Collections of identical, <u>indistinguishable</u> molecules

When we have N copies of a molecule and we know the single-molecule partition function $q(V,T)$, we can write:

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

this is the partition function for states available to <u>all</u> the particles

For nearly ideal gases (e.g. molecules like He or Ne) the single molecule partition function is

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

We'll derive this later, but for now we want to demonstrate what we can do with it:

Let's figure out the total <u>energy</u> of our N-particle system:

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = ?$$

$$\ln Q = N \ln q - \ln N!$$

$$\ln q = \frac{3}{2} \ln\left(\frac{2\pi m}{h^2 \beta}\right) + \ln V$$

$$N \ln q = \frac{3N}{2} \ln\left(\frac{2\pi m}{h^2 \beta}\right) + N \ln V$$

so:

$$\ln Q = \frac{3N}{2} \ln\left(\frac{2\pi m}{h^2 \beta}\right) + N \ln V - \ln N!$$

To get the energy, we want the derivative of this mess with respect to β, so lets separate it:

$$\ln Q = \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2}\right) - \frac{3N}{2}\ln\beta + N\ln V - \ln N!$$

$\therefore$

$$\frac{\partial \ln Q}{\partial \beta} = 0 - \frac{3N}{2\beta} + 0 - 0$$

$$-\frac{\partial \ln Q}{\partial \beta} = \frac{3N}{2\beta} = \frac{3}{2}Nk_BT$$

\# of molecules

$$\langle E\rangle_{translational} = \frac{3}{2}Nk_BT$$

\# of moles

$$= \frac{3}{2}nRT$$

$$U = \frac{\langle E\rangle}{n} = \frac{3}{2}RT$$

(U is the thermodynamic symbol for the internal energy of the system)

So the average energy of an ideal gas is $\frac{3}{2}nRT$

Heat Capacity is very important because this is what we typically measure in a calorimetry measurement (that doesn't involve a reaction or phase transition)

$$C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{N,V}$$

constant volume

$$C_V = \frac{3}{2}R$$

$\leftarrow$ ideal gases have a constant heat capacity.

More complicated Molecules

- Diatomics can vibrate, rotate, and translate
- If I have N identical, indistinguishable diatomics the total partition function is still

$$Q(N,V,T) = \frac{q(V,T)^N}{N!} \longleftarrow \text{single molecule partition function}$$

The thing that's different is the single molecule part:

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

$$q = q_{trans} \cdot q_{rot} \cdot q_{vib}$$

= product of the kinds of motion the molecule can undergo

(Again, we'll come back and derive these later but for now let's see what this does to $\langle E \rangle$)

$$\ln Q = N \ln q - \ln N!$$

We know that β is important, so let's pull it out:

$$\ln q = -\frac{3}{2}\ln\beta - \ln\beta - \frac{\beta h\nu}{2} - \ln\left(1-e^{-\beta h\nu}\right) + \boxed{\text{other terms without } \beta}$$

$$N\ln q = -\frac{3N}{2}\ln\beta - N\ln\beta - \frac{N\beta h\nu}{2} - N\ln\left(1-e^{-\beta h\nu}\right) + \text{others}$$

$$\left(\frac{\partial \ln Q}{\partial \beta}\right) = \frac{-3N}{2\beta} - \frac{N}{\beta} - \frac{N h\nu}{2} - \frac{N h\nu e^{-\beta h\nu}}{1-e^{-\beta h\nu}}$$

$$\langle E \rangle = \underbrace{\frac{3}{2} N k_B T}_{\text{translational contribution}} + \underbrace{N k_B T}_{\text{rotational contribution}} + \underbrace{\frac{Nh\nu}{2} + \frac{Nh\nu\, e^{-h\nu/kT}}{1-e^{-h\nu/kT}}}_{\text{vibrational contribution}}$$

for 1 mole

$$U = \frac{3}{2} RT + RT + \frac{N_A h\nu}{2} + \frac{N_A h\nu\, e^{-h\nu/kT}}{1-e^{-h\nu/kT}}$$

Again, we measure heat capacities, so if we take

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$$

$$= \underbrace{\frac{3}{2} R + R}_{\frac{5}{2} R} + \underbrace{R \left(\frac{h\nu}{kT}\right)^2 \frac{e^{-\beta h\nu}}{\left(1 - e^{-\beta h\nu}\right)^2}}_{\substack{\approx 0 \text{ at low } T \\ \approx R \text{ at high } T}}$$