Thermodynamics: Classical to Statistical
Prof. Sandip Paul
Department of Chemistry
Indian Institute of Technology Guwahati
Lecture - 01
Concepts of Heat and Work [First Law of Thermodynamics]

So, in next few classes, we will discuss briefly about the thermodynamics. You have all studied thermodynamics in 10+2 level. We will go through the laws of thermodynamics very briefly. So, we will start with the concept of work and heat. We define work by ‘w’ and heat by ‘q’ and they play important roles in thermodynamics. So, we need to know more about work and heat. We need to know what is work and what is heat? Both work and heat refer to the manner in which energy transferred between system and surroundings. We have introduced two new terminologies here, ‘systems’ and ‘surroundings’. So, what do you mean by system? How do we define a system then? System is defined as the part of the world we are investigating. Then, what is surroundings? Surroundings can be defined as everything else other than system. So, system is the part of the world we are investigating (See below Figure 1), and surroundings everything else. They are separated by a surface and surface can be movable also. So, now we know what is system and what is surroundings.

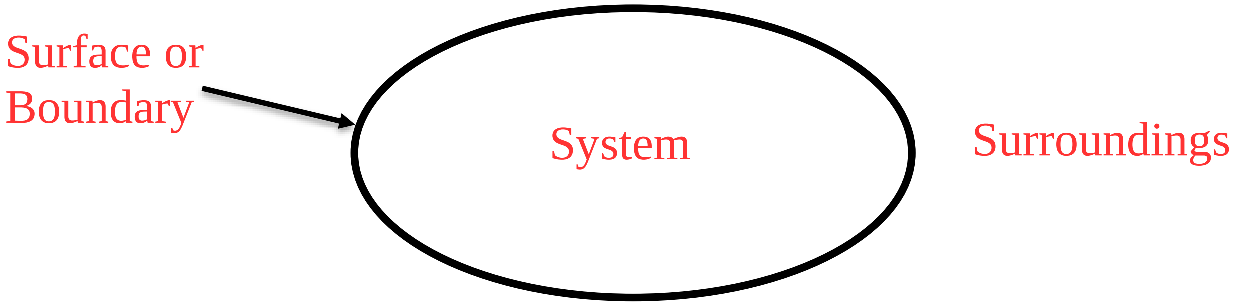

Figure 1

Next, let us define heat. What do we know about heat? Heat can be defined as energy transferred between system and surroundings due to temperature difference between them. Next, what is work? Work is energy transferred between system and surroundings, as a result of unbalanced forces between the two (system and surrounding). So, when there is an unbalanced forces between system and surroundings, we get work. So, we defined systems, we defined surroundings, we defined heat, and we defined work.

Now, what is the convention for heat and work? There has international convention for work and heat. Heat is positive, means heat input to the system. It is negative when heat is evolved by the system. Similarly, for work the convention is, work is considered as positive, means work done on the system and it is negative means work done by the system. So these are the conventions we will be using throughout the course.

q= + ve => heat input to the system

q= – ve => heat evolved by the system

w= + ve => work done on the system

w= – ve => work done by the system

Now let us see how we get heat and how we get work. We have a system having temperature T_1 and there is surroundings having a temperature T_2 and T_1 is not equal to T_2. Through this boundary, heat can exchange (heat exchange boundary). In this case, we get some heat. Similarly, suppose we have a container of ideal gas (see Figure 2) and the pressure of this container is P_{int}. And you have the external pressure, P_{ext}.

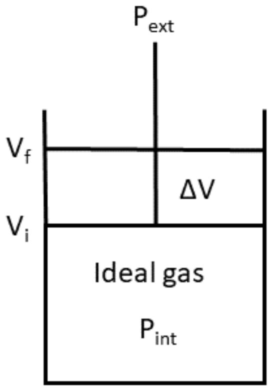

Figure 2

If P_{ext} is not equal to P_{int}, in that case, we get some work done. So, now we understood, how one can get heat, and one can get work. How do we quantify and calculate heat and work, etc. Consider the previous example, like we discussed now, we take one container like Figure 2, which is having internal pressure P_{int} or P_i. Initially we have ideal gas molecule confined in a cylinder. So, work done for this process, 'w' is nothing but ' - mgh', where, m is the mass of the piston, and, what is h? h is the expansion height. g is acceleration of gravity. So, this is the way we can calculate work done. We can further simplify this one is like:

$$W = -\,mgh \times (A/A)$$

Where, A is the area of the piston. The volume change due to expansion is $\Delta V = hA$.

$$\text{So, } W = -\,(mg/A) \times \Delta V$$

$$W = -\,P_{ext} \times \Delta V$$

We have initial volume here V_i and final volume V_f. So, ΔV is nothing but V_f minus V_i. So, we can calculate the work done as follows:

$$W = -\,P_{ext} \times \Delta V$$

This P_{ext} is nothing but final pressure.

$$W = -\,P_f \times \Delta V$$

This is applicable for irreversible process. Now, if pressure changes continuously during the process, then we can write:

$$W = -\int P_{ext}\, dV$$

This is very general expression and this is applicable for reversible process. Depending on the type of gas molecules, we can now calculate work done. Suppose, for ideal gas, we know P is nothing but nRT/V. So, we can calculate W by substituting the value of P. So, we get, $w = –nRT\ln(V_f /V_i)$.

For van der Waals gas we can substitute this P in the previous expression. For van der Waals gas, $P = ((nRT/V–nb) – (n^2 a/V^2))$. So, we can calculate W and so on. So, what we got so far? we got work done, W is $–P\Delta V$ for irreversible process and $–nRT\ln V_f /V_i$ for reversible process (for ideal gas).

We have one initial state, where the pressure was P_i and volume V_i , and we are going to final state here, where the pressure P_f, volume V_f . If the process is reversible one, we get one work done, and if the process irreversible one, we get different work done. So, depending on the process although we have started from the same initial state and we are going to the same final state, like if we go through reversible process or if we carry out irreversible process work done are different. So, work is not a state function. Rather, work is a path function. So, what do you mean by state function and what do you mean by path function? We will discuss this elaborately. A state function is a property that depends only upon the state of the system and not upon how the system was brought to that state. One important mathematical property of a state function is that its differential can be integrated in normal way. Suppose, U is a state function. So, we can do the integration of dU in normal way and we can get the value like this:

$$\int_{U_1}^{U_2} dU = U_2 - U_1 = \Delta U$$

So, this is how one can integrate one state function.

If A which is function of variables x and y, and is a state function, then dA is said to be perfect differential, like this.

So, state functions are perfect differential. So, if A is a state function so dA is said to be perfect differential if this condition holds:

$$\delta^2A/\delta x\delta y = \delta^2A/\delta y\delta x$$

A which is function of variables x and y:

$$dA = (\delta A/\delta x)_y dx + (\delta A/\delta y)_x dy$$

$$dA = f(x,y)dx + g(x,y)dy$$

where, $f(x,y) = (\delta A/\delta x)_y$ and $g(x,y) = (\delta A/\delta y)_x$

So, the necessary and sufficient comndition is:

$$(\delta f/\delta y)_x = (\delta g/\delta x)_y$$

Now, we will consider a simple function and we will try to prove this by following way:

$$A = x^2\sin(xy)$$

$$dA = (2x \sin(xy) + x^2y \cos(xy))\, dx + (x^3 \cos(xy)\, dy)$$

$$(\delta f/\delta y)_x = 3x^2 \cos(xy) – x^3y \sin(xy)$$

$$(\delta g/\delta x)_y = 3x^2 \cos(xy) – x^3y \sin(xy) = (\delta f/\delta y)_x$$

So, dA is a perfect differential. So, A is a state function.

Next we will prove work done is a path function. So, work is a path function or work is not a state function. So we will try to prove it in a very simple manner. So, we consider only PV work is involved here.

Proof: 0

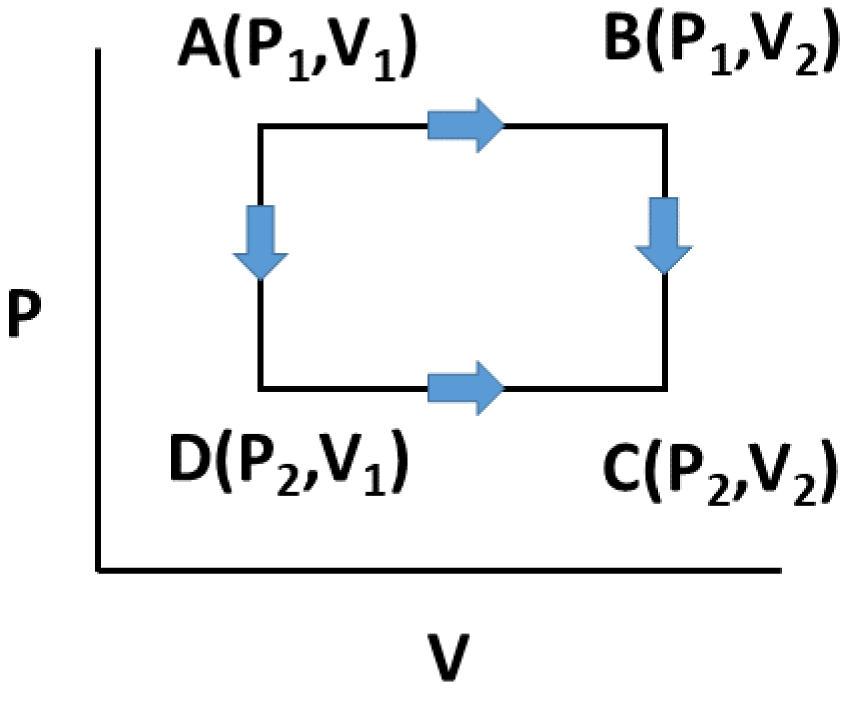

Figure 3

We have one initial state (in Figure 3) at point A where pressure is P_1 and volume is V_1. And we would like to reach a final state C, where pressure is P_2 and volume V_2. We can reach from point A to point C like this way. We will first reach at point B from point A, by keeping the pressure fixed we can increase the volume from V_1 to V_2. So this is our path 1. And we can reach in another fashion. We can first keep the volume fixed at V_1 and we can decrease the pressure from P_1 to P_2, and then, first, we can start from point A and then we reach to point D by keeping the volume fixed at V_1 and then we can decrease the pressure to P_2, so this is point D, where pressure is P_2 and volume is V_1 and then we can increase the volume at constant pressure P_2 from V_1 to V_2. So, this is path 2.

Now we will prove internal energy is a state function by taking Figure 4.

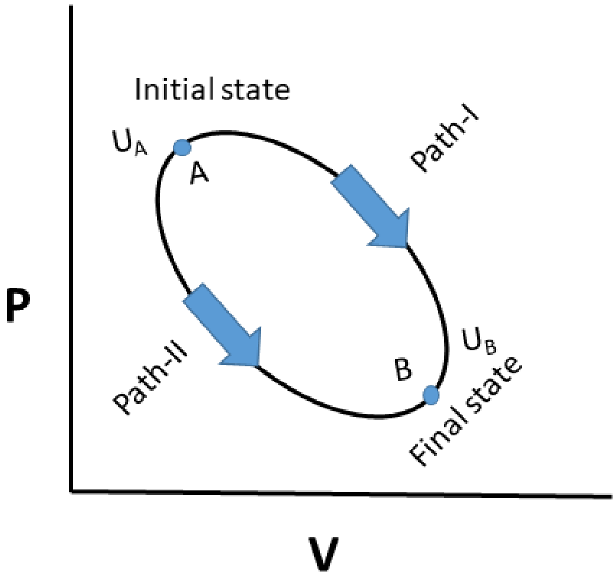

Figure 4

For path-I: $\Delta U_1 = U_B - U_A$

For path-II: $\Delta U_2 = U_A - U_B$

Assume, $|\Delta U_1|$ not equal to $|\Delta U_2|$, this implies we can generate some amount of energy by repeating this, but this is not possible.

$$\text{So, } |\Delta U_1| = |\Delta U_2|$$

So, U is a state function.

Now first law of thermodynamics:

If a state (A) having internal energuy U_A changes to another state (B) having internal energy U_B by taking +q amount of heat and w amount of work is done by the system, so,

$$\mathbf{U_A + q = U_B - w}$$

$$\mathbf{U_A - U_B = q + w}$$

$$\mathbf{\Delta U = q + w}$$

Now, for adiabatic process $dq = 0$,

So, $dU = dw$

In this special case dw becomes state function.

$C_V(T)\, dT = - P\, dV$

Where, $C_V = 3/2\, R$

$P = nRT/V$

So, $C_V(T)\, dT = - (nRT/V)\, dV$

By taking the temperature limit from T_1 to T_2 and volume limit V_1 to V_2 and integrating and putting the value of C_V, we get,

$(T_2/T_1)^{3/2} = (V_1/V_2)$

For expansion process, $V_2 > V_1$ and $T_1 > T_2$

By substituting the value of T, we get,

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$, where $\gamma = C_P/C_V$

$PV^{\gamma} = \text{constant}$

So, for adiabatic process, $PV^{\gamma} = \text{constant}$

For isothermal process, $PV = \text{constant}$, this is known as boyle law.

Now we will consider one simple diagram (Figure 5) and I will try to calculate work, internal energy, etc.

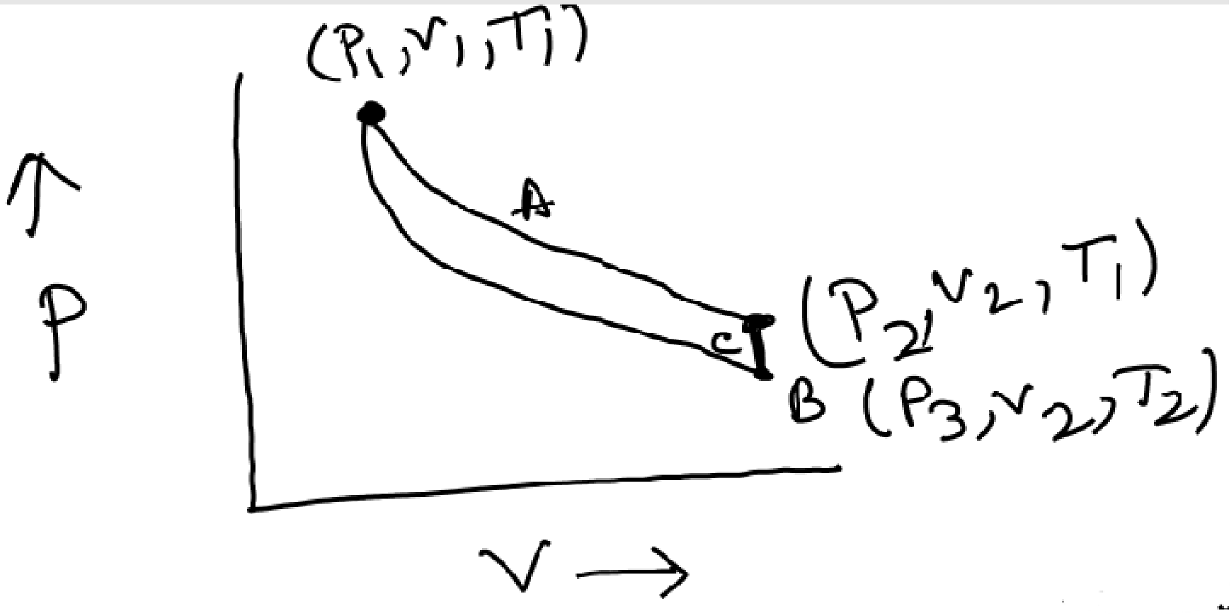

Figure 5

Path A is isothermal reversible process, path B is adiabatic process and for path C no PV work. So,

For path A: $\Delta U_A = 0$ **; So,** $q_A = -w_A$

For path B: $q_B = 0$ **;** $\Delta U_B = w_B$

For path C: $w_C = 0$ **;** $\Delta U_C = q_C$.

So in that fashion also we have just worked out here how we can calculate internal energy change, heat change or work done for different processes.