Thermodynamics: Classical to Statistical

Prof. Sandip Paul

Department of Chemistry

Indian Institute of Technology Guwahati

Lecture 17

Translational, Electronic and Nuclear Partition Function

We know translational partition function is

$$q_{\text{trans}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

We can rewrite the translational partition function like

$$q_{\text{trans}} = \frac{V}{\Lambda^3}$$

where $\Lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$ and it has no dimensions, so dimension less quantity. So, lambda has dimension of length. Now we will calculate the energy or average energy.

So, we calculate average translation energy is nothing but

$$<E_{\text{trans}}> = N <\varepsilon_{\text{trans}}>$$

So N times epsilon translation average is average translation energy, so epsilon translational is the average translational energy of a molecule and it can be writen as

$$<E_{\text{trans}}> = k_B T^2 \left(\frac{\partial \ln q_{\text{tr ans}}}{\partial T}\right)_V$$

remember q trans is a function of temperature and volume.

So, next will calculate average translational energy from the translational partition function. So if you take log of q trans we get

$$\ln q_{\text{trans}} = \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) + \frac{3}{2}\ln T + \ln V$$

. Now we will differentiate logarithm of q trans with respect to temperature at constant volume and we get

$$\left(\frac{\partial \ln q_{\text{trans}}}{\partial T}\right)_V = \frac{3}{2T}$$

because the first terms gives you 0, second term gives us $\frac{3}{2T}$ and third term is also 0. So average translational energy of a single particle is

$$<E_{\text{trans}}> = k_B T^2 \times \frac{3}{2T}$$

$$\Rightarrow <E_{\text{trans}}> = \frac{3}{2} k_B T$$

Again, classically we can write

$$<E_{\text{trans}}> = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

$$<E_{\text{trans}}> = \frac{3p^2}{2m}$$

So, if we equate them we get

$$\frac{3p^2}{2m} = \frac{3}{2} k_B T$$

So you get $p \sim (mK_B T)^{1/2}$

$$\Lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \sim \frac{h}{p}$$

so we get, Λ is of the order of h by p, Λ is known as thermal de Broglie's wavelength.

Next we discuss the significance of lambda. The condition for the applicability of classical or Boltzmann statistics is equivalent to the condition that $\frac{\Lambda^3}{V} \ll 1$ this suggests that the thermal de Broglie wave length must be small compare to the dimensions of the container. Or in other words it is similar to the condition that quantum effects decrease as the de Broglie wave length becomes small. Basically $\frac{\Lambda^3}{V}$ is very, very or is much smaller than 1, then classical statistics or quantum, or Boltzmann statistics can be applied.Next we consider electronic partition function. So we can write

$$q_{elec} = \sum_i w_{ei}\, e^{-\beta\varepsilon i}$$

where w_{ei} is the degeneracy of the ith level and ε_i is the energy of the ith level,

If $\varepsilon_1 = 0$ energy then $q_{elec} = w_{e1} + w_{e2}\, e^{-\beta\Delta\varepsilon 12} + w_{e3}\, e^{-\beta\Delta\varepsilon 13} + \ldots\ldots\ldots\ldots\ldots$

Where $\Delta\varepsilon 12 = \varepsilon 2 - \varepsilon 1$, $\Delta\varepsilon 13 = \varepsilon 3 - \varepsilon 1$ and so on

Neglecting higher terms it reduces to

$$q_{elec} = w_{e1} + w_{e2}\, e^{-\beta\Delta\varepsilon 12}$$

For nuclear partition function $q_{nucl} = \sum_i w_{ni}\, e^{-\beta\varepsilon i}$

where w_{ni} is the degeneracy of the ith nuclear energy level and ε_i is the energy of the ith nuclear energy level,

$$q_{nucl} = w_{n1} e^{-\beta\varepsilon 1} + w_{n2} e^{-\beta\varepsilon 2} + \ldots\ldots\ldots\ldots\ldots$$

We assume $\varepsilon_1 = 0$, zero energy concept

$$q_{nucl} = w_{n1} + w_{n2}\, e^{-\beta\Delta\varepsilon 12} + w_{n3}\, e^{-\beta\Delta\varepsilon 13} + \ldots\ldots\ldots\ldots\ldots$$

$\Delta\varepsilon_{ij}$ in most of the case $\sim 10^6$ ev, so $q_{nucl} = w_{n1}$

So for ideal monatomic gas the molecular partition function

$$q\,(V, T) = q_{trans} \times q_{elec} \times q_{nuc}$$

Now we will substitute the values of q trans, q electronic and q nuclear here and get

$$q\,(V,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V\, \{\, w_{e1} + w_{e2}\, e^{-\beta\Delta\varepsilon 12} \,\}\, w_{n1}$$

So this is the molecule partition function for ideal monatomic gas.

From here, we calculate total partition function or partition function for N number of particles. by using

$$Q\,(N, V, T) = \{q\,(V, T)\}^N \text{ or } \{q\,(V, T)\}^N / N!$$

depending on whether the particles are distinguishable or indistinguishable. So once we get capital Q, now we can calculate all macroscopic or thermodynamic quantities.

Next, we discuss thermodynamic functions. Here we need to remember the contribution of the electronic degrees of freedom to the energy is very small at ordinary temperatures. Since, we have neglected intermolecular potential, the contribution of the intermolecular potential to the total energy of the gas can be neglected, or can be omitted.

$$Q\ (N, V, T) = \{q\ (V, T)\}^N = q_{trans} \times q_{elec} \times q_{nucl}$$

Neglecting q_{elec}, q_{nuc}, we get

$$\ln Q\ (N, V, T) = N \ln q_{trans}\ (V, T)$$

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

$$\ln Q\ (N, V, T) = \frac{3}{2}\ N \ln \frac{2\pi m k_B}{h^2} + \frac{3}{2}\ N \ln T + N \ln V$$

Now, we can calculate average energy.

$$<E> \ = \ k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V$$

And $$\ln Q = \frac{3}{2}\ N \ln \frac{2\pi m k_B}{h^2} + \frac{3}{2}\ N \ln T + N \ln V$$

Now we differentiate lnQ with respect to temperature at constant volume, we get,

$$\left(\frac{\partial \ln Q}{\partial T}\right)_V = \frac{3N}{2T}$$

Now $$<E> = k_B T^2 \times \frac{3N}{2T}$$

$$\Rightarrow\ <E> = \frac{3}{2}\ N k_B T$$

This is the average energy and this average energy is nothing but the kinetic energy of the gas molecules.

Now

$$<E> = \frac{3}{2}\ N\ k_BT = \frac{3}{2}\ nRT$$

Where n = number of moles

$$N = nN_A \quad , \qquad N_A\ k_B = R$$

.So what is the contribution of C_V here?

$$C_V = \left(\frac{\partial <E>}{\partial T}\right)_V$$

The C_V of monatomic gas is $\frac{3}{2}nR$ or molar heat capacity or molar heat capacity $\overline{C_V} = \frac{3}{2}R$ where n is number of mole is 1.

Now, we calculate average pressure.

$$<P> = k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

If we differentiate ln Q with respect to V at constant N and T, we get

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

If you substitute that there, we get

$$<P>V = k_BT = nRT$$

This is the ideal gas equation that you have studied.

Similarly we can calculate,

$$A = -\ k_BT\ \ln Q$$

Next we discuss one very interesting thing that is known as Sackur-Tetrode equation. It is a classical problem related to distinguishable and indistinguishable particles. So by using Sackur-Tetrode equation we basically solve, the classical problem Gibbs Paradox. We know,

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$Q = \frac{q_{trans}}{N!}$$

we are considering translational degrees of freedom here and the particles are indistinguishable.

So it gives us

$$\ln Q = N \ln q_{trans} - \ln N!$$

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

we also know that

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3N}{2T}$$

If we substitute the value of ln Q and $\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$ in equation 1, we obtain

$$S = k_B \left[N \ln\left\{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V\right\} - \ln N! \right] + k_B T \times \frac{3N}{2T}$$

it further reduces to

$$S = N k_B \ln\left\{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{V e^{5/2}}{N}\right\} \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

this is Sackur-Tetrode equation

What is Gibbs Paradox? Consider two cases, suppose case 1 we have here a container which contains, two compartments and the volume of both the compartment is V and both of them contain N number of ideal gas molecules but in one compartment we have gas A and another compartment we have gas B and for simplicity you consider that they are ideal monatomic gases.

So here the catch is the density of the gas of both the compartments are equal, gas density means number density we are talking about here, so number of particles per unit volume are equal in both the compartments. Suppose, this thing is our initial states, so initially we have a container in which there is a partition there, which makes or which divides the container into two equal compartments and the volume of the each compartment is V and both the compartments campaign same number of particles N, but in one compartment we have gas molecule A and in other compartment we have gas molecule B, so this is our initial state.

Now, if we remove the partition, what will happen? We have N number of gas molecules of A and N number of gas molecules B, both are present in 2V volumes, so this is our final volumes, they will mix, so this will final state. If we remove the partition they will mix and we know this mixing process is entropy driven and ΔS final is greater than 0, it has some value.

Next, we consider another case with very similar experiment, but we will use same gas molecules in both the compartments. So in case two we have very similar arrangement, N number of particles, volume V and we have gas molecule A here and here also same gas molecule in both the compartment, again, if you remove the partition, what we get? They will mix, so we have 2N number of gas molecules A in 2V volume.

So initially we had a container in which there is a partition which divides the container into two compartments of equal volume V and in both the compartments we have N number of particles A and if you remove the partition they will mix and what is the value of ΔS_{mix} here or ΔS_{final} here is 0, so mathematically we will prove this with the help of Sackur-Tetrode equation.

So you can see tha in both experiments we have very similar arrangements except that in first case we considered two different gases and in second case we consider same gas molecules but in first case we get positive entropy mixing, and in second case there is no entropy change if you remove the partition.

So we will start with case 1, for case 1 before mixing the entropy of the initial state is nothing but entropy for gas A in the initial state plus entropy of gas B at initial state and if we now use the Sackur-Tetrode equation here, we can write,

$S_{initial} = (S_A)_{initial} + (S_B)_{initial}$

$$= Nk_B \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{2\pi m_A k_B}{h^2}\right) - \ln N + \frac{5}{2} \right] \Rightarrow \text{for gas A}$$

$$+ Nk_B \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{2\pi m_B k_B}{h^2}\right) - \ln N + \frac{5}{2} \right] \Rightarrow \text{for gas B}$$

Once we get the value of S final and S initial, the difference between them gives us the entropy of mixing or ΔS_{final}.

$$\Delta S_{final} = Nk_B \left[\ln 2V + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{2\pi m_A k_B}{h^2}\right) - \ln N + \frac{5}{2} \right] +$$

$$Nk_B \left[\ln 2V + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{2\pi m_B k_B}{h^2}\right) - \ln N + \frac{5}{2} \right]$$

$$\Delta S_{mix} = \Delta S = S_{initial} - S_{final}$$

$$S_{mix} = 2Nr \ln 2 > 0$$

For case 2,

$$S_{initial} = 2Nk_B \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{2\pi m_A k_B}{h^2}\right) - \ln N! + \frac{5}{2} \right]$$

$$S_{final} = 2Nk_B \left[\ln 2V + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{2\pi m_A k_B}{h^2}\right) - \ln(2N!) + \frac{5}{2} \right]$$

$$\Delta S_{mix} = \Delta S = S_{initial} - S_{final} = 0$$

Gibbs Paradox solved by using Sackur-Tetrode equation.