Introduction to Chemical Thermodynamics and Kinetics

Dr. Arijit Kumar De
Department of Chemistry
Indian Institute of Science Education and Research, Mohali

Lecture - 07
First law - part 2

All right. So, we have now, in an idea what is the Energy of the system? Now let us suppose, we do a transformation at constant volume. Now this experiment is known as Joules Experiment. It is another experiment carried out by James Prescott Joule. So, what he asked is, if we do our transformation, how the energy or internal energy of the system changes?

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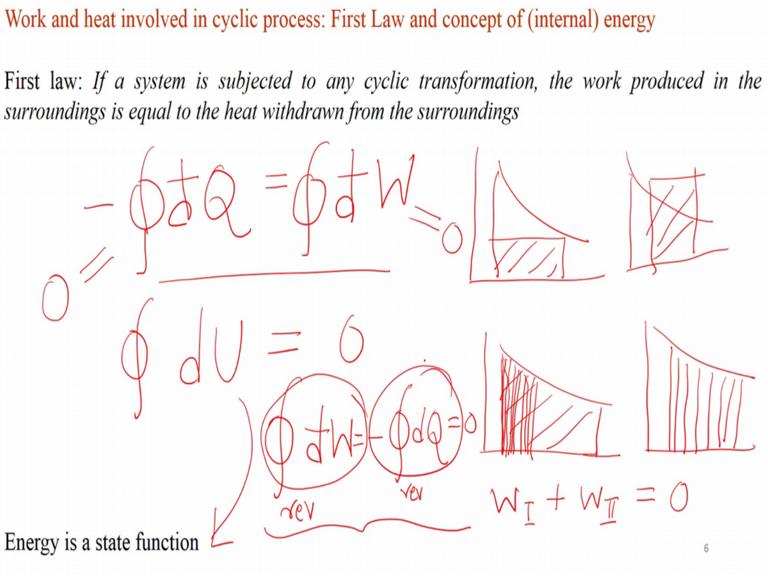

Work and heat involved in cyclic process: First Law and concept of (internal) energy

First law: *If a system is subjected to any cyclic transformation, the work produced in the surroundings is equal to the heat withdrawn from the surroundings*

Energy is a state function

So, let us now define the First Law more formally. So, here we say that if a system is subjected to any cyclic transformation, the work produced in the surrounding will be the heat withdrawn from the surrounding and that is how we formulated the First Law that d cross Q in the cyclic process will be d cross W.

We are keeping a negative sign, just to make sure that the convention is correct and then, by adding them we got d U, for any cyclic process is 0; which we stated in a different word that Energy is a state function, unlike heat and work. Now remember here, we gave an example of single step expansion, followed by single step compression and we know that the work done is very different. However, we said that work done which is the net work done by the surrounding was utilized in raising the temperature of the surrounding

Now, you may ask this question, if we had done it in a reversible way meaning changing the pressure of the system infinitesimal amount, changing the pressure of the system by infinitesimal amount; that will lead to the area under the curve same for the forward process as well as in the backward process. In this case these 2 areas cancel each other. So, if I write W in the first step and W in the second step that will be perfectly 0. So, in this particular case d cross W is equal to 0, d cross Q also is equal to 0 for the cyclic process.

For a reversible cyclic process then, we can write for any reversible process is nothing, but equal to 0. But remember that this is not always true, for any not a reversible process, which we will call as irreversible process this integral is nonzero. However, their addition must be 0.

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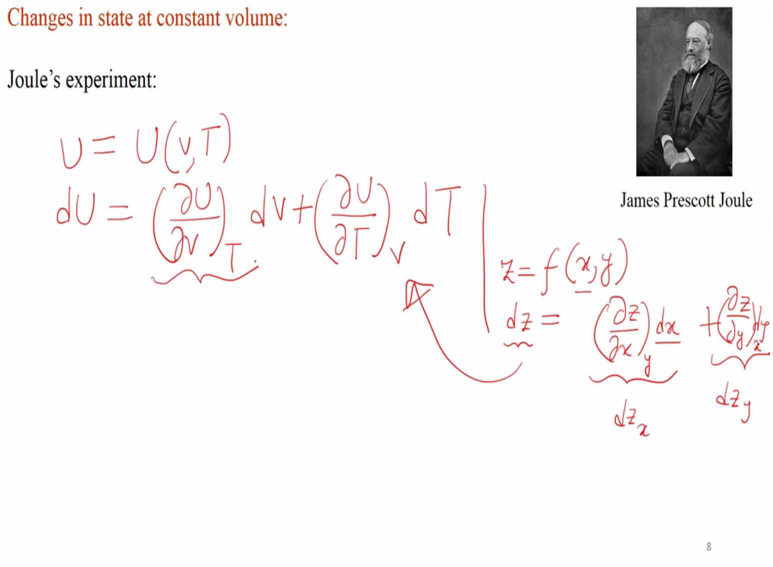

Changes in state at constant volume:

Joule's experiment:

$$U = U(v, T)$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial v}\right)_T}\, dv + \left(\frac{\partial U}{\partial T}\right)_v dT$$

$$z = f(x, y)$$

$$\underbrace{dz} = \underbrace{\left(\frac{\partial z}{\partial x}\right)_y dx}_{dz_x} + \underbrace{\left(\frac{\partial z}{\partial y}\right)_x dy}_{dz_y}$$

James Prescott Joule

Now, let us move on and ask this question, what happens if we do our transformation to the system at constant volume? Again, Joule did an very excellent experiment where he tried to understand, how this quantity which we just defined as the difference between work done and heat withdrawn, which we called as the Internal Energy of the system changes by change in volume, as we make the transformation.

So, for that mathematically, we can write the internal energy as a function of volume and temperature. Now which means the total differential d U can be written as a partial differential first with respect to volume; keeping the temperature constant and then, taking the partial differential with respect to temperature, keeping the volume constant.

Now this, comes from just the fact of differential and partial differential; the calculus which you learnt in 12th standard. If suppose Z is a function of x and y and if I ask this question, there is a transformation d Z which is the total differential offset and if I ask this question how much part of d Z actually is caused by changing in x alone. The answer will be I have to take the partial derivative with respect to x keeping y constant. So, we are not changing y and then multiply it by a change in d x.

So, that will be the part which we sometimes write as digit x and then, similarly there will be a part which is d Z y change in this differential d Z due to the change in y alone. In this case we keep that x fix. Now we have used the similar formula here. Now Joule asked this question that how one can measure this quantity? We will come back to it.

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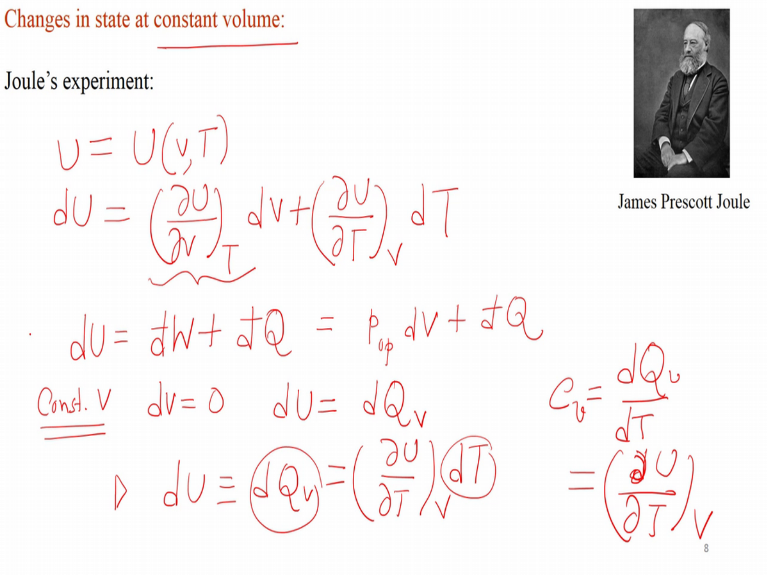

Changes in state at constant volume:

Joule's experiment:

James Prescott Joule

$$U = U(v,T)$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial v}\right)_T}_{} dv + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dU = \text{đ}W + \text{đ}Q = P_{op}\, dV + \text{đ}Q$$

$$\underline{\underline{\text{Const. }V}} \quad dV = 0 \quad dU = dQ_V \qquad C_v = \frac{dQ_v}{dT}$$

$$dU = \boxed{dQ_V} = \left(\frac{\partial U}{\partial T}\right)_V \boxed{dT} \qquad = \left(\frac{\partial U}{\partial T}\right)_V$$

Before that, let us do some mathematical tricks. We already know from first law that d U is d cross W plus d Q and d cross W we know that it is nothing but opposing pressure into d v plus d cross W.

Now, if we consider a constant volume process, d v must be 0. So, d U is nothing but d Q for constant volume. So, we can use this equation for a constant volume process d U is d Q v which is del U del T v d T. Now, we got a very interesting situation. If we divide d Q v by d T. We get the heat capacity at constant volume. Because remember that is the definition of heat capacity. How much heat is changed if we raise the temperature by say 1 degree at constant volume? So, that quantity is given by this partial derivative which is del U del T v.

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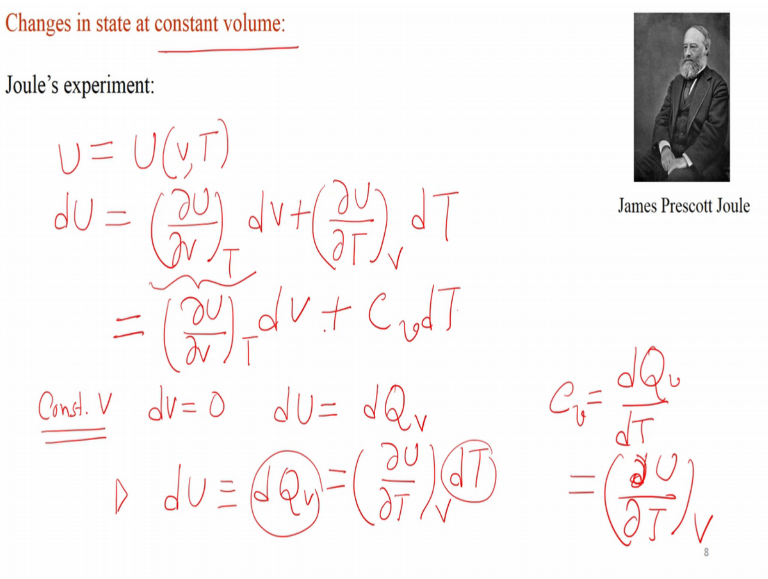

Changes in state at constant volume:

Joule's experiment:

James Prescott Joule

$$U = U(v,T)$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial v}\right)_T} dv + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$= \left(\frac{\partial U}{\partial v}\right)_T dV + C_v dT$$

Const. V $\quad dv = 0 \quad dU = dQ_v$

$$\triangleright \ dU = \boxed{dQ_v} = \left(\frac{\partial U}{\partial T}\right)_V \boxed{dT}$$

$$C_v = \frac{dQ_v}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

So, we can rewrite the total differential, which we just wrote for d U as d U is nothing but del U del V T d v plus C v d T. Now our task is to understand, what is this quantity del U del V T d v. So, that is why Joule did an very nice experiment to quantify this quantity.

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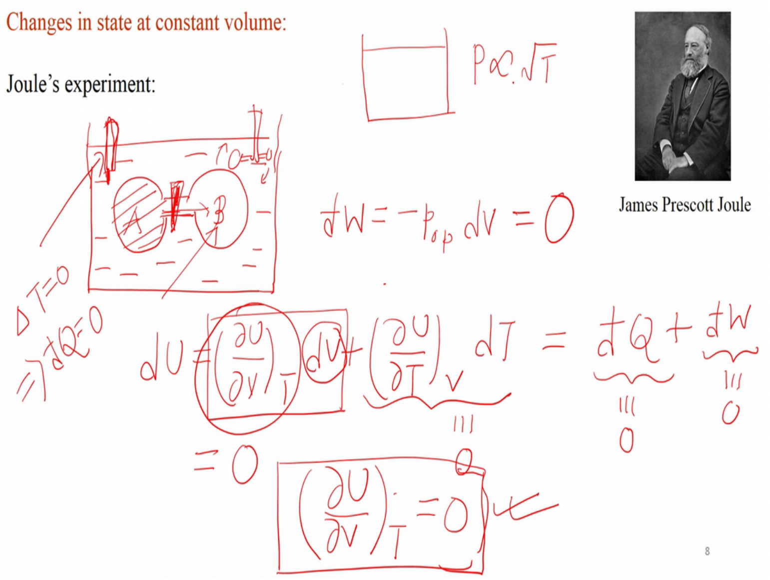
Changes in state at constant volume:

Joule's experiment:

James Prescott Joule

$P \propto \sqrt{T}$

$đW = -P_{op}\,dV = 0$

$\Delta T = 0 \Rightarrow đQ = 0$

$$dU = \boxed{\left(\frac{\partial U}{\partial V}\right)_T dV} + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V dT}_{\equiv 0} = \underbrace{đQ}_{\equiv 0} + \underbrace{đW}_{\equiv 0}$$

$= 0$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$$

Now, what Joule did? He took bucket of water and then, inside the bucket he kept 2 containers which are round bottom flasks like and with a stopcock in between. Initially, suppose there, I am leveling them as A and B; initially some gas filled the container, but the container B was empty and he was also used this entire system which is just 2 bulbs connected by a stopcock, immersed in a water where the temperature of the water can be monitored by a thermometer. And there was also an stirrer, in this case the stirrer actually just rotates in order to maintain the thermal equilibrium of the system.

Now, when the stopcock was open, the question, Joule asked is what is the associated change in the internal energy? Now remember we will just use the same notation here d cross Q or the work done is opposing pressure into d v. However, remember when the gas expanded the opposite pressure was 0.

Because initially, there was no gas in B. So, you can think that when the boundary of this gas changes, when the gas tries to fill in the other container. Always this boundary fills no opposing pressure, which means that P opposing was 0 in this case and the work done will be nothing but 0.

So, now from the First Law, we can write d U which was del U del V T; d v plus del U del T v d T which is nothing but d cross Q plus d cross W. But we just said that the d cross W is 0 in this case. The d cross Q was also 0; because Joule observed no rise in temperature. Since, delta T was 0, d cross Q also has to be 0. So, the right hand side of this equation is 0. Now since, the delta T was 0 which means d T was also 0, which means this term del U del V T must be zero since d v is nonzero. So, Joule said that del U del V T is 0 according to his measurement. We will come back to it, when you discuss the Joule Thomson Experiment.

Now, before we switch to other topics, let us briefly discuss, what is meant by this; why del U del V T is 0 for an ideal gas. Now let us have an analogy with our particle in a box model which we learnt in Quantum Mechanics. Now you know that as the length of the box changes, the energy levels also changes. So, from that perspective del U del V T should be nonzero; because it should be dependent on volume.

However, remember that this associated change in energy is already accounted for, why? Because we already discussed that, when work is done on the system or work is done by the system, there is a change in pressure; that pressure is proportional to the square root of temperature which is actually related to the supply of energy.

So, the energy we are talking of in this context is not the Kinetic energy. It is the internal energy of the system.

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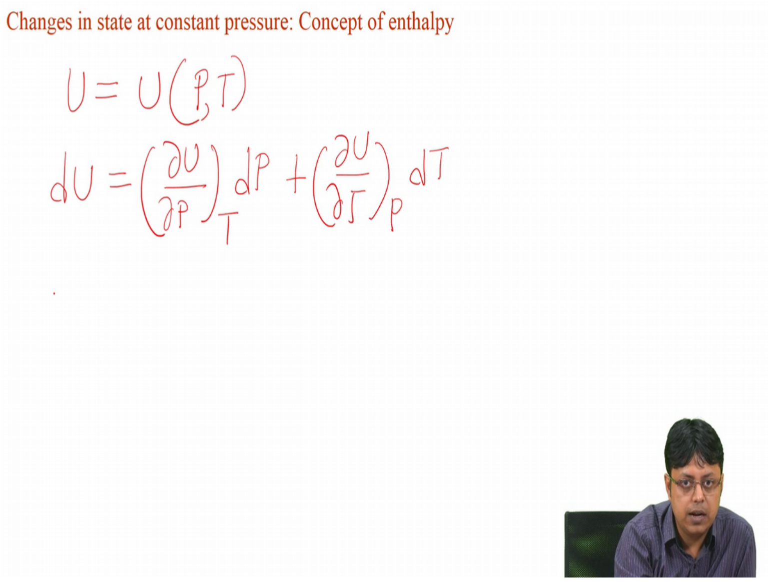

Changes in state at constant pressure: Concept of enthalpy

$$U = U(P,T)$$

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT$$

Now, let us consider another process in a similar way, where we would like to keep the pressure of the system constant. As before we will start with writing the energy as a function of instead of volume and temperature, this time we will write it as a function of pressure and temperature.

So, the total differential as before can be written as our differential with respect to pressure keeping the temperature constant, multiplied by the finite change in differential change in pressure and then, a partial derivative with respect to temperature keeping the pressure constant, multiplied by the finite change sorry differential change in temperature d T.

Now, similarly as before, we will consider a constant pressure process.

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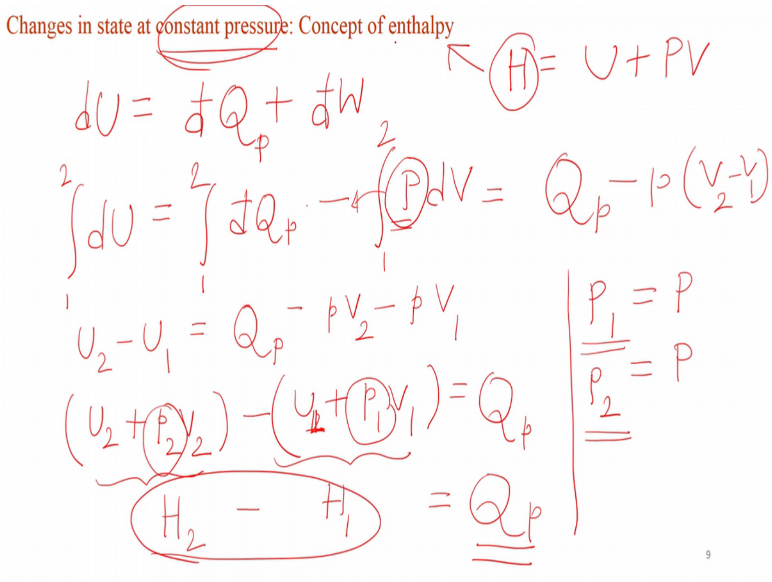

Changes in state at constant pressure: Concept of enthalpy

$$\boxed{H} = U + PV$$

$$dU = \text{đ}Q_p + \text{đ}W$$

$$\int_1^2 dU = \int_1^2 \text{đ}Q_p - \int_1^2 P\,dV = Q_p - P(V_2 - V_1)$$

$$U_2 - U_1 = Q_p - pV_2 - pV_1$$

$$(U_2 + P_2V_2) - (U_1 + P_1V_1) = Q_p$$

$$H_2 - H_1 = Q_p$$

$$P_1 = P$$

$$P_2 = P$$

So, let us write the internal energy using the First Law as d Q plus d W. In this case remember, we are considering a constant pressure process. So, I am just using a suffix P here; d U is d cross Q p plus d cross W; where, d cross Q p is the heat change associated with constant pressure process. Now if we ask this question, what will be the total differential going from say state 1 to 2, we have to integrate over each term and remember also that in this case the work done is nothing but minus P opposing into d V. But here, the opposite pressure will be nothing but the pressure of the system itself because it is a constant pressure process.

So, throughout the transformation the pressure was kept constant. So, since pressure was constant, during the change we can also keep it outside the integral. So, in our next step we will just write it as Q p; remember that we cannot write delta Q p because Q is a path function and the second integral is nothing but V 2 minus V 1. Now on the left hand side, I have a change in internal energy which we could write as U 2 minus U 1 and then, I have here the constant heat change as the constant pressure minus I have p into V 2 minus p into V 1.

Now, we can organize this in a slightly different fashion. We can write it as U 2 plus p 2 V 2 minus U 2 U 1 sorry plus p 1 V 1 is equal to Q p and in this case p 1 is the initial pressure; p 2 is the final pressure. However, p 1 is nothing but equal to P; because the pressure was constant. The p 2 is also nothing, but equal to P; because the pressure is constant. Just to maintain the equations similar looking, I am using instead of P p 2 and p 1, but the magnitude of p 2 and p 1 are equal to P.

So, we can define a new term which is H 2 and H 1 where, H is nothing but the U plus P V. Now we see that this difference H 2 minus H 1 is equivalent to the heat at constant pressure. Where, H is defined as a quantity, equivalent to U the internal energy plus pressure time's volume. So, the change in H, now is equivalent to the associated heat change at constant pressure and H this quantity we call as enthalpy.

Now note that this enthalpy must be a state function because we could write it as difference of H at 2 different states. H 1 corresponds to the enthalpy of the system when the system was in state 1 and H 2 corresponds to the enthalpy of the system, when the system was in state 2.

So, since we could write it as H 2 minus H 1 or a difference of the physical quantity at state 2 minus state 1, H must be a state function. It is not a path function. So, we got an interesting result where, we said that when we say that change in enthalpy of the system is nothing but the equivalent to the heat change at constant pressure. Now we will frequently use this concept. But before that, let us also discuss.

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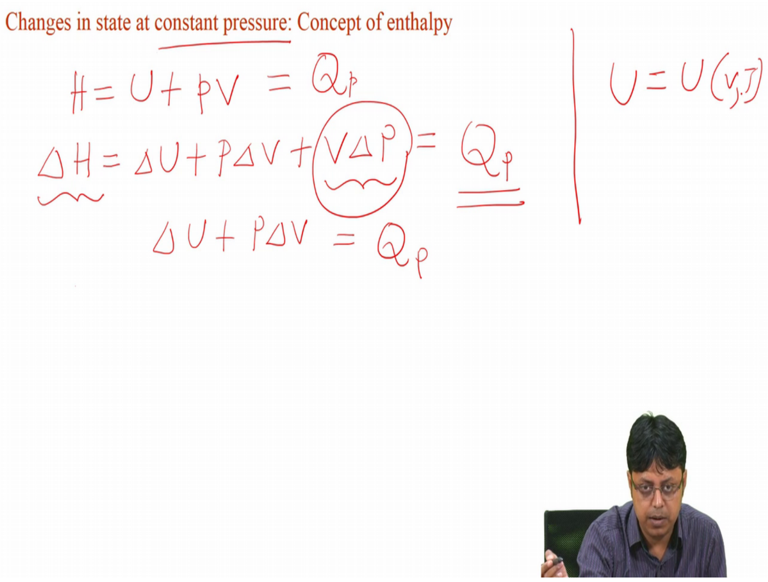

Changes in state at constant pressure: Concept of enthalpy

$H = U + pV = Q_p$

$\Delta H = \Delta U + P\Delta V + \boxed{V\Delta P} = \underline{Q_p}$

$\Delta U + P\Delta V = Q_p$

$U = U(V,T)$

So, we just defined enthalpy H as U plus p V. Now if we take the differential or the total differential of enthalpy, it must be equivalent to delta U plus P delta V plus V delta P. This is using the chain rule of differentiation.

Now, remember that this is equivalent to Q p or heat change at constant pressure. Now since, this is equivalent to heat at constant pressure, when we write delta H will write for a constant pressure process. We can actually drop this term. So, we can write delta U plus P delta V is nothing but Q p. Now let us try to understand, what is the, how a change in state at constant pressure happens?

Now as before where we wrote as U as a function of volume and temperature, in this case will write the newly defined quantity enthalpy as a function of pressure and temperature and then, compare the total derivative and write it in terms of the partial derivatives

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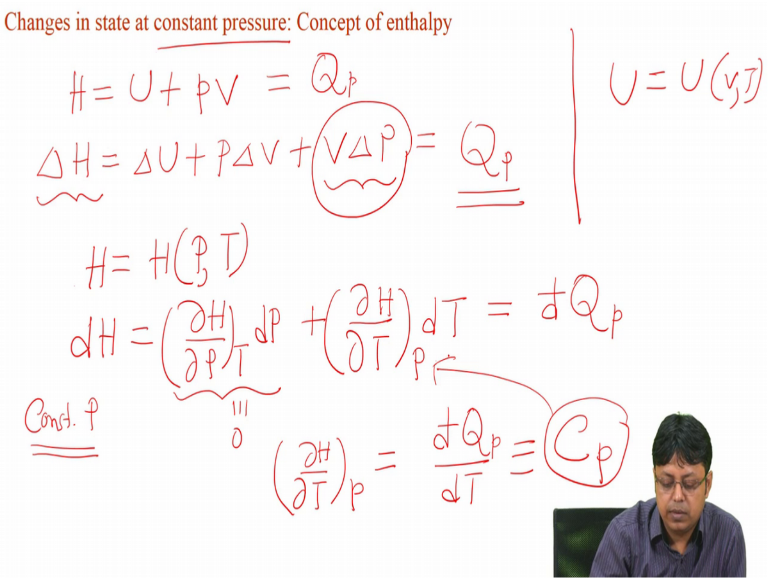

Changes in state at constant pressure: Concept of enthalpy

$$H = U + pV = Q_p$$

$$\Delta H = \Delta U + p\Delta V + \boxed{V\Delta p} = \underline{Q_p}$$

$$U = U(V,T)$$

$$H = H(p,T)$$

$$dH = \underbrace{\left(\frac{\partial H}{\partial p}\right)_T dp}_{0} + \left(\frac{\partial H}{\partial T}\right)_p dT = \text{đ}Q_p$$

Const. p

$$\left(\frac{\partial H}{\partial T}\right)_p = \frac{\text{đ}Q_p}{dT} = \boxed{C_p}$$

So, here d H is nothing but the partial derivative with respect to temperature plus partial derivative with respect to, we first write the H as a function of pressure and temperature. So, the total derivative is the partial derivative with respect to pressure keeping temperature constant, multiplied by the differential change in pressure plus the partial derivative taken with respect to temperature, keeping the pressure constant multiplied by the differential change in temperature.

Now as before we are considering a constant pressure process and then, you can easily figure out that at constant pressure this term goes to 0 and then, we know that d H and constant pressure is nothing, but d cross Q p and then we divide, if we divide both side by d T. Then, we get del H del T p is nothing but d cross Q p by d T.

Now, this quantity is nothing but heat change per unit rise in temperature, when the process is carried out at constant pressure; which means this is nothing but the heat capacity at constant pressure. Now this definition of heat capacity can be used in the original equation, where we can now write the total derivative for any process where the pressure might be constant. Now let us consider a process where we keep the pressure to be constant.

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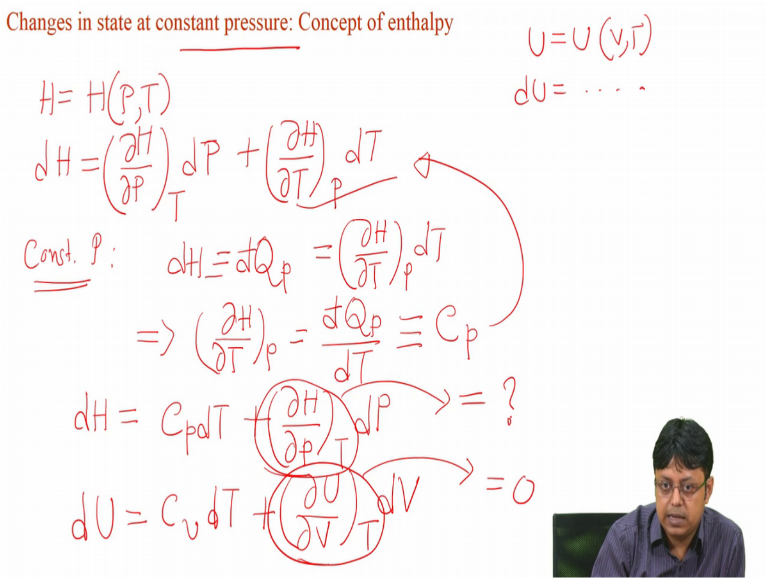

Changes in state at constant pressure: Concept of enthalpy

$U = U(V,T)$

$dU = \dots$

$H = H(P,T)$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

Const. P: $dH = đQ_p = \left(\frac{\partial H}{\partial T}\right)_P dT$

$$\Rightarrow \left(\frac{\partial H}{\partial T}\right)_p = \frac{đQ_p}{dT} \equiv C_p$$

$$dH = C_p dT + \boxed{\left(\frac{\partial H}{\partial p}\right)_T} dP \rightarrow = ?$$

$$dU = C_v dT + \boxed{\left(\frac{\partial U}{\partial V}\right)_T} dV \rightarrow = 0$$

So, just like before, we wrote the internal energy as a function of volume and temperature and then, wrote the total derivative d U in terms of the partial derivatives. In this case we will write the enthalpy as a function of volume and sorry pressure and temperature and then, write the partial derivative in total derivative of H as the partial derivative taken with respect to pressure, keeping the temperature constant plus the partial derivative taken with respect to temperature keeping the pressure constant.

Now as before, if we consider a constant pressure process then d P is 0, in that case only at constant pressure process we know d H is nothing but d Q p which is del H del T p d T. So, from that we can easily see that, this quantity del H del T p is nothing but d sorry I should used across Q d cross Q p by d T which is nothing but heat capacity at constant pressure. So, we can use this relation in the original equation and write d H is nothing but C p d T which is coming from the second term here and the other term which is del H del p T d P.

So, remember this has a very nice analogy, which we just got in the earlier case d U is C v d T plus del U del V T d V. By Jules experiment we saw that, this term is 0 and we also argued that for ideal gas, since it was 0. Since Joule showed that it is 0, the we saw from Jules experiment in the earlier case, we saw from Jules experiment that del U del V T is 0. Now the question is what is the value of del H del P T. For that, we will discuss an experiment which is known as Joule Thomson Experiment. But before that, we will discuss the relationship between these 2 quantities which is C p and C v which are heat capacities at constant pressure and heat capacity at constant volume.