface of the liquid was not maintained during the Rayleigh distillation.[199] The determination of the vapor pressure differences between ^{14}NO and $^{14}NO/^{15}NO$ mixtures as a function of ^{15}N content demonstrated that the vapor pressure difference is proportional to the ^{15}NO content. (Raoult's law is obeyed within the experimental precision, ±0.02 mm.)

The isotope effects are surprisingly large, about 3–5 times bigger than those of other diatomic molecules with similar boiling points. These large values for the separation factors imply that column distillation of NO can be employed for the enrichment of ^{15}N, ^{18}O, and ^{17}O isotopes.[200–203] An additional advantage is that the $^{14}N^{16}O + {}^{15}N^{18}O \rightleftharpoons {}^{15}N^{16}O + {}^{14}N^{18}O$ reaction comes rapidly to equilibrium, not only at room temperature,[204] but probably at low temperature as well.[59,202]

The original speculation that the abnormally large separation factors were due to association in the liquid phase was demonstrated experimentally by determining the separation factor over a dilute solution of NO in CH_4[203,205] and by a complete theoretical analysis due to Bigeleisen.[206] The experiments showed the separation factor in a 3% solution was more than a factor of 2 smaller than in the neat liquid. At higher dilution the value would supposedly decrease further, but at the same time it would be more difficult to carry out the measurements.

Bigeleisen's[206] theoretical analysis started from the observation that eq 39 was applicable, so that the isotope effect on the heat of vaporization can be expressed as

$$\delta(\Delta H)_{T,vap} = -2RT \ln (P'/P)_T \qquad (60)$$

A comparison between the experimental and calculated values is given in Table IX. The agreement is almost within the experimental error and shows that eq 39 is an adequate representation. It then follows that

$$\ln(P_{^{14}N^{16}O}/P_{^{15}N^{18}O}) = \ln (P_{^{14}N^{16}O}/P_{^{15}N^{16}O}) + \ln (P_{^{14}N^{16}O}/P_{^{14}N^{18}O}) \quad (61)$$

The same relationship had been empirically found by Clusius, Schleich, and Vecchi[59] as

$$P_{^{14}N^{16}O}P_{^{15}N^{18}O} = P_{^{15}N^{16}O}P_{^{14}N^{18}O} \quad (62)$$

The relative ^{18}O and ^{15}N effects can be written using eq 39 as

$$R = \frac{\ln (P_{^{14}N^{16}O}/P_{^{14}N^{18}O}')}{\ln (P_{^{14}N^{16}O}/P_{^{15}N^{16}O})} = \frac{(\mu' - \mu)_O(a_{ii} - b_{ii})_O}{(\mu' - \mu)_N(a_{ii} - b_{ii})_N} = 1.46\frac{(a_{ii} - b_{ii})_O}{(a_{ii} - b_{ii})_N} \quad (63)$$

The liquid NO consists of randomly oriented dimers which are negligibly dissociated in the liquid but completely dissociated in the gas phase. From structural considerations it follows that $(a_{ii} - b_{ii})_O$ is very close to $(a_{ii} - b_{ii})_N$, and thus the relative VPIE, R above, should equal 1.46. The experimental value is 1.38. The same value applies to the relative isotopic differences on the heat of vaporization and the triple point temperatures. (Experimental values are 1.45 and 1.40, respectively.) Finally a calculation of ln $(P_{^{14}N^{16}O}/(P_{^{15}N^{16}O})$ was made from molecular data. The contributions of the dimerization and of the translation and rotation of the dimers in the lattice to the VPIE were estimated as 0.021 and 0.006 at 115°K. This total, 0.027, is in good agreement with experiment (0.0295).

Friedmann[53] employed the experimental value 0.274 ± 0.004 for the ratio ln $(P_{^{15}N^{16}O}/P_{^{14}N^{18}O})$/ln $(P_{^{14}N^{16}O}/P_{^{14}N^{18}O})$ to deduce $2d/R = -0.061 \pm 0.002$ (eq 8), a value significantly smaller than the -0.230 ± 0.003 found for CO, thus demonstrating the virtual identity of the potential fields about the N and O atoms in this molecule. Using this value of $2d/R$ he found 0.719 ± 0.004 for the ratio ln $(P_{^{14}N^{18}O}/P_{^{15}N^{16}O})$/ln $(P_{^{15}N^{16}O}/P_{^{15}N^{18}O})$ as compared with the experimental, 0.726 ± 0.006.

5. Oxygen

The change in isotopic composition of oxygen during the technical distillation of air[207] and oxygen[208] was observed long ago. The application to production of ^{18}O isotopes came later.[185] More recent results obtained by Rayleigh distillation[187,209,210] generally do not agree with the isotope effects obtained by differential vapor pressure measurements.[58,211-213] According to Clusius, *et al.*,[212,213] the reason is to be ascribed to the many sources of error in the Rayleigh distillation method. Of the results obtained by the comparison of separated samples, those of Johns[58] and Clusius, *et al.*,[212] are practically the same. Groth's results[211] deviate slightly, but it must be taken into consideration that the ^{18}O content of this sample was as low as 6%. The results obtained by distillation below the boiling point[137] are about 6% smaller than those obtained by differential vapor pressure measurements.

6. Chlorine

The $^{35}Cl/^{37}Cl$ VPIE has been determined by distillation[214] and Rayleigh distillation.[215] The distillation experiment carried out at −36° gave 2 to 4 × 10^{-4} for ln $P_{^{35}Cl_2}/P_{^{35}Cl^{37}Cl}$. On the other hand, from the equations describing the results obtained by Rayleigh distillation in the temperature range −75 to −42°, it follows that $P_{^{35}Cl^{37}Cl} > P_{^{35}Cl_2}$. This is probably due to errors in the measurements.

TABLE IX. Calculated and Experimental Differences in Heat of Vaporization of NO Molecules ($^{x}N^{y}O$–$^{14}N^{16}O$)

	$^{15}N^{16}O$	$^{14}N^{18}O$	$^{15}N^{18}O$
Exptl	14.1	20.4	33.5
Calcd	13.5	18.7	32.3

[a] In cal mol^{-1} (T = 115°K). See ref 3 and 206.

7. The Hydrogen Halides (see Table X)

All available data on H/D effects for these compounds are more than 35 years old. The HF/DF measurements of Claussen and Hildebrand[216] show an inverse effect which is to be expected in view of the strong vapor phase association of this material. The HCl/DCl and HBr/DBr effects as measured by Lewis, Macdonald, and Schutz[217] and Bates, Halford, and Anderson[218] show rather large normal effects with strong negative temperature coefficients, but that reported for HI/DI[219] is reported as inverse and large (2%). The last result is surprising but must be viewed with skepticism in view of the experimental difficulties which these early authors faced. Wolff, Wolff, and Höppel[220] have given an interpretation of the results for HCl/DCl and HBr/DBr and correlated them with the spectroscopic data, but the agreement is not good. Holmberg[221] has made a detailed study of the properties of the maximum boiling aqueous azeotropes of HCl and HBr. It is interesting to note that even though the pressure ratios of both pure compounds, HOH/DOD and HX/DX, are greater than 1, that for the azeotropes, (HX in HOH)/(DX in DOD), is less than 1; the isotope effect is inverse. The chlorine isotope effects on Rayleigh distillation and distillation of HCl have been reported by Russian workers[214,222] who found that the separation factor is no more than 0.2%.

Clusius and Wolf[223] have made careful low-temperature heat capacity measurements on DCl, DBr, and DI and have reported isotope effects on a number of physical properties such as the triple points, heat of fusion, etc. These are shown in Table X.

D. Some Nonhydrogenic Effects in Polyatomics (Table VIII)

1. $B(OCH_3)_3$, $B(OC_2H_5)_3$, $B(OC_4H_9)_3$

Vapor pressure differences due to the isotopic substitution of ^{10}B and ^{11}B were measured at a single temperature on boric acidous methyl ester, ethyl ester and *n*-butyl ester using Rayleigh distillation and column distillation.[140,224,225] The absolute value of the inverse isotope effect decreases as total molecular weight increases.

2. BF_3

The vapor pressure difference between $^{10}BF_3$ and $^{11}BF_3$ has been determined by Rayleigh distillation,[226] distillation,[228-230] and differential manometry.[141,231-233] In all cases $^{11}BF_3$ was found to be more volatile than $^{10}BF_3$. However, results obtained by differential vapor pressure measurements[141,233] indicate that the inverse isotope effect decreases with increasing temperature (between −126.1 and −25.4°), while Rayleigh distillation data[226] show the opposite change over their temperature range (−115.9 to −104.6°). To explain the difference it was assumed[139] that the evaporation during Rayleigh distillation had not been carried out under equilibrium conditions. Even so, other calculations[127,143]

TABLE X. Some Isotope Effects of Hydrogen Halides[223]

	HCl	DCl	HBr	DBr	HI	DI
Melting point, °K	158.91	158.44	186.28	185.62	222.31	22.123
Melting pressure, mm	103.6	91.3	248	232	379	360
Heat of fusion, cal/mol	476.0	473.2	575.1	574.2	686.3	684.3
Transition temp II → I, °K	98.36	105.03	113.62 116.86	120.26	125.68	128.28
Heat of transition, cal/mol	284.3	320.1	264.5 (107.86–117.86°)	303.0 (111.26–121.26°)	359.9 (115.7–128.7°)	386.4 (115.7–128.7°)
Transition temp III → II, °K			89.75	93.5	70.1	77.3
Heat of transition, cal/mol			160.1 (85.75–93.75°)	196.7 (89.5–97.5°)	146.8 (62–73°)	175.6 (69.3–80.3°)

showed that the discrepancy between the experimental results is much larger than can be accounted for by this means.

A model calculation in the harmonic-cell approximation, using reasonable force fields, shows[234] that the temperature dependence of the VPIE observed by Rayleigh distillation experiments cannot be rationalized at all—it is of the wrong sign; that obtained by vapor pressure difference measurements seems to be too steep below the boiling point. Baertschi and Kuhn[64] calculated a value of −0.012 for $\ln P_{^{10}BF_3}/P_{^{11}BF_3}$ due to the contribution of infrared absorption bands (see section I.D.1) at the boiling point, while the weighted mean of the experimental results is −0.0085.

Distillations involving chemical exchange reactions (*e.g.*, ether boron trifluoro complexes) have been extensively studied as a means to isotope separation, but a discussion of this methodology is not within the scope of the present review.

3. BCl_3

The vapor pressure difference between $^{10}BCl_3$ and $^{11}BCl_3$ has been investigated by Rayleigh distillation[235] and distillation.[227,236] According to ref 235 below −61.7° $P_{10} > P_{11}$ and above −61.7° $P_{^{10}BCl_3} > P_{^{11}BCl_3}$. Distillation experiments at 23° showed that the vapor pressure of $B^{35}Cl_3$ is higher than that of $B^{37}Cl_3$.[227b] Both BF_3 and BCl_3 distillations have been thoroughly investigated[237–240] with a view toward industrial scale enrichment of ^{10}B. A larger separation factor speaks in favor of the BF_3 distillation, but the fact that the distillation has to be carried out at a lower temperature rules against it. (The boiling points of BF_3 and BCl_3 are −101.7 and 12.7°, respectively.) The only available calculation on the VPIE of the $^{10}BCl_3/^{11}BCl_3$ system is that of Urey[241] who predicted a higher vapor pressure for $^{10}BCl_3$ at the boiling point by using the available Raman frequencies. This is in contradiction to the experimental results obtained later, but the approximate nature of this calculation had been pointed out by Urey himself. The infrared contribution to the separation parameter was estimated by Baertschi and Kuhn[64] as −0.006 at the boiling point (experimental values −0.0030[235] and −0.0018[236]).

4. CO_2

Isotopic fractionation on liquid–vapor equilibrium of carbon dioxide has been measured by Grootes, Mook, and Vogel[242] for both carbon and oxygen in the temperature range −53 to +30°. The experimental results show $^{12}C^{16}O^{18}O$ as somewhat less, and $^{13}C^{16}O_2$ as slightly more volatile than $^{12}C^{16}O_2$. In both cases the fractionation approaches zero at the critical temperature (31°). The experimental results have been interpreted in terms of a theoretical expression derived by them;

$$\ln \alpha = \frac{3}{40}\left(\frac{\theta'}{T}\right)^2\left(\frac{m-m'}{m}\right) + \ln\left[\frac{Q_g' Q_l}{Q_g Q_l'} - \frac{L'-L}{RT}\right] \quad (64)$$

In eq 64, θ is the Debye characteristic temperature, m is the molecular mass, Q_g and Q_l are the internal partition functions in the gas and liquid phase, and L is the binding energy of the molecules in the liquid phase due to van der Waals forces. Since data on the vibrational and librational frequencies in the liquid phase were not available, the second term in the equation could not be evaluated. The magnitudes of the other terms were estimated along with the temperature dependence of the binding energy and the Debye temperature. A comparison with the experimental values shows that the internal effect, presumably caused by hindered rotation in the liquid phase, is relatively large. The isotopic difference in the van der Waals binding energy of molecules would seem to qualitatively explain the inverse isotope effect of $^{13}C^{16}O_2$. Nevertheless, the entire calculation is of a very approximate nature and subject to refinement. Vogel, Grootes, and Mook[243] also investigated the isotopic fractionation between gaseous CO_2 and an aqueous solution of the gas in the temperature range 0–60°. It was found that $^{13}C^{16}O_2$ is slightly less and $^{12}C^{16}O^{18}O$ slightly more soluble than $^{12}C^{16}O_2$. A theoretical expression was developed on the assumption that the interaction between solute and solvent could be treated in the same manner as the interaction between molecules in a pure liquid. In this fashion the vapor–liquid data were used to predict the sense of the effects in the vapor–solute system in satisfactory agreement with experiment.

Some interesting studies have been performed by Holmberg on the maximum boiling azeotropes which CO_2 forms with some primary and secondary amines. During the distillation of these compounds dissociation occurs in the gas phase, and there is an isotope effect for all atoms participating in the binding of the condensed phase complex. Isotope effects on carbon, oxygen, and nitrogen were determined by Rayleigh distillation in several systems.[244,245] Enrichment of ^{15}N, ^{18}O, and ^{12}C isotopes was found in the vapor phase. The boiling points of deuterated amine–CO_2 complexes were compared with those of nondeuterated, and it was found that the vapor pressure of the deuterated amine is 7–9% higher than that of the nondeuterated at the boiling point. Note that in the case of pure amines the vapor pressure of the nondeuterated compound is higher because of association in the liquid phase. When the carbon dioxide forms a compound with the amines, this can be qualitatively pictured as transforming the amine into "monomer" which exhibits inverse isotope effect. The ternary azeotropes $EtNH_2$–CO_2–EtOH and $BuNH_2$–CO_2–H_2O were also studied.[244]

5. $CFCl_3$

Distillation experiments[246] showed that the vapor pressure of $^{13}CFCl_3$ is higher by 0.3% than that of $^{12}CFCl_3$ at the boiling point (23.7°). Haberlandt[246] theoretically estimated a value of 0.5% for the inverse isotope effect using the approach of Baertschi and Kuhn (section II.D.1).

6. CS_2

During distillation of CS_2[64,246,247] it was observed at 46.5°

TABLE XI. Calculated and Experimental Values of Separation Parameters for the Isotopic N_2O Molecules at 184°K

Isotopic species	Rayleigh distillation[198]	Diff manometer[248]	Column distillation[151]	Theory[3,151]
$^{14}N^{14}N^{16}O$–$^{14}N^{14}N^{18}O$	$18 \pm 2 \times 10^{-4}$		$22 \pm 2 \times 10^{-4}$	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}
$^{14}N^{14}N^{16}O$–($^{15}N^{14}N^{16}O$–$^{14}N^{15}N^{16}O$)	$11.6 \pm 0.3 \times 10^{-4}$		$12 \pm 2 \times 10^{-4}$	13×10^{-4}

that the vapor pressure of $^{13}CS_2$ is higher by 0.1% than that of $^{12}CS_2$. Baertschi and Kuhn calculated a value of 0.16% for the infrared contribution.[64]

7. CCl_4

According to results obtained by distillation of CCl_4[62,64,128] and by Rayleigh distillation[128] at 35°, the vapor pressure of $^{13}CCl_4$ is higher (about 0.2%), while that of $C^{37}Cl_4$ is lower (about 0.01%) than the vapor pressure of $^{12}C^{35}Cl_4$. The reason[63,64] is that isotopic substitution of chlorine causes only weak shifts in the ir, but the frequency of the strong ir vibration of carbon undergoes a large change on isotopic substitution. These observations are in agreement with the evaluation of Wolfsberg[48] who considered the effect of the van der Waals interaction on the internal force constants using approximation methods. He predicted a considerably larger inverse effect for ^{12}C–^{13}C than for ^{35}Cl–^{37}Cl substitution (see Table I) and emphasized that in order to obtain agreement with the experimentally observed VPIE, other terms influencing the VPIE in CCl_4, *e.g.*, the effect of lattice frequencies, must also be taken into account (see section II.D.2).

8. N_2O

Kuhn, Narten, and Thürkauf[198] performed Rayleigh distillations on natural abundance material. They measured both ratios $^{14}N^{14}N^{16}O/^{14}N^{14}N^{18}O$ and $^{14}N/^{15}N$ (no distinction was made between $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$). The difference in the vapor pressure between $^{14}N^{14}N^{16}O$ and $^{15}N^{14}N^{16}O$ was measured by Clusius and Schleich[248] between the melting and boiling point (−90.9 to −89.6°), and the vapor pressures of $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, and $^{14}N^{14}N^{18}O$ were determined at 184.0 ± 0.6°K by Bigeleisen and Ribnikar[151] using column distillation. The experimental results of all these workers employing different methods are in satisfactory agreement (Table XI). The results show that the difference in the vapor pressure between $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ is as large as that between $^{14}N^{15}N^{16}O$ and $^{14}N^{14}N^{16}O$, and thus vividly demonstrate the important contribution of hindered rotation in the liquid. (The ratio of the moments of inertia $^{14}N^{14}N^{16}O/^{14}N^{15}N^{16}O$ is equal to 0.999932.) It is interesting to note that the hindered rotation so predicted was confirmed by far-infrared measurements 11 years later.[249]

The theoretical analysis proceeds similarly to that for NO. Equation 39 can be written[3,151]

$$R_1 = \frac{\ln (P_{^{14}N^{14}N^{16}O}/P_{^{15}N^{14}N^{16}O})}{\ln (P_{^{14}N^{14}N^{16}O}/P_{^{14}N^{15}N^{16}O})} = \frac{(a_{ii} - b_{ii})_{\text{end N}}}{(a_{ii} - b_{ii})_{\text{middle N}}} \quad (65a)$$

and

$$R_2 = \frac{\ln (P_{^{14}N^{14}N^{16}O}/P_{^{14}N^{14}N^{18}O})}{\ln (P_{^{14}N^{14}N^{16}O}/P_{^{15}N^{14}N^{16}O})} = 1.46 \frac{(a_{ii} - b_{ii})_0}{(a_{ii} - b_{ii})_{\text{end N}}} \quad (65b)$$

N_2O is a linear molecule and the molecules are randomly oriented end to end in the crystal lattice. If it is assumed that the change in the intramolecular force constants on condensation is negligibly small, then $(a_{ii} - b_{ii})_O = (a_{ii} - b_{ii})_{\text{end N}}$, and thus $R_1 = 1.46$ while the experimental value is 1.38 ± 0.07. The middle nitrogen is at the center of gravity; therefore the sole contribution to $(a_{ii} - b_{ii})_{\text{middle N}}$ arises from the potential restricting translation of the molecule, whereas $(a_{ii} - b_{ii})_{\text{end N}}$ also has a contribution from the rotation of the molecule. The authors assumed isotropic forces, an Einstein distribution for the rotation, and Einstein and Debye distributions for the translations. The agreement between the calculated (1.67 for Einstein and 2.11 for Debye translation) and the experimental (2.10 ± 0.10) value of the relative effect, R_1, is good. Absolute values of the separation parameters were also calculated (Table XI).

9. NO_2, N_2O_4

The $^{14}N/^{15}N$ separation factor between the vapor and liquid phase of N_2O_4 has been determined at the boiling point (21°) by column distillation, single-stage equilibrium, and Rayleigh distillation. The following values were obtained: 0.0038, 0.0031 ± 0.0015, and 0.0042.[250] The above results and an earlier value of 0.00275 ± 0.00003 obtained at 20.35°[198] clearly show that the ^{14}N concentrates in the vapor phase during the distillation.

10. SO_2

The $^{32}S/^{34}S$ separation factor for SO_2 has been investigated by distillation[214,251] and Rayleigh distillation.[252] According to ref 214, there is no difference between the vapor pressure of $^{32}SO_2$ and $^{34}SO_2$, while the values obtained by Rayleigh distillation,[252] 0.0030 ± 0.0016 (−23°) and 0.0018 ± 0.0005 (−35°), are one order of magnitude greater than the one, 0.00019 ± 0.00008 (−26°), obtained by column distillation.[251] The Rayleigh distillation data were obtained indirectly from results on $^{32}S/^{35}S$ separation factors and probably are too high.

The vapor pressure difference between $S^{16}O_2$ and $S^{18}O_2$ has been determined by Clusius, Schleich, and Bernstein[253] between the melting and boiling point. Because of the self-association in liquid SO_2 they expected a large isotope effect, but the values obtained are rather small (0.08–2.6%). The value of Pupezin and Ribnikar[251] found by column distillation at −26° compares favorably. These authors also investigated the $^{16}O/^{18}O$ and $^{32}S/^{34}S$ isotope effects occurring in the distillation of the azeotropic mixture between SO_2 and $(CH_3)_2O$. The results support the $(CH_3)_2O \cdots SO_2$ structure of the 1:1 complex. Eriksen[254] has recently considered sulfur isotope effects in the SO_2–HOH system.

11. $SiCl_4$

Orlov and Zhavoronkov[255] found during distillation of $SiCl_4$ (natural abundance) at the boiling point (57°) that the $^{30}SiCl_4$ and $^{29}SiCl_4$ isotopic species are slightly more volatile than $^{28}SiCl_4$. The $^{28}SiH_4$–$^{29}SiH_4$–$^{30}SiH_4$ compounds on the other hand display normal VPIE's.[255a]

12. $TiCl_4$

To separate Ti isotopes with masses of 46–50, $TiCl_4$ was fractionated in a column, and it was found that the vapor pressure of isotopic $TiCl_4$ species increases in the following order: $^{46}TiCl_4 < {}^{47}TiCl_4 < {}^{49}TiCl_4 < {}^{50}TiCl_4$.[256] The separation factor obtained by Rayleigh distillation in the same work

shows the vapor pressure of $^{50}TiCl_4$ to be higher by 0.2–0.4% than that of $^{46}TiCl_4$ at the boiling point (136.5°).

E. Effects in Hydrogenic but Nonassociated Molecules: Especially Hydrocarbons (Table XII)

Considerable information on isotope effects in hydrocarbon systems has been reported recently. Often this work includes studies on molar volume effects, enthalpic effects, virial coefficient effects, etc., and much of it has been theoretically analyzed in detail. In the present section we will summarize this literature, especially as it affects the theoretical analysis.

Protio–deutero isotope effects in hydrocarbons exhibit a rather wide variety of behavior depending on the intermolecular forces operating in the condensed phase. This is illustrated in Figure 3 where representative effects for a number of different hydrocarbons are compared with each other and with some associated compounds. In the case of substitution at saturated carbon the effects are generally dominated by red shifts in the infrared stretching motions which account for the observed inverse VPIE's. If substitution is made at groups which associate in the condensed phase, the pertinent modes generally blue-shift on condensation, and normal effects result. The contrast is nicely illustrated by comparing H/D effects for methylacetylenes substituted in methyl and methynic groups (Figure 3). In the case of molecules with small moments of inertia or masses (for example, methane), the contribution of the external modes is also important and may predominate.

1. Methanes

Isotope effects (including D, T, ^{13}C, and ^{14}C) on many of the physical properties of methane are known, and the available information is much more nearly complete than for any other polyatomic molecule. It is for this reason that we plan to discuss this system in considerable detail in the following paragraphs.

Methane isotope effects were among the earliest ones to be determined with precision. Clusius and coworkers reported thermal data and vapor pressure measurements both before[257-260] and after[166,261] World War II. Vapor pressure measurements on the entire series of deuterated methanes (solid and liquid) between approximately 75 and 110°K were made at the National Bureau of Standards during 1935–1938, although they were not reported until later (Armstrong, Brickwedde, and Scott[262,263]). The NBS data were obtained using differential oil and mercury manometry on purified samples of separated isotopes. The experimental precision was approximately 0.01 Torr. Johns[58] has determined the ^{14}C VPIE over the same temperature range by the same technique. His results are in good agreement with later measurements of Clusius, Endtinger, and Schleich,[261] but significantly higher than results obtained using Rayleigh distillation[210] or from measurements made on samples of lower isotopic purity.[184] Bigeleisen, Cragg, and Jeevanandam[81] nicely rounded out the available data by a series of determinations of the VPIE's of the $C^{14}H_4$–$C^{12}H_4$ and CH_3T–CH_4 pairs over the liquid range (91–120°K) using multistage column distillation. Grigor and Steele[264,265] extended measurements of the VPIE of CD_4–CD_4 as far as the critical temperature, although with less precision than is available at lower pressures. They also determined CH_4–CD_4 IE's on molar volumes and isothermal compressibilities of liquid and vapor and measured the critical parameters.

The VPIE data cited above have been gathered together and critically evaluated by Bigeleisen, Cragg, and Jeevanandam (BCJ)[81] who applied the appropriate corrections for molar volume and gas nonideality, and calculated the reduced partition functions, which were then fit to equations of the proper theoretical form, $\ln (f_c/f_g) = A/T^2 + B/T$. These are properly regarded as the currently best available descriptions of the VPIE's of isotopic methanes. They are quoted in Table XII and shown graphically in Figure 4. The data points included for one isomer illustrate the experimental dispersion. The second set of lines in the figure has been calculated by BCJ and is discussed in more detail below.

Other information on the IE's of methane includes a wealth of information on the low-temperature heat capacities and the low-temperature solid–solid phase transition temperatures of all of the deuterated methanes (Colwell, Gill, and Morrison[266-270]). These studies have extended the earlier calorimetric work of Clusius and others.[257-260,271-273] It is not our intent to discuss the heat capacity data in detail. However we do show the temperatures at which the two low-temperature λ transitions occur in the solid for each of the H/D isomers in Figure 5. The solid–liquid–vapor triple points and the crossover temperatures (as calculated from Table XII) are given in Table XIII and the critical parameters in Table XIV. Molar volume isotope effects for the pair CD_4/CH_4 have been measured by Grigor and Steele,[265] and by Fuks, LeGros and Bellemanns.[274] They are reviewed in Table XV. It is interesting to note that the effect changes smoothly from around 1% normal ($V_{CH_4} > V_{CD_4}$) at 100°K to 2% inverse near the end of the liquid range (180°K). The calorimetric heats of fusion and heats of vaporization are compared with those derived from vapor pressures in Tables XVI and XVII. The second virial coefficients of the vapors have been determined over the range 100–300°C for all of the deutero–protio isomers by Fang and Van Hook[275] and earlier for CH_4/CD_4 and $^{13}CH_4/CH_4$ by Thomaes and van Steenwinkel.[276] Also Gainar, Strein, and Schramm[277] recently report effects for CH_4/CD_4 over the range 200–510°K. Their data (in the region of overlap) are lower than those reported in ref 275 or 276. The authors[275] first cited report that, for the intermediate isomers, CH_3D, CH_2D_2, and CHD_3, the isotope effects obey the law of the mean to within the experimental precision (about ±0.2 cc/mol). That for CD_4/CH_4 is given by $B(CD_4) - B(CH_4) = (2.08 \pm 0.14) + (399.8 \pm 24.2)/T$. $\Delta B/B$ amounts to approximately 2% at 110°, increasing to 9% at 300°. The analysis indicated that the most important contribution to the virial coefficient isotope effect was due to the isotope effect on the molecular polarizability. The value for this effect, $\alpha_H/\alpha_D = 1.014$, extracted from the data was consistent with that derived from other measurements.[278,279] Finally the IE on viscosity has been reported for the methanes.[280,281]

The simple structure of the methane molecule considered together with the rather complete nature of the information available on the isotope effects would lead one to suppose that this system would be a prime candidate for a clear and unequivocal application of the theory. This, however, is not the case, and some matters of interpretation remain in serious dispute. One important issue involves the description of the rotational modes in the different phases of the solid and in the liquid. The discovery of the λ transition of CH_4 at 20.4°K[272] led rapidly to the suggestion that it was associated with the onset of free rotation.[282] However, the observation that not one, but two, such transitions exist for each isotopic isomer complicated that interpretation, as did other experiments including infrared[283,284] and Raman[285] spectroscopy, inelastic neutron scattering,[286] and the interpretation of the VPIE data itself[81] (*vide infra*). These experiments, taken as a whole, indicate that some kind of barrier to rotation must exist in the solid right up to the melting point, and, in fact, further on into the liquid phase. Even so, the precise nature of this rotation in any of the four different condensed phases has not yet been accurately delineated in

TABLE XII. VPIE's of Hydrocarbons, etc.[a]

Part A

Compound	Ref (date)	Type	Temp range, °C (or °K)	Method	Equation, table or graph	Ln R at low T and high T
Methane						
$^{12}CH_4$–$^{13}CH_4$	304 (56)	l	98–112°K	R	Ln $R = 2.7562/T - 0.01800$	
	58 (58)	l	91–105°K	DP	Ln $R_l = 85.0/T^2 - 0.442/T$	
		s	80–91°K	DP	Ln $R_S = 70.0/T^2 - 0.24/T$	
	210 (56)	l	91–110°K	R	Ln $R = 0.6686/T + 0.00396$	
	184 (54)	l	91–96°K	DP	Log $R = 4.19855/T + 0.077507 \log T$ -0.19588	
	261 (60)	l	91–112°K	DP	Ln $R = 166.82/T^2 - 2.072/T +$	Cf. Fig 4
	166 (63)				$+ 0.00817$	
	81 (67)	l, s	91–105°K	CR	Ln $f_l = 93.8/T^2 - 0.535/T$	
			80–91°		Ln $f_S = 64.3/T^2 - 0.175/T$	
	185 (58)	l	200 mm	D	$R^+ = 1.0108$	
$^{14}CH_4$–CH_4	81 (67)	l	91–120°K	D	4 pts: ln $f = 231.1/T^2 - 1.42/T$	Cf. Fig 4
	304a (62)	l	92.0–110.5°K	R	Log $R^+ = 1.1275/T - 0.0019$	
CH_3D–CH_4	262 (55)	s	75–91°K	DP	$T \log R = 110.2/T - 1.260$	
		l	91–112°	DP	$T \log R = 129.5/T - 1.328$	
	166 (63)	l	91–110°K	DP	7 pts, in good agreement with ref 262: earlier refs	
	81 (67)	s	75–91°K	CR	Ln $f_c/f_g = 277.3/T^2 - 3.168/T$	Cf. Fig 4
		l	91–120°K	CR	Ln $f_c/f_g = 292.2/T^2 - 2.995/T$	
CH_3T–CH_4	81 (67)	l	91–120°K	D	7 pts: ln $f = 502.8/T^2 - 4.827/T$	Cf. Fig 4
CH_2D_2–CH_4	262 (55)	s	75–91°K	DP	$T \log R = 222.2/T - 2.694$	Cf. Fig 4
		l	91–112	DP	$T \log R = 245.4/T - 2.671$	
	81 (67)	s	75–91	CR	Ln $f = 497.3/T^2 - 6.033/T$	Cf. Fig 4
		l	91–120	CR	Ln $f = 535.8/T^2 - 5.854/T$	
CHD_3–CH_4	262 (55)	s	75–91°K	DP	$T \log R = 351.7/T - 4.452$	
		l	91–112	DP	$T \log R = 343.8/T - 3.969$	
	81 (67)	s	75–91	CR	Ln $f = 831.3/T^2 - 10.486/T$	Cf. Fig 4
		l	91–120	CR	Ln $f = 748.5/T^2 - 8.687/T$	
CD_4–CH_4	262 (55)	s	75–91°K	DP	$T \log R = 410.5/T - 5.529$	
		l	91–112	DP	$T \log R = 421.1/T - 5.159$	
	264 (68)	l	120–183	P	24 pts plotted as a deviation function	
	81 (67)	s	75–91	CR	Ln $f = 888.5/T^2 - 12.083/T$	Cf. Fig 4
	262 (55)	l	91–120	CR	Ln $f = 894.77/T^2 - 11.097/T$	
Ethylene						
C_2H_4–C_2H_3D	302 (63)	l	−153 to −93	DP	Ln $R = 408.3/T^2 - 3.570/T$	−0.001
						−0.007
	303 (68)	l	−153 to −93	Th	Ln $R = 417.3/T^2 - 3.989/T$	−0.002
					$+ 0.00194$	−0.007
C_2H_4–$C_2H_2D_2$						
C_2H_4–$C_2H_2D_2$ (trans)	301 (63)	l	−153 to −93	DP	Ln $R = +716.0/T^2 - 6.865/T$	−0.008
						−0.016
$C_2H_2D_2$ (trans)–$C_2H_2D_2$ (cis)	301 (63)	l	−153 to −93	DP	Ln $P_t/P_c = 22.41/T^2 - 1.670 \times 10^{-4}$	0.0014
	300 (61)			D		0.0005
$C_2H_2D_2$ (trans)–$C_2H_2D_2$ (gem)	301 (63)	l	−153 to −93	DP	Ln $P_t/P_g = 22.86/T^2 - 4.395 \times 10^{-4}$	0.0011
						0.0003
C_2H_4–$C_2H_2D_2$ (trans)	303 (68)	l	−153 to −93	DP	Ln $f = +643.0/T^2 - 6.372/T$	−0.008
						−0.016
				Th − Cr	Ln $f = +711.9/T^2 - 6.891/T$	−0.006
					$+ 0.00180$	−0.016
C_2H_4–$C_2H_2D_2$ (cis)	303 (68)	l	−153 to −93	DP	Ln $R = +690.4/T^2 - 6.569/T$	−0.007
						−0.015
				Th − Cr	Ln $f = +751.0/T^2 - 7.059/T$	−0.007
					$+0.00211$	−0.014
C_2H_4–$C_2H_2D_2$ (gem)	303 (68)	l	−153 to −93	DP	Ln $R = +797.1/T^2 - 7.403/T$	−0.006
						−0.017
				Th − Cr	Ln $f = +800.2/T^2 - 7.570/T$	−0.004
					$+0.00303$	−0.014
C_2H_4–C_2HD_3	303 (68)	l	−158 to −93	DP	Ln $R = 1057.6/T^2 - 10.284/T$	−0.012 (−153)
						−0.024
	303 (68)	l	−153 to −93	Th	Ln $f = 1033.3/T^2 - 10.132/T$	−0.010
					$+ 0.00237$	−0.022
C_2H_4–C_2D_4	303 (68)	l	−158 to −93	DP	Ln $R = 1308.5/T^2 - 13.124/T$	−0.018 (−153)
						−0.033
	303 (68)		−153 to −93	Th	Ln $f = 1257.9/T^2 - 12.833/T$	−0.018
					$+ 0.00194$	−0.031

TABLE XII *(Continued)*

Part A

Compound	Ref (date)	Type	Temp range, °C (or °K)	Method	Equation, table or graph	Ln R at low T and high T
$^{12}CH_2{}^{12}CH_2$–$^{11}CH_2{}^{12}CH_2$	302 (63)			D	2 pts, $1.2 \pm 0.2 \times 10^{-3}$ and $4.0 \pm 0.3 \times 10^{-4}$	−139° −105°
	302 (63)		−153 to −93	Th	Ln $R = 58.7/T^2 - 0.281/T$	0.0017 0.0003
	304 (56)		−153 to −103	R	Ln $R = 0.00292 - 0.1879/T$	0.0014 0.0018
Ethane						
$^{12}C_2H_6$–$^{12}C^{13}CH_6$	304 (56)	I	−143 to −88	R	Ln $R = 0.9177/T - 0.00490$	0.0021 (−143) 0.0000 (−88)
CH_3CH_3–CH_3CH_2D	310 (66)	I	−158 to −73	DP	Table 59 pts. emp eq 5 par[b]	*Cf.* Fig 6
CH_3CH_3–CH_2DCH_2D	310 (66) 309 (64)	I	−158 to −73	DP	Table 45 pts; emp eq 5 par[b]	
CH_3CH_3–CHD_2CH_2D	310 (66) 309 (64)	I	−158 to −73	DP	Table 41 pts; emp eq 5 par[b]	*Cf.* Fig 6
CH_3CH_3–CHD_2CHD_2	310 (66)	I	−158 to −73	DP	Table 37 pts; emp eq 5 par[b]	*Cf.* Fig 6
CH_3CH_3–CD_3CHD_2	310 (66)	I	−158 to −73	DP	Table 21 pts; emp eq 5 par[b]	*Cf.* Fig 6
CH_3CH_3–CD_3CD_3	310 (66)	I	−158 to −73	DP	Table 38 pts; emp eq 5 par[b]	*Cf.* Fig 6
CHD_2CH_3–CH_2DCH_2D	310 (66)	I	−148 to −73	DP	Table 45 pts; emp eq 5 par	*Cf.* Fig 6
CD_3CH_3–CD_2HCH_2D	310 (66)	I	−148 to −73	DP	Table 41 pts; emp eq 5 par	*Cf.* Fig 6
CD_3CH_2D–CHD_2CHD_2	310 (66)	I	−148 to −73	DP	Table 37 pts; emp eq 5 par	*Cf.* Fig 6
Acetylene						
C_2H_2–C_2D_2	314 (70)	s	−148 to −83	DP	$10^4 \ln R = -382.71 + 91707/T$; $T > 147.4$ $10^4 \ln R = -8953.2 + 1.3551 \times 10^6/T$; $T < 147.4$	
C_2H_2–C_2HD			−148 to −88	DP	$10^4 \ln R = -204.12 + 51940/T$; $T > 150$	
Methylacetylene						
CH_3CCH–D_3CCCH	316 (67)	I	−106 to −18	DP	Table 47 pts; emp eq 5 par[b]	*Cf.* Fig 3
CH_3CCH–H_3CCCD	316 (67)	I	−106 to −18	DP	Table 32 pts; emp eq 5 par	*Cf.* Fig 3
CH_3CCH–D_3CCCD	316 (67)	I	−106 to −18	DP	Table 32 pts; emp eq 5 par	*Cf.* Fig 3
Propylene						
CH_3CHCH_2–CH_3CDCH_2	317 (70)	I	140–235°K	DP	Table 60 pts; emp eq 5 par[b]	0.008 −0.005
CH_3CHCH_2–CH_2DCHCH_2	317 (70)	I	140–235°K	DP	Table 40 pts; emp eq 5 par	−0.010 −0.008
CH_3CHCH_2–CH_3CHCD_2	317 (70)	I	140–235°K	DP	Table 52 pts; emp eq 5 par	0.000 −0.011
CH_3CHCH_2–CD_3CDCD_2	317 (70)	I	140–235°K	DP	Table 47 pts; emp eq 5 par	−0.059 −0.050
Benzene						
C_6H_6–C_6D_6	318 (53) 319 (64)	I	10–80	DP	Log $P = A + B/(C + t, °C)$ $A_H = 6.9121$ $A_D = 6.8887$ $B_H = -1214.65$ $B_D = -1196.38$ $C_H = 221.21$ $C_D = 219.21$	*Cf.* Fig 3
	2,319 (64)	s	−30 to +5	DP	Table (8)	0.01 (−30) −0.007 (+5)
	323 (72)	s	−39 to +4	DP	Eq 5 parameters[b]	
		I	6.4–160	DP	Eq 5 parameters[a]	
C_6H_6–p–$C_6H_4D_2$	323 (72)	I	6–21	DP	Ln $R_{D_2} = \ln R_{D_6}/3$	
C_6H_6–C_6H_5D	323 (72)	I	6–21	DP	Ln $R_{D_1} = \ln R_{D_6}/6$	
$^{12}C_6H_6$–$^{13}C^{12}C_5H_6$	62 (53)	I	34.6	D	Ln $R = -2.5 \times 10^{-4}$	−0.00025 (34.6)
$^{12}C_6H_6$–$^{13}C^{12}C_5H_6$	128 (61)	I	34.6; 78.0	D	Table (2)	−0.000230 (34.6) −0.000350 (78.0)
Toluene						
$C_6H_5CH_3$–$C_6D_5CD_3$	2,319 (64)	s, I	−20 to +15	DP	Table (8); graph	*Cf.* Fig 3
		I	20–90	P	Table (8)	
$C_6H_5CH_3$–p–$C_6H_4DCH_3$	323 (72)	I	−35 to 145	DP	Eq 5 parameter[b]	
$C_6H_5CH_3$–$C_6D_5CH_3$	319 (64)	I	−20 to +15	P	Table (8)	−0.06 (−20) −0.05 (+15)

TABLE XII *(Continued)* Part A

Compound	Ref (date)	Type	Temp range, °C (or °K)	Method	Equation, table or graph	Ln R at low T and high T
Cyclohexane						
C_6H_{12}–C_6D_{12}	318 (53)	I	10–80	DP	Log $P = A + B/(C + t, °C)$ $A_H = 6.8450$ $A_D = 6.8704$ $B_H = -1203.53$ $B_D = -1208.29$ $C_H = 222.86$ $C_D = 224.44$	*Cf.* Fig 3
	2,319 (64)	s	−40 to 5	DP	Ln $P_D/P_H \approx 0.11$, entire range	
	323 (72)	Glass, l	−61.1 to 130	DP	Eq 5 parameters[b]	
Neopentane						
$(CH_3)_4C$–$CD_3C(CH_3)_3$	327 (69)	s, l	−40 to +20	DP	Graph 10 pts $T_{trp}(CH_3)_4C = -16.34 \pm 0.02$ $T_{trp}(CH_3)_3CCH_3 = -16.90 \pm 0.02$	Liq: $-0.021 <$ ln $R < -0.019$ Solid: $-0.025 <$ ln $R < -0.022$ Max seen in the solid
Halogenated compounds						
CH_3Cl–CD_3Cl	328 (47)	l	183–249°K	P	Log $P_{CH_3Cl} = -1590.72/T - 3.9777$ log $T + 18.795$ Log $P_{CD_3Cl} = -1593.76/T - 4.06144$ log $T + 19.02286$	−0.039 (203) −0.031 (277)
$CH_3{}^{35}Cl$–$CH_3{}^{37}Cl$	214 (58)	l	Not cited	D	Ln $R \sim 0$	
CH_3Br–CD_3Br	328 (47)	l	203–277°K		Log $P_{CH_3Br} = -1696.91/T - 3.36805$ log $T + 17.23566$ Log $P_{CD_3Br} = -1683.89/T - 3.28743$ log $T + 17.00870$	−0.039 (203) −0.031 (277)
CH_3I–CD_3I	328 (47)	l	273–315°K	P	Log $P_{CH_3I} = -1476.2/T + 7.5549$ Log $P_{CD_3I} = -1471.9/T + 7.5613$	−0.054 (273) −0.047 (315)
$CHCl_3$–$CDCl_3$	2,319 (64)	l	233–283°K	DP	Table (10)	−0.040 (233) −0.016 (283)
$^{12}CHCl_3$–$^{13}CHCl_3$	62 (53)	l	34.6	D	Ln $R = -8 \times 10^{-4}$	−0.0008 (34.6)
$CH^{35}Cl^{37}Cl_2$–$CH^{37}Cl_3$	62 (53)	l	34.6	D	Ln $R = +10^{-4}$	0.0001 (34.6)
CH_3CCCl–CD_3CCCl	329 (54)	l	230–290	P	Log $P_H = -1480/T + 7.740$ Log $P_D = -1487/T + 7.782$	−0.029 (230) −0.039 (290)
CH_2BrCH_2Br–$CHDBrCH_2Br$	330 (49)	l	404.70°K 404.40°K	Bp		
CH_2BrCH_2Br–$CHDBrCHDBr$			404.05°K			
CH_2BrCH_2Br–CH_2BrCD_2Br			404.05°K			
CH_2BrCH_2Br–$CHDBrCD_2Br$			403.65°K			
CH_2BrCH_2Br–CD_2BrCD_2Br			403.30°K			
Silanes						
SiH_4	334 (39)	l	90–160°K	P	Log $P = -740.0/T + 1.75$ log T $- 79701 \times 10^{-7}T + 4.87448$	
SiD_4	334 (39)	l	90–160°K	P	Log $P = -793.0/T + 1.75$ log T $- 94026 \times 10^{-7}T + 5.31421$	0.12 (90) −0.010 (160)
$SiHD_3$	335 (69)	l	108–129°K	P	Log $P = -705.674/T + 7.29975$	
Si_2H_6	334 (39)	l	160–260°K	P	Log $P = 1380.2/T + 1.75$ log T $- 69309 \times 10^{-7}T + 5.78216$	
Si_2D_6	334 (39)	l	160–260°K	P	Log $P = -1394.3/T + 1.75$ log T $- 71510 \times 10^{-7}T + 5.91428$	−0.025 (160) −0.048 (260)
Si_3H_8–Si_3D_8	337 (39)	l	Normal boiling points reported			
Si_4H_{10}–Si_4D_{10}	333 (39)	l				
$^{28}SiH_4$–$^{29}SiH_4$–$^{30}SiH_4$	See Table VIII					
Borane						
B_5H_9–B_5D_9	337 (57)	l	25–57	DP	Log $P_H = 9.49191 - 1881.29/T$ $- 0.0028956T$ Log $P_D = 9.46916 - 180.70/T$ $- 0.0028783T$ Mp H = −46.8° D = −47.0° Bp H = 60.0°, D = 59.0°	 −0.056 (250) −0.034 (330)
Germanes						
GeD_4	336 (54)	l	10–800 mm	P	Log $P = -3744/4.575T + 7.327$ $T_m = 107$°K	
Ge_2D_6	336 (54)	l		P	Log $P = -6483/4.575T + 7.579$ $T_m = 165.3$	
Ge_3D_8	336 (54)	l		P	Log $P = -7876/4.575T + 7.367$ $T_m = 172.9$	

TABLE XII *(Continued)*

R	Part B. Fits to Ln $R = A + (B/T) + (C/T^2) + (D/T^3) + (E/T^4)$ ($R = P_D/P_H$) A	B	C × 10^{-5}	D × 10^{-7}	E × 10^{-9}
C_2H_5D-C_2H_6	−0.164392	+122.933	−0.327365	+0.389223	−0.172848
(1,2-$C_2H_4D_2$)-C_2H_6	−0.400038	+279.680	−0.705654	+0.798999	−0.340035
(1,1-$C_2H_4D_2$)-C_2H_6	−0.612092	+414.260	−1.01799	+1.11155	−0.452136
(1,1,2-$C_2H_3D_3$)-C_2H_6	−0.483517	+343.513	−0.873413	+0.999196	−0.429560
(1,1,1-$C_2H_3D_3$)-C_2H_6	−0.282277	+213.014	−0.556517	+0.658464	−0.291553
(1,1,1,2-$C_2H_2D_4$)-C_2H_6	−0.147808	+110.172	−0.253543	+0.275270	−0.113337
(1,1,2,2-$C_2H_2D_4$)-C_2H_6	−0.473811	+323.315	−0.776343	+0.844644	−0.346348
C_2HD_5-C_2H_6	−0.557990	+388.176	−0.945723	+1.04393	−0.433175
C_2D_6-C_2H_6	−0.298096	+229.639	−0.576798	+0.671692	−0.294238
CH_3CDCH_2-C_3H_6	0.3047	−212.71	0.5402	−0.5652	0.1918
CH_3CHCD_2-C_3H_6	0.8335	−582.60	1.5129	−1.7000	0.6927
CH_2DCHCH_2-C_3H_6	−1.2001	905.05	−2.5496	3.2047	−1.5120
CD_3CDCD_2-C_3H_6	0.5810	−405.49	1.1150	−1.3038	0.5521
CH_3CCD-C_3H_4	−0.89960	826.56	−2.81246	4.22582	−2.37971
CD_3CCH-C_3H_4	−0.51362	406.11	−1.14036	1.45534	−0.70580
CD_3CCD-C_3H_4	−2.24470	2005.52	−6.62015	9.72946	−5.36540
C_6H_{12}-C_6D_{12} (61.1-130.0°)	-1.80513×10^{0}	$+2.26910 \times 10^{3}$	−10.4158	$+21.2537 \times 10^{8}$	−15.9730
$C_6H_5CH_3$-p-$C_6H_4D.CH_3$ (35-145°)	$+8.41078 \times 10^{-1}$	-1.09835×10^{3}	+5.28158	-11.0315×10^{8}	+8.45987
C_6H_6-C_6H_6 (sol) (39-4.0°)	-1.47319×10^{1}	$+1.46710 \times 10^{4}$	−54.5863	$+90.0357 \times 10^{8}$	−55.5726
C_6H_6-C_6D_6 (liq) (6.4-160.0)	-6.02144×10^{1}	$+7.61293 \times 10^{2}$	−3.52802	$+73.8139 \times 10^{7}$	−5.84986

[a] l = liquid; s = solid; Th = theoretical evaluation; P = pressure; DP = differential pressure; D = distillation; Cr = critical evaluation, several workers. $R = P'/P$, $f = f_c/f_g$ = reduced partition function ratio; the prime refers to lighter isotope. [b] See Part B.

TABLE XIII. Some Isotope Effects on Transition Temperatures of Methanes[a]

	Triple Point ΔT_{trp}	Ref	Crossover $P_{CH_4}/P_X = 1$	Ref
$^{12}CH_4$				
CH_3D	0.265	268	87.5 (sol), 97.6 (liq)	262
	0.254	262	87.5 (sol), 97.6 (liq)	262
CH_2D_2	0.505	268	82.4 (sol), 91.5 (liq)	262
	0.492	262		
CHD_3	0.715	268	79.3 (sol)	262
	0.701	262		
CD_4	0.865	262	73.6 (sol)	262
	0.891	267		
$^{13}CH_4$	0.031	58		58
$^{14}CH_4$				
CH_3T			103.9 (liq)	81

[a] $T_{trp}(X) = T_{trp}(CH_4) - \Delta T_{trp}$; $T_{trp}(CH_4) = 90.660$ (ref 262); 90.675 (ref 267).

TABLE XIV. Critical Constants for CH_4 and CD_4[264,265]

	T_{cr}, °K	V_{cr}, cc/mol	P_{cr}, atm	ρ_{cr}, g/cc
CH_4	190.6 ± 0.1	98.7 ± 0.3	45.6 ± 0.1	0.1626 ± 0.0005
CD_4	189.2 ± 0.1	97.9 ± 0.3	46.0 ± 0.1	0.2045 ± 0.0005

TABLE XV. Molar Volume of Methanes

T, °K	V_{CH_4}	$V_{CH_4} - V_{CD_4}$	Ref
100	36.605	0.393	274
110	38.053	0.367	274
120	39.2	0.4	264
140	42.8	0.3	264
160	48.0	0.2	264
180	58.3	−1.3	264

spite of many theoretical studies of the rotational motion of molecules in restricting fields (ref 287–289, for example).

For the rotational contribution one finds in general that, as the restricting potential is increased, the free rotor energy levels split in a complex way which depends on the symmetry of both the molecule and the (crystal) field in which it is placed,

TABLE XVI. Heats of Fusion (cal/mol) of Isotopic Methanes at 90.675°K[a]

$\Delta(\Delta H_f)_{90.675} = (\Delta H_f)^{CH_4}_{90.675} - (\Delta H_f)^{x}_{90.675}$

x	From fits (ref) to VPIE	Calcd (ref)	Calorimetric[a] (ref)
CH_3D	1.6 (262)	1.6 (81)	−2.6 (268, 267)
CH_2D_2	2.5 (262)	2.5 (81)	0.8 (268, 267)
CHD_3	1.4 (262)	3.8 (81)	1.7 (268, 267)
CD_4	2.8 (262)	3.5 (81)	2.3 (267)
$^{13}CH_4$	0.6 (58)		

[a] Calculated from observed heat at triple point taking ΔT_{trp} from Table XIII and C_p(liq) − C_p(solid) = 2.25. $\Delta H_f^{CH_4}(90.675)$ = 221.9,[267] 225.2,[271] 224.[272]

TABLE XVII. Heats of Vaporization (cal/mol) at 100°K

$\Delta(H_v) = (\Delta H_v)_{CH_4} - (\Delta H_v)_{CD_4}$

	$(\Delta H_x)_{cal}$ (ref)	$\Delta(\Delta H_v)_{cal}$	$\Delta(\Delta H_v)_{VPIE}$[a]
CH_4	2034 ± 5 (269)		
CH_3D	2047 ± 2 (257)	−13 ± 5	−6
CH_2D_2	2058 ± 6 (269)	−24 ± 8	−9
CHD_3			−12
CD_4	2063 ± 5 (269)	−29 ± 7	−14
CH_3T			−10
$^{13}CH_4$			−3
$^{14}CH_4$			−8

[a] Calculated from equations in Table XII.

and finally coalesce at high fields into levels representing torsional oscillations (librations). The precise nature of the fields is not yet established, but Nakamura and Miyagi[289] have recently correlated the isotopic data on λ transition temperatures with a model calculation. They divided the crystal structure of the methanes (which are FCC) into four simple cubic sublattices. In phase II they assumed that molecules in three sublattices alternate in orientation along |100|, |010|, and |001| directions, and those in the fourth rotate freely. Phase III was taken as a layer structure with uniform orientation in the plane but alternate orientation in the |001| direction. The isotope effect on the (order–disorder) transition temperature was then developed by means of an expansion over quantum corrections where the rotational contribution predominates. In

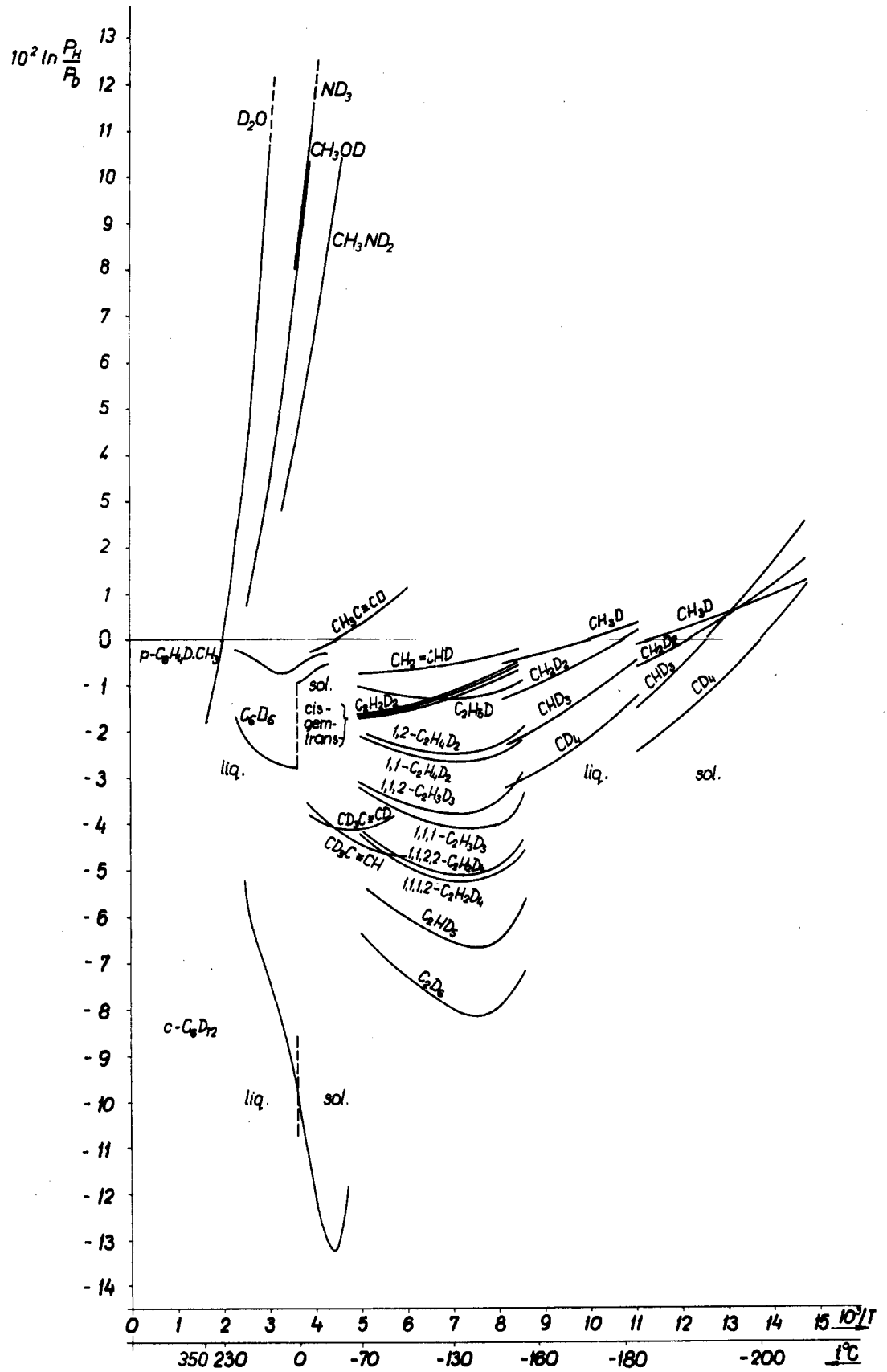

Figure 3. H/D VPIE of some compounds.

this way the transition temperatures are correlated with the rotational temperatures, $\theta = \hbar^2/I$ (spherical rotor) and $\theta = (\hbar^2/3)(2/I_1 + 1/I_3)$ (symmetrical rotor). The correlation is shown in Figure 5 and confirms the assignment of the transition as rotational in nature. It is interesting to note that this particular model calculation assumes that the rotation of the average methane molecule is significantly hindered even in the high-temperature phase.

Next we turn our attention to the properties of the high-temperature solid and liquid phases and consider the avail-

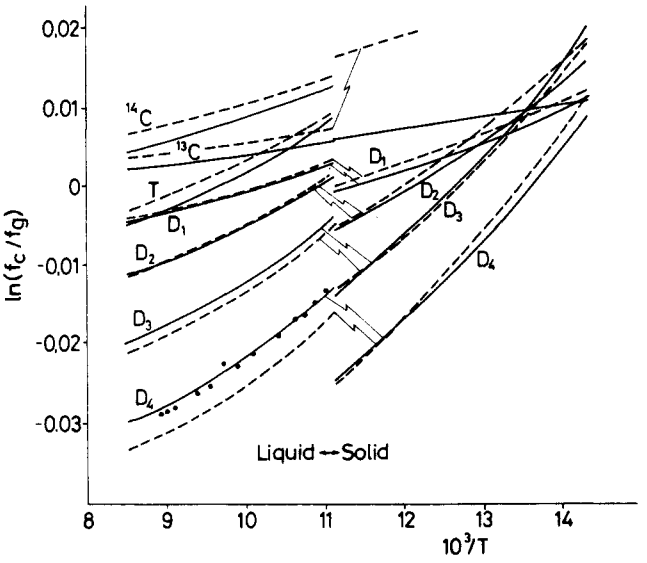

Figure 4. Vapor pressures of the isotopic methanes:[81] (——) fit to data; (- - - -) calculated.

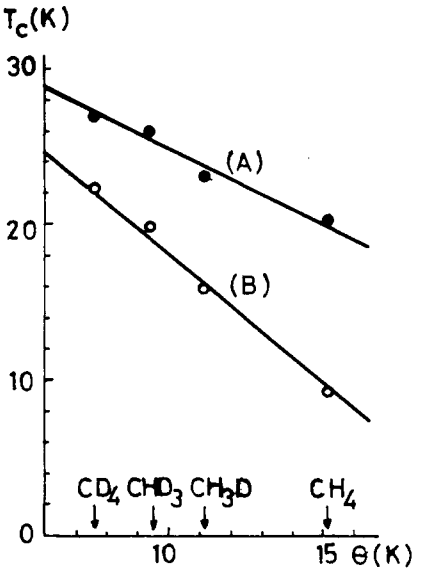

Figure 5. The upper (A) and lower (B) transition temperatures of the deuterated methanes. The lines are calculated from the theory of Nakamura and Miyagi.[289]

TABLE XVIII. Relative A Values for Isotopic Methanes

	Calcd for free rotor	Exptl		
		Solid (81)	Liquid (81)	Adsorbed (290)
CH_3D–$^{13}CH_4$	0.8	4.3	3.1	2.9
CH_2D_2–$^{14}CH_2$	0.9		2.3	
CH_3T–$^{14}CH_4$	0.7		2.2	

able VPIE following Bigeleisen, Cragg, and Jeevanandam.[81] These authors employed a harmonic oscillator model and calculated reduced partition function ratios using the Wilson *FG* matrix method *via* the approach of Stern, Van Hook, and Wolfsberg.[80] Due account was taken of the external–external and external–internal coupling. The calculation is worth considering in some detail because it embodies an approach which has been successfully employed in rationalizing the VPIE's of a number of different molecules. A similar calculation which focused on the methane(vapor) = methane(adsorbed) equilibria was made independently by Van Hook[290] who examined the application of Bigeleisen's theory[77] to the gas chromatographic separation factors for the isotopic methanes.[291–293] In the BCJ or VH calculations the problem of primary interest is the analysis of the rotational contribution. The discussion is most conveniently made in terms of the approximate relation, eq 36 or eq 42. The contribution of the internal modes is found primarily in the *B* term because these frequencies are large. The lattice contribution (*A* term) is from both translation and rotation. The effects may be sorted out, one from the other, by considering the behavior of molecules of the same total mass but different moments of inertia, *e.g.*, $CH_3D/^{13}CH_4$, $CH_2D_2/^{14}CH_4/CH_3T$, etc. In other words data from a single isotopic pair, such as CH_4/CH_3D, only fixes the total lattice contribution, which in turn could be consistent with a large number of ratios of rotational to translational contributions. The experimental determination of *A*'s (Table XVIII) for the different species unequivocally shows that rotation must contribute in the solid and liquid[81] and adsorbed[290] phases, and therefore must be hindered. It allows the ratio of librational to translational force constants to be fixed.

The detailed force fields used in the complete harmonic calculation are shown in Table XIX where the frequency shifts on phase change (which give rise to the isotope effects) are entered at the bottom. The agreement between the observed (spectroscopic) and calculated shifts is within the experimental precision with which the latter have been determined. The agreement between calculated and observed VPIE's is shown in Figure 4 where the calculated effects are plotted as the long dashes. The agreement is good in most details especially considering that one (isotope and temperature independent) approximate force field has been applied to calculate effects for seven different isotopic isomers. The agreement extends to the heats of fusion and vaporization as calculated from the slopes (Tables XVI and XVII) which are in reasonable agreement with the calorimetrically determined values; differences are on the order of a few calories per mole. Still, it is clear that the model is subject to refinement. It does not fit even all of the vapor pressure data simultaneously to within the experimental precision. This is particularly noticeable in the case of ^{13}C substitution. The authors[81] suggest that a refined calculation in which due account is taken of stretch–bend interactions and of the contribution of the anharmonicity in the external motions would improve the agreement. It is interesting, perhaps disturbing, to note that in the model the librational frequencies are found to be higher in the liquid than in the solid.

An alternative rationalization of the isotope effects has been presented by Steele[265,294,295] by means of an application of the de Boer–Lunbeck[33,36] theory of corresponding states. Strictly speaking this analysis disregards molecular structure and considers the effects in terms of isotope effects on the parameters which describe the form of the intermolecular potential. Steele, however, extends the treatment arriving, after approximation, at an expression which expresses the effects as a sum of quantum corrections on translational, rotational, and vibrational terms. He then presents arguments that the IE's on molar volume, isothermal compressibility, and critical constants (Tables XIV and XV) are primarily due to differences in the intermolecular potential function and from the data obtains values for the differences. He admits that the analysis of the VPIE data is considerably more complicated but even so chooses to ignore the rotational contribution. Bigeleisen and Wolfsberg[296] reacted strongly to Steele's analysis. They reemphasized the importance of the rotational contribution which they supposed Steele had overlooked because he was only examining data on a single pair of isotopic isomers. They went further, however, and claimed that the assumption of isotope dependent intermolecular potentials con-

TABLE XIX. F Matrix Elements for Isotopic Methanes

Gas		$F_{gas} - F_{sol}$	$F_{gas} - F_{liq}$	$F_{gas} - F_{ads}$
5.495	F_S, CH stretch, mdyn/Å	0.063	0.043	0.051
0.568	F_B, HCH bend, mdyn Å	0.000	0.003	0.002
0.165	F_{SB}, mdyn	0.000	−0.010	0.000
0.124	f_{SS}, mdyn/Å	0.000	0.000	0.001
0.019	f_{BB}, mdyn Å	0.000	0.000	0.000
0	F_t, CH_4 translation, mdyn/Å	−0.096	−0.057	−0.063
0	F_r, CH_4 rotation, mdyn Å	−0.008	−0.010	−0.021
	Ref	81	81	290
	Calculated Frequency Differences of $C^{12}H_4$ (cm^{-1}), $\nu_g - \nu_{cond}$			
3143.7_1 (A)	CH stretch	16.9	11.5	12.8
1574.2_2 (E)	HCH bend	0.0	3.9	2.3
3154.1_3 (F)	CH stretch	18.7	13.9	15.5
1357.4_4 (F)	HCH bend	0.0	4.8	2.3
Trans (F)		100.5	77.7	81.5
Rot (F)		63.5	72.3	106.0

stitutes unwarranted violation of the Born–Oppenheimer approximation. Steele, himself,[297] later admits the importance of the rotational contribution but defends his point of view on the matter of parametrizing around the intermolecular potential constants σ and ϵ. In this way, he claims, one can develop a satisfactory corresponding states treatment extending all the way to the critical point, while it is difficult to extend credibility to oscillator models over such broad ranges of temperature and density.

Van Hook and Fang[275] spoke to the problem in their discussions of methane virial coefficient isotope effects. Their analysis of virial coefficient data using the Lennard-Jones 6-12 potential yielded $\Delta\epsilon/\epsilon = (\epsilon_H - \epsilon_D)/\epsilon_H = 0.050$ and $\Delta\sigma/\sigma = (\sigma_H - \sigma_D)/\sigma_H = -0.013$. They note that other authors considering essentially identical data obtained 0.015 and +0.002, respectively. However, analysis shows that $\Delta\epsilon/\epsilon \approx 4\Delta\alpha/\alpha$, not $\Delta\epsilon/\epsilon \approx \Delta\alpha/\alpha$ as had previously been claimed. The authors made a careful distinction between σ_S, a size parameter characterizing the isolated and noninteracting molecule, and σ_0, the Lennard-Jones size parameter (that value of r at which the intermolecular potential happens to be zero). They indicate that the isotope effect on σ_S is available from molecular size effect data *via* electron diffraction measurements[299] which can be shown to be consistent wit the measured polarizability effects[278,279] (*via* a modified Slater–Kirkwood theory), and with the VCIE data above. In view of the fact that the isotope effect on the molecular size is well understood in terms of an isotope-independent intramolecular potential function, the authors claim that the effects ($\Delta\epsilon/\epsilon$ and $\Delta\sigma/\sigma$, above) on the effective intermolecular potential follow. They in no sense imply a violation of the Born–Oppenheimer principle, but rather are a consequence of well-understood IE's on the dynamical structure of the molecule. In applying the model to condensed-phase molar volume data, it was necessary to account for interaction between next-nearest and higher neighbors because of the longer range of the attractive potential. This was done and it was demonstrated that IE's on the effective intermolecular potential constants are smaller in the condensed than in the gas phase, in agreement with experiment. Finally the authors speculate as to whether it might not be sometimes convenient at this level of approximation to employ the formalism of isotope-dependent *effective* intermolecular potentials in the handling of external translational modes in VPIE calculations. Such an approach would avoid the necessity of explicitly considering higher order terms in the handling of the dynamical analysis of the intramolecular part.

2. Ethylenes

An exhaustive series of measurements of the VPIE's of the six different deuterated ethylenes (including the three equivalent isotopic isomers *cis-*, *trans-*, and *gem*-$C_2H_2D_2$) has been reported by Bigeleisen and coworkers.[300-303] The isotopic pressure differences were determined manometrically. This group also measured the $^{13}C/^{12}C$ effect with a low-temperature distillation column.[302] The only previous study had been a determination of the ^{13}C effect by Yagodin, Uvarov, and Zhavoronkov[304] which is in reasonable agreement only at the lowest temperatures. The American authors claim that the positive temperature coefficient reported by Yagodin, *et al.*, is not theoretically reasonable.

The ethylene measurements have been analyzed in detail by Stern, Van Hook, and Wolfsberg[80] (d_0, d_1, d_2), and this analysis was later refined by Bigeleisen and Ishida[303] who had data available on all of the isotopic isomers. To begin with, the experimental data were found to conform to the approximate form predicted by theory, ln $R = A/T^2 + B/T$, because, for ethylene, the condensed-phase frequencies nicely factor into 6 low-lying lattice modes (A/T^2) and 12 much stiffer internal frequencies (B/T) which are then handled in the ZPE approximation. The original authors[302] chose to employ relations between the various A terms as imposed by the geometry and mass distributions, together with all of the available data on all isotopes, in making one simultaneous least-squares fit and thereby deriving a consistent set of "normalized" equations. The normalized A and B parameters were then compared with the results of a complete solution of the eigenvalue problem in the average cell approximation.[80,303]

In the detailed calculation[80] the cell model was solved giving 18 harmonic oscillator eigenvectors and eigenvalues for each isotopic isomer. The potential energy matrix for the internal coordinates was obtained by modifying the 12 dimensional gas-phase force field while requiring consistency with the available condensed-phase spectroscopic data. Only diagonal elements were considered for the six translational and rotational coordinates (but this constraint was removed in the refined calculation[303]). The translational elements were derived from heat capacity data, and the rotational ones in part from the VPIE data itself. No temperature dependency was assumed for the condensed phase constants. The kinetic energy matrix (G matrix) was calculated in the $3n$ dimensional space and included terms coupling internal with internal, external with external, and external with internal frequencies depending on the molecular symmetry. The resulting eigenvalues were then substituted into the complete equation (eq 32); the VPIE's were deduced as a function of temperature, and fit by least squares to give theoretical equations to be compared with experiment (*cf.* Table XII). The agreement with experiment was good. The vapor pressure differences between *cis-*, *trans-*, and *gem*-$C_2H_2D_2$ were shown to be principally

due to hindered rotation in the liquid (*i.e.*, the principal moments of inertia are different for these three molecules), but in addition, superimposed on this effect, there is a ZPE effect due to coupling of the hindered rotation with certain internal vibrations. The specific internal frequencies which couple with the rotation are symmetry dependent. The same effect is manifested by the shifts in the internal frequencies themselves on condensation (*i.e.*, in the B as well as the A term). In the absence of the effect, the law of the geometric mean would be obeyed, and $B(d_2)/B(d_1) = 2.00$. The symmetry dependent perturbations may theoretically be shown to necessarily lower this value. The calculated and experimental values are compared below:

	$(B(d_2)/B(d_1))_{\text{theor}}$	$(B(d_2)/B(d_1))_{\text{expt}}$
trans	1.83	1.88
cis	1.89	1.93
gem	1.92	1.98

Agreement in the ordering trans–cis–gem is cited as particularly strong evidence in favor of the correctness of the approach. Note that the order is symmetry, not model, dependent. The magnitude of the shift does depend on the parameters inserted into the calculation.

In the refined analysis by Ishida and Bigeleisen,[303] the force field was expanded to include off-diagonals coupling the external frequencies one to the other. In addition effects associated with expansion of the liquid as the temperature increases were considered. These are anharmonic effects and in first order are accounted for by eq 42, $\ln R = A/T^2 + B/T + C$. The authors also report new measurements on the dideutero isomers which are in good agreement with the earlier data.[301] They correct both the new and old data for molar volume, nonclassical rotation, and gas imperfection, thereby deriving values for the reduced partition function ratios which are then directly compared with theory. The set of derived equations are in excellent agreement with the experimental data. The agreement extends to details of rather subtle rotational effects and also shows consistency with spectroscopic studies within the experimental precision of the latter.

Molar volume isotope effects between C_2H_4 and *trans*-$C_2H_2D_2$ and C_2D_4 between 105 and 175°K have been measured by Menes, Dorfmüller, and Bigeleisen.[305] They observed an effect of approximately 0.05 cm^3/mol per D (H > D) which decreased with temperature. Calculations based on an anharmonic potential showed that hindered rotation made a significant contribution to the effect. The authors succeeded in correlating the MVIE and the VPIE data through a common force field. Their treatment of the MVIE should be compared with that earlier advanced by Bartell and Roskos.[652] The later authors, using a simplified model, showed that the most important contribution to the MVIE of larger molecules is due to a molecular size effect caused by isotope effects on the zero-point intramolecular motions of the molecules. The overall motion in the intermolecular potential also contributes, but that contribution is negligible for the molecules they considered (H and D benzene, toluene, cyclohexane, and methylcyclohexane). Dorfmüller and Gopel[306–308] have determined virial coefficient isotope effects for C_2D_4 and *trans*- and *gem*-$C_2H_2D_2$.

3. Ethanes

Yagodin and coworkers[304] have determined separation of factors for $^{12}C_2H_6/^{12}C^{13}CH_6$ by Rayleigh distillation. Van Hook[309,310] has measured the vapor pressures of all ten deutero–protio isomers between 115 and 200°K by manometry. The H/D isotope effects are inverse and all go through maxima between 125 and 140°K (Figure 6). At the maxima the effects are of the order of 1.2% per D atom. The observation of the maxima is consistent with theoretical expectation. Deviations from the law of the mean are small but occur between all three sets of equivalent isomers (1,1- and 1,2-$C_2D_2H_4$, 1,1,1- and 1,1,2-$C_3D_3H_3$, and 1,1,1,2- and 1,1,2,2-$C_2D_4H_2$). In each case the more unsymmetrically substituted compound was found to have the higher vapor pressure. Near the maxima (~140°) the effect between equivalent isomers is about 0.2%.

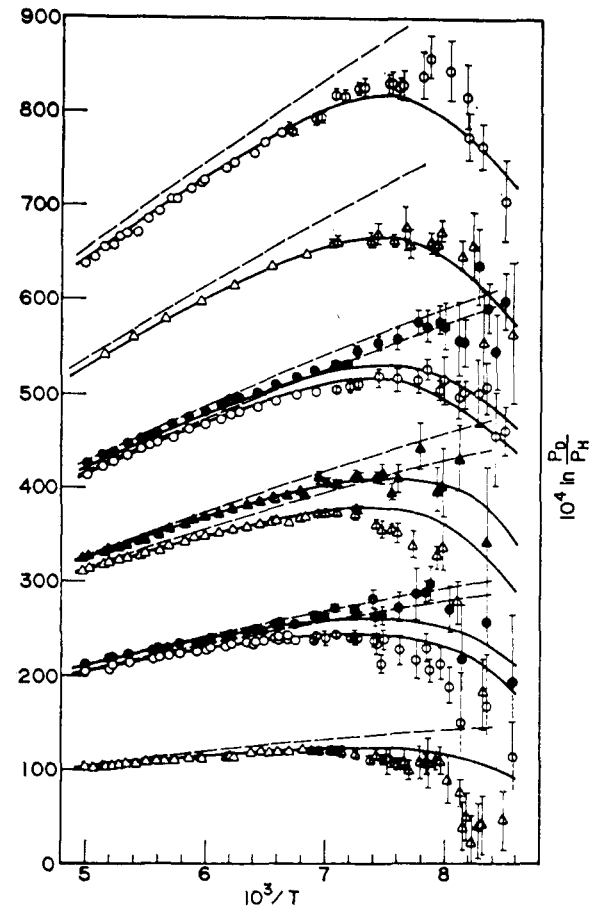

Figure 6. Vapor pressures of the deuterated ethanes:[310] points, experimental; lines, calculated; — temperature-dependent force field; - - - - -, temperature-independent force field. Reading up in order, D is equal to C_2H_5D; 1,2-$C_2H_4D_2$; 1,1-$C_2H_4D_2$; 1,1,2-$C_2H_3D_3$; 1,1,1-$C_2H_3D_3$; 1,1,2,2-$C_2H_2D_4$; 1,1,1,2-$C_2H_2D_4$; C_2HD_5; C_2D_6.

The data were interpreted in detail using a harmonic cell model following the method developed by Stern, Van Hook, and Wolfsberg.[80] The calculated shifts in the internal frequencies on condensation were in good agreement with the spectroscopic measurements. The calculations revealed that the torsional motion (the internal rotation) must be blue shifted on condensation and is the single most important factor determining the isotope effect between equivalent isomers. In order to take care of anharmonic effects caused by the expansion of the lattice, temperature-dependent force constants were invoked for the low-frequency lattice modes. (The theoretical justification for this approach was later formalized by Ishida and Bigeleisen.[303]) The results of the model calculation are compared with the experimental data in Figure 6. The general theoretical approach is nicely confirmed here (as above for CH_4 and C_2H_4) by the fit to all (ten in this case) of the isotopic isomers with one single set of isotopically independent force constants. The unequivocal prediction of the sign and magnitude of the equivalent isomer effect for all three pairs was also invoked as substantiating the approach.

Independent experimental evidence for the existence of maxima comes from the melting point data of Burnett and

Muller.[311] These authors report melting points as follows: CH_3CH_3, 89.82 ± 0.03°K; CH_3CD_3, 89.13 ± 0.03; CHD_2CHD_2, 89.89 ± 0.03; CHD_2CD_3, 89.82 ± 0.03. An nmr technique was employed. Following arguments of the kind recently articulated by Jeevanandam,[124] we may conclude from the lack of isotopic ordering in the data, and from the quite small magnitude of the effects, that crossover temperatures for these molecules must occur somewhere near their triple points. This in turn predicates the existence of a maximum in the VPIE at some higher temperature. It is interesting that a maximum is also found in the glc (gas–liquid chromatography) separation factors for C_2H_6/C_2D_6 reported by Van Hook and Phillips[312] and Van Hook and Kelly.[313]

4. Acetylenes

Phillips and Van Hook[314] have investigated the VPIE for C_2D_2/C_2H_2 between 125 and 190°K by manometry. They also determined the VPIE of an enriched (from the statistical $d_2:d_1:d_0::1:2:1$) sample of C_2HD. The enrichment had been effected by a gas chromatographic method.[315] Only a small amount of the C_2HD was available and that experiment was limited to temperatures above 150°K. The acetylenes are solid over the temperature range of both experiments. The effects are normal. The VPIE for C_2D_2 showed a sharp break at 147.4°K which was interpreted as due to the orthorhombic–cubic phase transition in C_2D_2. The corresponding transition for C_2H_2 is at 133°K and the isotope effect on this transition temperature is unusually large, 14°. The C_2HD data do not extend to a low enough temperature to detect the corresponding transition for that molecule. A model calculation was made using the available spectroscopic data and the agreement was satisfactory.

5. Methylacetylenes

Van Hook has determined the VPIE for three of the deutero isomers of methylacetylene, CH_3CCD, CD_3CCH, and CD_3CCD.[316] The experiments extended from 167 to 255°K. (Earlier more crude results had been reported by Leitch and Renaud.[316a]) Deuteration on the methyl group resulted in an inverse isotope effect of about 1.6%/d at 167°K falling smoothly to 1.2% at 255°. Acetylenic deuteration showed a 2% normal effect at 167° which rose smoothly to an inverse effect of 0.2% at 255°. The VPIE for the totally deuterated compound was observed as slightly less than the sum of effects for D_3CCCH and H_3CCCD.

The data were interpreted with the aid of a model calculation. A force field was chosen consistent with the spectroscopic data, but, as in the C_2H_6 case, it was found necessary to postulate temperature-dependent lattice frequencies in order to rationalize the behavior of the deuteriomethyl compound. The behavior of the deutero–methynic compound is unusual and was interpreted as indicating considerable molecular association in the condensed phase which is itself temperature dependent. This interpretation was shown to be consistent with the results of an independent nmr investigation of the chemical shift of the methynic hydrogen as a function of temperature, and by spectroscopic studies.

6. Propylenes

The VPIE's of certain of the deutero isomers of propylene have been reported by McDaniel and Van Hook;[317] the effects are mostly inverse but deuteration on the ethylenic group causes crossovers to a normal effect as the temperature is lowered for both molecules studied (~165°K for CH_3CDCH_2, ~144°K for CH_3CHCD_2). The inverse effect shows a monotonous increase as the temperature is raised although at the highest temperatures the slope of the VPIE–(1/T) curve is about zero. Around these highest temperatures, the law of the mean is very nearly obeyed for the two compounds studied although, as expected, wide deviations show up as the crossover region is approached. The data on these two compounds thus appear entirely consistent with each other and with the earlier work on ethylene, but the effect per deuterium is significantly smaller for the propylenes—small enough so the crossover which is only indicated in extrapolation for the ethylenes is actually observed for propylene.

The deuteration on the methyl group shows a larger inverse effect per deuterium than does ethylenic substitution. A definite maximum in the inverse effect is observed. At the higher pressures the effect lies intermediate to that found for CH_2DCH_3[310] and expected for $CH_2DC{\equiv}CH$[316] demonstrating consistency with these other compounds. The order is that expected if one assumes the shifts in methyl group frequencies on condensation are approximately the same for the three different liquids. In that event the predicted VPIE's are principally determined by the reduced moments of inertia for the internal methyl rotation and the predicted order of inverse VPIE's is that observed—methylacetylene > propylene > ethane.[6]

A surprising feature of the propylene data is the fact that the observed effect for C_3D_6 is significantly higher than the value predicted by the (admittedly crude) relation

$$C_3D_6 \approx 3CH_2DCHCH_2 + CH_3CD{=}CH_2 + CH_3CH{=}CD_2 \quad (66)$$

The difference over most of the temperature range is larger than 10%, and it persisted when more accurate calculations were made using the average molecule harmonic oscillator cell model.

7. Other Hydrocarbons

Davis and Schiessler[318] determined the VPIE for the benzene–perdeuteriobenzene and the cyclohexane–perdeuteriocyclohexane pairs between 10 and 85°. The measurements were extended well into the solid region (−40°) by Rabinovich[319] with good agreement where the data overlapped. The later author also reports data for perdeuteriotoluene over the same temperature range. Measurements on the benzene system had been earlier reported by Ingold and coworkers[30] and interpreted by Bailey and Topley,[29] but the precision does not compare well with the later work. Measurements of the $^{12}C/^{13}C$ effects for C_6H_6 were made by Narten and Kuhn.[128] The Davis–Schiessler data[318] has been interpreted by Grosh, *et al.*,[121] using significant structure theory. The isotope effects, as expected, are inverse for all these compounds. That for benzene is larger for the liquid than for the solid, but just the reverse is true for the cyclohexane. (Toluene effects were not measured in the solid region.) The optical dispersions, viscosities, refractive indices, and ultrasonic velocities have also been determined for the C_6H_6–C_6D_6 and C_6H_{12}–C_6D_{12} pairs.[320-322]

Quite recently Kiss, Jakli, and Illy[323] have reported extensive measurements on a number of cyclic hydrocarbons. The completely deuterated isomers of benzene and cyclohexane were studied over a 180° temperature range, as was *p*-deuteriotoluene. The results are found in Table XII. Over the range where comparison is possible, the agreement with earlier work is satisfactory. It is interesting to note that while the IE for C_6D_6 showed the expected discontinuity at the freezing point, that for cyclohexane showed none at all. The authors explain that this is a consequence of the fact that this material is not really freezing but simply being transformed to a glassy state of disordered structure. They also made mea-

surements on statistically deuterated benzenes containing 16, 30, 60 and 94% D, as well as on monodeuteriobenzene and *p*-dideuteriobenzene and verified that the VPIE for benzene is linearly dependent on the D content, thus experimentally verifying the calculational predictions of Bigeleisen and Goldstein,[324] Bigeleisen, Weston, and Wolfsberg,[325] and Wolfsberg.[326] However, they point out that a more definitive experiment would be one in which the vapor pressure of *o-m-*, and *p*-dideuteriobenzenes are intercompared in a direct test of the law of the geometric mean.

Höpfner and Parekh[327] have measured the VPIE between neopentane and $(CH_3)_3(CD_3)C$ in the solid and liquid phases. The effects are inverse and show a discontinuity at the melting point. No interpretation was given.

8. Halogenated Hydrocarbons

Beersmans and Jungers[328] investigated the properties of the CH_3X/CD_3X systems with X = Cl, Br, or I many years ago. Their fits are quoted in Table XII. The effects approximate the expected 1 to 1.5% per atom D and are inverse. Rabinovich[2,319] has also reported measurements on the chloroform system $CHCl_3/CDCl_3$ which are as large as 4% (−40°) falling off rapidly to about 1.5% at 10°. Chlorine isotope effects for CH_3Cl[214] and for $CHCl_3$[62] have also been reported and are small. Finally Morse and Leitch[329] have reported deuterium effects for the chloro derivatives of methylacetylene, and Verhulst and Jungers[330] have investigated H–D isomers of dibromoethane in the region of the boiling point. Wolff[331] has correlated the data on CH_3Cl and CH_3Br with the available spectroscopic information, and Rabinovich and Nikolaev[332] have reported on measurements of effects in the two-component system ($CHCl_3$–acetone/$CDCl_3$–acetone).

9. Silanes, Germanes, and Boranes

The vapor pressure of the isotopic silanes, SiH_4, SiD_4, Si_2H_6, and Si_2D_6, was investigated many years ago by Stokland[333,334] and the results of his investigation are reported in Table XII. The behavior of these compounds is similar to that we have already seen for CH_4 and C_2H_6. More recently Klein, Morrison, and Weir[335] have measured the low-temperature heat capacities of SiH_4 and SiH_3D. They were particularly interested in comparing the thermal properties of these materials with those of the corresponding methanes, but also reported the vapor pressure of SiH_3D between 108 and 129°K and the triple points. It is interesting to note that in the isotopic silanes there is only one λ transition (SiH_4, 63.75°K; SiH_3D, 66.05°K; and SiD_4, 67 ± 1°K), in contrast to the two such transitions found for each of the isotopic methanes. The residual entropy of the $SiHD_3$ species was found to be approximately R ln 4.

The vapor pressures of deuterated mono-, di-, and trigermanes have been reported by Zeltmann and Fitzgibbon[336] between 10 and 800 mm. They also reported triple point temperatures. Unfortunately the vapor pressure of the nondeuterated isomer was not determined in the same laboratory. Shapiro and Ditter[337] have reported an inverse VPIE for perdeuteriopentaborane.

F. Associated Compounds Containing Hydrogen (Table XX)

1. Methanol

The effect of isotopic substitution (^{13}C, ^{14}C, ^{18}O, D) on the vapor pressure of methanol has been thoroughly studied. A compilation of the different investigations and the temperature ranges they cover is shown in Table XXI.

The data for the VPIE of CH_3OH–CH_3OD obtained by Beersmans and Jungers[338] (0 to 65.5°) are in fair agreement with the values reported by Kiss, *et al.*,[74,339,340] (−22.3 to 120°) and Rabinovich[2,73,319] (20 to 210°), but above the normal boiling point the results of the two latter sets of measurements differ considerably and neither set agrees with data obtained by Rayleigh distillation[341] (35.0 to 64.7°). Results for the CD_3OH–CH_3OH and CD_3OD–CH_3OH pairs obtained by Beersmans and Jungers[338] and Rabinovich, *et al.*,[2,319] also differ considerably. The temperature dependence of Rabinovich's data seems to be too large. A normal effect reported for the CD_3OH–CH_3OH pair as obtained in distillation experiments[342] is probably in error.

Recently Borowitz and Klein[343] have studied the effect of ^{18}O and ^{13}C substitution on the vapor pressures of CH_3OH, CH_3OD, CD_3OH, and CD_3OD, in a distillation experiment. Their data are in fair agreement with previous measurements.[62,146,247,344] The results show that ^{14}C, ^{13}C, and D substitution in the methyl group increases the vapor pressure of methanol at ordinary temperatures while ^{18}O and D substitution in the hydroxyl group decreases it.

Wolff, *et al.*, made measurements of vapor pressure isotherms in the two-component systems CH_3OH–hexane, CH_3OD–hexane, and CH_3OH–CCl_4 (but not CH_3OD–CCl_4)[345-348] and observed that the normal isotope effect (in the partial pressures) goes over into an inverse effect at mole fractions of methanol below 0.05. An approximate calculation[331] showed that the inverse vapor pressure isotope effect is primarily due to the changes in intramolecular vibrations from the solvation. In another interpretation Wolff, Wolff, and Höppel[220] made an evaluation of the VPIE for the CH_3OH–CH_3OD and CD_3OH–CD_3OD isotopic pairs at three temperatures with Bigeleisen's theory (see section II.F). They used experimentally observed infrared frequencies in the partition functions. The results are in poor agreement with experiment probably because of accumulating experimental errors in the isotopic frequency shifts, the neglect of hindered rotation of the OH in the gas phase, and inadequacies in the harmonic cell model. In a similar vein Rabinovich[2,73] has carried out an approximate calculation of the isotope effect on association energy and vapor pressure of CH_3OH–CH_3OD at 25° applying eq 16 (see also section II.E.3). He obtained a value for the VPIE which was in satisfactory agreement with the experimental one. Rabinovich states[2,73] that the energy of association is increased by substitution of deuterium for hydrogen in the hydroxyl group, and this claim is echoed by the conclusions of Wolff and Höppel[346,347] (from vapor pressure measurements on CH_3OD–hexane system), Benjamin and Benson[349] (from heats of mixing of CH_3OH and H_2O, and CH_3OD and D_2O), and Staveley and Gupta[350] (from heats of evaporation of CH_3OH and CH_3OD). On the other hand, Cardinaud[351,352] obtained a higher energy of association for CH_3OH from spectroscopic data on solutions of CH_3OH and CH_3OD in CCl_4 and C_6H_6. The results of infrared investigations on CCl_4 solutions containing CH_3OH and CH_3OD led Bonner[353] to the same conclusion, namely, that the hydrogen bonding is more extensive than the deuterium bonding. Whalley and Falk[68] examined the intermolecular potentials of CH_3OH and CH_3OD using the difference in the heats of vaporization at 0°K obtained from thermal data and vibrational frequencies and found that the hydrogen bond in CH_3OH has about the same strength or is a little stronger than the deuterium bond in CH_3OD.

Borowitz and Klein[343] interpreted their experimental results in terms of the *AB* equation (see section II.F.4). They concluded from an examination of the experimentally obtained *A* values for ^{18}O substitution in CH_3OH, CH_3OD, and CD_3OH that the mean intermolecular force in CH_3OH is smaller than in CH_3OD and in CD_3OH ($\langle F^2_{CH_3OH}\rangle/\langle F^2_{CH_3OD}\rangle$ = 0.83 ±

TABLE XX. VPIE's of Associated Compounds Containing Hydrogen

Compound	Ref (date)	Type	Temp range, °C	Method	Equation, table or graph	Ln R, low T, high T
Alcohols						
$CH_3{}^{16}OH$-$CH_3{}^{18}OH$	344 (39)	I	a	D	$P_{CH_3{}^{16}OH} > P_{CH_3{}^{18}OH}$	
CH_3OH-CH_3OD	338 (47)	I	0–65.5	DP	Log $R = 59.86/T + 0.26699 \log T - 0.84049$	0.06712 (0) 0.02692 (65.5)
CH_3OH-CD_3OH	338 (47)	I	0–65.5	DP	Log $R = 24.15/T + 0.16972 \log T - 0.50384$	−0.00442 (0) −0.00732 (65.5)
CH_3OH-CD_3OD	338 (47)	I	0–65.5	DP	Log $R = 24.07/T - 0.00236 \log T - 0.05450$	0.06417 (0) −0.02443 (65.5)
$CH_3{}^{16}OH$-$CH_3{}^{18}OH$	146 (51)	I	a	D	Ln $R^+ > 0$	
CH_3OH-CH_3OD	146 (51)	I	a	D	Ln $R^+ > 0$	
CH_3OH-CH_2DOH	146 (51)	I	a	D	Ln $R^+ \approx 0$	
$^{12}CH_3OH$-$^{13}CH_3OH$	146 (51)	I	a	D	Ln $R^- \approx 0$	
$CH_3{}^{16}OH$-$CH_3{}^{18}OH$	62 (53)	I	34.6	D	Ln $R = 0.003$	0.003 (34.6)
$^{12}CH_3OH$-$^{13}CH_3OH$	62 (53)	I	34.6	D	Ln $R = -0.0002$	−0.0002 (34.6)
CH_3OH-CH_3OD	62 (53)	I	34.6	D	$P_{CH_3OH} > P_{CH_3OD}$	
$CH_3{}^{16}OH$-$CH_3{}^{18}OH$	247 (58)	I	64.7	D	Ln $R^+ = 0.0029$	0.0029^+ (64.7)
$^{12}CH_3OH$-$^{13}CH_3OH$	247 (58)	I	64.7	D	Ln $R^+ = -0.00043$	-0.00043^+ (64.7)
$^{12}CH_3OH$-$^{14}CH_3OH$	247 (58)	I	64.7	D	Ln $R^+ = -0.0010$	-0.0010^+ (64.7)
CH_3OH-$CHOD$	247 (58)	I	64.7	D	Ln $R^+ = 0.0096$	0.0096^+ (64.7)
CH_3OH-CD_3OH[b]						
CH_3OH-CH_3OD	341 (61)	I	35–64.7	R	Log $R^+ = -0.0772 + 27.7/T$; table (4)	0.0292 (35) 0.0110 (64.7)
CH_3OH-CH_3OD	342 (62)	I	64.8	D	Ln $R^+ = 0.0099_5$	0.0099_5^+ (64.8)
CH_3OH-CD_3OH	342 (62)	I	64.8	D	Ln $R^+ = 0.0049$	0.0049^+ (64.8)
CH_3OH-CH_3OD	2,319 (64)	I	20–60	P	Table (5); graph[c]	0.056_6 (20) 0.035_6 (60)
CH_3OH-CH_3OD	2,319 (64)	I	70–210	DP	Table (15); graph	0.033_6 (70) −0.0003 (210)
CH_3OH-CD_3OH	2,319 (64)	I	20–60	P	Table (5); graph	-0.021_8 (20) -0.011_9 (60)
CH_3OH-CD_3OD	2,319 (64)	I	20–60	P	Table (5); graph	0.041_9 (20) 0.028_4 (60)
CH_3OH-CH_3OD	339 (65) 74 (67) 340 (67)	I	−22.3 to 120	DP	Ln $R^+ = 16039/T^2 - 38.03/T$	0.1033^+ (−22.3) 0.0070^+ (120.0)
$CH_3{}^{16}OH$-$CH_3{}^{18}OH$	343 (71)	I	35–64	D	Ln $R^+ = 2200/T^2 - 5.6/T$	0.0050^+ (35) 0.0027^+ (64)
$CH_3{}^{16}OD$-$CH_3{}^{18}OD$	343 (71)	I	39, 51, 64	D	Ln $R^+ = 2500/T^2 - 6.7/T$	0.0042^+ (39) 0.0021^+ (64)
$CD_3{}^{16}OH$-$CD_3{}^{18}OH$	343 (71)	I	51, 64	D	Ln $R^+ = 4100/T^2 - 11.6/T$	0.0032^+ (51) 0.0017^+ (64)
$CD_3{}^{16}OD$-$CD_3{}^{18}OD$	343 (71)	I	39, 51, 64	D	Ln $R^+ = 3500/T^2 - 9.9/T$	0.0042^+ (39) 0.0010^+ (64)
$^{12}CH_3OH$-$^{13}CH_3OH$	343 (71)	I	35–64	D	Ln $R^+ = 300/T^2 + 0.7/T$	-0.00036^+ (35)[d] -0.00028^+ (64)[d]
$^{12}CH_3OD$-$^{13}CH_3OD$	343 (71)	I	39, 51, 64	D	Ln $R^+ = -300/T^2 + 0.7/T$	-0.00047^+ (39)[d] -0.00029^+ (64)[d]
$^{12}CD_3OH$-$^{13}CD_3OH$	343 (71)	I	51, 64	D	Ln $R^+ = -200/T^2 + 0.5/T$	-0.00042^+ (51)[d] -0.00034^+ (64)[d]
$^{12}CD_3OD$-$^{13}CD_3OD$	343 (71)	I	39, 51, 64	D	Ln $R^+ = -500/T^2 + 1.3/T$	-0.00061^+ (39)[d] -0.00020^+ (64)[d]
Two-component systems	347 (68) 346 (68) 345 (68)					
C_2H_5OH (EtOH)						
EtOH-EtOD	354 (39)	I	80 mm; 750 mm	D	Table (2)	0.034^+ (80 mm) 0.019^+ (750 mm)
$Et^{16}OH$-$Et^{18}OH$	355 (42)	I	a	D	$P_{Et^{16}OH} > P_{Et^{18}OH}$	
EtOH-EtOD	2,319 (64)	I	15–75	P	Log $P_H = 24.1133 - 2898.1/T - 5.1012 \log T$ Log $P_D = 24.4530 - 2932.6/T - 5.2009 \log T$ Table (9); graph	0.058_0 (15) 0.029_5 (75)
C_2H_5OH-C_2D_5OH	2,319 (64)	I	15–75	P	Table (9); graph	-0.05_1 (15) −0.017 (75)
C_2H_5OH-C_2D_5OD	2,319 (64)	I	15–75	P	Table (9); graph	0.000_0 (15) 0.005 (75)
EtOH-EtOD	339 (65) 74, 340 (67)		−14.5 to 140	DP	Ln R^+ $18343/T^2 - 44.45/T$ (−15 to 78°) Ln $R^+ = 17960/T^2 - 43.96/T$ (78 to 140°)	0.1023^+ (−14.5) -0.0012^+ (140.2)

TABLE XX *(Continued)*

Compound	Ref (date)	Type	Temp range, °C	Method	Equation, table or graph	Ln R, low T, high T
Two-component systems	356 (68)					
C_3H_7OH (PrOH)						
PrOH–PrOD	73a (64)	I	20–70	P	Log $P_H = 35.9487 - 3670.6/T - 9.0230 \log T$	0.0698 (20)
	2 (70)				Log $P_D = 36.2509 - 3706.1/T - 9.1087 \log T$	0.0426 (70)
					Table (6); graph	
PrOH–PrOD	339 (65) 340 (67) 359 (68)	I	4.6–98.3	DP	Ln $R^+ = 19015/T^2 - 44.39/T$; table (58)	0.0867^+ (4.6) 0.0183^+ (98.3)
$CH_3CH(OH)CH_3$ (iPrOH)						
iPrOH–iPrOD	358 (55)	I	15–80	P	Table (8); graph	0.063_0 (15) 0.028_6 (80)
iPrOH–iPrOD	341 (61)	I	40–82.5	R	Log $R^+ = -0.0817 + 31.7/T$	0.0449^+ (40) 0.0170^+ (82.5)
^{12}C iPrOH–^{13}C iPrOH	342 (62)	I	82.5	D	Ln $R^+ = 0.0009_9$	0.0009_9^+ (82.5)
^{12}C iPrOH–^{14}C iPrOH	342 (62)	I	82.5	D	Ln $R^+ = 0.0012$	0.0012^+ (82.5)
iPr^{16}OH–iPr^{18}OH	342 (62)	I	82.5	D	Ln $R^+ = 0.0021$	0.0021^+ (82.5)
H iPrOH–D iPrOH	342 (62)	I	82.5	D	Ln $R^+ = 0.0089_5$	0.0089_5^+ (82.5)
iPrOH–iPrOD	342 (62)	I	82.5	D	Ln $R^+ = 0.0154$	0.0154 (82.5)
iPrOH–iPrOD	73a (64) 2 (70)	I	20–80	P	Log $P_H = 25.8692 - 3079.7/T - 5.6153 \log T$	0.0598 (20)
					Log $P_D = 26.3754 - 3121.0/T - 5.7739 \log T$	0.0343 (80)
					Table (7); graph	
iPrOH–iPrOD	340 (67) 359 (68)	I	−10.3 to 133	DP	Ln $R^+ = 13830/T^2 - 31.33/T$; table (42)	0.0810^+ (−10.3) 0.0067^+ (133)
$CH_3(CH_2)_3OH$ (BuOH)						
BuOH–BuOD	358 (55)	I	20–100	P	Table (10); graph	0.061 (20) 0.030_5 (100)
BuOH–BuOD	73a (64) 2 (70)	I	20–80	P	Ln $P_H = 30.6838 - 3648.4/T - 7.1166 \log T$	0.0682 (20)
					Log $P_D = 31.2820 - 3695.4/T - 7.3062 \log T$	0.0408 (80)
					Table (7); graph	
BuOH–BuOD	359 (68) 340 (67)	I	2.1–97.5	DP	Ln $R^+ = 19840/T^2 - 44.80/T$; table (17)	0.0991^+ (2.1) 0.0235^+ (97.5)
$(CH_3)_2CHCH_2OH$ (iBuOH)						
iBuOH–iBuOD	73a (64) 2 (70)	I	20–80	P	Log $P_H = 31.6360 - 3631.4/T - 7.4415 \log T$	0.0412 (20)
					Log $P_D = 31.3106 - 3634.7/T - 7.3123 \log T$	0.0128 (80)
$CH_3CH_2CH(OH)CH_3$ (sBuOH)						
sBuOH–sBuOD	73a (64) 2 (70)	I	20–80	P	Log $P_H = 33.5787 - 3628.5/T - 8.1468 \log T$	0.0361 (20)
					Log $P_D = 34.0127 - 3664.0/T - 8.2800 \log T$	0.0136 (80)
					Table (7); graph	
sBuOH–sBuOD	359 (68) 340 (67)	I	0.7–150	DP	Ln $R^+ = 13860/T^2 - 31.94/T$; table (36)	0.0682^+ (0.7) 0.0019^+ (150.0)
$(CH_3)_3COH$ (tBuOH)						
tBuOH–tBuOD	359 (68) 340 (67)	I	30.7–128	DP	Ln $R^+ = 15710/T^2 - 37.19/T$; table (30)	0.0478^+ (30.7) 0.0049^+ (128.0)
$C_5H_{11}OH$						
$C_5H_{11}OH$–$C_5H_{11}OD$	360 (39)	I	25–130	DP	Table (9)	0.157 (25) 0.045_7 (130)
$CH_3CH_2CH(OH)CH_2CH_3$ (sAmOH)						
sAmOH–sAmOD	359 (68) 340 (67)	I	24.8–94.8	DP	Ln $R^+ = 12850/T^2 - 31.15/T$; table (18)	0.040_2^+ (24.8) 0.0103^+ (94.8)
Octanols (Ocol)						
Ocol-(1)–Ocol-(1)-OD	361 (66)	I	20–80	P	$P/P' = 1.042 - 20.76/(154.3 + t)$; table (7)	0.080 (20) 0.048 (80)
Ocol-(2)–Ocol-(2)-OD	361 (66)	I	10–80	P	$P/P' = 1.055 - 20.46/(154.3 + t)$; table (8)	0.072_6 (10) 0.032_5 (80)
Ocol-(3)–Ocol-(3)-OD	361 (66)	I	10–80	P	$P/P' = 1.073 - 20.51/(154.3 + t)$; table (8)	0.053 (10) 0.015 (80)
Ocol-(4)–Ocol-(4)-OD	361 (66)	I	10–80	P	$P/P' = 1.036 - 20.24/(154.3 + t)$; table (8)	0.042^e (20) 0.011^e (80)

TABLE XX *(Continued)*

Compound	Ref (date)	Type	Temp range, °C	Method	Equation, table or graph	Ln R, low T, high T
Thiols						
C_2H_5SH						
C_2H_5SH–C_2H_5SD	360 (39)	I	0–40	DP	Table (6)	0.093_2 (25)[f]
Alkyl hydrogen peroxide						
$(CH_3)_3COOH$–$(CH_3)_3COOD$	2, 73a (64)	I	20–90	P	Log $P_H = 9.369 - 2493.9/T$	0.079 (20)
					Log $P_D = 9.416 - 2517.8/T$; table (15)	0.043 (90)
$(CH_3)_2C(C_6H_5)OOH$– $(CH_3)_2C(C_6H_5)OOD$	2, 73a (64)	I	10–50	g	Log $P_H = 10.760 - 3649.1/T$	0.076 (10)
					Log $P_D = 10.812 - 3673.2/T$	0.052 (50)
Amines						
CH_3NH_2						
CH_3NH_2–CH_3ND_2	363 (37)	I	−60 to −10	P	Table (9)	0.187 (−60)
						0.050_9 (−10)
CH_3NH_2–CH_3ND_2	364 (65)	I	−55 to +20	DP	Table (11)	0.111 (−55)
						0.039 (+20)
CH_3NH_2–CH_3ND_2	340 (67)	I	−60 to +30	DP	Ln $R^+ = 9876/T^2 - 24.17/T$	0.1040^+ (−60)
	365 (71)					0.0277^+ (+30)
CH_3NH_2–CD_3NH_2	366 (67)	I	−55 to +20	DP	Table (11)	-0.042_9 (−55)[h]
						-0.030_4 (+20)[h]
CD_3NH_2–CD_3ND_2	366 (67)	I	−55 to +20	DP	Table (11)	0.105_4 (−55)[i]
						0.038_8 (+20)[i]
CH_3ND_2–CD_3ND_2	366 (67)	I	−55 to +20	DP	Table (11)	-0.042_6 (−55)[j]
						-0.029_3 (+20)[j]
CH_3NH_2–CD_3ND_2	366 (67)	I	−55 to +25	DP	Table (12)	0.072_4 (−55)[k]
						0.008_5 (+20)[k]
Two-component systems	387 (62)					
	364 (65)					
	366 (67)					
$C_2H_5NH_2$ ($EtNH_2$)						
$EtNH_2$–$EtND_2$	367 (39)	I	−50 to +10	P	Table (7)	0.083 (−50)
						0.044_8 (+10)
$EtNH_2$–$EtND_2$	364 (65)	I	−55 to +20	DP	Table (10)	0.087 (−55)
						0.029 (+20)
$EtNH_2$–$EtND_2$	340 (67)	I	−60 to +90	DP	Ln $R^+ = 9032/T^2 - 22.87/T$	0.0915^+ (−60)
	365 (71)					0.0055^+ (+90)
Two-component systems	383 (64)					
	364 (65)					
	244 (62)					
$C_3H_7NH_2$($PrNH_2$)						
$PrNH_2$–$PrND_2$	244 (62)	I	48.7	k	$R = 1.0125$	0.0124 (48.7)
$PrNH_2$–$PrND_2$	340 (67)	I	−25 to +65	DP	Ln $R^+ = 8131/T^2 - 23.33/T$	0.0380^+ (−25)
	365 (71)					0.0021^+ (+65)
$C_4H_7NH_2$						
Two-component systems	244 (62)					
$(CH_3)_2NH$						
$(CH_3)_2NH$–$(CH_3)_2ND$	367 (39)	I	−50 to +5	P	Table (6)	0.053 (−50)
						0.035_3 (+5)
$(CH_3)_2NH$–$(CH_3)_2ND$	368 (70)	I	−50 to +20	P	Table (8)	0.050_7 (−50)
						0.0220 (+20)
$(CH_3)_2NH$–$(CD_3)_2NH$	368 (70)	I	−50 to +20	P	Table (8)	-0.079_3 (−50)
						−0.0478 (+20)
$(CH_3)_2NH$–$(CD_3)_2ND$	368 (70)	I	−50 to +20	P	Table (8)	-0.016_3 (−50)
						−0.0253 (+20)
Two-component systems	388 (66)					
	368 (70)					
	244 (62)					
$CH_3(NH)C_2H_5$						
$CH_3(NH)C_2H_5$–$CH_3(ND)C_2H_5$	244 (62)	I	35	k	$R = 1.0092$	0.0092 (35)
Two-component systems	244 (62)					
$(C_2H_5)_2NH$						
$(C_2H_5)_2NH$–$(C_2H_5)_2ND$	244 (62)	I	55.5	k	$R = 1.0071$	0.0071 (55.5)
Two-component systems	244 (62)					
$C_6H_5NH_2$						
$C_6H_5NH_2$–$C_6H_5ND_2$	358 (55)	I	50 to 80	P	Table (7)	0.035 (50)
						0.006 (80)
$C_6H_5NH_2$–$C_6H_5ND_2$	2, 73a (64)	I	−5 to +9	g	Table (5)	0.051 (−5)
						0.037_6 (+9)
$C_6H_5NH_2$–$C_6H_2D_3NH_2$	2, 73a (64)	I	−5 to +9	g	Table (5)	−0.034 (−5)
						-0.029_1 (+9)

TABLE XX *(Continued)*

Compound	Ref (date)	Type	Temp range, °C	Method	Equation, table or graph	Ln R, low T, high T
$C_6H_5NH_2$-$C_6H_2D_3ND_2$	2,73a (64)	l	−5 to +9	g	Table (5)	0.014_5 (−5) 0.011_1 (+9)
Organic Acids						
CH_3COOH						
CH_3COOH-CH_3COOD	28 (34)	l	50–90	P	Table (4)	−0.075 (50) −0.03 (90)
CH_3COOH-CD_3COOD	393 (35)	l	20–100	DP	Log $R = -3.94/T - 0.0106$; table (17)	−0.0554 (20) −0.0487 (100)
CH_3COOH-CH_3COOD	391 (36)	l	21–83.6	DP	Table (9)	−0.009 (21)[i] -0.032_9 (83.6)[i]
CH_3COOH-CD_3COOH	391 (36)	l	21–83.6	DP	Table (9)	$+0.012_3$ (21)[i,m] -0.032_2 (83.6)[i]
CH_3COOH-CD_3COOD	391 (36)	l	21–83.6	DP	Table (9)	-0.043_9 (21)[i] -0.027_0 (83.6)[i]
CH_3COOH-CD_3COOD	392 (54)	l	25–125	P	Log $P_H = 7.4275 - 1558.03/(224.79 + t)$ Log $P_D = 7.4397 - 1556.17/(224.82 + t)$	−0.0539 (25) −0.0412 (125)
CH_3COOH-CH_3COOD	358 (55) 2,73a (64)	l	15–110	P	Log $P_H = 15.5792 - 2480.4/T - 2.4528$ log T Log $P_D = 16.9073 - 2542.0/T - 2.9016$ log T	-0.023_9 (15) -0.018_4 (110)
Two-component systems	396 (59)					
$CH_3CH_2CH_2COOH$ (PrCOOH)						
PrCOOH-PrCOOD	358 (55) 2,73a (64)	l	55–115	P	Log $P_H = 12.0365 - 2828.0/T - 1.0168$ log T (50–90°) Log $P_D = 12.0305 - 2821.8/T - 1.0154$ log T (55–90°) Log $P_H = 12.0505 - 2828.0/T - 1.0168$ log T (95–115°) Log $P_D = 12.0505 - 2821.8/T - 1.0154$ log T (95–115°) Table (13)	-0.037_8 (55) -0.045_1 (115)
$(CH_3)_2CHCOOH$						
$(CH_3)_2CHCOOH$-$(CH_3)_2CHCOOD$	358 (55) 2,73a (64)	l	50–90	P	Log $P_H = 8.8395 - 2532.7/T - 0.0068$ log T Log $P_D = 9.9303 - 2615.0/T - 0.3379$ log T Table (9)	−0.0122 (50) −0.0380 (90)
$(CH_3)_2CHCH_2COOH$						
$(CH_3)_2CHCH_2COOH$-$(CH_3)_2CHCH_2COOD$	358 (55) 2,73a (64)	l	55–110	P	Log $P_H = 11.6256 - 2972.1/T - 0.7826$ log T Log $P_D = 11.8738 - 2982.6/T - 0.8621$ log T Table (12)	−0.037 (55) −0.035 (110)
Inorganic acids						
HBr-DBr	218 (35)	s	174–184°K	P	Log $P_H = 8.309 - 1103/T$ Log $P_D = 8.306 - 1103/T$	0.007 (174) 0.007 (184)
		l	187–205°K	P	Log $P_H = 7.465 - 945.7/T$ Log $P_D = 7.517 - 956.5/T$	0.0132 (187) 0.0016 (205)
HI-DI	219 (35)	s	191.4–207.8°K	P	Log $P_H = 10.493 - 0.003167T - 0.377$ log $T - 1406/T$ Log $P_D = 10.505 - 0.003167T - 0.377$ log $T - 1406/T$	−0.028 (191.4) −0.028 (207.8)
		l	223–233.9°K	P	Log $P_H = 26.119 + 0.002293T - 7.111$ log $T - 1636/T$ Log $P_D = 26.129 + 0.002293T - 7.111$ log $T - 1636/T$	−0.023 (223) −0.023 (233.9)
HCl-DCl	217 (34)	s	152.6–157.6°K	P	Log $R = -57.7/T + 0.387$ Table (4)	0.020 (152.6) 0.048 (157.6)
		l	159.5–200.9°K	P	Log $R = 15.4/T - 0.075$ Table (7)	0.050 (159.5) 0.003_8 (200.9)
$H^{35}Cl$-$H^{37}Cl$	222 (59)	l	167, 173, 181°K	R	Ln $R^+ = 1.2846/T - 0.0055$ Table (3); graph	0.0022+ (167) 0.0016+ (181)
$H^{35}Cl$-$H^{37}Cl$	214 (58)	l	−88	D	Ln $R^+ = 6\text{-}4 \times 10^{-4}$	0.0006–0.0004+ (−88)
HF-DF	216 (34)	l	240–290°K	P	Log P_H (cm) $= 6.3739 - 1316.79/T$ Log P_D (cm) $= 6.2026 - 1261.16/T$	-0.139_3 (240) -0.047_3 (290)
HNO_3-DNO_3	397 (58)	l	0	P	Table P vs. x at 0°	−0.07 (0)

TABLE XX *(Continued)*

Compound	Ref (date)	Type	Temp range, °C	Method	Equation, table or graph	Ln R, low T, high T
HNO_3–DNO_3	397 (58)	l	0	P	Table P vs. x at 0°	−0.07 (0)
Ammonia						
NH_3–ND_3	402a (71)	l	10–90	D	Log $R^+ = 10.796/T - 0.02756$	0.0243^+ (10) 0.0050 (90)
NH_3–ND_3	402 (69)	l	−55 to 0	DP	Table (13); graph	0.168 (−55) 0.080 (0)
NH_3–ND_3	401 (63)	l	250 to 760 mm	D	Ln $R^+ = (0.0395 \pm 0.0004) - (0.0128 \pm 0.0029)(x - 0.424) - (0.01246 \pm 0.00065)$ ln $(\pi/760)^n$; Table (20)	
NH_3–ND_3	140 (62)	s	−115 to −80	DP	Log $R = 105.4/T - 0.4210$	0.565_2 (−115) 0.287_1 (−80)
		l	−74 to −30	DP	Log $R = 42.36/T - 0.1244$	0.203_3 (−74) 0.114_7 (−30)
NH_3–ND_3	398 (56)	l	0–20	DP	$P_{NH_3}/P_{ND_3} = 2.2105 \times 10^8 T^{-3.8869} + 1$ (±0.0002); Table (31) $P_{NH_3}/P_{NH_2D} = 4.8118 \times 10^7 T^{-3.8156} + 1$ (±0.0001)^o	0.0723 (0) 0.0552 (20)
NH_3–ND_3	193 (42)	s	189.7–195.3°K	DP	Log $R = 49.69/T - 0.1305$; table (15)	0.3023 (189.7) 0.2852 (195.3)
		l	202.03–235.74°K	DP	Log $R = 46.25/T - 0.14003$; table (15)	0.2047 (202.03) 0.1293 (235.74)
$^{14}NH_3$–$^{15}NH_3$	404 (40)	l	197.7–239.5°K	DP	Log $R = 1.3665/T - 0.004632$	0.00525 (197.7) 0.00247 (239.5)
$^{14}NH_3$–$^{15}NH_3$	405 (36)	l	n	D	$R = 1.0025 \pm 0.003$	0.0025
$^{14}NH_3$–$^{15}NH_3$	406 (35)	l	o	D	$R = 1.0052 \pm 0.0013$	0.0052
NH_3–ND_3	27 (33)	l	202.3–238.6°K	DP	Table (5)	0.20 (202.3) 0.128 (238.6)
NH_3–NT_3	72 (59)	l			$\Delta T_{trp} = 0.0118$°K	
Two-components: NH_3–ND_3 (propane)	402 (69)					
HCN–DCN	394 (34)	s	200–260°K	P	Log $P^H_{mm} = 9.372 - 1877/T$	
		l	260–284°K	P	Log $P^H_{mm} = 7.795 - 1467/T$	
		s	200–260°K	P	Log $P^D_{mm} = 9.476 - 1907/T$	
		l	260–294°K	P	Log $P^D_{mm} = 7.695 - 1440/T - 175/T^2$	
	413 (69)	s	210–260°K	P	Log $P^H_{mm} = -943.642/T + 1.42653 + 0.016844T$	
		l	260–305°K	P	Log $P^H_{mm} = -1681.25/T + 9.35845 - 0.0028593T$	
		s	210–260°K	P	Log $P^D_{mm} = -1993.81/T + 10.2580 - 0.0017516T$	
		l	260–305°K	P	Log $P^D_{mm} = -1790.05/T + 10.0954 - 0.0041111T$	
$HC^{14}N$–$HC^{15}N$	413 (69)	s	210–260°K	P	Log $P^{15}_{mm} = -922.01/T + 2.13604 + 0.013670T$	
		l	260–275°K	P	Log $P^{15}_{mm} = -2836.13/T + 17.9479 - 0.018835T$	
DMSO						
$(CH_3)_2SO$–$(CD_3)_2SO$	411 (72)	l	323–463°K	DP	Ln $R = 43454.6/T^2 - 219.449/T + 0.25996$ $T^D_m - T^H_m = 2.30 \pm 0.02$ Table (47), graph	
H_2S–D_2S	407 (70)	l	−78; −30 to +30°C	P	Log $P^{atm}_H = 26.82579 - 1538.461/T - 9.00784 \log T + 0.0064489T$	Cf. Fig 9
				P	Log $P^{atm}_D = 29.06074 - 1601.543/T - 9.89939 \log T + 0.0070815T$ Table (1 pt −78+, 20 pts −30 to +30)	
	140 (62)	s	148–188°K	DP	Log $P_D/P_H = 0.1003 - 19.80/T$	Cf. Fig 9
		l	189–205°K	DP	Log $P_D/P_H = 0.0529 - 11.40/T$	
$H_2{}^{32}S$–$H_2{}^{34}S$	214 (58)	l	−60	D	Ln R = 0.001 − 0.0008	0.001 − 0.0008 (−60)
$H_2{}^{32}S$–$H_2{}^{34}S$	252 (58)	l	−76, −65	R	Table (2)	0.0035^+ (−76)^p 0.0038^+ (−65)^p
$(CH_3)_2{}^{16}O$–$(CH_3)_2{}^{18}O$	251 (70)	l	−26	D	Ln $R^+ = (24 \pm 4) \times 10^{-4}$	0.0024^+ (−26)

[a] The temperature of measurement is not given in the paper. [b] The authors did not differentiate between the deuterium in the OH and in the methyl group. [c] The same equation is given as in ref 338. [d] The value was taken from Table II of ref 343 since the value calculated from the equation does not agree with the experimental result. [e] l = liquid; s = solid; P = pressure; DP = differential pressure; D = distillation; [f] The absolute vapor pressure of EtSH is not given at 40°. [g] The vapor pressures were measured by the Knudsen effusion method.[362] [h] The vapor pressure difference was taken from Table II of ref 366 and the absolute vapor pressure of CH_3NH_2 from ref 383. [i] The value was calculated from the vapor pressures of isotopic species (Table 1a and 1b in ref 366). [j] The vapor pressure of CH_3ND_2 and CD_3ND_2 was taken from Table 1 of ref 364 and Table 1b of ref 366, respectively. [k] The boiling points of the two isotopic compounds were compared. [l] The vapor pressure difference was taken from Table II of ref 393 and the absolute vapor pressure of CH_3COOH calculated from the equation given in ref 392. [m] According to the authors this positive value may not be significant. [n] π is the system pressure in mm and x is the mole fraction of deuterium in liquid. A weak dependence of the separation factor on deuterium concentration was observed. [o] This equation was obtained by assuming the validity of the expression $P_{NH_3}/P_{NH_2D} = (P_{NH_3}/P_{ND_3})^{1/3}$. [p] These values were obtained from Rayleigh distillation data on $^{32}S/^{35}S$ isotope effect by correcting for the mass difference between ^{34}S and ^{35}S.

TABLE XXI. Temperatures of VPIE Measurements for Isotopic Methanol Molecules[a]

Isotopic pairs	Method of measurement			
	Pressure differences	Absolute pressures	Distillation	Rayleigh distillation
$^{12}CH_3OH$–$^{13}CH_3OH$			34.6[62]	
			64.8[247]	
			35–64[343 b]	
			×[146]	
$^{12}CH_3OH$–$^{14}CH_3OH$			64.8[247]	
$CH_3{}^{16}OH$–$CH_3{}^{18}OH$			34.6[62]	
			64.8[247]	
			35–64[343 b,c]	
			×[146]	
CH_3OH–CH_3OD	0–65.5[338]		34.6[62]	
	70–210[2]		64.8[247 d]	
	−22.3 to +120[74,339,340]	20–60[2,73,319]	64.8[342 b]	
			×[146]	35–64.7[341]
CH_3OH–CD_3OH	0–65.5[338]	20–60[3,319]	64.8[342]	
			×[146]	
CH_3OH–CD_3OD	0–65.5[338]	20–60[2,319]		

[a] The temperature range covered and the references are given. × denotes that a temperature is not given in the paper. [b] The $^{12}C/^{13}C$ separation factors have been also measured in CH_3OD, CD_3OH, and CD_3OD. [c] The $^{16}O/^{18}O$ separation factors have been also measured in CH_3OD, CD_3OH, and CD_3OD. [d] The authors did not differentiate between CH_3OD and CD_3OH.

0.2; $\langle F^2_{CD_3OH}\rangle/\langle F^2_{CH_3OH}\rangle = 2.2 \pm 0.2$). However, the contribution of the librational motion of the molecules to the *A* terms was not taken into consideration, and so the above conclusions are to be questioned. In order to explain the relative magnitudes of ^{13}C and ^{18}O effects Borowitz and Klein[343] used Friedmann's approach[53] (section II.C.2) which can be hardly justified in the extension to the isotopic methanols.

2. Ethanol

The effect of the D substitution at the OH group on the vapor pressure of ethanol has been investigated by Widiger and Brown,[354] Rabinovich, *et al.*,[2,73,319] between 15 and 75°, and Kiss, *et al.*,[74,339,340] between −14.5 and 140°. The agreement is poor. The VPIE is normal as far as the crossover temperature of 135.4°,[74] above which the C_2H_5OD is the more volatile. The determination of the vapor pressures of C_2D_5OH and C_2D_5OD[2,319] show that the isotopic substitution of hydrogen bound directly to carbon causes the expected inverse effect. One crude measurement on O^{18} substitution has been reported.[355]

The vapor pressures of H_2O–C_2H_5OH and D_2O–C_2H_5OD mixtures in the concentration range of 0–30 mol % ethanol have been determined by Linderstrom-Lang and Vaslow[356] using a static method. An interesting result was obtained in that the isotope effect expressed as the logarithm of the ratio of the activity coefficients of the two ethanols ln (γ_H/γ_D) changes sign (from positive to negative) at about 0.08 mol fraction and then becomes relatively constant above 0.12. The results were discussed on the basis of current ideas of the structure of alcohol–water mixtures.[357]

3. Other Alcohols

The vapor pressures of a series of deuterated alcohols, propanol-1 and -2, butanol-1 and -2, and 2-methylpropanol-1 have been measured by Rabinovich.[2,73,358] Differences between the vapor pressures of propanol-1 and -2, butanol-1 and -2, 2-methylpropanol-2, pentanol-3, and their derivatives deuterated at the hydroxyl group have been determined by Kiss, *et al.*,[340,359] over a wide range of temperatures. The comparison of the results with those of Rabinovich, *et al.*, is made difficult by the discrepancies between Rabinovich's data as shown in tables and the equations he formulated for the description of the results. The values for the separation factor obtained by Efremov and Zel'venskii[341] for propanol-2 using Rayleigh distillation are in satisfactory agreement with the manometric data of Kiss, *et al.* We have seen that agreement between these two techniques is a seldom thing. The data[340,359] were least-square fitted to the *AB* equation (eq 36). Approximately the same *B* values were obtained for the primary, the secondary alcohols, and for methanol and 2-methyl-2-propanol, respectively. This was interpreted as arising from the similarity in the ir spectra of alcohols of the same order.

In another series of experiments Russian workers studied the distillation of propanol-2. At 760 mm the ^{13}C and ^{14}C isotopes enriched at the top of the column, the ^{18}O and D isotopes at the bottom.[342] Whereas the value of α obtained for C_3H_7OH–C_3H_7OD is in reasonable agreement with ref 340, 341, and 359, the normal isotope effect reported for the D substitution on methyl or ethyl is in contradiction to those obtained for methanol[2,319,328] and ethanol[2,319] and probably is in error.

The differences in the vapor pressures between the light and heavy forms of pentanol-1 and ethylthiol, respectively, were determined by Hobden, *et al.*,[360] as early as 1939. The numerical values of the VPIE seem excessive (*e.g.*, 15.7% at 25° for pentanol-1); nevertheless, they do show that the deuterium substitution at the OH and SH group decreases the vapor pressure of the alcohol and thiol, respectively.

The vapor pressures of isomeric octyl alcohols (octanol-1, -2, -3, and -4) and their derivatives deuterated in the OH group have been measured by Geiseler, Fruwert, and Hüttig.[361] According to the results the normal VPIE decreases in the series octanol-1, -2, -3, -4.

4. Two Organic Peroxides

Rabinovich and Kozlov[2,73] determined the vapor pressures of *tert*-butyl hydrogen peroxide ($(CH_3)_3CO$–OH) and isopropylbenzene peroxide ($(CH_3)_2C(C_6H_5)O$–OH) and their derivatives deuterated at the OH group using a glass membrane manometer and the Knudsen effusion method,[362] respectively. Since the deuterium substitution was in the group responsible for the association, a normal isotope effect (4–8%) was observed in accord with expectations.

5. Amines

a. Methylamine

The absolute vapor pressures of CH_3NH_2 and CH_3ND_2 have been determined by Emeleus and Briscoe[363] (−60 to −10°) and the isotopic pressure differences by Wolff and

Höpfner[364] (−55 to +20°) and by Kiss, *et al.*[340,365] (−60 to +30°). The results obtained by Wolff and Höpfner are 6–12% higher than those of Kiss. The very early data of Emeleus scatter badly and show a questionable temperature dependence. The vapor-pressure differences between the isotopic pairs CD_3NH_2–CH_3NH_2, CD_3ND_2–CD_3NH_2, CD_3ND_2–CH_3ND_2, and CD_3ND_2–CH_3NH_2 have been measured by Wolff and Höpfner[366] between −55 and +20°. The results show that the deuterium substitution in the amino group decreases the vapor pressure, and substitution in the methyl group increases it. The NH_2/ND_2 effect is markedly temperature dependent, but the methyl group effects display scarcely any change with temperature. An approximate calculation to aid in the interpretation of the VPIE of CH_3NH_2–CD_3NH_2 and CH_3ND_2–CD_3ND_2 systems has been reported by Wolff.[331] Contributions of the methyl bending and stretching vibrations in the gaseous and condensed phase were represented in the zero-point energy approximation, and effects caused by intermolecular vibrations were neglected. The results agree qualitatively with experiment.

The VPIE of methylamine in inert solvents has been also studied (see section IV.F.6).

b. Ethylamine

The absolute vapor pressures of $C_2H_5NH_2$ and $C_2H_5ND_2$ have been determined by Emeleus, *et al.*,[367] (−50 to +10°), and isotopic differences by Wolff and Höpfner[364] (−55 to +20°) and by Kiss, *et al.*[74,365] (−60 to +90°). The data of Emeleus again display an improper temperature dependence. Those of Wolff and Höpfner are 2–19% higher than those of Kiss. The VPIE of $C_2H_5NH_2$ has been measured in hydrocarbon solutions[364] (see section IV.F.6).

c. Propylamine

The vapor pressure difference between $C_3H_7NH_2$ and $C_3H_7ND_2$ has been measured by Kiss, *et al.*,[74,365] between −25 and +65°. Holmberg[244] compared the boiling points of the two compounds and obtained a value for the VPIE which is nearly twice as high as that of Kiss. The VPIE results for methyl-, ethyl-, and *n*-propylamine[74,365] have been fit to the *AB* equation (eq 36) by least squares and it was found that, just as for alcohols, the value of *B* is nearly independent of the length of the alkyl chain. This can be understood if one considers that *B* is connected with shifts in the zero-point energies of the internal vibrations on condensation (see eq 38) and is mainly determined by the vibrations of the amine group.

d. Dialkylamines

The absolute vapor presures of $(CH_3)_2NH$ and $(CH_3)_2ND$ have been determined by Emeleus, *et al.*,[367] between −50 and +5°. The VPIE values calculated from these data scatter badly around the later results of Wolff and Würtz.[368] The later authors also measured the vapor pressures of $(CD_3)_2NH$ and $(CD_3)_2ND$ both as the pure compounds and in hexane solution. The inverse VPIE's found for $(CH_3)_2NH$–$(CD_3)_2NH$ and $(CH_3)_2ND$–$(CD_3)_2ND$ are about twice that for CH_3NH_2–CD_3NH_2 and CH_3ND_2–CD_3ND_2. This was explained[368] (in terms of eq 32) by considering that the VPIE in the above systems is mainly determined by the methyl group vibrations. The factor corresponding to these vibrations appears twice for the dimethyl compound, only once for the monomethyl. The smaller normal effect observed for $(CH_3)_2NH$–$(CH_3)_2ND$ and $(CD_3)_2NH$–$(CD_3)_2ND$ as compared with the corresponding isotopic methylamine molecules were explained in terms of a weaker association of dimethylamine resulting in lower frequencies for the intermolecular vibrations.

The boiling points of methylethyl- and diethylamines deuterated at nitrogen were compared with those of the nondeuterated compounds by Holmberg.[244] Normal isotope effects of 0.9 and 0.7% were obtained for $(CH_3)(C_2H_5)NH$ and $(C_2H_5)_2NH$, at the boiling points.

e. Aniline

The vapor pressures of $C_6H_5NH_2$, $C_6H_5ND_2$, $C_6H_2D_3NH_2$, and $C_6H_2D_3ND_2$ have been determined by Rabinovich and Kozlov[2,73] between −5 and +9° using the Knudsen effusion method.[362] The results of an earlier measurement of the vapor pressures of $C_6H_5NH_2$ and $C_6H_5ND_2$ (also carried out by Rabinovich, *et al.*,[358] between 50 and 80° but by a different technique) are not consistent with the low-temperature data. However, the latter seem internally consistent and show that deuterium substitution in the amine group decreases, and on the benzene ring increases, the vapor pressure of aniline.

6. Two-Component Systems with Amines

Wolff and his coworkers have carried out detailed investigations of the thermodynamic properties of solutions of several different amines in inert solvents. These studies have been supplemented with infrared and Raman spectral studies of the amines in the gaseous and condensed states.[369–383] Vapor pressure isotherms of various solutions of deuterated and nondeuterated amines have been determined, and isotope effects on association constants, association energies, vapor pressures, etc., were extracted from the data. The systems studied are shown in Table XXII. For undiluted amines a normal VPIE was observed for deuterium substitution at nitrogen and an inverse effect for substitution at carbon. In solution the VPIE (expressed as the logarithm of the ratio of partial pressures of isotopic species at a given concentration) for substitution at carbon was found inverse, in contrast to the normal NH/ND effect. The NH/ND effect shows a strong temperature and concentration dependence, and in fact the effect goes over into an inverse effect on high dilution with inert solvents (*e.g.*, *n*-hexane, *n*-butane). However, if the CH_3NH_2–CH_3ND_2 system is diluted with $(CH_3)_3N$, the normal effect persists to very low concentrations of the monomethylamine.[384] The implication is that in this case strong association takes place between methylamine and the trimethylamine in contrast to the VDW bonded monomers which would exhibit an inverse effect. The inverse VPIE of such monomers results primarily from the solvent shift of the intramolecular vibrations; the intermolecular vibrations are low in frequency and do not contribute significantly.[331,385]

The concentration dependence of the VPIE for $(CH_3)_2NH$–$(CH_3)_2ND$ and CH_3NH_2–CH_3ND_2 in *n*-hexane has been interpreted with a two-state model[368,386]

$$\frac{P}{P'} = \left(\frac{P}{P'}\right)^{1-x}_{\text{bonded}} \left(\frac{P}{P'}\right)^{x}_{\text{free}} \qquad (67)$$

P/P' is the ratio of partial pressures of the heavy and light isotopic species at a mole fraction, x, of molecules with free amino groups. $(P/P')_{\text{bonded}}$ and $(P/P')_{\text{free}}$ are the vapor pressure ratios at the hypothetical states of complete association and at infinite dilution. These ratios can in principal be evaluated from the frequencies of intramolecular vibrations of the isotopic species in the gaseous state and from the frequencies of intra- and intermolecular vibrations of monomers or associated compounds in the liquid state (see eq 32). The fraction of free groups, x, can be obtained from activity coefficients and association constants[387,388] using a theory of ideal associated solutions.[389] Calculations for the methylamine–*n*-hexane system at −10 and +20°, in the concentration range 0.1–0.3, show that the expected linear depen-

TABLE XXII. Two Component Systems of Amines Studied by Wolff and His Coworkers

Amine	Second component of the mixture[a]				
	n-Hexane	*n*-Butane	CCl_4	*n*-Nonane	$(CH_3)_3N$
CH_3NH_2	387^+, 369, 379, 380	383^+, 380	382^+	383^+, 380	384^+
CH_3ND_2	364^+, 379, 380, 386				384^+
CD_3NH_2	366^+, 380, 379				
CD_3ND_2	366^+, 379, 380				
$C_2H_5NH_2$	383^+, 369, 380	383^+, 380			
$C_2H_5ND_2$	364^+, 380	364^+, 380			
$C_3H_7NH_2$	383^+, 369, 380				
$(CH_3)_2NH$	388^+, 368^+, 390, 369, 380		388^+, 380		
$(CH_3)_2ND$	368^+, 390				
$(CD_3)_2NH$	368^+, 390				
$(CD_3)_2ND$	368^+, 390				
$(CH_3)_3N$	382^+		382^+		

[a] The references in which experimental results can be found are marked with a +.

dence of ln P/P' on x is satisfied. Using values of P/P' at $x = 0$ obtained by extrapolation, together with experimentally determined vapor pressure ratios of undiluted compounds, estimates of the fraction of free groups in the undiluted amines were obtained: 46 and 33% for methylamine at +20 and −10°; and 64 and 44% for dimethylamine at +20 and −20°. The smaller value for methylamine indicates stronger association. We note that while the above two-state equation neglects the isotope effect on the degree of association, the results of VPIE measurements[390,366] have been interpreted as showing the deuterated derivative to be more strongly associated than the nondeuterated compound.

7. *Organic Acids*

a. Acetic Acid

The vapor pressures of CH_3COOH and CH_3COOD were determined by Lewis and Schutz[28] (50 to 90°) and Rabinovich, *et al.*[2,73,358] (15 to 110°). The latter results are much lower than those obtained by Lewis and Schutz and also deviate considerably from the difference measurements of Halford and Anderson[391] (21 to 84°). According to Rabinovich's data the inverse VPIE goes through a maximum around 50° (see Figure 7). It is interesting that Potter and Ritter[392] observed methyl–carboxyl hydrogen exchange in CH_3COOD and concluded that there is no stable compound corresponding to CH_3COOD. However, a recent study[392a] of the catalytic exchange of deuterium between carboxylic acids and hydrogen indicates that no exchange occurs between the methyl hydrogen of acetic acid and deuterium. The vapor pressures of CH_3COCH and CD_3COOD were determined by Potter and Ritter[392] (25 to 125°) and the vapor pressure differences by Wilson[393] (20 to 100°), and Halford and Anderson[391] (21 to 84°) (who also measured the effects between CH_3COOH and CD_3COOH). The most reliable data seem to be those of Potter and Ritter.[392]

All of these results indicate that deuterium substitution in the methyl group and even in the carboxyl group increases the vapor pressure of the acid. The reason for this was long ago attributed by Lewis and coworkers[28,394] to the fact that organic acids are considerably associated not only in the liquid, but also in the vapor. More recently Rabinovich[2,17,73] gave a qualitative explanation of the VPIE for organic acids. According to him the combined effects of two factors must be taken into consideration: deuterium substitution in the carboxyl group increases the energy necessary to break the hydrogen bond and decreases the proportion of associated complexes decomposing on evaporation. The first of these factors increases, while the second, which is a consequence of the first, decreases, the heat of evaporation. Since the proportion of hydrogen bonds decomposing depends exponentially on the bonding energy, the effect of the second factor dominates and the vapor pressure of RCOOD is therefore higher than that of RCOOH. The maximum observed in the inverse VPIE of the CH_3COOH–CH_3COOD system[2,73,358] is explained in terms of the temperature dependence of the vapor phase association. This explanation is supported by the fact that Potter, *et al.*,[395] show from experimental data on vapor density that the energy of dimerization and the dimerization constant are higher by about 300 cal/mol and 17% (at 120°), respectively, for CD_3COOD than for CH_3COOH.

Holmberg[396] prepared azeotropes with CH_3COOH or CH_3COOD as one component and pyridine, trimethylamine, or triethylamine as the other component. He determined the boiling point differences and isotope fractionation for the amino nitrogen of the amine, and carbon and oxygen fractionation in the carboxyl group using Rayleigh distillation. The ratio of the vapor pressures of the H and D azeotropes at the boiling point of the H form was found to be larger (1.03–1.038) than the corresponding ratio for acetic acid at its normal boiling point (1.017). While the observed separation factors for N isotopes are quite large, those for ^{13}C and ^{18}O isotopes were small. The latter results seem to indicate that the C and O atoms on carboxyl group are very little influenced by the formation of an azeotrope between the acetic acid and an amine.

b. Butyric and Valeric Acids

The effect of deuterium substitution in the carboxyl group on the vapor pressures of $CH_3CH_2CH_2COOH$, $(CH_3)_2CHCOOH$, and $(CH_3)_2CHCH_2COOH$ has been investigated by Rabinovich, *et al.*[2,73,358] An inverse VPIE was found in each case with a maximum for *n*-butyric acid (see Figure 7).

8. *Inorganic Materials*

a. Acids

The isotope effects displayed by the halogen halides HF, HCl, HBr, and HI have been described in section IV.C.7. In ad-

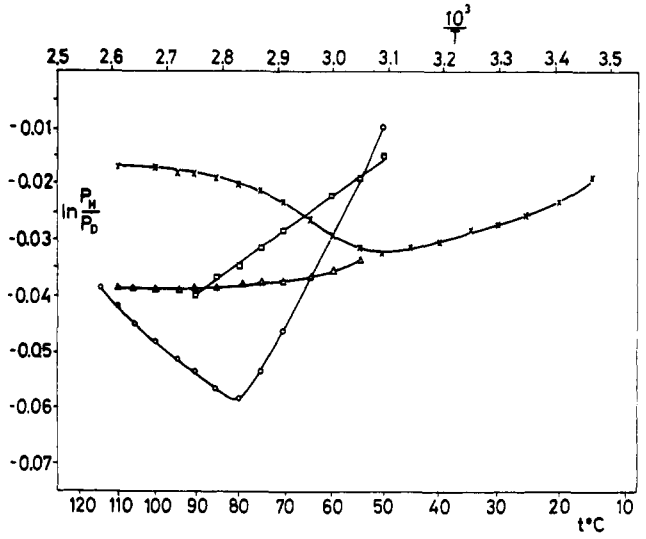

Figure 7. Vapor pressure isotope effects for organic acids deuterated at the carboxyl position:[358] X, CH_3COOH; O, $CH_3CH_2CH_2COOH$; □, $(CH_3)_2CHCOOH$; △, $(CH_3)_2CHCH_2COOH$.

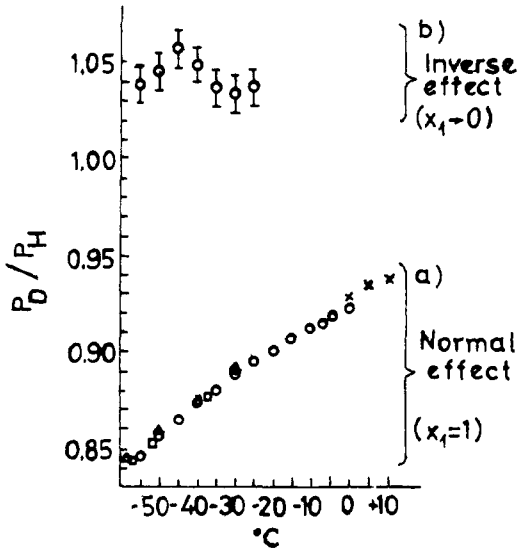

Figure 8. Vapor pressure isotope effect for NH_3/ND_3: (a) Pure ammonia, O, Wolff and Höpfner;[402] □, Kirshenbaum and Urey;[193] △, Kiss, Matus, and Opauszky;[140] X, Groth, Ihle, and Murrenhoff.[398] (b) At infinite dilution in propane: Wolff and Hopfner.[402] x_1 = mole fraction of ammonia.

dition, Dawbar and Wyatt[397] have reported on measurements on the D_2O–N_2O_5 system, and Holmberg[221] has reported on measurements of N^{15} and D enrichment factors for the maximum boiling azeotrope formed between nitric acid and water. He finds the D form of the azeotrope more volatile. Similarly the vapor pressure of 84.37% N_2O_5 in DOD (DNO_3) was found to be 7% higher than the vapor pressure of HNO_3 at 0°.[397] These results indicate that the vapor is associated to a considerable extent.

b. Ammonia

The substitution of deuterium for the three protons in NH_3 results in a large VPIE which has been well studied over the years. The work of Kirschenbaum and Urey,[193] Groth, Ihle, and Murrenhoff,[398] Kiss, Matus, and Opauszky,[140] and others[399-401] has been summarized and extended by Wolff and Höpfner.[402] This summary is nicely displayed in Figure 8 which generally shows satisfactory agreement between different laboratories. The separation factor in the high temperature region (10–90°) was determined by Bakin and Zel'venskii.[402a] Self-association in condensed-phase ammonia is strong, and this is reflected in large normal isotope effects. Wolff and Höpfner[402] also examined H/D effects in the two-component system ammonia–propane and found, as expected, that the normal effect falls off dramatically with ammonia concentration as the self-association is destroyed. In fact, at very low concentrations the molecule shows an approximate 4.3% inverse effect (−25 to −55°). Thus the monomer, which is only experiencing van der Waals intermolecular forces in solution, shows the quite common 1 to 1.5 % per D inverse effect. Wolff, Rollar, and Wolff[403] have made a detailed spectroscopic study of solid ammonia and its deuterium derivatives and have correlated this information with the VPIE by means of a model calculation. Eyring and coworkers have also made model calculations on the NH_3/ND_3 system.[121]

The effect of N^{15} substitution has been considered.[404-406] A small normal effect is observed. Devyatykh and Shavarin[72] have reported on the VPIE of NT_3.

Several authors[400,401] have looked into the engineering feasibility of using ammonia fractionation for the production of deuterium because of the large separation factor but have concluded that under present circumstances it is not economical.

The density and viscosity of the ND_3/NH_3 pair have recently been determined by Alei and Litchman[406a] between −25 and 30°. At any given temperature, the ratio of densities ρ_{ND_3}/ρ_{NH_3} is 1.187 ± 0.001 and the ratio of viscosities η_{ND_3}/η_{NH_3} is 1.20 ± 0.01. The density ratio indicates that the molecular volume of NH_3 in the liquid is ~1% larger than that of ND_3, while the viscosity ratio indicates that the viscosity varies directly as M/V_m (V_m = molar volume) for these two liquids.

c. Hydrogen Sulfide

The vapor pressure difference between H_2S and D_2S was measured by Kiss, Matus, and Opauszky[140] from 148 to 204°K, and from 243 to 303° by Clarke and Glew.[407] Solid–solid transitions occur in H_2S and D_2S at 103.5 and 126.2 and 107.8 and 132.9°K, respectively.[408] The isotope effects are normal in the solid. A discontinuity occurs on melting and the liquid VPIE crosses over to an inverse effect at approximately 225°K.[409] The S^{32}/S^{34} effect has been reported by Russian workers,[214,252] and Clarke and Glew[410] have examined the H_2S–H_2O, D_2S–D_2O systems.

The theory of H_2S/D_2S effects in the solid phase has been considered approximately by Wolff, Wolff, and Höppel[220] and in detail by Gellai and Jancso.[409] The later authors also considered the liquid data and made a full nine-dimensional model calculation in both phases using a force field consistent with the spectroscopic measurements. The force fields were taken to be temperature independent. The agreement with experiment was quite satisfactory and in fact is within the experimental precision as far as −10°. Above that temperature the experimental curvature exceeds the calculated (Figure 9). The authors point out that this result is hardly surprising, especially if one considers that the pressure in the high-temperature range varies from 7.5 to 22.5 atm. At these pressures correction terms should be large and difficult to evaluate.

d. Miscellaneous (HCN, DMSO)

The VPIE's and triple points of dimethyl sulfoxide (DMSO) and perdeuteriodimethyl sulfoxide have been reported by Jakli and Van Hook.[411] The effects are inverse and small, and display the theoretically expected maximum. Chan and Van Hook have investigated the DMSO–HOH and DMSO–DOD systems in considerable detail[412] and report isotope effects

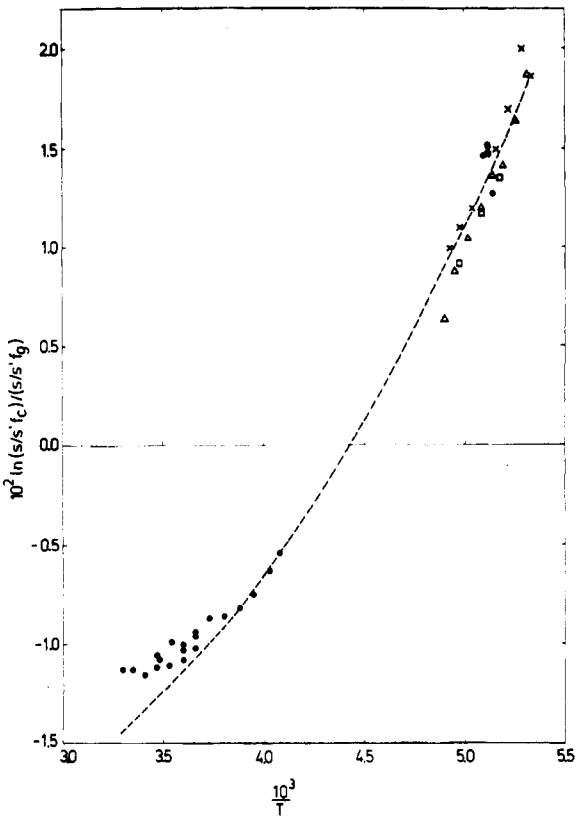

Figure 9. Comparison of experimental liquid partition function ratios of H_2S–D_2S with model calculation: (●), Clarke and Glew;[410] ■, △, □, Kiss, Matus, Opauszky;[140] - - - -, calculated line.[409]

on excess free energies and heats and excess heats of solution.

The H/D VPIE for the system HCN–DCN has been investigated by Lewis and Schutz[394] and by Appleton[413] in both liquid and solid phases. Appleton also reports values for the N^{15} effect. The N^{15} effect is normal over the entire temperature range, but that for DCN shows a crossover to an inverse effect near 300°K. Appleton states that the analysis of his data was hindered by a number of difficulties peculiar to the HCN. First the high lability of the proton in HCN introduced significant problems in synthesis, purification, and storage. Secondly gas-phase polymerization was observed to occur at moderate pressures, and the subsequent dissolution of the polymer species in the liquid sample tended to depress the vapor pressure and to destroy the experimental accuracy. This effect should be particularly important at low absolute pressures, and the rather large VPIE's which may be calculated for the solid from the equations reported in Table XX should be viewed with skepticism. The H/D effects in the liquid are small, just over 1% normal around the triple point, crossing to inverse near 300°K. The agreement between ref 394 and 413 is judged to be satisfactory in view of the experimental difficulties. Appleton feels that his data are to be preferred because his DCN pressures lie systematically higher than those of Lewis and Schutz. This probably indicates that the latter authors were working with a sample which had a higher concentration of dissolved polymeric impurity.

V. Isotope Effects in Aqueous Systems

The isotopic isomers of water itself are among the most thoroughly studied of all systems as far as effects on vapor pressure, molar volume, etc., are concerned. Additionally a great deal of information on isotope effects in aqueous solutions is available (*i.e.*, effects on heats of solution and dilution, activities, partial molal volume, etc.). One practical reason for this is the engineering interest in the utilization of enrichment processes on water flow streams for the industrial scale preparation of deuterium and the heavy oxygen isotopes. A second stems from a recently renewed interest in the problem of water and aqueous solution structure due to the central role that such solutions play in the living cell, as well as in such practical areas as water desalination, etc.

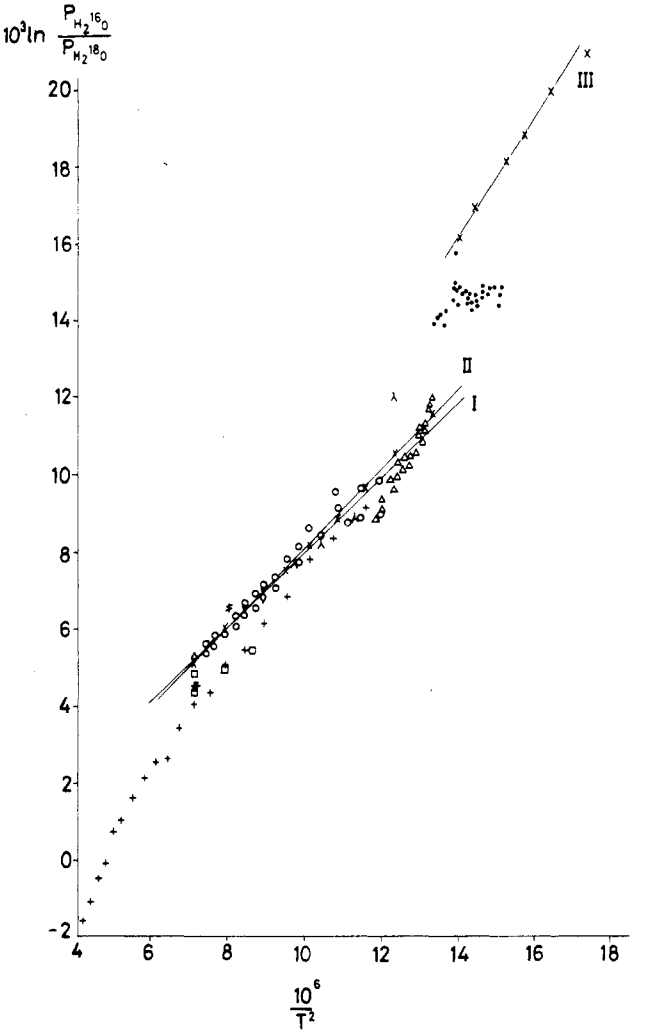

Figure 10. Vapor pressure isotope effect for $H_2{}^{18}O/H_2{}^{16}O$: (X) Majoube;[425,426] (O) Szapiro and Steckel;[416] △, Pupezin, Jakli, Jancso, and Van Hook (liquid);[75] ●, PJJVH (solid);[75] □, Riesenfeld and Chang;[417] +, Uvarov, *et al.*;[418] ⅄, Wahl and Urey;[420] ◊, Baertschi and Thürkauf;[420a] *, Sakata and Morita;[421] ≠, Dostrovsky, *et al.*[422] The data fits I, II, and III are referred to in the text.

Isotope effects on the properties of water have been reviewed earlier on a number of occasions. The works of Kirshenbaum[414] and Whalley[415] summarize the early data quite nicely.

A. Isotope Effects of Pure Water and Ice

1. VPIE. Results

a. Oxygen Isotopes

Most of the data which are available for the VPIE of $HH^{18}O$–$HH^{16}O$, and which are also in substantial agreement from laboratory to laboratory, are reviewed in Figure 10. The data include measurements of separated isotopes by Szapiro and Steckel[416] and Pupezin, Jakli, Jancso, and Van Hook,[75] distillation experiments by Riesenfeld and Chang,[417] Uvarov, *et al.*,[418,419] Wahl and Urey,[420] and others,[138,421–424] as well as the results of Majoube[425–427] on the separation factor which were obtained by a mass spectrometric sampling tech-

TABLE XXIII. Selected Best Equations Describing the VPIE's of the Isotopic Waters

Isotope isomer[a]	Ref	Experimental methods[b]	Phase	Temp range, °C	
(1) $HH^{18}O$	426 (75, 416, 425, 431)	SS, DP	Liq-vapor	0-100 (0-370)	$\ln \alpha = 1137/T^2 - 0.4156/T - 0.00207$
(2) $HH^{18}O$	425	SS	Solid-vapor	0 to −40	$\ln \alpha = 11.839/T - 0.028224$
(3) $HH^{17}O$	416	DP, Cr	Liq-vapor	40-90	$(\alpha_{HH^{17}O} - 1)/(\alpha_{HH^{18}O} - 1) = 0.564 \pm 0.014$
(4) $DD^{18}O$	416	DP, Cr	Liq-vapor	40-90	$(\alpha_{DD^{18}O} - 1)/(\alpha_{HH^{18}O} - 1) = 0.825 \pm 0.022$
(5) $DD^{16}O$	75	DP	Solid-vapor	0 to −40	$\ln R = 56783/T^2 - 206.62/T + 0.23688$
(6) $DD^{16}O$	75	DP	D_2O(solid-vapor) H_2O(liquid-vapor)	−2 to 4	$\ln R = -889582/T^2 + 7405.4/T - 14.9472$
(7) $DD^{16}O$	75	DP	Liq-vapor	−5 to 80	$\ln R = 57320.6/T^2 - 209.412/T + 0.202524$
(8) $DD^{16}O$	This paper	Cr	Liq-vapor	80-350	$\ln R = 57320.6/T^2 - 209.412/T + 0.202524 - 7.146(t - 80) \times 10^{-5} - 1.7202(t - 80)^2 \times 10^{-7}$
(9) $HD^{16}O$	435	Cr	Solid-vapor	0 to −40	$(\ln R_{DDO})/(\ln R_{HDO}) = 1.89 \pm 0.02$
(10) $HD^{16}O$	435	Cr	Liq-vapor	0-200	$(\ln R_{DDO})/(\ln R_{HDO}) = 1.91 \pm 0.02$
(11) TTO	440	P	Ice-vapor	0 to −10	$\ln R \approx 302/T - 0.808$
(12) TTO	440	DP	Liq-vapor	0-110	$\ln R = -103.87/T + 46480/T^2$
(13) THO	435, this paper	Cr	Liq-vapor	0-200	$(\ln R_{TTO})/(\ln R_{HTO}) = 1.86 \pm 0.03$

[a] Estimates of the VPIEs of all of the other isotopic isomers of water have been made by Van Hook[432,435] using a model calculation. These results should not be used for the isotopic isomers of oxygen in the solid phase. [b] SS = single-stage equilibration; DP = differential pressure measurement; Cr = critical evaluation; P = pressure.

nique. In addition to the data on the graph, the results of Craig, Gordon and Horibe[428] and Bottinga and Craig[429] over the range 0–100° are in quantitative agreement with Majoube[426] and Szapiro and Steckel,[416] although they are not shown so as to avoid clutter. Also O'Neil and Adami[430] have determined the reduced oxygen partition function (−2 to 85°) using a CO_2 equilibration technique. Finally Bottinga[431] has reported on fractionation measurements between 100° and the critical point (374°). While those results are not available to us, Majoube[426] says that they lie substantially above the high-temperature results of Uvarov[418,419] and join smoothly with the curves drawn on Figure 10. He reports that his equation (eq 1, Table XXIII) fits these high-temperature data to within 0.4% across the entire range. In particular it is to be noted that Bottinga does not report a high-temperature crossover to an inverse effect in contrast to the claim of the Russians. The data presented in Figure 10 are plotted on a T^{-2} diagram in accord with the theoretical expectation.[77,432] For the liquid they are in substantial agreement, one with the other, except that the Russian work[418-419] and the very early data of Riesenfeld and Chang[417] are definitely low. Some of the data reported on the graph have been smoothed in order to avoid clutter. The agreement between French,[425-427] Israeli,[416] and American[75] workers is especially noteworthy. Two lines are drawn through the liquid points. The first, I on the graph ($\ln R = 982.4/T^2 - 0.00193$), is a least-squares fit reported by Pupezin, *et al.*, to the data in ref 416 and 75, while the second, II ($\ln R = 1137/T^2 - 0.4156/T - 0.002067$), is a fit to the data of Majoube.[425-427] In either case the temperature dependence is approximately proportional to T^{-2} (in the latter equation the contribution of the second term only amounts to some 10% of the first over the range of interest). Between 0 and 100° the two curves differ at most by 0.0004 ln R unit. We have already indicated the excellent agreement with Craig.[428] The data on the ice phase are not as good. They include those of Matsuo and Matsubaya[433] (not shown, unreasonably low), Pupezin *et al.*,[75] and Majoube.[425] The temperature dependence of the American data ($\ln R = 2.110/T + 0.00656$) is small as compared to the French results[425] ($\ln R = 11.839/T - 0.02822$), but both give reasonable values for the effect at the ice point ($\alpha - 1 = 0.0143$ and 0.0151, respectively). We feel that the French data are to be preferred in view of its theoretically more reasonable slope. The combination of the liquid–vapor and solid–vapor separation factors at the melting point gives a value, 1.0034 ± 0.0003, for the solid liquid fractionation (O^{18} concentrates in the solid), which is to be compared with the lower limit reported by O'Neil[434] as 1.0030 ± 0.0002, and the 1.0030 ± 0.0003 found in ref 75. The agreement is satisfactory. The triple point for $HH^{18}O$ as calculated from these results is 0.38 ± 0.05° and is the only reliable estimate available.

Szapiro and Steckel have compared the VPIE's of $HH^{17}O$ and $DD^{18}O$ with $HH^{18}O$ in a careful series of measurements.[416] They also review the (rather sparse) information which had been previously available on these systems. In the case of O^{17} substitution the authors observed an approximately 11% deviation from the law of the mean which was temperature independent over the range of their experiment, 40–90° ($\ln R^{17}/\ln R^{18} = 0.564 \pm 0.014$). This result was shown to be consistent with theory by model calculations due to Van Hook.[432,435] Similarly the lowering of the VPIE observed on deuteration[416] is also temperature independent and in reasonable agreement with the calculated value ($(\alpha(DD^{18}O - 1)/(\alpha(HH^{18}O - 1) = 0.825 \pm 0.022$ as measured (0.86 calculated)).

b. Deuterium and Tritium Isotopes

The differential vapor pressures for the separated isomers DOD and HOH have been measured by at least three different groups for the ices and by nine different laboratories for the waters. By and large the results are in good agreement.

Measurement on ice-I VPIE's have been made to as low as −40° by Kiss, Jakli, and Illy,[130] Matsuo, Kuniyoshi, and Miyake,[436] Pupezin, Jakli, Jancso, and Van Hook,[75] and Johannin-Gilles and Johannin.[437] The first three sets of measurements are in good agreement, but the PJJVH results display considerably better precision above −20° and are preferred. The least-squares fit to these data is reported in Table XXIII. The effects are large and normal. $\ln R = \ln (P_{HOH}/P_{DOD})$ ranges from 0.2415 at 0° to 0.395 at −40°, and is somewhat more than an order of magnitude larger than that for the O^{18} effect.

The available data on the VPIE ratio for liquid DOD and HOH as obtained from nine different laboratories over a 40-year period are shown in Table XXIV.[26,75,130,438-443] We have chosen to compare smoothed values at 10° intervals. The data extend from the supercooled liquid at −5°, all the way to the critical point. They show generally satisfactory agreement from laboratory to laboratory except that the results of Riesenfeld and Chang[438] below 100° are consistently lower

TABLE XXIV. VPIE of DDO (Smoothed)[a]

Worker(s)	Ref (year)	Method	0	10	20	30	40	50	60	70	80	90	100	110
Lewis and Macdonald	26 (33)	P			152	134	118	103.8	91.0	79.6	69.4	60.2	52.0	
Riesenfeld and Chang	438 (36)	DP		158	138	122	109	96.5	85.5	75.8	67.2	58.7	51.0	44.3
Miles and Menzies	439 (36)	DP		173	153	135	119	104.0	90.8	79.2	68.5	59.1	50.9	43.4
Kiss, Jakli, and Illy	130 (66)	DP	198	171										
Beasley and Bottomley	443 (73)	P	204.2	178.9	157.0									
Pupezin, Jaki, Jancso, and Van Hook	75 (72)	DP	204.1	177.9	155.2	135.5	118.3	103.4	90.4	79.1	69.2	60.1	53.0	
Jones	440 (68)	DP		171	151	134	118	103.6	91.0	79.6	69.2	59.8	51.4	44.1
Liu and Lindsay	441 (70)	P												43.8
Oliver and Grisard	442 (56)	DP												
Eq 7 and 8, Table XXIII	This paper		204.1	177.9	155.2	135.5	118.3	103.4	90.4	79.1	69.2	59.8	51.5	44.1

Worker(s)	Method	120	140	160	180	200	220	250	275	300	325	350	370.6
Lewis and Macdonald													
Riesenfeld and Chang	DP	37.8	26.5	17.6	10.7	5.3	1.0						
Miles and Menzies	DP	37.0	26.3	17.9	11.3	5.9	1.0						
Kiss, Jakli, and Illy													
Besley and Bottomley													
Pupezin, Jakli, Jancso, and Van Hook													
Jones													
Liu and Lindsay	P	37.3	26.7	17.8	10.7	4.9	0.2	−5.5	−9.1	−12.2			
Oliver and Grisard	DP					4.7	0.1	−5.4	−9.2	−12.2	−14.9	−17.9	−20.6
Eq 7 and 8, Table XXIII		37.6	26.6	17.8	10.7	4.9	0.2	−5.4	−9.1	−12.3	−15.1	−17.6	−23.7

[a] Units are 10^3 ln (P'/P).

than those of other workers. Also below room temperature the recent results of PJJVH[75] and Beasley and Bottomley,[443] which are in good agreement one with the other, lie higher than those of most other workers. Both these groups had considerably more precision than was available to early workers in the low-pressure range due to improved manometry. The higher results are to be preferred. (We note that the relation quoted by PJJVH is deduced from an examination of pure solvent data as well as of the concentration dependence of the VPIE of four different dilute salt solutions. The VPIE for the pure waters obtained by extrapolation of solution data to infinite dilution agrees quantitatively with the fit to the pure solvent data alone.) Above 30° or so the agreement between laboratories generally improves; this is a consequence of the increase in the value of $P_H - P_D$ as the total pressure increases.

We have carefully considered the data in Table XXIV and have indicated our preferred choice in heavy outline. These data define the pressure ratio, ln (P_{HOH}/P_{DOD}) over the range −5 to 370° with an average standard deviation of about ±0.0002 ln R unit. They consist of results from four different laboratories. The VPIE itself varies from about 20% normal at the ice point to about 2% inverse at the critical point. An equation which reproduces these selected data (−5 to 350°) with $\sigma = \pm 0.0001$ ln R unit and a maximum deviation of 0.0003 unit is quoted in Table XXIII.

The reliability of eq 7, Table XXIII, in the low-temperature region is further substantiated by a comparison of the fractionation factors for the hypothetical process

$$HOH_{sol} + DOD_{liq} = HOH_{liq} + DOD_{sol} \quad (0°) \quad (68)$$

Thus a value of 1.0381 ± 0.0004 is found from eq 5 and 7, Table XXIII, as compared with the 1.0384 ± 0.0002 obtained by Weston[444] or 1.0380 ± 0.0002 by Kuhn and Thürkauf[445] from thermodynamic data. Similarly PJJVH[75] obtained data between the triple points of HOH and DOD (eq 6, Table XXIII). Simultaneous solution of eq 5 and 6, and 6 and 7, Table XXIII, gives 3.83 ± 0.04 and −0.03 ± 0.04 for the two triple points, in good agreement with the accepted values 3.83 and 0.01.

The measurement of the VPIE of HOD has been approached in a number of different ways. Majoube[426] and Merlivat and Nief[446] have measured HOH–HOD separation factors by a mass spectrometric technique over the range −30 to 100°, while Kiss, Jakli, and Illy[130] and Combs, Googin, and Smith[447] made measurements of the total pressure exerted by mixtures of HOH, HOD, and DOD in efforts to deduce the VP of HOD, and Zieborak[448] made ebulliometric measurements on similar mixtures between 80 and 220°. The results of Majoube and Zieborak are superior. The data have been considered in detail by Van Hook[435,449] who concludes that the ratio $RR = 1.91 \pm 0.02$ (liquid)

$$RR = \frac{\ln (P_{HOH}/P_{DOD})}{\ln (P_{HOH}/P_{HOD})} \quad (69)$$

and is independent of temperature (0 to 200°) and HOD concentration (*i.e.*, solutions of HOD and DOD in HOH are perfectly ideal to within the precision of the presently available measurements). He also finds that RR(liquid) − RR(solid) = 0.02 by the analysis of measurements of the freezing points of HOH–HOD–DOD solutions.[450,451] The 4.5% lowering from the value of 2.0 which is predicted by the law of the geometric mean was shown to be consistent with the theory, by means of a model calculation. It is also supported by an examination of the measured fractionation factors for the process

$$HOH(solid) + HOD(liquid) = HOH(liquid) + HOD(solid) \quad (0°) \quad (70)$$

which lie consistently (1.0211 ± 0.0007,[452] 1.0171 ± 0.0005,[445] 1.0235,[446] 1.0195,[434] 1.0195,[453] 1.0208[454]) above the value 1.0189 ± 0.0002 predicted from the law of

TABLE XXV. Physical Properties of Isotopic Waters

		HOH	DOD	TOT	$HH^{18}O$	$HH^{17}O$	$DD^{18}O$	HOD	HOT
Triple point, °C		0.0	3.82	4.49	0.38 ± 0.05	0.21 ± 0.05[a]	4.13 ± 0.05[a]	2.04 ± 0.05	2.4 ± 0.1[a]
Boiling point, °C		100.00	101.42[b]	101.51	100.15 ± 0.05	100.08[a] ± 0.05	101.54 ± 0.05[a]	100.74 ± 0.05[a]	100.8 ± 0.1[a]
Critical temp, °C		374.15	370.9 ± 0.1						
Critical pressure, atm		218.3	215.7						
Crossover temp with HOH, °C			220.9[b] 220.77 ± 0.05	190 ± 10	Does not cross	Does not cross?[a]	<220.8[a]	217	...
$(L_x - L_{H_2O})_{liq}$, cal/mol	0°		418[b]	469	15.7[b]	8.9[b]	431[b]	219[b]	252[b]
	25°		348,331 ± 8	413	14.3	8.1	360	182	222
	50°		289	365[c]	13.2	7.4	300	151	196
	75°		238	324	12.2	6.9	248	125	174
	100°		194	289	11.3	6.4	203	102	155
$(L_x - L_{H_2O})_{sol}$	0°		416[b]	~600[a]	23.5[b]	13[a]	427[a]	220[b]	...
	−25°		498						
ΔH_{fus}[e]	0°	1436	1424[c], 1501 at 3.82°						
C_p at 25°[e]		17.99	20.16						
C_v at 25°		17.80	20.0						
Compressibility, 25°		45.29 × 10^{-6} atm^{-1}	46.56 × 10^{-6} atm^{-1}						
Dipole moment[f]									
In benzene (25°C)		1.76	1.78						
Vapor at 100–200°		1.84	1.84						
Refractive index, $n^{20}D$		1.33300	1.328299		1.33334				
Viscosity, (Cp)	5°	1.5192	1.9820						
	70°	0.4039	0.4732						
		(d)	(d)						
Surface tension (25°)[g]		71.97	71.93						
2nd virial coef, cm^3/mol,	200°	−223	−226						
	300°	−117.2	−117.9						
	400°	−71.0	−71.1						

[a] Estimated, this paper. For other entries, see text for references, especially ref 522. [b] Calcd from Table XXIII. [c] Calcd from C_p and ref 463. [d] DOD: $\log \eta/\eta_{20} = 1.3580(20 - t) + 6.7 \times 10^{-4}(t - 20)^2/(96.71 - t)$; $\eta_{20} = 1.2471$, ref 484. [e] Cal/mol. [f] Debyes. [g] Dyne cm.

the mean and the HOH–DOD separation factor. The number calculated from $RR_{liq} = 1.91$ and $RR_{sol} = 1.89$ is 1.0199 in good agreement with the bulk of the measured values above.

Data on the VPIE of solid and liquid TOT has been reported by Jones[440] and for the liquid by Popov and Tazetdinov.[455] The data are much less precise than those for DOD because of the necessity of making rather large corrections for radiolytic heating and gas production. They extend from approximately −10 to about 110° and over most of the range lie significantly above the corresponding DOD effects (Table XXIII). Separation factors for the HOT–HOH system have been measured between 20 and 60° by Smith and Fitch,[456] at 72.5 and 100° by Avinur and Nir,[457] and between 40 and 100° by Zel'venskii, *et al.*[458] Earlier TOT–HOT data are due to Libby and Cornog[459] and Price.[460] There is considerable scatter from laboratory to laboratory but still general agreement that the value of the ratio $RRR = (\ln (P_{HOH}/P_{TOT})/(\ln (P_{HOH}/P_{HOT}))$, lies between 1.6 and 2.0. We feel that the best assessment of this ratio is obtained by correcting that found *via* a model calculation[435] (1.83) by the factor which corrects the corresponding DOD ratio to the observed value. This gives $RRR = 1.86 \pm 0.03$ where the error is arbitrarily estimated. The most reliable VPIE's for HOT are then obtained by combining this number with the experimental data of Jones for TOT.[440]

2. Isotope Effects on Other Physical Properties of Water

A variety of effects on the physical properties of the waters are presented in Tables XXV and XXVI. The effects on the triple points, boiling points, and relative enthalpies of vaporization and sublimation have with few exceptions been calculated from the vapor pressure data in Table XXIII. The exceptions include direct measurements of the triple points of DOD and TOT[461] and the measurements of the enthalpy of vaporization (25°) and of fusion (3.81°) as measured by Rossini, *et al.*,[462] and Long and Kemp,[463] respectively. The agreement between these values and those derived from the vapor pressure is within the combined experimental errors of the two techniques. It is interesting to note that the isotope effect on the enthalpy of fusion at the ice point (0°) as calculated from the measured values for HOH (0°) and DOD (3.83°)[463] and $c_{sat} \approx c_p$ for DOD[464] (or from the vapor pressures) is inverse and very small. In fact, the effect for DOD appears to be no larger in magnitude than that for $HH^{18}O$ although of opposite sign. This is to be contrasted with the more crudely determined value for TOT which is much larger and normal. Certain of the enthalpy effects in the table (for example, those for HOD or $HH^{17}O$) have been approximated from the relations in Table XXIII and are to be interpreted as approximations only. The enthalpies of vaporization when combined with the zero-point energy differences of the gas-phase molecules[465,466] give an approximate value for the enthalpy of formation of HOD in solutions of HOH or DOD ($\Delta H_{HD} \simeq [ZPE_{HD} - \frac{1}{2}(ZPE_{HH} + ZPE_{DD})] - [\Delta(\Delta L^V_{HD}) - \Delta(\Delta L^V_{DD})/2] \approx 13$ cal/mol, which is in satisfactory agreement with the much more precise 15.75 cal/mol directly measured by Duer and Bertrand[467] and earlier workers.[468,469] Narten[470,471] in an earlier theoretical calculation estimated 17.2 cal, but this calculation did not incorporate the Wolfsberg[97,98] G° correction term.

We note here that earlier disagreements between harmon-

TABLE XXVI. Coefficients and Properties of Functions Representing Density of Water[473] (Refer to Eq 71)

Coeff, g/cc	H_2O	D_2O	$H_2{}^{18}O$	$D_2{}^{18}O$	T_2O
a_0	0.9998396	1.104690	1.112333	1.215371	1.21293
10^3a_1	18.224944	20.09315	13.92547	18.61961	11.7499
10^6a_2	−7.922210	−9.24227	−8.81358	−10.70052	−11.612
10^9a_3	−55.44846	−55.9509	−22.8730	−35.1257	
$10^{12}a_4$	149.7562	79.9512			
$10^{15}a_5$	−393.2952				
10^3b_1	18.159725	17.96190	12.44953	15.08867	9.4144
Range of function, °C	0–150	3.5–100	1–79	3.5–72	5–54
Est accuracy, ppm	0.5–20	10	50	100	200
Temp of max density, °C	3.984	11.185	4.211	11.438	13.403
Max density, g/cc	0.999972	1.10600	1.11249	1.21688	1.21501
Ref		474–484	479, 481	479	482

ic (K = 3.82)[98] and anharmonic (K = 3.45)[472] calculations of the disproportionation constant for the process

$$HOH + DOD = 2HOD$$

have been resolved by Wolfsberg[97,98] and Hulston[99] (see section II.F.4.c) who pointed out an error which had been incorporated into the earlier anharmonic calculations. Both the harmonic and the corrected anharmonic calculations now appear to be in reasonably close agreement with experiment. Values are as follows:

T, °C	K_{vap} (exptl)[96]	K_{vap} (theor)[97-99]	$K_{liq} - K_{vap}$[449]
0	3.74	3.82	0.04
75	3.80	3.89	0.01

Molar volume isotope effects at 1 atm pressure may be obtained from the smoothed density functions reported in Table XXVI by multiplying by the molecular weights. The table, due to Kell,[473] reports coefficients of fit of extant data[474-483] to the function

$$\rho = \sum_{n=0}^{5} a_n t^n/(1 + b_1 t) \qquad (71)$$

Millero, Dexter, and Hoff[484] recently redetermined the density of DOD between 5 and 70° in excellent agreement with the values tabulated in Table XXVI. Hebert, *et al.*,[485] have measured the densities of heavy water, liquid and vapor, between 250° and the critical point. It is interesting to note that the molar volumes of the isotopic waters are in the order TOT > DOD > HOH > $HH^{18}O$ over the entire liquid range. Rivkin and Akhundov[485a] have also reported on density measurements at elevated temperatures and pressures for DOD.

New viscosity data for DOD between 5 and 70° have been presented by Millero, Dexter, and Hoff[484] who have also reviewed the older data.[486-492] The effects are large; the ratio η_D/η_H, 1.305 at 5°, decreases gradually to 1.172 at 70°. No interpretation of the results was made. Viscosity data on electrolyte solutions in HOH and DOD are also available.[493,494]

The isothermal compressibility of DOD has been carefully measured between 5 and 65° by Millero and Lepple[495] who present comparisons of their work with the older data[464,496-498] on DOD and with the best compilation[499] on HOH. The compressibility of water is anomalous in that it decreases with increasing temperature, finally going through a minimum around 45°. The compressibility of DOD follows a similar pattern. It lies above the curve for HOH by 4.7% at 5°, but this decreases to 1.5% at 65°. Over this range the DOD compressibility is fit within experimental error by the relation

$$10^6\beta_{DOD} = 53.61 - 0.4717t + 0.9703 \times 10^{-2}t^2 - 0.1015 \times 10^{-3}t^3 + 0.5299 \times 10^{-6}t^4 \qquad (72)$$

The minimum in the curve occurs at approximately 49.5°, or about 4° higher than that for HOH. Rabinovich[2] has measured the isotope effect on compressibility by experimentally determining ultrasonic velocities in the two media. The results lie generally a few per cent lower than those reported by Millero, *et al.*,[495] but the isotope effects are comparable in magnitude. Rabinovich also reports similar measurements on a variety of other compounds.

Rabinovich[2] and Mehu and Johannin-Gilles[500] have reviewed the rather extensive data[501-511] which are available on the refractive index and the dispersion of light in liquid HOH, DOD, and $HH^{18}O$. Values of the refractive index at one temperature are entered in Table XXV. We note that although the refractive index of $HH^{18}O$ lies higher than that for normal water the polarizability of the latter is nonetheless about 0.05% larger because the O^{18} water displays a smaller molar volume. It is also interesting that both HOH and DOD show an anomalous temperature dependence for the polarizability, which falls with increasing temperature up to about 60° where it goes through a minimum. Rabinovich speculates that this effect, like the anomalies on density and compressibility, is caused by peculiarities in the structure of liquid water.

The dielectric constants for HOH and DOD have been carefully intercompared between 0 and 40° by Vidulich, Evans, and Kay[512] and earlier by Malmberg[513] and Wyman and Ingalls.[514] The isotope effect is very small over the entire temperature range. Data for the isotope effects on the polarizability and the dipole moments of the isolated molecules (in the vapor or in dilute solution) are old and hard to find. The surface tensions of HOH and DOD differ insignificantly at room temperature,[515-517] but above 100° the differences begin to be appreciable and at 220° DOD has a surface tension some 3% less than that of HOH.[518] The isotope effect on the second virial coefficient of the vapor has been reported by Kell, McLaurin, and Whalley.[496] They show a smooth decrease in the difference, $(B_{HOH} - B_{DOD})/B_{HOH}$, from 1.3% at 200° to 0.1% at 450°. The results were discussed in terms of a model involving dimerization. Juza, *et al.*,[519] have determined Joule–Thomson coefficients for H_2O and D_2O (130 to 190°, 1 to 2 atm).

3. *Interpretive Calculations on Isotopic Waters*

Workers from a number of different laboratories have

more or less systematically engaged in model calculations in an effort to interpret isotope effects on the physical properties of water. Most calculations have been made either in the average molecule cell model calculation or by using some form of mixture model. In the later category the extended calculation by Nemethy and Scheraga[520] and the application of significant structure theory to the HOH–DOD system by Jhon, Grosh, Ree, and Eyring[521] are the most noteworthy. The Nemethy–Scheraga calculation for DOD, with but one exception, employed a set of parameters which was consistent with the analogous[522] calculation on HOH. The calculation is a complex one and will not be discussed in detail here. The authors concluded that a somewhat larger fraction of hydrogen bonds are broken in DOD than in HOH but that the cluster sizes in DOD are significantly larger than in HOH. The calculation reproduced the general features of the molar volume, thermal expansion, and compressibility data (extending to the prediction of minima in the temperature dependence of these properties), but the agreement was hardly quantitative. The VPIE's were not calculated. Certain statistical arguments incorporated in the Nemeththy–Scheraga model have been criticized.[523] A particularly fine description of this model as well as other mixture models for water has been given by Davis and Jarzynski.[524]

In the application of significant structure theory to water and heavy water, Eyring and his coworkers[521] assumed three kinds of water molecules in the condensed phase. By a systematic methodology they developed a set of parameters for HOH and DOD, but these unfortunately differ, and no theoretical rationale is given for the differences. This is the chief criticism of the approach which does reproduce the physical properties with about the same precision as the earlier Nemethy–Scheraga calculation. In neither case is the calculated VPIE (apparently the most sensitive test) in good agreement with experiment. Somewhat later Jhon, Van Artsdalen, Grosh, and Eyring applied the model in a calculation of the surface tensions of light and heavy water.[525]

Average molecule cell model calculations really make no pretense of developing a realistic partition function for the condensed phase. In this approach each molecule is assigned a set of $3n = 9$ intermolecular (6) and intramolecular (3) oscillator frequencies. The approach described in section II.F.3 is employed, and to date all calculations have been made in the harmonic approximation. Since only one kind of condensed phase molecule has been assumed, these models cannot realistically reproduce the temperature dependence of such properties as the molar volume, the compressibility, etc. The philosophy, however, has not been to predict the value of the property itself but only the isotope effect thereon. The calculations have been strictly limited to the VPIE. The (harmonic) frequencies are used to derive ratios of partition functions which then give the VPIE with the use of the Bigeleisen equation (eq 32). Authors who have employed this general approach include Majoube,[425] Jones,[440] Wolff,[526,527] Van Hook,[432,435] and O'Ferrall, Koeppl, and Kresge.[528,529] The principal factor which determines the value of the isotope effects is the very large red shift in the two OH stretching frequencies on condensation. This is more than compensated for by the appearance of three rather large librational frequencies. Therefore, although the intramolecular red shift is in the direction of an inverse effect, the net effect remains normal because of the strong intermolecular bonding in the liquid. There is a relatively small blue shift in the bending mode upon condensation.

The spectra of liquid water is broad and difficult to assign,[465,530] especially in the intermolecular region. Still, certain problems may be circumvented by studying the decoupled spectra of dilute solutions of HOD.[531–533] The exact isotope effect which results from the calculation strongly depends on the relative assignments of the intermolecular and the librational modes. Thus, for example, Majoube[425] made internal assignments of 3340, 1645, and 3440 cm^{-1} at 0° (gas-phase values are 3657, 1595, and 3756[466]) and lattice mode assignments at 454, 590, and 860 (librational) and 176 (translational), while Van Hook[432,435] (40°) gives 3450, 1645, and 3630 cm^{-1}, and 500, 497, 495, and 162 cm^{-1}. Notice that in the later assignment the rather smaller intramolecular red shift is compensated for by the assignment of smaller frequencies to the librational modes. Both sets of frequencies give satisfactory agreement with the observed isotope effects. The higher librational frequencies appear more reasonable on spectroscopic grounds, but so does the second set of intramolecular frequencies. In any event the model is highly approximate, especially for water where the motions of each molecule are strongly coupled to its neighbors, and where anharmonicity in the condensed phase plays an important role. This is underscored by the fact that temperature-dependent force constants must be employed in order to obtain agreement with experiment over the whole temperature range. Although the temperature dependencies employed are consistent with the spectroscopic observations, the approach remains somewhat unsatisfactory. The attempt of Wolff to improve the situation by using a two state model suffers from problems arising from the doubling of the number of parameters. Similarly the calculation of O'Ferrall, *et al.*,[528,529] which treats a tetrahedrally coordinated model of a hydrogen bonded water involves the assignment of a large number of parameters. The VPIE calculated by these authors is in poor agreement with experiment, probably because their rather high librational assignments are not compensated for with large intramolecular red shifts.

In summary we must conclude the harmonic oscillator calculations of water VPIE's are much too oversimplified to be useful aids in deducing the structure of condensed phase water. They are, however, quite useful in correlating and systematizing the data on the different isotopic isomers. In this context the calculations of either Majoube[425] or of Van Hook[432] as ammended[435] should prove most useful. In particular, the prediction of the VPIE for an as yet unstudied isotopic isomer such as (for example) $TT^{17}O$ from a model which gives good agreement with experiment for $TT^{16}O$ and $HH^{17}O$ should be highly reliable, but this does not imply that the model accurately describes the physical state of any of the isotopic waters.

B. Aqueous Solvent Isotope Effects

An extensive literature has accumulated on solvent isotope effects in HOH–DOD systems. It is convenient to divide the discussion and treat electrolyte and nonelectrolyte solutions separately. In neither case will we attempt a comprehensive discussion.

1. *Solvent Isotope Effect in Electrolyte Solutions*

a. Introduction

The treatment of solvent isotope effects in aqueous solutions has been discussed in considerable detail by Friedman and Krishnan[9] and Arnett and McKelvey.[8] Two important quantities which must enter any discussion of solution chemistry are the definitions of the concentration scale and the standard state. In the treatment of solvent isotope effects, concentration is normally expressed in aquamolality units.[534] A 1 aquamolal solution corresponds to 1 mol of solute per 55.508 mol of solvent. For HOH this reduces to the conventional kilogram of solvent. The standard state for the solutions is taken as the hypothetical 1 *m* solution having the properties of infinite dilution. For any given thermodynamic parame-

TABLE XXVII. Standard Free Energies of Transfer of Electrolytes to D_2O from H_2O[a,b]

X	$(G°_x)_{d←w}$	X	$(G°_x)_{d←w}$	X	$(G°_x)_{d←w}$	X	$(G°_x)_{d←w}$
LiF	−58	NaI	230	$RbPh_4$	269	t-$BuMe_2SNPi_2$	260
	(−140)		(180)		(265)		(270)
LiCl	32	KF	−3	$RbBAn_4$	369	$(CH_2)_4MeSBAn_4$	279
	110		(5)		(373)		(278)
	202[560]						
	30	KCl	130	CsCl	170	$(CH_2)_4MeSNPi_2$	279
			180		(170)		(280)
LiBr	67		225				
	(50)		121[534]	$CsBPh_4$	212	$TolMe_2SBAn_4$[e]	269
			219		(210)		(278)
LiI	100		140[75]				
	(100)		210[563]	$CsBAn_4$	316	$TolMe_2SNPi_2$	288
			(175)		(318)		(280)
NaF	−28						
	(−60)	KBr	180	$CsNPi_2$[d]	316	n-Bu_4NBAn_4	42
			(195)		(320)		(128)
NaCl	140						
	110	KI	240	Me_3SBAn_4	279	n-Bu_4NNPi_2	140
	116[534]		(245)		(273)		(130)
	212[560]						
	170[75]	$KBPh_4$	269	Me_3SNPi_2	269	NH_4Cl[f]	164
	(110)		(215)		(275)		(164)
NaBr	170	$KBAn_4$[c]	377	t-$BuMe_2SBAn_4$	279	Me_4NCl[f]	134
	(130)		(323)		(268)		(134)
$MgCl_2$	280	$CdCl_2$	436	$C_3H_7CO_2Na$[f]	−46[546]	$AgIO_3$	270[559]
	(280)		(436)		(−46)		
						AgCl	47[562]
$CaCl_2$[f]	300[548]	HCO_2Na[f]	−19[546]	$C_4H_9CO_2Na$[f]	−39[546]		
	(300)		(−19)		(−39)	$CdCl_2$	436[560]
$SrCl_2$[f]	300[548]	CH_3CO_2Na[f]	−34[546]	$C_5H_{11}CO_2Na$[f]	−39[546]		
	(300)		(−34)		(−39)		
$BaCl_2$[f]	340	$C_2H_5CO_2Na$[f]	−45[546]	$AgBrO_3$	190[550]		
	(340)		(−45)				
				$Cu(IO_3)_2$	520[551]		

[a] Values in cal/mol at 25°. Standard states: hyp 1 aquamolal. The electrolyte data (unless specified) are taken from the compilations given by Arnett and McKelvey[3] or Friedman and Krishnan.[9b] Values in parentheses are calculated from single-ion values in Table XXX to test the degree to which the data are made up of additive ionic contributions. [c] BAN_4^- is the tetraanisylborate ion. [d] NPi_2 is the dipicrylamide ion. [e] Tol = $C_6H_5CH_2$. [f] These data were obtained by an emf method employing an anion exchange membrane to separate the H_2O and D_2O solutions. A correction for solvent transport has not been made and the results are subject to uncertainties of the order of 20%.

ter, X, one then defines the desired complete set, $X_1°$, $X_2°$, X_1^{ex}, and X_2^{ex}. The subscripts 1 and 2 refer to solvent and solute, respectively, and the superscript ° refers to the process which proceeds from the solute (2) or the solvent (1) in its standard state to the standard solution. The excess properties, X^{ex}, are defined, $X^{ex} = X - X°$, and refer to the change in X per mole for a process which proceeds from the standard state of the solution to a solution of finite concentration. The excess functions depend on both temperature and concentration, the standard functions on temperature alone.

Isotope effects are usually reported in terms of transfer properties. Thus the notation $\Delta X_2°(d←w)$ refers to the change in a property X_2 characterizing the solute, when 1 mol of solute is transferred from normal water to heavy water, both at infinite dilution. Similarly the notation $\Delta X_2^{ex}(d←w)$ refers to the isotope effect on the transfer from the solution at finite concentration to the standard state solution. The corresponding properties, $\Delta X_1°(d←w)$ and $\Delta X_1^{ex}(d←w)$, exist for solvents too, but we note that the $\Delta X_1°$'s do not differ from pure solvent isotope effects. The ΔX_2^{ex}'s can be obtained from the ΔX_1^{ex}'s *via* a Gibbs–Duhem–Bjerrum integration if sufficient data are available to allow the extrapolation to infinite dilution. The formulation of the description of the properties of electrolyte solutions in terms of excess thermodynamic properties is due to Friedman.[535]

Before proceeding to the data, we briefly mention the model which is currently in vogue for the discussion of the results. This has been variously labeled as the "Gurney cosphere model" [536] or the "Samoilov hydration model" [537] and has been developed in considerable detail by Friedman (*cf.* ref 9 and citations therein) on both a qualitative and a detailed theoretical plane. In its simplest form the model pictures two kinds of water, cosphere water in the immediate neighborhood of the solute particles and bulk water which retains the properties of the pure solvent. One thus has a two state model for the solvent, and the thermodynamics of the isotope effects on the equilibrium between the two kinds of water are phrased in terms of the equilibrium between bulk and cosphere water. This equilibrium is readily associated with the differences in the standard state properties, $\Delta X_2°(d←w)$. The detailed theory invokes several different kinds of cosphere water.* If it is possible to assume that the coordination

* The notation employed for the different kinds of cosphere water, as due to Friedman and Krishnan,[9] is as follows.

I. Hydration of the first kind: states in which the water is oriented by ionic fields or other directional solute–solvent forces.

State I_c: characteristic of the inner cospheres of small cations.

State I_a: characteristic of the inner cospheres of small anions.

State I_{hb}: characteristic of the inner cospheres of hydroxyl groups or R_3NH^+ ions.

II. Hydration of the second kind: states in which the water is perturbed by the proximity of a solute particle, but the effect cannot be ascribed to directional solute–solvent forces.

State II_{rg}: characteristic of the cosphere of a rare gas atom.

State II_{al}: characteristic of the cosphere of an alkyl group.

State II_{ar}: characteristic of the cosphere of an aromatic group.

State II_{sb}: characteristic of the outer cospheres of small ions, the seat of the so-called structure-breaking phenomenon.

TABLE XXVIII. Calorimetric Heats of Transfer to D_2O from H_2O (kcal/mol) at 25°[a]

X	$(H°x)_{d←w}$	Ref	X	$(H°x)_{d←w}$	Ref
LiF	−0.155	538	$MeSO_3Na$	0.29	543
LiCl	0.40	539	$PhSO_3Na$	0.29	543
LiBr	0.535	539	p-$TolSO_3Na$	0.29	543
LiI	0.675	539	Na_2CO_3	0.418	545
$LiClO_4$	0.40	540, 541	Na_2SO_3	0.388	545
LiO_2CCF_3	0.03	541	Na_2SO_4	0.591	545
NaF	0.00	543	HCO_2Na	0.195	546
	0.01	538		0.205	546
NaCl	0.53	543	CH_3CO_2Na	0.068	546
	0.56	539		0.065	546
	0.59	8			
	0.54	544	$C_2H_5CO_2Na$	0.016	546
	0.547	569			
			$C_3H_7CO_2Na$	−0.017	546
NaBr	0.695	539			
	0.68	544	i-$C_3H_7CO_2Na$	−0.036	546
	0.649	569			
			$C_4H_9CO_2Na$	−0.054	546
NaI	0.835	539			
	0.83	544	$C_5H_{11}CO_2Na$	−0.099	546
$NaClO_4$	0.60	541	KF	0.06	539
	0.57	539			
			KCl	0.61	539
NaO_2CCF_3	0.10	541, 542		0.73	8
				0.61	541
$NaNO_3$	0.49	539		0.75	547
	0.481	545		0.55	544
$NaClO_3$	0.53	541	KBr	0.75	539
$NaBPh_4$	0.78	541	KI	0.89	539
	0.77	8			
KCN	0.50	539	$BaCl_2$	1.36	548
				1.36	549
KNO_3	0.51	541		1.28	547
$KBrO_3$	0.52	539	NH_4Cl	0.26	541
RbCl	0.60	540, 541	$NH_4O_2CCF_3$	−0.23	541
RbBr	0.80	539	Me_4NCl	0.48	541
RbO_2CCF_3	0.17	541		0.38	8
CsCl	0.65	541	Me_4NBr	−0.37	542, 552
CsBr	0.81	539	Me_4NI	0.71	540, 541
CsO_2CCF_3	0.21	541			
			Et_4NCl	−0.20	541
AgCl	0.20	562	Et_4NBr	0.30	542, 552
$AgNO_3$	0.42	539	Et_4NI	0.41	541
$AgBrO_3$	0.80	550	Pr_4NCl	−0.12	541, 552
AgIO	0.12	559	Pr_4NBr	0.04	552
			Pr_4NI	−0.15	541, 552
$Hg(CN)_2$	0.20	539			
			Bu_4NCl	−0.26	541, 552
$Cu(IO_3)_2$	0.23	551			
			Bu_4NBr	−0.15	552
$MgCl_2$	0.87	548			
	0.751	549	Pen_4NCl	−0.44	541, 545
$CaCl_2$	1.20	548	Pen_4NBr	−0.28	552
	1.05	549			
	1.01	547	Ph_4AsCl	0.10	552
$SrCl_2$	1.27	548	Ph_4PCl	0.12	552
	1.22	549			
	1.15	547	$Bu_3N(CH_2)_8NBu_3Br_2$	−0.04	541
$MeNH_3Cl$	−0.02	557	$OctNH_3Cl$	−0.29	557
$EtNH_3Cl$	−0.05	557	$MeNH_3Br$	0.064	569
$PrNH_3Cl$	−0.11	557	$PrNH_3Br$	−0.026	569
$BuNH_3Cl$	−0.16	557	$BuNH_3Br$	−0.067	569
$PenNH_3Cl$	−0.20	557	$OctNH_3Br$	−0.214	569
$HexNH_3Cl$	−0.24	557	Me_3SI	0.21	8
$HepNH_3Cl$	−0.27				

[a] After Friedman and Krishnan,[9] in major part. Data have been corrected to infinite dilution where necessary.

TABLE XXIX. Single-Ion Standard Free Energies of Transfer to D_2O from H_2O[a] Based on the Convention that $(Na^+)^G_{d\leftarrow w} = 0$ as due to Friedman and Krishnan[9]

X	Li^+	Na^+	K^+	Rb^+	Cs^+	Me_3S^+	t-$BuMe_2S^+$	$(CH_2)_4MeS^+$	
$(\Delta G°)^X_{d\leftarrow w}$	−80	0	65	115	60	15	10	20	
X	$TolMe_2S^+$	NH_4^+	Me_4N^+	n-Bu_4N^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Cd^{2+}
$(\Delta G°)^X_{d\leftarrow w}$	20	54	24	−130	60	80	80	120	216
X	F^-	Cl^-	Br^-	I^-	BPh_4^-	BAn_4^-	NPi_2^-	HCO_2^-	$CH_3CO_2^-$
$(\Delta G°)^X_{d\leftarrow w}$	−60	110	130	180	150	258	260	−19	−34
X	$C_2H_5CO_2^-$	$C_3H_7CO_2^-$	$C_4H_9CO_2^-$	$C_5H_{11}CO_2^-$					
$(\Delta G°)^X_{d\leftarrow w}$	−45	−46	−39	−39					

[a] Values in cal/mol. Standard states: hyp 1 aquamolal.

TABLE XXX. Single-Ion Standard Enthalpies of Transfer of Solutes to D_2O from H_2O[a] Based on the Convention $(AsPh_4^+)^H_{d\leftarrow w} = (BPh_4^-)^H_{d\leftarrow w}$ as due to Friedman and Krishnan[9]

X	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$(\Delta H°)^X_{d\leftarrow w}$	450	610	660	680	710	540	970	1300	1370	1460
X	NH_4^+	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+	Pen_4N^+	Ph_4As^+	Ph_4P^+		
$(\Delta H°)^X_{d\leftarrow w}$	300	430	210	−50	−230	−380	160	170		
X	$DiBu^{2+}$	$MeNH_3^+$	$EtNH_3^+$	$PrNH_3^+$	$BuNH_3^+$	$PenNH_3^+$	$HexNH_3^+$			
$(\Delta H°)^X_{d\leftarrow w}$	−220	30	0	−60	−110	−150	−190			
X	$HepNH_3^+$	$OctNH_3^+$	Hg^{2+}	Me_3S^+	F^-	Cl^-	Br^-	I^-		
$(\Delta H°)^X_{d\leftarrow w}$	−220	−240	−120	−20	−610	−50	90	230		
X	$CF_3CO_2^-$	ClO_4^-	NO_3^-	CN^-	ClO_3^-	BrO_3^-	BPh_4^-	CO_3^{2-}		
$(\Delta H°)^X_{d\leftarrow w}$	−510	−40	−120	−160	−80	−140	60	−800		
X	SO_3^{2-}	SO_4^{2-}	HCO_2^-	$CH_3CO_2^-$	$C_2H_5CO_2^-$	$C_3H_7CO_2^-$	i-$C_3H_7CO_2^-$			
$(\Delta H°)^X_{d\leftarrow w}$	−830	−630	−420	−540	−590	−630	−650			
X	$C_4H_9CO_2^-$	$C_5H_{11}CO_2^-$								
$(\Delta H°)^X_{d\leftarrow w}$	−660	−710								

[a] Values in cal/mol at 25°.

number (*i.e.*, the size of the cosphere) is isotope independent, the interpretation proceeds straightforwardly (*vide infra*).

The effects on the excess properties are not as easily interpreted. They arise from the fact that as the concentration increases the cospheres between neighboring ions begin to overlap, and at that point some water is squeezed out. The pertinent equilibrium, at least at lower concentrations, would therefore be that between cosphere "monomer" and cosphere "dimers" or "oligmers." The effect should be much smaller than those on the standard state properties.

b. Data on Standard Transfer Properties

The available data for HOH–DOD solvent isotope effects on the standard state properties, $\Delta H°$ (ref 8, 9, 538–559) and $\Delta G°$ (ref 8, 9, 75, 548, 550, 551, 559–563) are reviewed in Tables XXVII and XXVIII. The bulk of the information is taken from the compilations of Friedman and Krishnan[9] or of Arnett and McKelvey.[8] The data in the tables have been corrected to infinite dilution where possible. The corresponding entropy effects may be readily derived. Suggested sets[9] of single ion parameters (apparently additive to within the precision of the data) are quoted in Tables XXIX, XXX, and XXXI for the standard ionic free energy, enthalpy, and entropy, respectively. Other authors[8,564] have suggested different criteria.

Friedman and Krishnan[9] have also considered the available $^{18}O/^{16}O$ fractionation data over saline solutions as gathered by Taube and coworkers[565,566] and obtained standard transfer effects from them. Zel'venskii, *et al.*,[567] report similar fractionation data. The effects are quite small.

Only a limited amount of information is available on the partial molal heat capacities $(C_p°)^x_{d\leftarrow w}$. Davies and Benson report −6.8 gibbs/mol for NaCl,[543] and a value of −8.8 gibbs/mol may be obtained from the data of LaMer and Noonan[547] for KCl. Craft and Van Hook[544] have measured isotope effects on the heats of solution of NaCl, KCl, NaBr, and

TABLE XXXI. Quantities Related to the Solvent Isotope Effect[a] in Single-Ion Hydration Entropies after Ref 9

Species X	$(TS°)^X_{d\leftarrow w}$ Exptl[b]	Exptl[c]
Li^+	0.49	0.05
Na^+	0.57	0.13
K^+	0.56	0.11
Rb^+	0.53	0.07
Cs^+	0.61	0.17
F^-	−0.51	−0.07
Cl^-	−0.12	0.33
Br^-	0.00	0.45
I^-	0.09	0.54
Mg^{2+}	0.84	
Ca^{2+}	1.13	
Sr^{2+}	1.19	
Ba^{2+}	1.25	
Me_4N^+	0.37	
HCO_2^-	−0.35	
$CH_3CO_2^-$	−0.47	
$C_2H_5CO_2^-$	−0.51	
$C_3H_7CO_2^-$	−0.54	
$C_4H_9CO_2^-$	−0.59	
$C_5H_{11}CO_2^-$	−0.63	

[a] All quantities in kcal/mol at 25°. [b] Single-ion values based on $T(Na^+)^X_{d\leftarrow w} = 0.57$ kcal/mol. [c] Single-ion values based on $T(F^-)^S_{d\leftarrow w} = -0.07$ kcal/mol.

NaI at 10, 25, 50, and 75°. They obtained (in that order) −7.3, −9.0, −7.8 and −8.7 gibbs/mol for $C_p°$ at 25°, but their data (which are not of the highest precision) indicate that these values approximately double as the temperature falls to 0°. At 75° they are some 60% of the 25° value. Much more precise values of the transfer heat capacities (25° only) have been reported for the tetraalkylammonium bromides by Philip and Desnoyers[568] using a high precision calorimeter specifically designed just for heat capacity measurements. The method is precise enough to investigate concentration depen-

TABLE XXXII. The Solvent Isotope Effect in the Partial Molal Volume[570]

Solute, X	$(\Delta V^\circ)^X_{d\leftarrow w}$ ml/mol
NaF	−1.42
	−1.93[571]
NaCl	−0.83
NaBr	−0.34
NaI	−1.35[571]
$C_6H_5SO_3Na$	−5.96[571]
KCl	−0.37
KBr	−0.19
Me_4NBr	−0.12
Et_4NBr	0.20
	0.25[572]
n-Pr_4NBr	0.42
n-Bu_4NBr	0.94
$(HOC_2H_4)NHBr$ } $(DOC_2H_4)_3NHBr$ }	−2.70
HOD	0.56
Pyridine	0.20

dence. The standard transfer heat capacities are large at 25° and sensitive to the size of the alkyl chain. They amounted to −61.5, −33.5, +111, and +156 cal/(mol deg) for the tetramethyl, tetraethyl, tetrapropyl, and tetrabutyl bromides, respectively. No detailed interpretations of the heat capacity effects are yet available. Desnoyers, Francescon, Picker, and Jolicoeur[569] have also measured the standard and excess transfer enthalpies for a series of n-alkylamine hydrobromides with high precision. They (and also earlier authors examining other homologous series) report smooth progressions in standard and excess properties with carbon number.

The standard partial molal volumes of transfer available in the literature[570-572] are shown in Table XXXII. Corresponding single ion parameters have been derived from them,[9,570] but the trends appear to be anomalous.[9]

An area of research very closely related to the present discussion deals with the measurement and interpretation of isotope effects on the ionization constants of weak acids and bases. Bates and his coworkers Paabo and Robinson have reported solute and solvent isotope effects on acetic acid,[573-575] bicarbonate ion,[576] and phosphoric acid,[577] and have reviewed the earlier work in the field.[578] They[579] and Lietzke and Stoughton[580] report measurements on the HCl/HOH–DCl/DOD system. A number of other workers have also reported on similar isotope effects.[581] All of these results have been of material aid in establishing an operational pD scale.[582,583] At 25° they report pK(DOD) = 14.955 (molality scale). This corresponds to K(HOH)/K(DOD) = 7.35 to be compared with other values of 7.06 (Goldblatt and Jones[584]), 7.2 (Gold and Lowe[585]), and 7.47 (Salomaa[564]). Goldblatt and Jones report a value of 16.4 for the ratio K(HOH)/K(TOT).

An extensive literature on the measurement and interpretation of isotope effects in mixed solvent (HOH–HOD–DOD) systems has accumulated. We regard this interesting area as outside the scope of this review. A good discussion of many aspects of this problem has recently been given by Halevi[586] and by Gold.[587]

Gold and Grist[588] and Friedman and Krishnan[589] have recently instituted programs of study of solvent isotope effects in the CH_3OH and CH_3OD system. The comparisons with the corresponding data for aqueous systems are interesting.

c. Data on Excess Transfer Properties

Not a great deal of information is available on excess transfer properties. The determination of the excess transfer free energies is equivalent to measuring the isotope effect on the activity coefficients, $(\Delta G_2^{ex})_{d\leftarrow w}$, or on the osmotic coefficients, $(\Delta G_1^{ex})_{d\leftarrow w}$. Pupezin, Jakli, Jancso, and Van Hook determined solvent VPIE's in HOH and DOD[75] over solutions of NaCl, KCl, CsCl, and LiCl over broad temperature (0 to 90°) and concentration ranges. The measurements have more recently been extended to NaBr, NaI, KF, Na_2SO_4, and $CaCl_2$ solutions by Van Hook and Jakli[590] and Van Hook and Chan.[591] Similarly Googin and Smith,[592] Combs and Smith,[593] Selecki and coworkers,[594-596] and Becker, *et al.*,[597] have determined separation factors over saline solutions.

In the treatment of the VPIE data the authors[75] applied the extended Debye–Hückel theory. Under the assumption that the leading term (the electrostatic part) is isotope independent, the isotope effect on the osmotic coefficient, which is proportional to the difference of the VPIE's between the pure solvents and the solution, was shown to be of the form

$$m(\phi_H - \phi_D) = \frac{55.508}{\nu}\left[\ln\left(\frac{P_H}{P_D}\right)_0 - \ln\left(\frac{P_H}{P_D}\right)_m\right] \doteq bm^2 + cm^3 + \ldots \quad (73)$$

The effects were found to be small and, within experimental precision, positive for all the salts investigated. This observation is consistent with the separation factor studies[592-596] where it was found that the addition of salt invariably lowered the factor from the pure solvent value. The result is, however, in conflict with the conclusions reached by Kerwin[534] and Bonner[598,599] (whose work is referenced to Kerwin) from isopiestic data, but in agreement with other isopiestic work of Robinson.[600,601] The solvent excess free energies are readily deduced from the osmotic coefficients, and the excess solvent transfer enthalpies follow from the temperature dependence. Extrapolation of the isotope effects to infinite dilution and the use of the Gibbs–Duhem–Bjerrum equation allows the isotope effect on the mean ionic activity coefficients and the excess solute transfer free energies and enthalpies to be evaluated.

$$\ln\left[\gamma_\pm(H_2O)/\gamma_\pm(D_2O)\right] = 2bm + \tfrac{3}{2}cm^2 + \ldots \quad (74)$$

The results are in satisfactory agreement with those determined calorimetrically (Table XXXIII) and would seem to establish the procedure as reasonable. The calorimetric data are to be preferred because of their higher precision. Depending on the point of view of the observer, the extrapolation is acceptably short (over a very small isotope effect)[75] or unacceptably long (over a wide concentration range—as much as $2m$),[602,603] and the methodology has therefore been questioned. It has been suggested that there may be a nonzero constant of integration,[602] which could arise if the assumption of an isotope independent DH leading term were incorrect. The resolution of this point must await precise data on small effects at low concentration. The matter is an important one and pertains to both excess and standard transfer free energies. For example, if $\phi_H - \phi_D$ (and $\ln(\gamma_H/\gamma_D)$) is known as a function of concentration to the solubility limit, and if the IE on the solubility (or solute free energy in the case of hydrates) is known, then the standard transfer free energies may be deduced provided the constant of integration is known. [For the saturated solutions $(G_2^\circ)_{crys} = (G_2)_m{}^{H_{soln}} = (G_2)_m{}^{D_{soln}}$. Data on $(m_H/m_D)_{sat}$ (see ref 2, 493, 550, 551, 563, 604–613) and hydrate VPIE's (ref 614–620, 620a) are available.] Although a number of the data entered in Table XXXIII have been so obtained, comparison with other methods does not resolve the matter of an integration constant because experimental scatter is too large. In the case where the solubilities are small, the contribution of the excess transfer free energies may be neglected, and the isotope effect on the solubility gives the standard transfer free energy directly.[562]

TABLE XXXIII. Some Excess Properties of Transfer at 2 *m*

	$K = [(\phi_H - \phi_D)/m] \times 10^3$			$-\Delta H_2^{ex}/m$, cal/mol					$-\Delta C_{p2}^{ex}$, cal/(mol°)	
Ref	75	601	534[d]	621[a]	542[a]	544[a]	569[a]	75,[b] 590,[b] 412[b]	544[a]	75[b]
NaCl	1.8	2.3	−1.2 (1.8)	39	34	32	36	34 ± 6	−1.2	−1.2
KCl	3.1	3.9	0.0 (3.0)	39	40	33		15 ± 25	−1.1	−0.2
CsCl	10	4.1	0.8 (3.8)					90 ± 35		−2.3
LiCl	−0.4	1.1	−5.8 (2.8)	12	47 ± 8			−6 ± 7		−0.3
NaBr	0.9		−5.0 (2.0)				36	19 ± 6		
NaI	2.1		−3.1 (3.7)					42 ± 10		
KF	3.0							84 ± 15		
Na_2SO_4	3.2							130 ± 20		
$CaCl_2$	36.7							300 ± 50		
$MeNH_3Br$							18			
$EtNH_3Br$							6			
n-$PrNH_3Br$							1			
n-$PrNH_3Br$							(115)[c]			
n-$OctNH_3Br$							(549)[c]			

[a] Calorimetric. [b] From VPIE *via* Van't Hoff. [c] Extrapolated. [d] Values in parentheses referenced to (NaCl) = 1.8[75]

Calorimetric data at 25° on $\Delta(\Delta H_2^{ex})_{d\leftarrow w}$ for a number of salts has been obtained by Friedman and Wu,[542] Wood, Rooney, and Braddock,[621] Philip and Desnoyers,[568] and Craft and Van Hook.[544] The last authors have also obtained data on a few salts at several other temperatures. Comparisons are found in Table XXXIII. Generally the agreement is satisfactory. In most instances it is within 0.001 unit on K ($K = (\phi_H - \phi_D)/m$), and within several calories on $(\Delta H_2^{ex})_{d\leftarrow w}$. This is reasonable in view of the fact that the effects are small and difficult to measure, and the comparisons are between workers in different laboratories using different techniques. The values in the table are quoted at a concentration of 2 *m*. Generally the excess functions show pronounced concentration dependencies, but these are not discussed in detail here in the interest of conserving space. The calorimetric enthalpies are to be preferred over those obtained from the VPIE measurements. It is gratifying that the agreement between the two methods is as good as it is. The excess transfer enthalpies for the inorganic salts are negative, and those excess heat capacities of transfer which have been measured are all positive and appreciably large at 25°.

d. Discussion

The isotope effects on both the standard and the excess transfer properties appear to be consistent with extensive evidence on a wide variety of other processes related to hydration phenomena. This other evidence has recently been summarized by Lumry and Rajender[622] who point out in particular that around 25° one very often finds the Barclay–Butler rule obeyed with T^* somewhat less than 300°K.

$$\Delta G(X) = \Delta H(X) - (T - T^*)\Delta S(X) \qquad (75)$$

Typically the enthalpy–entropy compensation is of such a magnitude that only about 10% or so of the X dependence shows up in the free energy. The expression of the compensation phenomena is sometimes called "Lumry's law." It is apparent that this type of phenomena is operating in the isotopic solvent transfer phenomena as presented in Tables XXVII through XXXI,[8,9] where there is a large measure of enthalpy–entropy compensation. Friedman[9] claims that much of the data are consistent with the assumption that the enthalpy change associated with the process

$$\text{water (bulk)} = \text{water (type II cosphere)} \qquad (76)$$

is about 5% larger for DOD than for HOH.

The standard transfer data can usefully be considered in terms of the *AB* equation (eq 32). In applying eq 32 to the bulk = cosphere equilibria, one is concerned with the frequency shifts of the water molecules between bulk and cosphere. The implicit assumption of no isotope effect on the cosphere coordination number is often made, but this may limit the application to strongly coordinated cospheres.[75] To our knowledge no attempts to formulate the problem in more general terms in order to evaluate the isotope effect on cosphere structure (as opposed to properties) have been attempted. In any case granting the necessary assumption and applying the *AB* equation, one may straightforwardly obtain a relation

$$\frac{\Delta G^\circ}{RT} = \frac{A^\circ - A^c}{T^2} + \frac{B^\circ - B^c}{T} \qquad (77)$$

which taking the external modes as the *A* frequencies, and employing the normal approximations, gives eq 78. In eq 77 and 78, the superscript o's refer to unchanged bulk water, superscript c's to cosphere water, subscript r's to a suitably averaged librational frequency, subscript t's to the hindered translational frequencies, and the *G*'s to the *G* matrix elements of the intramolecular vibrational modes.

$$\frac{\Delta G^\circ}{RT} \cong \frac{1}{24}\left(\frac{hc}{K}\right)^2 \frac{1}{T^2}\left[3\,(\bar{\nu}_r{}^{o2} - \bar{\nu}_r{}^{c2})\left(1 - \frac{I_H}{I_D}\right) + 3\left\{(\nu_t{}^{o2} - \nu_t{}^{c2})\left(1 - \frac{M_H}{M_D}\right)\right\}\right] + \frac{1}{T}\left[\frac{hc}{2k}\sum_{int}(\nu_i{}^{o} - \nu_i{}^{c})\left(\frac{G_D}{G_H}\right)^{1/2}\right] \qquad (78)$$

Swain and Bader, some years ago,[623] performed an interesting calculation which amounted to lumping the entire effect into the librational contribution (which forms the major part of the *A* term). The intramolecular parts of the partition functions were ignored completely. They obtained numbers which were in reasonable agreement with the observations at 25°, and the agreement extended to the prediction of trends from ion to ion. The ΔA term was positive, indicating that the librational frequencies red-shift in going from bulk to cosphere. The standard transfer enthalpies were positive in agreement with experiment but were also predicted to be temperature invariant. This last point is not in agreement with experiment.[75,543] The observation of significantly large heat capacities of transfer indicates that more sophisticated models are required. No refined calculations have yet been reported, but we anticipate that a proper calculation will first account for the compensatory changes in intramolecular frequencies (the *B* term) as well as in the *A* terms. Following that, the possibility of isotope effects on the structure of the

TABLE XXXIV. Standard Transfer Properties for Some Nonelectrolytes

	$(\Delta G°)°_{d\leftarrow w}$	$(\Delta H°)°_{d\leftarrow w}$	Method[a]	Ref
Argon	−48	−237	S	627
CH_4	−30	−400	S	625
C_2H_6	−33	−400	S	625
C_3H_8	−14	−222	S	625
n-C_4H_{10}	+8	−900	S	
	−17	−142		
Benzene	49	−50	S	625
	0 ± 15			
Biphenyl	−23	−50	S	625
Toluene	25 ± 15		S	635
m-Xylene	45 ± 12		S	635
o-Xylene	84 ± 20		S	635
Naphthalene	108 ± 15		S	635
$C_6H_5NO_2$	157		S	636
Picric acid (18°)	809		S	637
CH_3F (29°)	−12	489	S	638
CH_3Cl (29°)	20	140	S	638
CH_3Br (29°)	38	76	S	638
CH_3I (29°)	57	369	S	638
t-BuCl (15°)	−14		S	640
Dimethyl sulfate	130		S	639
I_2	110	−269	S	8
CO_2	−1.7		S	8
Ketones				
Acetone	0 ± 15	−160 ± 16	S, C	635
2-Butanone	7 ± 20	−232 ± 10	S, C	635
3-Pentanone	−18 ± 23	−318 ± 12	S, C	635
3-Hexanone	0 ± 15	−419 ± 1	S, C	635
Cyclohexanone	+52 ± 10	−186 + 18	S, C	635
Hexane-2,5-dione	0 ± 15	−18 ± 10	S, C	635
3,3-Dimethylacetyl-acetone	+41 ± 40	+70	S, C	635
3-Methylacetyl-acetone (keto)	+25 ± 40		S, C	635
3-Methylacetyl-acetone (enol)	+200		S, C	635
Deuterioquinone	+110		Emf	623
Alcohols				
Methanol		−230	C	8
		−182 ± 16	C	624
Ethanol		−350	C	866
		−311 ± 2	C	624
Deuterioethanol		−320	C	8
1-Propanol		−383 ± 2	C	624
2-Propanol		−405 ± 4	C	624
		−384 ± 2	C	635
1-BuOH		−290	C	8
		−469 ± 16	C	624
2-BuOH		−433 ± 6	C	624
t-BuOH		−510	C	8
		−450 ± 17	C	624
1-Pentanol		−495 ± 4	C	624
3-Pentanol		−514 ± 6	C	635
Cyclohexanol		−449 ± 12	C	635
Benzyl alcohol		−285 ± 18	C	624
Ethylene glycol		−160	C	8
Glycerol		−120	C	8
Amides				
$HCONH_2$		−30	C	8
CH_3CONH_2		−70	C	8
t-$C_4H_{10}ONH_2$		−270	C	8
$CH_3CONHCH_3$		−140	C	8
$CH_3CONHC_2H_5$		−420	C	8
$CH_3CONH(n$-$C_4H_9)$		−390	C	8
$CH_3CONH(t$-$C_4H_9)$		−410	C	8
$CH_3CON(CH_3)_2$		−130	C	8
$CH_3CON(C_2H_5)_2$		−360	C	8
Amino acids				
$RCH(NH_2)COOH$				
Glycine (R = H)	−28 ± 4	−190 ± 27	S, C	624
DL-Alanine (R = Me)	−24 ± 3	−328 ± 17	S, C	624
DL-α-Aminobutyric acid (R = Et)	−3 ± 1	−374 ± 21	S, C	624
DL-Norvaline (R = n-Pr)	13 ± 0	−429 ± 23	S, C	624
DL-Norleucine (R = n-Bu)	13 ± 0	−512 ± 7	S, C	624
L-Phenylalanine (R = Bz)[b]	127 ± 1	−308 ± 24	S, C	624

[a] S = from solubility or liquid–liquid extraction as appropriate. C= calorimetric. [b] Bz = $C_6H_5CH_2$–). Units are cal/mol.

cosphere must be considered (perhaps in terms of an isotope effect on the coordination number).

No calculations, either qualitative or quantitative, have been performed on the excess transfer properties, but these have been discussed in general terms in a number of places.[75,542,569]

2. Nonelectrolyte Solutions

Solubility data have been obtained as a function of temperature (0 to 50°) for propane and butane by Kresheck, Schneider, and Scheraga,[624] and for methane, ethane, butane, benzene, and biphenyl by Ben Naim, Wolf, and Yacobi.[625] Guseva and Parnov[626] also give some hydrocarbon solubilities in HOH and DOD. Ben Naim[627] had earlier reported similar data for argon. In all cases the transfer free energies were obtained directly from the solubilities and the transfer enthalpies from the temperature coefficients. The values at 25° are reported in Table XXXIV. The agreement between Ben Naim, *et al.*,[625] and Scheraga, *et al.*,[624] for n-butane, the one solute which both workers used, is not good. Moule[628] examined the other end of the concentration scale by determining the solute isotope effect on solubility and activity for water in benzene. He has given an interpretation of the observed effects with a calculation based on the Bigeleisen approach (section II.F). Glasoe and Schultz[629] have also reported solubilities of HOH and DOD in hydrocarbons and in CCl_4.

The results on the solubility of simple hydrocarbon gases are of particular interest in that they shed considerable light on the phenomenon of hydrophobic bonding.[630] Ben Naim suggests that the data be used to compute thermodynamic parameters for the following "reactions" in solution.

$$\begin{aligned} &2 \text{ methane} = \text{ethane} \\ &2 \text{ ethane} = \text{butane} \\ &4 \text{ methane} = \text{butane} \\ &2 \text{ benzene} = \text{biphenyl} \end{aligned} \qquad (79)$$

The idea here is that the parameters describing the reactions above are equivalent[631-634] to the process of bringing two solute particles from fixed positions at infinite separation to some close distance—the whole process being carried out in the liquid at constant pressure and temperature. Except for the last case (which is probably not a good model for the hydrophobic bond because of specific directional forces), the free energies and enthalpy changes for the reactions as written above are stronger in HOH than in DOD. This might be attributed to a decrease in the "structure of the water" as the two solute particles approach each other. It, for example,

implies that two methane molecules in solution have more "structure" associated with them than does one ethane molecule. It would be interesting to compare this idea with measurements of excess thermodynamic properties of hydrocarbon solutions. However, these could be obtained only with great experimental difficulty.

We note that further stuies of the type discussed above are to be much recommended. Many, in fact the great majority of earlier discussions of hydrophobic bonding, have centered about the properties of charged species in solution, generally tetraalkylammonium ions. For these ions, like any ions, the greatest part of effects which are actually measured are due to the electrostatic forces. Still, the point of interest—the hydrophobic bond itself—is connected with the residue. The experiments of Ben Naim and of Kresheck point more directly toward that effect. Ben Naim has discussed the interpretation of isotope effects on the reactions in eq 79, but only in general and qualitative terms.[625]

The standard transfer free energies and enthalpies on tlhe simple hydrocarbons are presented in Table XXXIV together with what other data[8,624,635-640] are available. In particular, studies have been made on homologous series of alcohols,[624] ketones,[635] amides,[8] amino acids,[624] and aromatic compounds,[625,635] as well as on all of the methyl halides[638] and other selected compounds.[641] Isotope effects on critical micelle concentrations have also been measured.[642] The usual methcd employed to determine the free energy differences was by measuring the isotope effect on the solubilities, but in those cases where the solubility was high, liquid–liquid extractions with organic materials were employed. The enthalpic effects were taken either from Van't Hoff plots of the solubilities or (more generally) from calorimetric measurements. It is fair to say that experimental difficulties are much more pronounced in these studies of nonelectrolyte solutes than they were for the salt solutions, and this accounts for the sometimes large disagreement between workers which is noted in the table; Kresheck[640] has reported standard transfer heat capacities for the amino acids.

Dahlberg[635] and Arnett and McKelvey[8] have pointed out the pronounced enthalpy–entropy compensation which is exhibited by these isotope effect data. They have elaborated on their remarks with some speculations concerning the structure of the solutions. We have already mentioned the somewhat different, but still qualitative, approach of Ben Naim[625] to the problem. To our knowledge no quantitative theoretical discussion of the kind of effects reported in Table XXXIV has yet been reported.

In addition to the rather extensive studies on dilute solutions as discussed above, a number of authors have examined isotope effects on the properties of aqueous solutions over wider concentration ranges. Thus Linderstrom-Lang and Vaslow[356] have examined the VPIE's of ethyl alcohol–water–heavy water solutions, and Van Hook and Chan[412] have made measurements on the DMSO–HOH–DOD system over the complete concentration range and from 30 to 100°. Their work included calorimetric as well as vapcr pressure studies. Glew and Watts[643] made enthalpic measurements on the ethylene oxide–HOH–DOD systems. "S" shaped enthalpy of mixing–composition curves were obtained, and these were interpreted in terms of hydrogen bonding changes in the solution. A detailed discussion was given. Earlier Glew, Mak, and Rath[644] had reported freezing points and activity coefficients of ethylene oxide dissolved in DOD. Clarke and Glew examined the solubilities of the H_2O–H_2S and the D_2O–D_2S systems.[410] Giguere and coworkers[645,646] have measured the calorimetric properties of the systems H_2O_2–H_2O and D_2O_2–D_2O as well as the density, viscosity, surface tension, etc., and Benjamin and Benson[349] report heats of mixing for CH_3OH–HOH and CH_3OD–DOD. Rabinovich[2,319] has examined the pyridine–water–heavy water system over the entire concentration range. Finally there have been a considerable number of solvent IE studies on upper and lower consolute temperatures in partially miscible liquid–liquid systems[2,319,641,647-649] (Schrier, Loewinger, and Diamond[647] have given a brief but interesting discussion).

VI. Isotope Effects on Miscellaneous Other Properties

We believe that a reasonably balanced discussion of condensed phase isotope effects has been presented in the preceding sections. However, certain topics which we have neglected deserve to be set aside and at least labeled as distinct and separate fields of interest. At the same time we will indicate leading references.

A. Molar Volume Effects

Considerable work has been reported on the molar volume isotope effect. Papers prior to 1965 are reviewed by Rabinovich.[2] Brown has recently reported calculations on the rare gases using an anharmonic potential.[650,651] For polyatomic molecules, the work of Bartell and Roskos[652] and of Bigeleisen, Dorfmüller, and Menes[305] are of especial interest. These sets of authors propose alternative explanations of the effects (section IV.E.2). In the present review we have given some consideration to the molar volume problem in the sections on water, methane, and ethylene (sections IV.E.1, IV.E.2, V.A.2). Other references which may be of interest are 47, 274, 392, 407, 418, 419, 473, 646, and 653–659.

B. Gas Chromatographic Effects

The utilization of the techniques of gas–solid and gas–liquid chromatography for the separation of isotopic isomers and for the measurement of separation factors and other thermodynamic properties has been aggressively pursued in the recent years. The Italian group under Liberti has been most active in this area (ref 292, 293, 660–671). Van Hook[672] has reviewed the literature prior to 1968 including the work from his own laboratory (ref 290, 291, 312, 313, 315). Other work which has been reported recently includes ref 673–685. We might comment that the chief advantage of gc studies in the context of the present article is that they afford a convenient method to obtain isotope effects on solute activity coefficients in the Henry's law region for two-component systems between (generally) small and volatile solutes and the (generally) large involatile solvents which form the column substrate. In the case of gas–solid chromatography, it is of course the isotope effect on adsorption which is investigated.

C. Surface Tension

The isotope effect on surface tension has been discussed by Deutch, Kinsey, and Oppenheim in theoretical terms.[686] Eyring and coworkers[525] have applied significant structure theory to the calculation of the surface tension isotope effect of water, and Bartell and Roskos[652] have discussed surface tension effects of hydrocarbon–deuterocarbons in qualitative terms. Rabinovich[2] has reviewed the earlier data.

D. Viscosity

Rabinovich[2] has listed the earlier data, and we have commented above on the effects for the isotopic waters. Other references which may be of interest are 320, 484, 492–494, 646, and 687–693.

VII. Conclusion

The experimental and theoretical work reviewed in the present article appears to have unequivocally established that condensed phase isotope effects without notable exception can be understood in terms of present ideas concerning the condensed phase. These ideas include the notion that the *properly* calculated potential energy surface describing the liquid is isotope independent. This granted, the interpretation of observed effects has provided and is providing a powerful tool to aid in the understanding of the details of that surface, and hence of the condensed phase. We are confident that further progress in this area will unfold, particularly as more sophisticated techniques for handling problems of anharmonicity, rotation–vibration coupling, etc., are developed.

VIII. Addendum

The general field covered by this review has remained active since submission of the manuscript to the editor (alas! a complaint common to all reviewers). In this addendum we briefly list some recent contributions.

Symposia which included extensive discussions of some aspects of condensed phase isotope effects were held at Cluj, Romania, in 1973 and Los Angeles, California, in 1974. Proceedings of both are in press.[694,695] A review article by Bigeleisen, Lee, and Mandel which includes some discussion of condensed phase effects has appeared in the *Annual Review of Physical Chemistry*.[696] In addition Staschewski[696a] has reviewed a good part of the literature on oxygen isotope effects, and the monograph on heavy water by Kazavchinskii, Kessel'man, Kirillin, Rivkin, Sheindlin, Shpil'rain, Sychev, and Timrot has been translated into English.[696b]

Eshelman, Torre, and Bigeleisen[697] have extended measurements of the $^{15}N/^{14}N$ fractionation factors for the NO molecule to 110–173°K and interpreted the data using a detailed theoretical analysis. Ustinov and Petropavlov[698] find the vapor pressure ratio ln $(P(^{12}CF_4)/P(^{13}CF_4)) = -0.0045$ at 90°K. The temperature dependence of the VPIE of acetone and acetone-d_6 was determined by Duer and Bertrand[699] using an isoteniscope. The published result shows the vaporization of acetone-d_6 (25°C) as 150 ± 90 more endothermic than acetone. The authors determined heats of solution of acetone/acetone-d_6 and chloroform/chloroform-*d* in various solvents. They conclude that hydrogen bonds involving $CDCl_3$ are about 20 cal/mol stronger than for $CHCl_3$. The same conclusion had earlier been reached from heats of mixing measurements.[700] Galimov and Ivlev[700a] have reported on carbon isotope effects in straight-chain alkanes.

Considerable work on isotope effects on the properties of the pure waters has been reported. Equilibrium D/H and $^{18}O/^{16}O$ fractionations between ice and water are given as 1.0206 + 0.0005 and 1.0028 ± 0.0001.[701] Some properties of supercooled D_2O have been investigated.[702-704] Deuterium isotope effects on surface tension,[705] vapor phase dipole moment,[706-708] dielectric constant,[709] self-diffusion,[710] viscosity,[711,712] and other structural parameters[713,714] have been studied. Viscosity and density effects have also been investigated for the oxygen isomers.[715,716] High-precision volumetric heat capacity measurements on $H_2{}^{18}O$ and $D_2{}^{18}O$ and their heats of mixing have been reported by Picker, Fortier, and Steckel.[717] The results are in good agreement with earlier reports by Steckel and coworkers.[718]

Work on investigations of the properties of solutions in D_2O[719-739] and $H_2{}^{18}O$[719,740,741] has been reported. Solubility studies continue[742-744] as do studies on salt hydrate systems.[740,745-750]

In other areas several reports on viral coefficient isotope effects (but with differing interpretation) have appeared.[275,751-753] The absorption of sound in liquid NH_3 and ND_3 has been studied.[754] Rock and coworkers have reported on the thermodynamics of lithium isotope exchange reactions,[755] and Boettcher and Drago[756] have reported on calorimetric experiments involving adducts of phenol and phenol-*d*. Finally, Kleinman and Wolfsberg[757] have made a careful analysis of the magnitude of corrections on the Born–Oppenheimer approximation and their effects on isotopic equilibria.

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