Isotope Effects on Vapor Pressure

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ABSTRACT. The isotope effect of pure liquid on vapor pressure is examined, and the vapor pressure ratios of two different isotopes are calculated. Based on the Significant Structure Theory of Liquids, the effect of molecular weight and the effect of moments of inertia are dominant in ordinary/trans-\(d_2\) ethylene isotopes; the effect of hindered rotational zero-point energy is dominant in trans-\(d_2\)/cis-\(d_2\) ethylene isotopes; and the effect of intermolecular potential difference is found in CH\(_4\)/CH\(_3\)OD isotopes. In the isotopes of CH\(_4\)/CD\(_4\), SiH\(_4\)/SiD\(_4\) and GeH\(_4\)/GeD\(_4\), the weight effect decrease in the order of CH\(_4\)/CD\(_4\)>SiH\(_4\)/SiD\(_4\)>GeH\(_4\)/GeD\(_4\).

1. INTRODUCTION

The isotope effect on vapor pressure is an old problem. Recently, Jansco and Van Hook\(^1\) have reviewed this topic. When an isotopic mixture of liquid (e.g. H\(_2\)O+D\(_2\)O) is in equilibrium with its vapor, the ratio of concentrations of two isotopes in liquid phase is not equal to the ratio of vapor phase. The separation factor (\(\alpha\)), which is defined as the equilibrium constant of isotopic exchange reaction, is equal to the vapor pressure ratio of pure isotopes.

Usually \(\alpha=1\), and this is called “Isotope Effect on Vapor Pressure (IEVP)”.

If \(\alpha>1\), the light isotope is more volatile, which is called “Normal Isotope Effect”.

If \(\alpha<1\), the heavy isotope is more volatile, which is called “Inverse Isotope Effect”.

There are four significant factors which govern the IEVP. First, molecular weight: The translational motion of gas-like molecules is not same as that of solid-like molecules in the liquid. The latter is rather lattice motion. Since these motions are function of molecular weight, the change of molecular weight by isotopic substitution results the vapor pressure change. Second, moments of inertia: The
rotational motion of gas-like molecules in the liquid is not same as that of solid-like molecules. The latter is generally torsional lattice motion. Since the rotation and torsion are function of moments of inertia, the change of moments of inertia by isotopic substitution gives the IEVP. Third, zero-point energy: The zero-point energy of lattice vibration is related to the vapor pressure. The change of zero-point energy of lattice motion by isotopic substitution gives the IEVP. Fourth, intermolecular potential: The intermolecular interaction of liquid molecules may be altered by isotopic substitution, and result the IEVP.

Various effects described above occur simultaneously, and it is a problem of statistical thermodynamics to analyze the IEVP in terms of the above four effects. The problem can be solved by utilizing the partition function of the "significant structure theory of liquids".

2. THEORY

According to the significant structure theory of liquids, the partition function of polyatomic molecule is generally written as

\[
f = \left( \frac{e^{E_f /RT} - e^{-E_f /RT}}{(1 - e^{-E_f /RT})^N} \right)^N \]

\[
= \frac{a (2\pi m kT)^{3/2}}{\hbar^3} e^{V_f /kT} \frac{e^{-V_f /kT}}{N! f_{\text{int}}} \frac{\nu_V \nu_e}{\nu_{f_{\text{int}}}} f_{\text{int}}^N
\]  

(1)

where \( V \) and \( V_f \) are molar volume of the liquid and solid respectively; \( N \) is Avogadro's number; \( \theta \) is Einstein characteristic temperature; \( E_f \) is the sublimation energy at 0 K; \( f_{\text{deg}} \) is the partition function of positional degeneracy; \( f_{\text{IR}} \) and \( f_{\text{rot}} \) are the hindered rotational partition function of solid-like molecules and the rotation of gas-like molecules respectively; \( f_{\text{int}} \) is the partition function of internal vibration.

Utilizing the relation, \( A = -kT \ln f, \ G = A + PV \), and the condition that the liquid is in equilibrium with its vapor, the following expression of vapor pressure is obtained assuming the ideality of the gas phase.

\[
\ln P = \frac{V_f}{V} \left[ -\frac{E_f}{RT} + 3 \ln(1 - e^{-E_f /RT}) \right]
\]

\[
\ln f_{\text{deg}} - \ln f_{\text{IR}} + \ln \left( \frac{2\pi m kT}{\hbar^3} \right) \frac{3}{2} \]

\[
+ \ln f_{\text{rot}} + \ln \left( \frac{N_f}{e^f} \right) - \frac{V_f}{V} - \ln V
\]

\[
+ \frac{PV}{RT} + \ln RT - 1
\]

(2)

Neglecting the minor terms, the expression of vapor pressure ratio of the two isotopes is obtained

\[
\ln \frac{P'}{P} = \frac{V_f}{V} \left[ -\frac{E'_f - E_f}{RT} \right]
\]

\[
+ 3 \left\{ \frac{1}{2} \ln \frac{m'}{m} - \ln \frac{1 - e^{-E'_f /RT}}{1 - e^{-E_f /RT}} \right\}
\]

\[
+ \left\{ \frac{1}{2} \ln \frac{A'B'C'}{ABC} - \ln \frac{f_{\text{int}'}}{f_{\text{int}}} \right\}
\]

(3)

The prime represents the light isotopes, \( A, B \) and \( C \) are the principle moments of inertia of a molecule, \( m \) is the molecular weight. To obtain the equation (3), the following approximations are used

\[
\frac{V_f}{V} \approx \frac{V_f'}{V'}
\]

(4)

\[
\ln f_{\text{deg}} = \ln f_{\text{deg}'}
\]

(5)

In equation (3), the term of \( 3 \left\{ \frac{1}{2} \ln \frac{m'}{m} - \ln \frac{1 - e^{-E'_f /RT}}{1 - e^{-E_f /RT}} \right\} \) means the effect of molecular weight, and the term of \( \frac{1}{2} \ln \frac{A'B'C'}{ABC} - \ln \frac{f_{\text{int}'}}{f_{\text{int}}} \) means the effect of moments of inertia. The term of \( -\frac{E'_f - E_f}{kT} \) means both the zero-point energy effect and the effect of intermolecular potential, since \( E_i \) is defined as the depth of the lowest energy state of lattice mode. It is evident that the effects of molecular weight and moments of inertia contribute to the inverse IEVP, and the effect of the sublimation energy (EVP) contributes to the normal IEVP.

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3. APPLICATION

3.1. Ethylene, Ethylene-\(d_2\) (trans), Ethylene-\(d_2\) (cis). The measurements of vapor pressure ratios of the isotopic isomers, cis-\(d_2\) and trans-\(d_2\) ethylenes, have been reported by Biegeleisen and coworkers. According to them, the trans-dideuterated isomer is more volatile than the cis-dideuterated isomer. Since the molecular weight of the two isomeric isotopes are same, there is no effect of the molecular weight; but the moments of inertia of the two are not same. Generally, the molecules in liquid do not rotate freely. When the molecules rotate freely in the liquid state, the moments of inertia do not effect the IEVP.

The hindered rotational degree of freedom of molecules are discussed in Appendix. In Table 1, the moments of inertia, the torsional frequencies and the zero-point energy of hindered rotation for ordinary, trans-\(d_2\) and cis-\(d_2\) ethylenes are given. The potential barrier of hindered rotation is taken as 500 cal.

In the trans-cis isomeric system, the trans-\(d_2\) ethylene has higher zero-point energy than the cis-\(d_2\) ethylene. This is the reason that the trans-\(d_2\) ethylene is more volatile than the cis-\(d_2\) ethylene. The vapor pressure ratio equation for this system is

\[
\ln \frac{P_d}{P_c} = \frac{V}{V} \left[ -\frac{E_d - E_c}{RT} \right] \\
+ \frac{1}{\gamma} \ln \left( \frac{P_d}{P_c} \right)_{\text{th}} - \frac{1}{\gamma} \ln \left( \frac{P_d}{P_c} \right)_{\text{cal}}
\]

(6)

Table 1. The moments of inertia, frequencies of torsional vibration and the hindered rotational zeropoint energy of ordinary, trans-\(d_2\), and cis-\(d_2\) ethylene.

<table>
<thead>
<tr>
<th></th>
<th>Ordinary</th>
<th>trans-(d_2)</th>
<th>cis-(d_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A \times 10^9) (gcm(^2))*</td>
<td>5.75</td>
<td>8.06</td>
<td>8.45</td>
</tr>
<tr>
<td>(B \times 10^9) (gcm(^2))*</td>
<td>28.09</td>
<td>33.70</td>
<td>33.09</td>
</tr>
<tr>
<td>(C \times 10^9) (gcm(^2))*</td>
<td>33.75</td>
<td>41.72</td>
<td>41.48</td>
</tr>
<tr>
<td>(\theta_a) (°K)</td>
<td>83.88</td>
<td>70.91</td>
<td>69.26</td>
</tr>
<tr>
<td>(\theta_b) (°K)</td>
<td>38.65</td>
<td>34.68</td>
<td>35.00</td>
</tr>
<tr>
<td>(\theta_c) (°K)</td>
<td>34.65</td>
<td>31.17</td>
<td>31.26</td>
</tr>
<tr>
<td>(E_{z} = \frac{1}{2} R (\theta_a + \theta_b + \theta_c)) (cal/mole)</td>
<td>155.6</td>
<td>135.9</td>
<td>134.7</td>
</tr>
</tbody>
</table>

*The moments of inertia of ethylene are from ref. 4.

The following parametric values to calculate the vapor pressure ratios are used: \(E_0 = 500\) cal/mole, \(V_V = 40\) cc/mole, \(\alpha = 0.0271\) and \(n = 24.16\):

- \(E_\theta = 4241.8\) cal/mole and \(\theta = 131.68°K\) for ordinary,
- \(E_\theta = 4272.6\) cal/mole and \(\theta = 129.7°K\) for trans-\(d_2\),
- \(E_\theta = 4273.8\) cal/mole and \(\theta = 129.7°K\) for cis-\(d_2\) respectively. The difference of \(E_\theta\), \(E_{z} = E_{\theta} - E_{\phi}\), is taken as being equal to the difference of the zero-point energy. The results of calculation are shown in Table 2, and Fig. 1.
In the system of ordinary and trans-\(d_2\) ethylene, both the mass effect and the moments of inertia effect appear. The \(E_t\) difference should be considered as \(\Delta E_{t,p} (\text{lat}) + \Delta E_{t,p} (\text{rot})\), where \(\Delta E_{t,p} (\text{lat})\) is the zero-point energy difference of lattice vibration and \(\Delta E_{t,p} (\text{rot})\) is that of hindered rotation. The vapor pressure ratio equation for this system is as follows.

\[
\ln \frac{P_{\text{ord}}}{P_{\text{rot}}} = \frac{V_f}{V} \left[ -\frac{E_{\text{ord}}^\prime - E_{\text{rot}}^\prime}{RT} + 3 \frac{11}{2} \ln \frac{m_{\text{ord}}}{m_{\text{rot}}} - \ln \frac{1}{1 - e^{-\text{rot}/T}} \right] + \frac{1}{2} \ln \left( \frac{(ABC)^{\text{ord}}}{(ABC)^{\text{rot}}} \right) - \ln \frac{f_{\text{ord}}^{\text{rot}}}{f_{\text{rot}}^{\text{rot}}} \tag{7}
\]

The parametric values of ordinary ethylene have been obtained using the routine technique, and the potential barrier of hindered rotation is fixed using the data of molar entropy. \(\theta^{\prime}\) is obtained according to the equation \(\theta^{\prime} = \sqrt{\frac{m_{\text{ord}}}{m_{\text{rot}}}}\), and \(E_{t}^{\prime}\) is obtained by using the formula \(E_{t}^{\prime} = E_{\text{ord}}^{\prime} + \Delta E_{t,p} (\text{lat}) + \Delta E_{t,p} (\text{rot})\).

In the ordinary-trans system, the ratio of the moments of inertia is much larger than that of the trans-cis isomeric system.

\[
\frac{1}{2} \ln \left( \frac{(ABC)^{\text{ord}}}{(ABC)^{\text{rot}}} \right) = -0.367, \quad \frac{1}{2} \ln \left( \frac{(ABC)^{\prime}}{(ABC)^{\prime\prime}} \right) = -0.612
\]

The difference of molecular weight and moments of inertia are

\[
\frac{3}{2} \ln \frac{m_{\text{ord}}}{m_{\text{rot}}} = -0.104
\]

According to the experimental measurement of vapor pressure, the trans-\(d_2\) ethylene is more volatile than the ordinary ethylene. The inverse isotopic effect of this system is due to the fact that the effect of moments of inertia and molecular weight are dominant in comparison with the effect of zero-point energy. In other words, the zero-point energy effect cannot overcome the effect of moments of inertia and molecular weight. Hence, the inverse isotope effect of this system results. The results of calculation are given in Table 3 and Fig. 2.

**Table 3.** Vapor pressure ratios of ordinary and trans-\(d_2\) ethylene and molar volume of ordinary ethylene.

<table>
<thead>
<tr>
<th>(T) (°K)</th>
<th>(V) (cc/mole)</th>
<th>(10^3 \times \ln \frac{P_{\text{ord}}}{P_{\text{rot}}}) (calc.)</th>
<th>(10^3 \times \ln \frac{P_{\text{ord}}}{P_{\text{rot}}}) (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>116.79</td>
<td>43.88</td>
<td>-6.93</td>
<td>-6.25</td>
</tr>
<tr>
<td>127.61</td>
<td>44.68</td>
<td>-9.97</td>
<td>-9.83</td>
</tr>
<tr>
<td>136.86</td>
<td>45.91</td>
<td>-11.55</td>
<td>-11.78</td>
</tr>
<tr>
<td>155.26</td>
<td>46.89</td>
<td>-13.27</td>
<td>-14.51</td>
</tr>
<tr>
<td>165.84</td>
<td>47.88</td>
<td>-14.41</td>
<td>-15.36</td>
</tr>
<tr>
<td>173.42</td>
<td>48.67</td>
<td>-15.10</td>
<td>-15.78</td>
</tr>
</tbody>
</table>

**Fig. 2.** Vapor pressure ratio of ordinary, and trans-\(d_2\) ethylene (−: calc; ○: obs).
not so large in the CH$_3$OH/CH$_3$OD isotopic substitution, but one sees large normal IEVP. This is due to the difference of intermolecular potential of the two isotopes.

The equation of vapor pressure ratio is

\[
\ln \frac{P^H}{P^D} = \frac{V_s}{V} \left( -\frac{E^H - E^D}{RT} \right) \\
+ 3 \left\{ \frac{1}{2} \ln \frac{m^H}{m^D} \frac{m^D}{m^H} - \ln \frac{1 - e^{-\theta V_s/T}}{1 - e^{-\theta V_s/T}} \right\} \\
+ \frac{1}{2} \ln \left( \frac{(ABC)^H}{(ABC)^D} \right) - \ln \left( \frac{m_H^{10}}{m_H^{10}} \right)
\]  

(8)

The superscripts H and D means CH$_3$OH and CH$_3$OD respectively.

In this system, the $E_i$ difference is 103.2 cal/mole, and the difference of the zero-point energy is $\Delta E_{zp}$ (lat) $+ \Delta E_{zp}$ (rot) = 21.5 cal. Accordingly the difference of intermolecular potential minimum is 103.2 - 21.5 = 81.7 cal/mole. In 1961, Walley and Palk have examined the difference of intermolecular potential of CH$_3$OH and CH$_3$OD using the thermal and spectroscopic data. They have reported the value of potential difference as $110 \pm 62$ cal/mole. This value is consistent with the value 81.7 cal/mole which is obtained from the calculation of vapor pressure ratio.

The calculated results are given in Table 4 and Fig. 3, and the following input data are used: $B_0 = 3.000$ cal/mole, $V_s = 34.30$ cc/mole, $a = 0.464 \times 10^{-3}$; for CH$_3$OH, $A = 6.579 \times 10^{-60}$ gcm$^2$, $B = 34.01 \times 10^{-60}$ gcm$^2$, $C = 35.30 \times 10^{-60}$ gcm$^2$, $E_i = 10338.8$ cal/mole and $\theta = 204.23$ K; for CH$_3$OD, $A = 7.67 \times 10^{-60}$ gcm$^2$, $B = 35.76 \times 10^{-60}$ gcm$^2$, $C = 43.55 \times 10^{-60}$ gcm$^2$, $E_i = 10442.0$ cal/mole, and $\theta = 201.10$ K. (The moments of inertia are from reference 9).

3.3 Methane(CH$_4$/CD$_4$), Silane(SiH$_4$/SiD$_4$), Germane(GeH$_4$/GeD$_4$). The molecules of methane, silane and germane are assumed to rotate freely in the liquid phase. The equation of vapor pressure ratio becomes

\[
\ln \frac{P^H}{P^D} = \frac{V_s}{V} \left( -\frac{E^H - E^D}{RT} \right) \\
+ 3 \left\{ \frac{1}{2} \ln \frac{m^H}{m^D} \frac{m^D}{m^H} - \ln \frac{1 - e^{-\theta V_s/T}}{1 - e^{-\theta V_s/T}} \right\} \\
+ \frac{1}{2} \ln \left( \frac{(ABC)^H}{(ABC)^D} \right) - \ln \left( \frac{m_H^{10}}{m_H^{10}} \right)
\]  

(9)

The inverse IEVP of these systems are due to the effect of molecular weight. The magnitudes of the ratio of the ratio of the molecular weight $\frac{3}{2} \ln \frac{m^H}{m^D}$ are as follows: $-0.336$ for CH$_4$/CD$_4$, $-0.177$ for SiH$_4$/SiD$_4$ and $-0.077$ for GeH$_4$/GeD$_4$.

The effect of molecular weight decreases according to the order of CH$_4$/CD$_4$ $>$ SiH$_4$/SiD$_4$ $>$ GeH$_4$/GeD$_4$.

But the term $\frac{E^H - E^D}{RT}$ gives the normal IEVP. These two effects are in opposite direction, which result the inverse IEVP of CH$_4$/CD$_4$, the normal IEVP of GeH$_4$/GeD$_4$ and the

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Table 4. Vapor pressure ratios of CH$_3$OH, CH$_3$OD and molar volume of CH$_3$OH.

<table>
<thead>
<tr>
<th>($T$) °K</th>
<th>$V$ (cc/mole)</th>
<th>$\ln \frac{P^H}{P^D}$ (calc.)</th>
<th>$\ln \frac{P^H}{P^D}$ (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>274.899</td>
<td>37.54</td>
<td>.140</td>
<td>.136</td>
</tr>
<tr>
<td>282.069</td>
<td>37.75</td>
<td>.136</td>
<td>.133</td>
</tr>
<tr>
<td>281.702</td>
<td>38.04</td>
<td>.130</td>
<td>.128</td>
</tr>
<tr>
<td>302.663</td>
<td>38.39</td>
<td>.124</td>
<td>.124</td>
</tr>
<tr>
<td>313.185</td>
<td>38.75</td>
<td>.119</td>
<td>.120</td>
</tr>
<tr>
<td>320.591</td>
<td>39.01</td>
<td>.116</td>
<td>.117</td>
</tr>
<tr>
<td>330.891</td>
<td>39.40</td>
<td>.111</td>
<td>.114</td>
</tr>
</tbody>
</table>

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Fig. 3. Vapor pressure ratio of CH$_3$OH/CH$_3$OD ($-\cdot$ calc; $\bigcirc$ obs).
Table 5. Parameters of CH₄/CD₄, SiH₄/SiD₄ and GeH₄/GeD₄.

<table>
<thead>
<tr>
<th></th>
<th>Eₜ (cal/mole)</th>
<th>θ (°K)</th>
<th>V (cc/mole)</th>
<th>n</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄*</td>
<td>2200.7</td>
<td>71.34</td>
<td>31.06</td>
<td>11.65</td>
<td>3.64×10⁻³</td>
</tr>
<tr>
<td>SiH₄</td>
<td>3374.5</td>
<td>63.54</td>
<td>46.80</td>
<td>13.85</td>
<td>4.52×10⁻⁵</td>
</tr>
<tr>
<td>GeH₄</td>
<td>4239.5</td>
<td>60.22</td>
<td>47.00</td>
<td>15.21</td>
<td>2.58×10⁻³</td>
</tr>
<tr>
<td>CD₄</td>
<td>2220.3</td>
<td>65.81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiD₄</td>
<td>3359.0</td>
<td>61.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeD₄</td>
<td>4263.0</td>
<td>60.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Parameters of CH₄ are from ref. 5.

Table 6. Vapor pressure ratios of CH₄/CD₄ and molar volume of CH₄.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>V (cc/mole)</th>
<th>ln P⁹⁴/₉⁵ (cal.)</th>
<th>ln P⁹⁴/₉⁵ (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.65</td>
<td>33.63</td>
<td>-.0139</td>
<td>-.0135</td>
</tr>
<tr>
<td>95.00</td>
<td>34.17</td>
<td>-.0174</td>
<td>-.0177</td>
</tr>
<tr>
<td>99.67</td>
<td>34.71</td>
<td>-.0207</td>
<td>-.0213</td>
</tr>
<tr>
<td>102.90</td>
<td>35.32</td>
<td>-.0238</td>
<td>-.0245</td>
</tr>
<tr>
<td>111.67</td>
<td>36.11</td>
<td>-.0272</td>
<td>-.0276</td>
</tr>
</tbody>
</table>

Table 7. Vapor pressure ratios of SiH₄/SiD₄ and molar volume of SiH₄.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>V (cc/mole)</th>
<th>ln P⁹⁴/₉⁵ (cal.)</th>
<th>ln P⁹⁴/₉⁵ (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>103.2</td>
<td>48.21</td>
<td>.021</td>
<td>.041</td>
</tr>
<tr>
<td>113.2</td>
<td>49.98</td>
<td>.012</td>
<td>.028</td>
</tr>
<tr>
<td>123.2</td>
<td>49.82</td>
<td>.006</td>
<td>.001</td>
</tr>
<tr>
<td>133.2</td>
<td>50.75</td>
<td>-.001</td>
<td>-.002</td>
</tr>
<tr>
<td>143.2</td>
<td>51.79</td>
<td>-.005</td>
<td>-.010</td>
</tr>
<tr>
<td>153.2</td>
<td>52.93</td>
<td>-.009</td>
<td>-.011</td>
</tr>
</tbody>
</table>

Table 8. Vapor pressure ratios of GeH₄/GeD₄ and molar volume of GeH₄.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>V (cc/mole)</th>
<th>ln P⁹⁴/₉⁵ (cal.)</th>
<th>ln P⁹⁴/₉⁵ (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>50.18</td>
<td>.021</td>
<td>.027</td>
</tr>
<tr>
<td>140</td>
<td>51.25</td>
<td>.015</td>
<td>.021</td>
</tr>
<tr>
<td>150</td>
<td>52.19</td>
<td>.010</td>
<td>.013</td>
</tr>
<tr>
<td>160</td>
<td>53.17</td>
<td>.005</td>
<td>.002</td>
</tr>
<tr>
<td>170</td>
<td>54.21</td>
<td>.001</td>
<td>-.011</td>
</tr>
<tr>
<td>180</td>
<td>55.35</td>
<td>-.002</td>
<td>-.028</td>
</tr>
</tbody>
</table>

crossover phenomenon of SiH₄/SiD₄. The calculated results and parameters are given in Table 5~8, and Fig. 4.

4. Discussion

The effect of molecular weight and moments of inertia contributes to the inverse IEVP, but the effect of lattice vibrational and hindered rotational zero-point energy contribute to the normal IEVP. In the C₂H₄/C₂H₂D₂ (trans) isotopes, the effect of molecular weight and moments of inertia is more dominant. But in the C₂H₂D₂ (trans)/C₂H₄D₂ (cis) isotopic isomers, there is no effects of molecular weight, the effect of hindered rotational zero-point energy is significant.

In the CH₃OH/CH₃OD isotopes, the large normal IEVP is due to the intermolecular potential difference of the two species, the deuterium bond is stronger than the hydrogen bond by 81.7 cal/mole.

For the molecules rotating freely in the liquid state, there is no effect of moments of inertia but the weight effect contribute to IEVP. In the isotopes of CH₄/CD₄, SiH₄/SiD₄, and GeH₄/GeD₄, the weight ratio of the two species decreases according to the order of CH₄/CD₄ > SiH₄/SiD₄ > GeH₄/GeD₄. This may be the reason why the volatility of the heavy isotopes decrease in the order of CH₄/CD₄ > SiH₄/SiD₄ > GeH₄/
Fig. 4. Vapor pressure ratio of CH₄/CD₄, SiH₄/SiD₄, and GeH₄/GeD₄ (—: calc; ○: obs).

**APPENDIX**

McLaughlin and Eyring\(^1\) suggested the approximate hindered rotational partition function, \(f_{HR}\), as

\[
f_{HR} = f_{rot} + e^{-E/RT} (f_{rot} - f_{vib}) \tag{A1}
\]

where \(f_{rot}\) and \(f_{vib}\) are the free rotational and the vibrational partition function, \(B_0\) is the barrier height of the hindered rotation.

The potential energy which restricts the rotation may be approximated as a cosine function\(^1\),

\[
V = \frac{B_0}{2} (1 - \cos m\phi) \tag{A2}
\]

where \(m\) is the symmetry number and \(\phi\) is the angle of rotation. The frequency of vibration is

\[
\nu = \frac{m}{2\pi} \sqrt{\frac{B_0}{2I}}
\]

where \(I\) is moments of inertia, and the partition function of vibration is

\[
f_{vib} = \frac{1}{1 - e^{-\nu RT}} \tag{A4}
\]

The partition function of one-dimensional rotation is

\[
f_R = \frac{2\pi \sqrt{2\pi mI}}{m \hbar} = \frac{0.27931}{m} \sqrt{RT \times 10^{20}} \tag{A5}
\]

For the non-linear three-dimensional rotator, there are three rotational axes. The partition function of three-dimensional hindered rotation is expressed as

\[
f_{HR}^A = f_{HR}^B f_{HR}^C \tag{A6}
\]

where the superscripts \(A, B\) and \(C\) mean the three rotational axes.

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**REFERENCES**