Advanced Physical Chemistry II
HW

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December 25, 2019

18 Partition Functions and Ideal Gases

5,8,13,16,20,24,29,32,38

18-5

$$f_2 = \frac{2\,\mathrm{e}^{-\beta E_2}}{2 + 2\,\mathrm{e}^{-\beta E_2} + 4\,\mathrm{e}^{-\beta E_3} + 2\,\mathrm{e}^{-\beta E_4}} \tag{18.1}$$

where

$$E_2 = 14\,903.66\,\mathrm{cm}^{-1} \tag{18.2}$$
$$E_3 = 14\,904.00\,\mathrm{cm}^{-1} \tag{18.3}$$
$$E_4 = 27\,206.12\,\mathrm{cm}^{-1} \tag{18.4}$$
$$\beta = \frac{1}{0.6950\,\mathrm{cm}^{-1}\cdot\mathrm{K}^{-1} \times T} \tag{18.5}$$

thus

$$f_2(300K) = 9.05 \times 10^{-32} \tag{18.6}$$
$$f_2(1000K) = 4.86 \times 10^{-10} \tag{18.7}$$
$$f_2(2000K) = 2.20 \times 10^{-5} \tag{18.8}$$

18-8

$$\Theta_{vib}(\mathrm{H_2}) = \frac{hc\tilde{\nu}_{\mathrm{H_2}}}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J}\cdot\mathrm{s}\cdot 2.998 \times 10^{10}\,\mathrm{cm}\cdot\mathrm{s}^{-1}\cdot 4401\,\mathrm{cm}^{-1}}{1.381 \times 10^{-23}\,\mathrm{J}\cdot\mathrm{K}^{-1}} = 6330\,\mathrm{K} \tag{18.9}$$
$$\Theta_{vib}(\mathrm{D_2}) = \frac{hc\tilde{\nu}_{\mathrm{D_2}}}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J}\cdot\mathrm{s}\cdot 2.998 \times 10^{10}\,\mathrm{cm}\cdot\mathrm{s}^{-1}\cdot 3112\,\mathrm{cm}^{-1}}{1.381 \times 10^{-23}\,\mathrm{J}\cdot\mathrm{K}^{-1}} = 4476\,\mathrm{K} \tag{18.10}$$

18-13 Since

$$\varepsilon_J = \frac{\hbar^2 J(J+1)}{2I} = k_\mathrm{B}T \tag{18.11}$$

thus

$$J(J+1) = \frac{2Ik_\mathrm{B}T}{\hbar^2} = \frac{T}{\Theta_{rot}} \tag{18.12}$$

For N_2(g) at 300 K,

$$J(J+1) = \frac{300}{2.88} = 104.167 \tag{18.13}$$

thus

$$J = 9.72 \approx 10 \tag{18.14}$$

18-16

$$\sum_{v=0}^{\infty} \mathrm{e}^{-\beta(v+1/2)h\nu} = \mathrm{e}^{-\Theta_{vib}(v+1/2)/T} = \mathrm{e}^{-\Theta_{vib}/2T} \sum_{v=0}^{\infty} \mathrm{e}^{-\Theta_{vib}v/T} \tag{18.15}$$

Let

$$f(v) = \mathrm{e}^{-\Theta_{vib}v/T} \tag{18.16}$$

we have

$$\begin{aligned} f'(v) &= -\frac{\Theta_{vib}}{T}\,\mathrm{e}^{-\Theta_{vib}v/T} \\ f'''(v) &= -\left(\frac{\Theta_{vib}}{T}\right)^3 \mathrm{e}^{-\Theta_{vib}v/T} \end{aligned} \tag{18.17}$$

thus

$$\begin{aligned} \sum_{v=0}^{\infty} \mathrm{e}^{-\beta(v+1/2)h\nu} &= \mathrm{e}^{-\Theta_{vib}/2T}\left[\int_0^{\infty} \mathrm{e}^{-\Theta_{vib}v/T}\,\mathrm{d}v + \frac{1}{2}(1-0) - \frac{1}{12}\left(-\frac{\Theta_{vib}}{T} - 0\right) + \frac{1}{720}\left(\left(-\frac{\Theta_{vib}}{T}\right)^3 - 0\right) + \mathcal{O}(T^{-3})\right] \\ &= \mathrm{e}^{-\Theta_{vib}/2T}\left[\frac{T}{\Theta_{vib}} + \frac{1}{2} + \frac{1}{12}\frac{\Theta_{vib}}{T} + \mathcal{O}(T^{-3})\right] \end{aligned} \tag{18.18}$$

For O_2, $\Theta_{vib} = 2256\,\mathrm{K}$, thus

$$q_{vib} = \mathrm{e}^{-2256/600}\left(\frac{300}{2256} + \frac{1}{2} + \frac{1}{12}\frac{2256}{300}\right) = 0.0293 \tag{18.19}$$

while

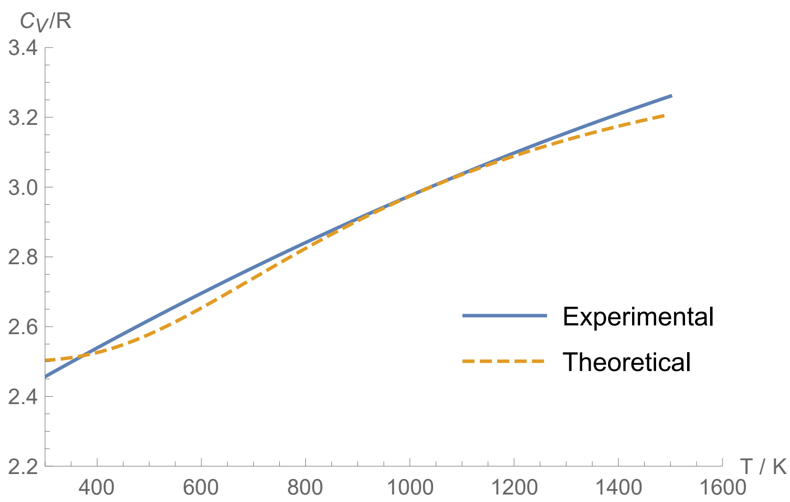
$$q_{vib}(\text{exact}) = \frac{\mathrm{e}^{-2256/600}}{1 - \mathrm{e}^{-2256/300}} = 0.0233 \tag{18.20}$$

thus the error is about 26%.

18-20 Eq. 18.41 gives

$$\frac{\bar{C}_V}{R} = \frac{5}{2} + \frac{\Theta_{vib}^2}{T^2}\frac{\mathrm{e}^{-\Theta_{vib}/T}}{(1-\mathrm{e}^{-\Theta_{vib}/T})^2} \tag{18.21}$$

where $\Theta_{vib} = 3103\,\mathrm{K}$ for CO(g).
thus the theoretical and experimental curve are as follows



18-24

$$\Theta_{rot} = \frac{\hbar^2}{2Ik_\mathrm{B}} = \frac{(1.045 \times 10^{-34}\,\mathrm{J \cdot s})^2}{2 \times 18.816 \times 10^{-47}\,\mathrm{kg \cdot m^2} \times 1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 2.10\,\mathrm{K} \tag{18.22}$$

$$\Theta_{vib,1} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 2096.7\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 3016\,\mathrm{K} \tag{18.23}$$

$$\Theta_{vib,2} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 713.46\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 1026\,\mathrm{K} \tag{18.24}$$

$$\Theta_{vib,3} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 3311.47\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 4763\,\mathrm{K} \tag{18.25}$$

Since HCN is linear

$$\begin{aligned}\frac{\bar{C}_V(3000\,\mathrm{K})}{R} &= \frac{5}{2} + \sum_j g_j \frac{\Theta_{vib}^2}{T^2} \frac{\mathrm{e}^{-\Theta_{vib}/T}}{(1-\mathrm{e}^{-\Theta_{vib}/T})^2} \\ &= \frac{5}{2} + \left(\frac{3016}{3000}\right)^2 \frac{\mathrm{e}^{-3016/3000}}{(1-\mathrm{e}^{-3016/3000})^2} + 2\left(\frac{1026}{3000}\right)^2 \frac{\mathrm{e}^{-1026/3000}}{(1-\mathrm{e}^{-1026/3000})^2} + \left(\frac{4763}{3000}\right)^2 \frac{\mathrm{e}^{-4763/3000}}{(1-\mathrm{e}^{-4763/3000})^2} \\ &= 6.214 \end{aligned} \tag{18.26}$$

thus

$$\bar{C}_V(3000\,\mathrm{K}) = 6.214R \tag{18.27}$$

18-29

$$\Theta_{vib,1} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 1319.7\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 1898\,\mathrm{K} \tag{18.28}$$

$$\Theta_{vib,2} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 749.8\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 1078\,\mathrm{K} \tag{18.29}$$

$$\Theta_{vib,3} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 1617.75\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 2327\,\mathrm{K} \tag{18.30}$$

$$\Theta_{rot,A} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 8.0012\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 11.51\,\mathrm{K} \tag{18.31}$$

$$\Theta_{rot,B} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 0.433\,04\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 0.623\,\mathrm{K} \tag{18.32}$$

$$\Theta_{rot,C} = \frac{hc\tilde{\nu}_1}{k_\mathrm{B}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s} \times 2.998 \times 10^{10}\,\mathrm{cm \cdot s^{-1}} \times 0.410\,40\,\mathrm{cm^{-1}}}{1.381 \times 10^{-23}\,\mathrm{J \cdot K^{-1}}} = 0.590\,\mathrm{K} \tag{18.33}$$

$$\begin{aligned}\frac{\bar{C}_V(1000\,\mathrm{K})}{R} &= 3 + \sum_j g_j \frac{\Theta_{vib}^2}{T^2} \frac{\mathrm{e}^{-\Theta_{vib}/T}}{(1-\mathrm{e}^{-\Theta_{vib}/T})^2} \\ &= 3 + \left(\frac{1898}{1000}\right)^2 \frac{\mathrm{e}^{-1898/1000}}{(1-\mathrm{e}^{-1898/1000})^2} + \left(\frac{1078}{1000}\right)^2 \frac{\mathrm{e}^{-1078/1000}}{(1-\mathrm{e}^{-1078/1000})^2} + \left(\frac{2327}{1000}\right)^2 \frac{\mathrm{e}^{-2327/1000}}{(1-\mathrm{e}^{-2327/1000})^2} \\ &= 3 + 0.747 + 0.908 + 0.649 \\ &= 5.30 \end{aligned} \tag{18.34}$$

thus

$$\bar{C}_V(1000\,\mathrm{K}) = 5.30R \tag{18.35}$$

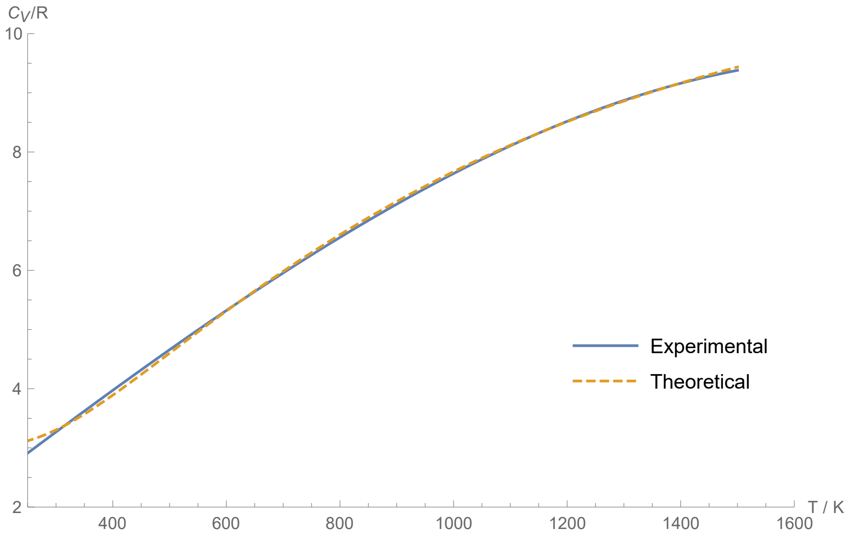
18-32 The theoretical heat capacity is

$$\frac{\bar{C}_V}{R} = 3 + \sum_{j}^{9} \frac{\Theta_{vib,j}^2}{T^2} \frac{\mathrm{e}^{-\Theta_{vib,j}/T}}{(1-\mathrm{e}^{-\Theta_{vib,j}/T})^2} \tag{18.36}$$

where

$$\begin{aligned}
\Theta_{vib,1} &= 4170\,\mathrm{K} \\
\Theta_{vib,2} &= \Theta_{vib,3} = 2180\,\mathrm{K} \\
\Theta_{vib,4} &= \Theta_{vib,5} = \Theta_{vib,6} = 4320\,\mathrm{K} \\
\Theta_{vib,7} &= \Theta_{vib,8} = \Theta_{vib,9} = 1870\,\mathrm{K}
\end{aligned} \tag{18.37}$$

thus the theoretical and experimental curve are as follows



18-38 A 2-dimensional diatomic molecule has 2 translational degrees of freedom, 1 vibrational degrees of freedom, 1 rotational degrees of freedom. Thus, in total, 4 degrees of freedom.
The rotational partition function is

$$\begin{aligned}
q_{rot} &= \frac{1}{\sigma} \int_0^\infty g_J \, \mathrm{e}^{-\epsilon_J/k_\mathrm{B}T} \, \mathrm{d}J \\
&= \frac{1}{\sigma} \int_0^\infty g_J \, \mathrm{e}^{-\Theta_{rot}J^2/T} \, \mathrm{d}J \\
&= \sqrt{\frac{\pi T}{\Theta_{rot}}}
\end{aligned} \tag{18.38}$$

while

$$q_{trans} = \frac{2a^2 \pi m k_\mathrm{B} T}{h^2} \tag{18.39}$$

$$q_{vib} = \frac{\mathrm{e}^{-\Theta_{vib}/2T}}{1-\mathrm{e}^{-\Theta_{vib}/T}} \tag{18.40}$$

thus

$$q(T) = \frac{2a^2 \pi m k_\mathrm{B} T}{h^2} \sqrt{\frac{\pi T}{\Theta_{rot}}} \frac{\mathrm{e}^{-\Theta_{vib}/2T}}{1-\mathrm{e}^{-\Theta_{vib}/T}} \tag{18.41}$$

thus

$$\begin{aligned}
\langle E\rangle &= Nk_{\mathrm{B}}T^2\left(\frac{\partial \ln q}{\partial T}\right)_V \\
&= Nk_{\mathrm{B}}T^2\,\frac{\partial\left[\ln T+\frac{1}{2}\ln T-\frac{\Theta_{vib}}{2T}-\ln\bigl(1-\mathrm{e}^{-\Theta_{vib}/T}\bigr)\right]}{\partial T} \\
&= Nk_{\mathrm{B}}T^2\left[\frac{3}{2}\frac{1}{T}+\frac{\Theta_{vib}}{2T^2}+\frac{\mathrm{e}^{-\Theta_{vib}/T}}{1-\mathrm{e}^{-\Theta_{vib}/T}}\frac{\Theta_{vib}}{T^2}\right] \\
&= Nk_{\mathrm{B}}\left[\frac{3}{2}T+\frac{\Theta_{vib}}{2}+\Theta_{vib}\frac{\mathrm{e}^{-\Theta_{vib}/T}}{1-\mathrm{e}^{-\Theta_{vib}/T}}\right] \qquad (18.42)
\end{aligned}$$