CHEM304 - HW 4

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1 Chapter 3 Questions

3-14) Use the following partition function for a monotomic van der Waal gas to calculate the heat capacity, then compare it to a the monotomic ideal gas law result.

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}(V-Nb)^N e^{\frac{aN^2}{Vk_BTT}}$$

So, to find the heat capacity C_V, we must first find the average energy using this partition function, thus we need to use the following equation,

$$\langle E\rangle = k_B T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

then, given log rules,

$$\begin{aligned}
\ln Q &= \ln\left(\frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}(V-Nb)^N e^{\frac{aN^2}{Vk_BTT}}\right)\\
&= \ln(N!) + \frac{3N}{2}\ln(2\pi m k_B T) - \frac{3N}{2}\ln(h^2) + \ln(V-Nb)^N + \ln\left(e^{\frac{aN^2}{Vk_BT}}\right)\\
&= \frac{3N}{2}\ln(2\pi m k_B T) + \frac{aN^2}{Vk_BT} + \text{terms not involving T}
\end{aligned}$$

thus,

$$\begin{aligned}
\langle E\rangle &= k_B T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}\\
&= -aN^2 + \frac{3}{2}k_B N T
\end{aligned}$$

where, using this to find C_V,

$$\begin{aligned} C_V &= \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} \\ &= \frac{\partial}{\partial T}\left(-aN^2 + \frac{3}{2}k_B NT\right)_{N,V} \\ &= \frac{3}{2}k_B N \end{aligned}$$

Now, comparing this to the heat capacity of an ideal gas, $C_V = \frac{3}{2}R$, we see that we have the same result. Thus, the heat capacity for a monotomic van der Waal gas is the same for a monotomic ideal gas. $\square$

3-15) Use the following partition function

$$Q(N,V,T) = \frac{[q(V,\beta)]^N}{N!}$$

to show pressure of a diatomic gas obeys $PV = k_B NT$ where

$$q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^3 /2V \cdot \frac{8\pi^2 I}{h^2\beta} \cdot \frac{e^{-\beta hv/2}}{1-e^{-\beta hv}}$$

To find pressure, we must solve the following formula for pressure

$$\langle P \rangle = P_{obs} = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

where we must first simplify $\ln Q$, so

$$\begin{aligned} \ln Q &= N \ln q - \ln(N!) \\ &= N(\frac{3}{2}\ln(2\pi m) - \frac{3}{2}\ln(h^2\beta) + \ln(V) + \ln(8\pi^2 I) - \ln(h^2\beta) + \frac{\beta hv}{2} + \ln(1-\beta hv)) \\ &= N\ln(V) + \text{terms not involving } V \end{aligned}$$

thus,

$$\begin{aligned} P_{obs} &= k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} \\ P_{obs} &= \frac{k_B NT}{V} \\ P_{obs}V &= k_B NT \end{aligned}$$

thus, we have shown the pressure of a diatomic gas obeys $P_{obs}V = k_B NT$.
$\square$

3-16) If

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

where $q(V,T) = f(T)V$, where $f(T)$ is some function of temperature, show that the the ideal gas law results. To show this result, we wish to solve for pressure,

$$\langle P \rangle = P_{obs} = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta}$$

where we first solve for $\ln Q$, so

$$\begin{aligned} \ln Q &= \ln \left(\frac{[q(V,T)]^N}{N!} \right) \\ &= \ln \left(\frac{[f(T)V]^N}{N!} \right) \\ &= N \ln(f(T)V) - \ln(N!) \end{aligned}$$

therefore, when we solve for pressure

$$\begin{aligned} P_{obs} &= k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} \\ &= \frac{k_B N T}{V} \end{aligned}$$

where $P_{obs} V = k_B N T$ is the ideal gas law, thus we have shown the desired result. □

3-32) Give the following partition function:

$$Q(N_1, N_2, V, T) = \frac{[q_1(V,T)]^{N_1}}{N_1!} \cdot \frac{[q_2(V,T)]^{N_2}}{N_2!}$$

where,

$$q_j(V,T) = \left(\frac{2\pi m_j k_B T}{h^2} \right)^{\frac{3}{2}} V, \; j = 1, 2$$

Find $\langle E \rangle$ and P. To find $\langle E \rangle$, we will use the following expression

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

thus, we must find $\ln Q$. Following the pattern of simplifying $\ln Q$ to just terms of T,

$$\begin{aligned} \ln Q &= N_1 \ln(q_1) + N_2 \ln(q_2) - \ln(N!) \\ &= \frac{3}{2} N_1 \ln(2\pi m_1 k_B T) + \frac{3}{2} N_2 \ln(2\pi m_2 k_B T) + N_1 \ln(V) + N_2 \ln(V) \\ &- \ln(N!) \\ &= \frac{3}{2} N_1 \ln(2\pi m_1 k_B T) + \frac{3}{2} N_2 \ln(2\pi m_2 k_B T) \\ &+ \text{terms not involving } T \end{aligned}$$

Where the terms involving V are not included. Thus, using this $\ln Q$

$$\begin{aligned}\langle E\rangle &= k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \\ &= k_B T^2 \left(\frac{N_1+N_2}{V}\right)\frac{3}{2} \\ &= \frac{3k_B T^2}{2V}(N_1+N_2)\end{aligned}$$

therefore, we have found $\langle E\rangle$ Now, we must find P. We know that

$$\langle P\rangle = P_{obs} = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

Where, when we construct $\ln Q$ such that we isolate the V terms, then

$$\begin{aligned}\ln Q &= N_1 \ln(q_1) + N_2 \ln(q_2) - \ln(N!) \\ &= \frac{3}{2}N_1 \ln(2\pi m_1 k_B T) + \frac{3}{2}N_2 \ln(2\pi m_2 k_B T) + N_1 \ln(V) + N_2 \ln(V) \\ &- \ln(N!) \\ &= N_1 \ln(V) + N_2 \ln(V) + \text{terms not involving } V\end{aligned}$$

Thus, solving for pressure now

$$\begin{aligned}\langle P\rangle = P_{obs} &= k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} \\ &= k_B T \left(\frac{N_1+N_2}{V}\right) \\ &= (N_1+N_2)\frac{k_B T}{V}\end{aligned}$$

where we proven the results the question asks us to prove. □

3-38) Given our definition for the average energy of a system

$$\langle E\rangle = U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

show that the standard deviation of our system is the following:

$$\sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2 = k_B T^2 C_V$$

To achieve this result, we will differentiate $\langle E\rangle$ by β. We will also use the fact that $\langle E\rangle = \frac{\sum_i E_i e^{-\beta E_i}}{Q(N,V,\beta)}$. For notation sake, we will also consider $Q(N,V,\beta) = Q$. So, through the quotient rule and simplification, we get

the following result:

$$\frac{\partial}{\partial\beta}\left(\frac{\sum_i E_i e^{-\beta E_i}}{Q}\right) = \frac{-E_i Q \sum(E_i e^{-\beta E_i}) - \frac{\partial Q}{\partial\beta}\sum E_i e^{-\beta E_i}}{Q^2}$$
$$= \frac{-\sum E_i{}^2 e^{-\beta E_i}}{Q} - \frac{\frac{\partial Q}{\partial\beta}\sum E_i e^{-\beta E_i}}{Q^2}$$

Recall that $\frac{\partial\langle E\rangle}{\partial\beta} = -k_B T^2 C_V$. Since $\frac{-\sum E_i{}^2 e^{-\beta E_i}}{Q}$ is just $\langle E^2\rangle$, $\frac{\frac{\partial Q}{\partial\beta}}{Q} = \frac{\partial \ln Q}{\partial\beta}$, and $\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial\beta}\right)_{N,V}$, then

$$\frac{-\sum E_i{}^2 e^{-\beta E_i}}{Q} - \frac{\frac{\partial Q}{\partial\beta}\sum E_i e^{-\beta E_i}}{Q^2} = \langle E^2\rangle - \frac{\langle E\rangle\sum E_i e^{-\beta E_i}}{Q}$$
$$= -\langle E^2\rangle + \langle E\rangle^2$$

Therefore,

$$\frac{\partial\langle E\rangle}{\partial\beta} = -k_B T^2 C_V = -\langle E^2\rangle + \langle E\rangle^2$$
$$k_B T^2 C_V = \langle E^2\rangle - \langle E\rangle^2 \text{ (def. of Standard Deviation)}$$
$$= \sigma_E^2$$

Thus, we have shown our desired result. What this result shows is that as Heat Capacity increases, the standard deviation of the average energy of the system increases. This makes sense from a physical standpoint where a molecule that can hold more heat can hold higher energy levels. Now consider the relative magnitude of the spread of $\langle E\rangle$ given be the following magnitude:

$$\frac{\sigma_E}{\langle E\rangle} = \frac{(k_B T^2 C_V)^{1/2}}{\langle E\rangle}$$

To understand the size of this ratio, use the values of $\langle E\rangle$ and C_V for a monotomic ideal gas, $\frac{3}{2}k_B NT$ and $\frac{3}{2}k_B N$, and show that $\frac{\sigma_E}{\langle E\rangle}$ goes as $N^{-1/2}$. Considering the monotomic ideal gas, we can simplify our equation

as follows:

$$\begin{aligned}
\frac{\sigma_E}{\langle E\rangle} &= \frac{(k_B T^2[\frac{3}{2}k_B N])^{\frac{1}{2}}}{\frac{3}{2}k_B NT} \\
&= \frac{(\frac{3}{2}k_B{}^2 NT^2)^{1/2}}{\frac{3}{2}k_B NT} \\
&= \frac{(\frac{3}{2}N)^{\frac{1}{2}}k_B T}{\frac{3}{2}k_B NT} \\
&= \left(\frac{3}{2}N\right)^{\frac{1}{2}}\left(\frac{3}{2}N\right)^{-1} \\
&= \left(\frac{3}{2}\right)^{-\frac{1}{2}}(N)^{-\frac{1}{2}}
\end{aligned}$$

Where we can see with our final result that as the number of particles increases, our magnitude of the spread of $\langle E\rangle$ decreases. □

2 Chapter 4 Questions

4-6) Show that each dimension contributes $\frac{R}{2}$ to molar transitional heat capacity. The partition function for any polytomic molecule is the following:

$$q(V,T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V$$

where this equation is considered in three dimensions. To find C_V, we must first find $\langle E\rangle$, so

$$\langle E\rangle = k_B T^2\left(\frac{\partial \ln Q}{\partial T}\right)$$

where recall that $Q(N,V,T) = \frac{[q(N,V,T)]^N}{N!}$, and,

$$\begin{aligned}
\ln Q &= N\ln(q) - \ln(N!) \\
&= \frac{3N}{2}\ln(2\pi M k_B T) + \text{ terms not involving } T
\end{aligned}$$

thus,

$$\begin{aligned}
\langle E\rangle &= k_B T^2(\frac{3N}{2T}) \\
&= \frac{3k_B NT}{2}
\end{aligned}$$

And, now solving for C_V,

$$\begin{aligned} C_V &= \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} \\ &= \frac{3R}{2} = 3(\frac{R}{2}) \end{aligned}$$

Where we this final equation, we can see how there are three contribution of $\frac{R}{2}$ in the final equation for C_V, showing how transitional energy is made up of three components from the x, y, z coordinates. □

4-8) We have $\tilde{v}_{H_2} = 4401\ \text{cm}^{-1}$ and $\tilde{v}_{D_2} = 3112\ \text{cm}^{-1}$. So, to find $\Theta_{vib,j}$, we must use the following formula:

$$\Theta_{vib,j} = \frac{hc\tilde{v}}{k_B}$$

Using this formula, we get the following results (where the calculations were done on Desmos):

$$\begin{aligned} \Theta_{vib,H_2} &= \frac{(6.62\times10^{-34}\ \text{J s})(3.0\times10^{8}\ \text{m s}^{-1})(440100\ \text{m}^{-1})}{1.38\times10^{-23}\ \text{J/K}} \\ &= 6334\ \text{K} \\ \Theta_{vib,D_2} &= \frac{(6.62\times10^{-34}\ \text{J s})(3.0\times10^{8}\ \text{m s}^{-1})(311200\ \text{m}^{-1})}{1.38\times10^{-23}\ \text{J/K}} \\ &= 4479\ \text{K} \end{aligned}$$

and thus, we have finished the question. □

4-21) Calculate the contribution of each normal mode for Molar Vibrational Heat Capacity, $\overline{C}_V$ of H_2O(g) at 600 K. Using table 4.4, we obtain the following Characteristic Vibrational Values: $\Theta_{vib,a} = 5360\ \text{K}, \Theta_{vib,b} = 5160\ \text{K}, \Theta_{vib,c} = 2290\ \text{K}$. Where, to find $\overline{C}_V$, we must use the following formula:

$$\overline{C}_V = \sum_{j=1}^{\alpha}\left(\frac{\Theta_{vib,j}}{T}\right)^2 \frac{e^{-\Theta_{vib,j}/T}}{(1-e^{-\Theta_{vib,j}/T})^2}$$

Thus, solving for $\Theta_{vib,a}$:

$$\begin{aligned} \overline{C}_V &= \left(\frac{5360\ \text{K}}{600\ \text{K}}\right)^2 \frac{e^{-5360\ \text{K}/600\ \text{K}}}{(1-e^{-5360\ \text{K}/600\ \text{K}})^2} \\ &= 0.105 \end{aligned}$$

and, for $\Theta_{vib,b}$:

$$\begin{aligned} \overline{C}_V &= \left(\frac{5160\ \text{K}}{600\ \text{K}}\right)^2 \frac{e^{-5160\ \text{K}/600\ \text{K}}}{(1-e^{-5160\ \text{K}/600\ \text{K}})^2} \\ &= 0.0136 \end{aligned}$$

and, finally for $\Theta_{vib,c}$:

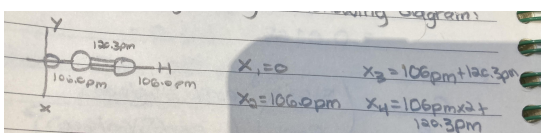
$$\begin{aligned}\overline{C}_V &= \left(\frac{2290\text{ K}}{600\text{ K}}\right)^2 \frac{e^{-2290\text{ K}/600\text{ K}}}{(1-e^{-2290\text{ K}/600\text{ K}})^2} \\ &= 0.335\end{aligned}$$

Where we have calculated all of our contributions to $\overline{C}_V$. □

4-25) There are two lines of symmetry for Acetylene and with two lines of symmetry, that means we have 4 symmetry numbers. To find the moment of inertia, we must first find the center of mass. This, for Acetylene, can trivially be seen as the center of the molecule since the molecule is linear and symmetric on both sides of the middle. To find the moment of inertia, we will use the following equation:

$$I = \sum_i = m_i d_i^2$$

where d_i is the distance of the nucleus to the center of mass. With the diagram above, our center of mass is 166 pm



Where we plug in our values for m_i and d_i into python and yield the following result:

$$I = 2.94 \times 10^{-24}\text{ kg} \cdot \text{m}$$

Thus, using this result, we can find Θ_{rot} to be the following:

$$\begin{aligned}\Theta_{rot} &= \frac{h^2}{8\pi^2 I k_B} \\ &= \frac{(6.62\times10^{-34}\text{ J}\cdot\text{s})^2}{8\pi^2(2.94\times10^{-24}\text{ kg}\cdot\text{m})(1.38\times10^{-23}\text{ J/K})} \\ &= 1.705\text{ K}\end{aligned}$$

Where we have found $\Theta_{rot} = 1.705$ K. To find $\Theta_{vib,j}$, we must use the following formula:

$$\Theta_{vib,j} = \frac{hc\tilde{v}_j}{k_B}$$

I create a function to calculate the five $\Theta_{vib,j}$ associated with each vibrational frequency constant provided with us. The code for that can be found at the end of this document. I calculated the values to be the

following:

$$\Theta_{vib,\tilde{v}_1} = 2842 \text{ K}$$
$$\Theta_{vib,\tilde{v}_2} = 4849 \text{ K}$$
$$\Theta_{vib,\tilde{v}_3} = 4715 \text{ K}$$
$$\Theta_{vib,\tilde{v}_4} = 1049 \text{ K}$$
$$\Theta_{vib,\tilde{v}_5} = 863.2 \text{ K}$$

With these values, we can now calculate the Molar Heat Capacity, $\overline{C}_V$ for polytomic molecule. Here is the formula for $\overline{C}_V$:

$$\overline{C}_V = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{\alpha} g_i \left(\frac{\Theta_{vib,j}}{T}\right)^2 \frac{e^{-\Theta_{vib,j}/T}}{(1 - e^{-\Theta_{vib,j}/T})^2}$$

Where to calculate $\overline{C}_V$, I created a python program to complete that task. Using python, I found $\overline{C}_V$ to be the following value:

$$\overline{C}_V = 4.34 \text{ R}$$

Thus, I have found the Molar Heat Capacity, Characteristic Rotational Value, Characteristic Vibrational Values, and the symmetry number for Acetylene. □

3 Question about Most Populated J State

To calculate the most populated J state, we will create a graph that plots the Boltzmann Factor of J vs. associated J value. The Boltzmann Factor equation is calculated through the following:

$$\text{Population} = g_j \exp\left(\frac{-\beta J(J+1)\hbar^2}{2I}\right)$$

where g_j is degeneracy which is equal to $2J + 1$. My methology of how I did this can be found within Python, where I found the most populated J state to be $J = 9$. □