Isotope effects on vapor phase
2nd virial coefficients

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Abstract Vapor phase 2nd virial coefficient isotope effects (VCIE’s) are interpreted. A useful correlation is developed between \( \Delta(\mathcal{B} - \mathcal{B}_\text{bo})/\mathcal{B}_\text{bo} = -(\text{VCIE}) \) and the reference condensed phase reduced isotopic partition function ratio \([\ln(f_c/f_g)]^*\). \( \mathcal{B} \) is the second virial coefficient, \( \mathcal{B}_\text{bo} = 2\pi\sigma^3/3 \), \( \sigma \) is the Lennard-Jones size parameter, and \( \Delta \) is an isotopic difference, light-heavy. \([\ln(f_c/f_g)]^* \) can be obtained from vapor pressure isotope effects for \( T/T_{\text{CRITICAL}} < 0.7 \). Also \( -(\text{VCIE}) = \ln(f_p/f_g^2) \), where \( \ln(f_p/f_g^2) \) is the reduced isotopic partition function ratio describing the equilibrium between monomers and interacting pairs. At temperatures well removed from crossovers in \( \ln(f_p/f_g^2) \) or \([\ln(f_c/f_g)]^* \), \( \ln(f_p/f_g^2) = (0.4\pm0.2) \ [\ln(f_c/f_g)]^* \).

Key words isotope effects • Lennard-Jones potential • reduced partition function ratio • vapor phase • vapor pressure isotope effects • virial coefficients

Introduction

This paper reviews recent work on isotope effects (IE’s) on intermolecular interaction in the vapor including comparison with condensed phase IE’s [19]. It is well established that IE’s on condensed phase molar volume (MVIE), vapor pressure (VPIE), virial coefficients (VCIE), and molecular polarizability (PIE) share a common origin in the vibrational properties of the interacting molecules. Even so, the details of the connections between PIE, MVIE, VCIE and VPIE have been argued for years, sometimes contentiously [1, 3, 4, 5–7, 17, 18]. The confusion arose because it is convenient to express virial coefficients (and VCIE’s) in terms of the parameters of intermolecular potentials of the Lennard-Jones type and IE’s thereon (\( \varepsilon, \sigma, \Delta\varepsilon/\varepsilon \) and \( \Delta\sigma/\sigma \)) [4, 8], but in the description of MVIE and VPIE one introduces a formalism which uses a set of vibrational frequencies, frequency shifts, and isotope dependences [2, 10]. In the worst case this can result in interpretations which violate the Born-Oppenheimer (BO) approximation. That approximation, of course, has been axiomatic in the theory of equilibrium isotope chemistry [11, 12, 20]. In the present development we compare free energy differences between condensed phase molecules or gas phase dimers, on the one hand, and the dilute gas phase reference on the other. The resulting correlation supports the conclusion that the two effects share a common origin.
Background

The VPIE

Bigeleisen [2, 10] has shown the logarithmic isotopic vapor pressure ratio, \( \ln(P/P') \), is related to the reduced partition function ratio, condensed to gas, \( \ln(f_{g}/f'_{g}) \).

\[
\ln(f_{g}/f'_{g}) = \ln(P/P') - \Delta(PV')/(RT) + (2B_{o}P - 2B_{o}'P)
\]

\( P \) and \( P' \) are equilibrium vapor pressures, \( \Delta(PV') = (PV' - PV'') \), light-heavy. \( V' \) and \( V'' \) are condensed phase molar volumes, \( B_{o} \) and \( B_{o}' \) are virial coefficients. At low enough temperatures, say between \( T_{\text{TRIPLE}} \) and \( -0.7 T/T_{\text{CRITICAL}} \), the corrections (last two terms) are small, and VPIE \( \approx \ln(f_{g}/f'_{g}) \) is the size of functions. \( T \) is the kinetic energy operator and the \( \phi(r) \) correspond to \( \phi_{1}(r) \) or \( \phi_{2}(r) \) of Eq. (4). We are led again to Eq. (5) except that now \( \bar{K} \) is formulated quantum mechanically and is isotope dependent. In the model below, we consider \( K \) in the “harmonic approximation”, replacing it by a bound dimer (pair) harmonic-rigid-rotor partition function divided by the square of the monomer partition function, \( \ln(f_{g}/f'_{g}) \).

Since \( b_{o} = (2/3)\pi\sigma^{3} \) is isotope independent (\( \sigma \) is the size parameter), one focuses the discussion of VCEIE on \((2\pi-b_{o})\) which is directly related to the association equilibrium constant \( K \). \( \ln(K/K') = \ln(f_{g}/f'_{g}) \) in precise analogy to Eq. (5). We define VCEIE

\[
\ln (K/K') = -\ln(K/K') = \ln(f_{g}/f'_{g}) = (7)
\]  

\[
= -\ln[(2\pi-b_{o})]/(2\pi-b_{o})] = (-\text{VCIE}) = A_{p}/T^{2} + B_{p}/T
\]

The reason for the minus sign is that \( K \) involves the equilibrium (2 monomer = pair) but the vapor pressure equilibrium is (condensed phase monomer = vapor phase monomer). The sum in the expression for \( A_{p} \) for non-linear polyatomic molecules extends over twelve frequencies corresponding to the external degrees of freedom. In the monomers these are the rotations and translations of the two molecules, in the dimer they are the three rotations and three translations of the dimer molecule (null frequencies), plus six frequencies which correspond to one monomer-monomer stretch, and five other low lying frequencies (loose monomer-monomer bending modes or hindered internal rotations). The remaining internal frequencies of the \( n \)-atomic monomers map into internal frequencies of the dimer, slightly shifted from the monomer. These frequencies appear in the \( B_{p} \) term. The result is consistent with an earlier formalism [15].

The \( A \) contribution to \( \ln(f_{g}/f'_{g}) \) or \( \ln(f_{g}/f'_{g}) \) is necessarily positive and in the direction of a normal isotope effect (light > heavy). The \( B \) terms, on the other hand, involve the sum of dimer-monomer or condensed-vapor isotopic frequency differences, and can be either positive or negative. For monatomic species \( B_{o} = B_{p} = 0 \) (there are no internal modes). For molecules with structure the situation is more complicated. If the net shift in internal modes on condensation/dimerization is to the blue, the \( A \) and \( B \) terms are both positive and reinforce one another. The IE will be positive and large. More often, the net shift in isotope sensitive internal frequencies is to the red (the ordinary case for noncomplexed H/D substitution) and \( B \) is of opposite sign to \( A \). Over some range of temperature \( B/T \) may be, and often is, larger in magnitude than \( A/T^{2} \). In such cases the net isotope effect will be negative (inverse), it is a small difference between competing positive and negative terms with distinctly different temperature dependences. These matters have been thoroughly discussed so far as application to VPIE is concerned [2, 9, 10]. Similar considerations carry over to (VCIE). That is the point of concern of the present paper.

Comparing \( \ln(f_{g}/f'_{g}) \) and \( \ln(f_{g}/f'_{g}) \) the important features of the model are summarized in Figure 1. When a molecule is transferred from its ideal gas reference to dimer, or to the condensed phase, significant
changes occur in both internal and external degrees of freedom. We refer to a 3n dimensional potential energy surface, PES, which describes how the molecular potential energy depends on the distortion of various atoms or groups of atoms (internal modes), and on the position or orientation of the molecule itself (externals). Fig. 1 represents the shifts in intermolecular potential energy and in the internal vibrational potential energy of a single normal mode, as two or more molecules vary their distance of intermolecular separation $R_{\text{INTERMOL}} = R_{12}$. A similar diagram can be constructed for each of the 3n-6 internal degrees of vibrational freedom. The upper curve, $\alpha$, sketches the transfer between the dilute gas reference state (on the right at large $R_{12}$) and the complexed (dimerized) vapor molecule at the bottom of the upper well to the left. Similarly, the lower curve, $\beta$, shows transfer from dilute vapor to condensed phase. In the first case $u(R_{12})$ represents the pair potential energy; and in the second, it represents the projection on the $r$ axis of the intermolecular potential of a single molecule embedded in the field of (N-1) neighbors. That accounts for the significantly deeper and sharper well which describes condensation. During the change from dilute gas to condensed phase PES$_{\text{INTERMOL}}$ shifts to lower energy, and, of at least equal importance, the curvature in the intramolecular dimension is perturbed by virtue of the coupling between internal and external degrees of freedom.

Figure 1 illustrates the truism that the intermolecular interactions accounting for $\ln(f_f/f_g^r)$ (upper curve) and $\ln(f_f/f_g)^*$ (lower curve) differ not in kind, but in degree. One concludes that $[\ln(f_f/f_g^r)] = -(\text{VCIE})$ should be roughly proportional to $\ln(f_f/f_g)^*$, and the constant of proportionality should be less than unity (because of differences in the well depths and curvatures of the effective intermolecular potentials). The well depth for the gas-gas pair interaction is “available” from fits of $\Xi$ for the parent molecule, and that for the condensed phase can be obtained by combining measured energies of vaporization with the zero point energies of the condensed and ideal vapor phases. Typically for attractive forces limited to the van der Waals dispersion interaction, $\varepsilon_{\text{DIMER}}/\varepsilon_{\text{COND}} \approx 0.1$ [13]. In the condensed phase the average potential energy per molecule in a condensed system of N molecules becomes $u(R_{12}) = (s_n C_{12} R_{12}^{s_n} - s_n C_c/R_{12}^{s_n})/2$ where $s_n$ and $s_c$ are tabulated constants obtained from lattice or smeared lattice sums. With the (gas + gas = dimer) interaction as reference, the effect of condensation is to bring the molecules some 3 to 5% closer, and to increase the well depth by nearly an order of magnitude, at the same time increasing the curvature at the bottom of the intermolecular well (i.e. increasing force constants of the equivalent harmonic oscillators, $k_c > k_f$), and shifting the associated external frequencies commensurately, $(\nu_d^{2}/\nu_g^{2} - (1/2.7)^{1/2} - 0.6$, and $\nu_d^{2}/\nu_g^{2} = (k_c/k_f)(\mu_d/\mu_g) - 0.4$). In the condensed state the average potential energy is greater than the near pairs value, $(c/2)\varepsilon_{\text{DIMER}}$ by 40 to 60 per cent or more [13]. In addition, and importantly for present purposes, one expects the zero point energy shifts to scale similarly.

The discussion, strictly interpreted, refers to intermolecular modes only. With modest generalization we expect similar arguments to apply to intramolecular modes as well. Most commonly the internal and external contributions to $\ln(f_f/f_g^r)$ and $\ln(f_f/f_g)^*$ are of opposite sign and are usefully described using the A, B formalism. The ratio $[\ln(f_f/f_g)/\ln(f_f/f_g)^*] = \Delta \ln(\nu_f^{2}/\nu_g^{2})/\Delta \ln(\nu_f^{2}/\nu_g^{2}) = \nu_f^{2}/\nu_g^{2}$ is zero at the crossover temperature for (VCIE), $T_{\text{CROSSC}} = -A_c/B_c$, and is unbounded at the crossover temperature for $\ln(f_f/f_g)^*$. $T_{\text{CROSSC}} = -A_c/B_c$. By crossover is meant that temperature at which one or the other isotope effect, $\ln(f_f/f_g)$ or $\ln(f_f/f_g)^*$, goes through zero and changes sign. At temperatures near crossovers it is more useful to report ratios of A and B parameters separately, and not ratios of overall isotope effects.

**Comparisons of VCIE and VPIE data**

We have reviewed data for the 14 compounds (24 sets of isotopomer pairs) on which data for both VCIE and VPIE are available [19]. Another two pairs, H$_2$/D$_2$ and He$_3$/He$_4$, are light. Their quantum corrections are large and the thermodynamics complicated by nuclear spin effects. They are not considered in present context.

In the comparisons one notes in almost every case that $\ln(f_f/f_g)$ is of the same sign and smaller in magnitude, yet commensurate, with $\ln(f_f/f_g)^*$. VCIE’s are consistent with the correlation introduced above. VPIE and (-VCIE), $\ln(f_f/f_g)$ and $\ln(f_f/f_g)^*$, are subject to the same underlying principles. That is the point of concern of the present paper. In Table 1 we review (A, B) parameters of fit to Eq. (3) for averaged $\ln(f_f/f_g)^*/\Delta M$ and $\ln(f_f/f_g^r)/\Delta M$. In spite of large uncertainties, the averaged ratios, $<(A_f/A_c) = \lambda_{\text{VCIE}}/\lambda_{\text{VPIE}}>$ = 0.4±0.2 and $<(B_f/B_c) = B_{\text{VCIE}}/B_{\text{VPIE}}>$ = 0.4±0.1, are consistent with the expectations of the model. The large uncertainties are a consequence of experimental uncertainty in the VCIE data. Figure 2 shows another test of the correlation between
Table 1. A and B parameters for fits to (-VCIE) and VPIE for selected molecules (per ∆M unit).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>VPIE</th>
<th>(-VCIE)/VPIE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>36Ar/34Ar</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>CH3CD3</td>
<td>233</td>
<td>-2.34</td>
</tr>
<tr>
<td>CH3CD4</td>
<td>97</td>
<td>-0.91</td>
</tr>
<tr>
<td>CH3CD3</td>
<td>53</td>
<td>-0.74</td>
</tr>
<tr>
<td>C(CH3)2CD(CD3)4</td>
<td>10.2</td>
<td>-0.51</td>
</tr>
<tr>
<td>NH3/ND3</td>
<td>2630</td>
<td>-5.43</td>
</tr>
<tr>
<td>CH3NH2/CH3ND2</td>
<td>1960</td>
<td>-2.70</td>
</tr>
<tr>
<td>H2O/D2O</td>
<td>4277</td>
<td>-6.14</td>
</tr>
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</table>

Average 0.4±0.2 0.4±0.1

Fig. 2. The correlation of ln(f_c/f_g) = (-VCIE) with ln(f_c/f_g)*/ΔM at the temperatures of the VCIE measurements. The correlation line is: ln(f_c/f_g) = 0.49 ln(f_c/f_g)* + 1.2×10^{-2}, R^2 = 0.6. Open circles = argon, darkly shaded circles = CH3F/CD3F, small squares = methanes, lightly shaded triangles = ethanes, small diamonds = ethylenes, shaded hexagons = neopentanes, large inverted triangles = ammonia, large inverted crossed triangles = methyl amines (CD3), upright dotted triangles = methyl amines (ND3), upright open triangles = methyl amines (CD3ND3), crossed shaded circles = H2O/D2O.

Table 2. LJ calculations of (A_υ = A_(υVCIE))/ΔM and (A_υ = A_(υVPIE))/ΔM compared with experiment [19].

<table>
<thead>
<tr>
<th>System</th>
<th>(ε/κ)K</th>
<th>σ/A</th>
<th>ν_υ/cm⁻¹</th>
<th>ν_υ/cm⁻¹</th>
<th>A_υ/K²</th>
<th>A_υ/K²</th>
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</thead>
<tbody>
<tr>
<td>36Ar/34Ar</td>
<td>118</td>
<td>3.4</td>
<td>26</td>
<td>47</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>CH3CD3</td>
<td>148</td>
<td>3.82</td>
<td>44.72b</td>
<td>72.72b</td>
<td>288</td>
<td>238</td>
</tr>
<tr>
<td>CH3CD4</td>
<td>243</td>
<td>3.95</td>
<td>40</td>
<td>69</td>
<td>42</td>
<td>132</td>
</tr>
<tr>
<td>CH3NH2/CH3ND2</td>
<td>4277</td>
<td>-0.14</td>
<td>0.4±0.1</td>
<td>0.2±0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remarks:

a See Ref. [19] for discussion of uncertainties.
b Frequencies are listed in the order: LJ pair frequency, hindered rotation in pair (vapor phase); or lattice translation, lattice libration (condensed phase).

Conclusion

Isotope effects on the vapor phase second virial coefficient and on vapor pressure share a common origin. They are approximately proportional, ln(f_c/f_g)^* = (-VCIE) = (0.4±0.2)* ln(f_c/f_g), provided the comparisons are made not too close to either crossover temperature. Both depend on temperature in a complicated fashion, ln(δVCIE or VPIE) = A/T^2 + B/T. For many compounds, the A and B terms are of opposite sign but of commensurate magnitude, and in such cases lnR amounts to a small difference between much larger terms. This difficulty, compounded by experimental uncertainty in the VCIE data, accounts for most of the uncertainty in the correlations above.

We have carried out more detailed calculations for 36Ar/34Ar, the series of methane/deuteromethanes, and other molecules, developing a set of LJ force constants from the potential parameters, and demonstrating consistency between those parameters and VCIE, VPIE and independent spectroscopic observation (Table 2). Details may be found in the earlier report [19].

References

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