Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 08
First law – part 3

Let us now find.

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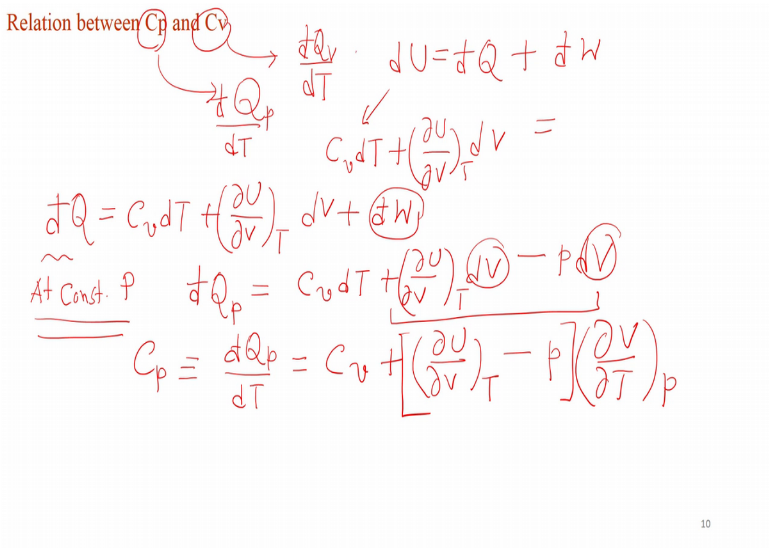

Relation between Cp and Cv

$C_p \rightarrow \frac{\text{đ}Q_p}{dT}$ $\quad C_v \rightarrow \frac{\text{đ}Q_v}{dT}$

$dU = \text{đ}Q + \text{đ}W$

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

$\text{đ}Q = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + \boxed{\text{đ}W}$

At Const. P $\quad \text{đ}Q_p = C_v dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T dV - p\,dV}$

$C_p = \frac{\text{đ}Q_p}{dT} = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T - p\right]\left(\frac{\partial V}{\partial T}\right)_p$

A relationship between **C** p and C v, C p is heat capacity at constant pressure and C v is heat capacity at constant volume. Now in order to find a relation we have to write either C p or C v in terms of associated heat change divided by the temperature for C p it is d cross Q p by d T for C v it is d cross Q v by d T.

Now we can start from the first law using d U is d cross Q plus d cross W and then we can impose some conditions where I will use the fact that d U is nothing, but C v d T plus del U del v T d v and similarly on the right hand side I can actually use the relationship for enthalpy which we just discovered. So, we rewrite this equation as d cross Q is nothing, but d U minus d cross W now d U we are writing as C v d T plus del U del v T d v plus d cross W.

Now, in order to get a relation between C p and C v I have to write this d cross Q p as C p. So, we are considering a constant pressure process. So, at constant pressure what will happen I will have d cross Q p is nothing, but C v d T plus del U del v T d v minus. Now the expression for d cross W is minus p opposing into d v, but since it is a constant pressure process the opposing is nothing, but p which is pressure of the system.

So, we can write it as minus p d v and then we can divide both side by T and define C p as d cross Q p divided by d t. So, the right hand side becomes C v plus del U del v T remember we are dividing by d T both side. So, before that we can take the d v factor common and write it as this and since we divided both side by d T at constant pressure we can write that C p is nothing, but equal to C v plus del U del v T minus p into del v del T p.

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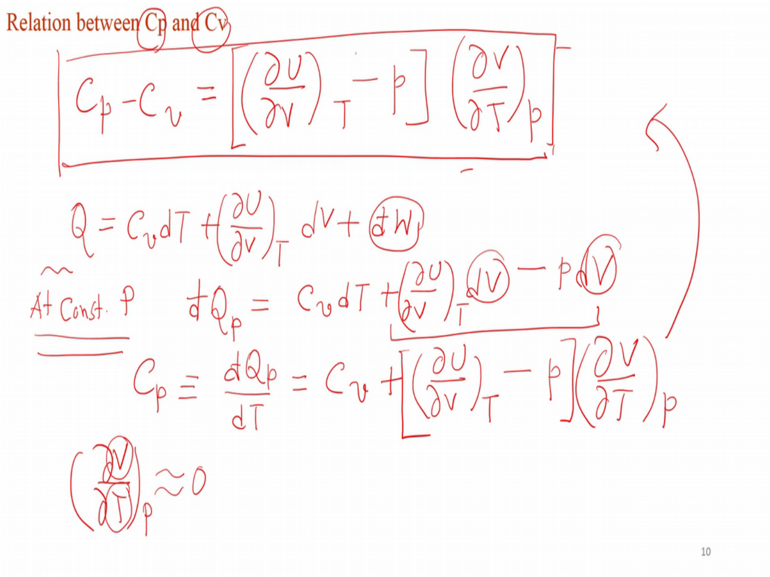

Relation between Cp and Cv

$$\boxed{C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T - p\right]\left(\frac{\partial V}{\partial T}\right)_p}$$

$$Q = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + \bar{d}W$$

At Const. P

$$\bar{d}Q_p = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV - p\,dV$$

$$C_p = \frac{\bar{d}Q_p}{dT} = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T - p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{\partial V}{\partial T}\right)_p \approx 0$$

Let me rewrite it once again and then we will discuss what are the values of C p minus C v for different systems. So, from here we are writing C p minus C v is del U del v T minus p into del v del T p now think about a solid for solid this term del v del T p which is the change in volume with respect to temperature keeping the pressure constant that will be almost negligible. So, C p minus C v for solids is almost 0.

Now, let us consider what will happen for an ideal gas.

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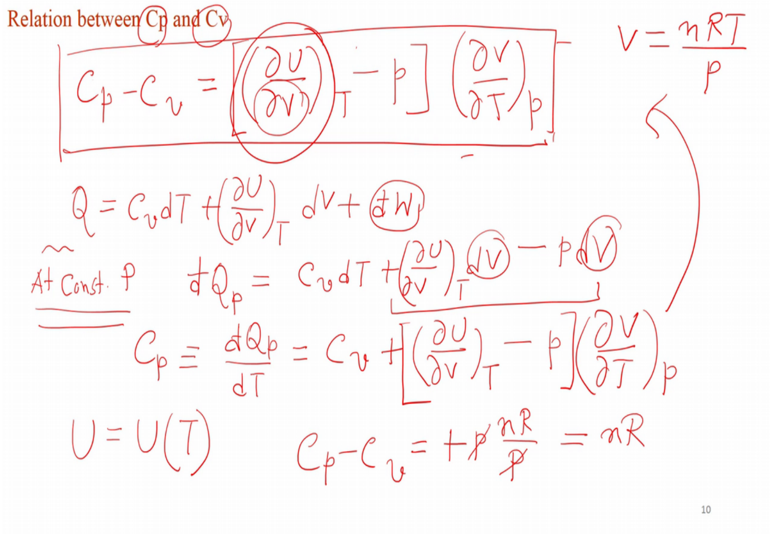

Relation between Cp and Cv

$$\boxed{C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T - p\right]\left(\frac{\partial V}{\partial T}\right)_p}$$

$$V = \frac{nRT}{p}$$

$$Q = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + \text{đ}W$$

At Const. p

$$\text{đ}Q_p = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV - p\,dV$$

$$C_p = \frac{\text{đ}Q_p}{dT} = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T - p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

$$U = U(T)$$

$$C_p - C_v = +\cancel{p}\,\frac{nR}{\cancel{p}} = nR$$

For an ideal gas we have del U del v T is 0 why because the internal energy is only a function of temperature for ideal gas and joules experiment showed that there is no change in internal energy with respect to volume. So, if the first term gets 0 then what we have what we are left with is C p minus C v is nothing, but minus p into del v del T p now what is del v del T p at that point we can use the ideal gas equation we can write v as n R T by p. So, del v del T p will be nothing, but n R by p. So, this will be n R by p with a negative sign that makes the total thing as positive, this thing gets cancelled, C p minus C v is nothing, but n R.

If we consider in terms of one mole of substance then instead of writing C p and C v.

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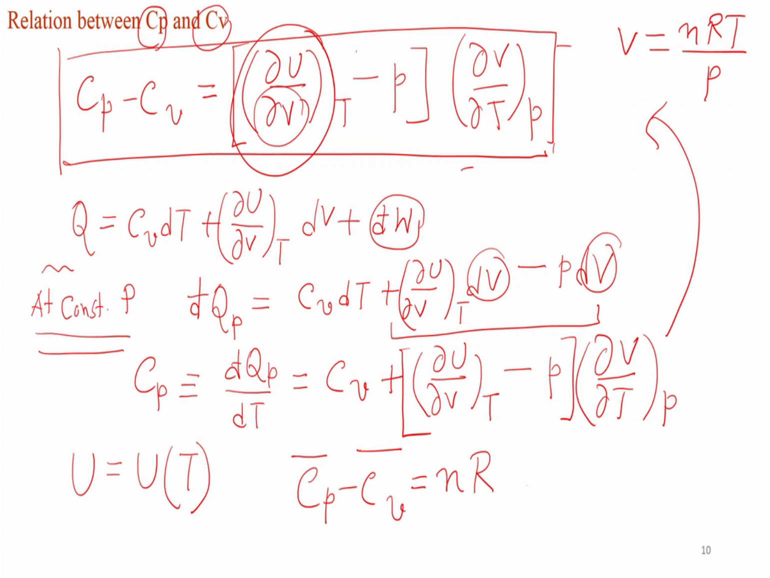

Relation between Cp and Cv

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$$Q = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + \text{đ}W$$

At Const. P $\quad \text{đ}Q_p = C_v dT + \underline{\left(\frac{\partial U}{\partial V}\right)_T dV - p\,dV}$

$$C_p = \frac{\text{đ}Q_p}{dT} = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T - p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

$U = U(T) \qquad \bar{C}_p - \bar{C}_v = nR$

We can write them as C p bar by C v bar by dividing both sides by the number of moles.

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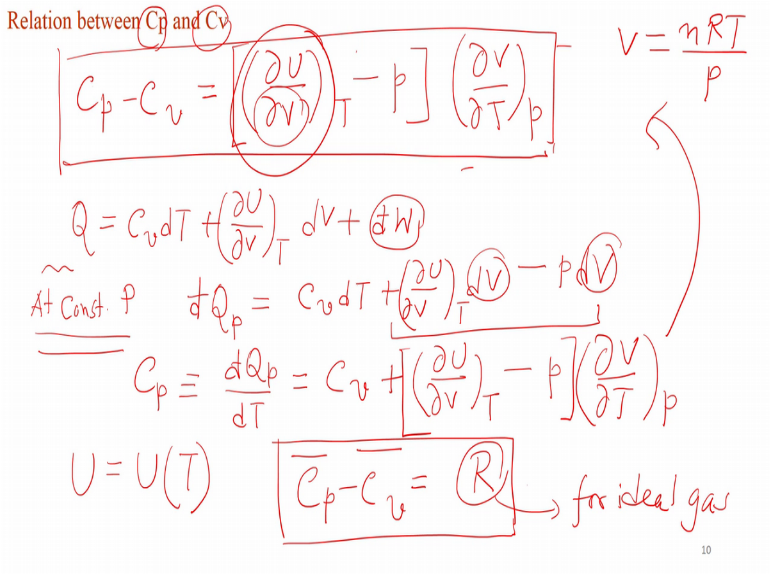

Relation between Cp and Cv

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$$V = \frac{nRT}{p}$$

$$Q = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + \text{đ}W$$

At Const. P $\quad \text{đ}Q_p = C_v dT + \underline{\left(\frac{\partial U}{\partial V}\right)_T dV - p\,dV}$

$$C_p = \frac{\text{đ}Q_p}{dT} = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T - p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

$U = U(T) \qquad \boxed{\bar{C}_p - \bar{C}_v = R} \rightarrow$ for ideal gas

So, the molar heat capacities C p bar and C v bar are related as C p bar minus C v bar is R or this molar gas constant for an ideal gas.

Now, let us discuss what happens if we do at change of the system at constant pressure.

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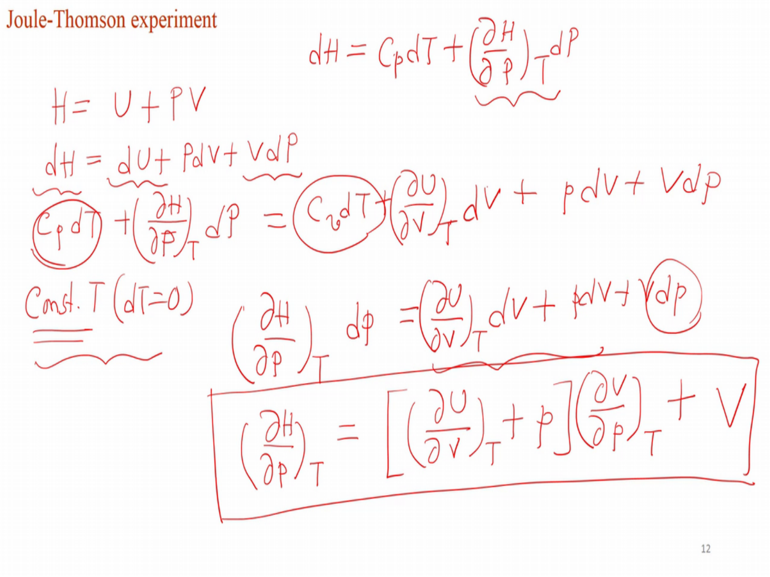

Joule-Thomson experiment

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$H = U + PV$$

$$dH = dU + PdV + Vdp$$

$$C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV + Vdp$$

Const. T $(dT = 0)$

$$\left(\frac{\partial H}{\partial p}\right)_T dp = \left(\frac{\partial U}{\partial V}\right)_T dV + pdV + Vdp$$

$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial p}\right)_T + V}$$

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We already discussed that we got a relation that the total derivative for the enthalpy is nothing, but C p d T plus del H del p T d p and we are left with the task how to measure this del H del p T for that we will discuss something known as Joule Thomson experiment, but before that let us discuss what is the total derivative for enthalpy now enthalpy was defined as U plus P V.

So, the derivative d H is nothing, but d U plus p d v plus v d p this remember that this v d p will be 0, but only for if we consider a constant pressure process now we can write this d H as C p d T plus del H del p T d p and similarly we can also write the equation for d U which was C v d T plus del U del v T del U del v p d v plus we have p d v plus v d p. Now consider a constant temperature process if we have constant temperature which means d T is 0 these 2 terms cancel these 2 terms become 0.

So, we have del H del p T d p is del U del v T d v plus p d v plus v d p as before we can divide both side by d p and keep in mind that we are doing it at constant temperature. So, this quantity del H del p T is expressed as again before I divide both sides by d p I can actually write this 2 term as del U del v T plus p times d v now we are taking a partial derivative with respect to pressure at constant temperature plus if I divide by d p this term becomes just v. So, now, we get an expression for del H del p T for any system.

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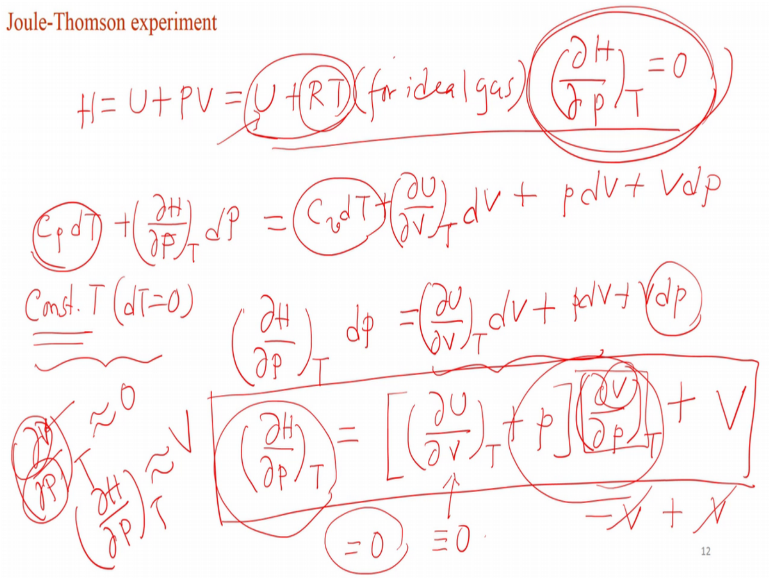

Joule-Thomson experiment

$$H = U + PV = U + RT \text{ (for ideal gas) } \left(\frac{\partial H}{\partial p}\right)_T = 0$$

$$C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p dV + V dp$$

Const. T $(dT = 0)$

$$\left(\frac{\partial H}{\partial p}\right)_T dp = \left(\frac{\partial U}{\partial V}\right)_T dV + p dV + V dp$$

$$\left(\frac{\partial V}{\partial p}\right)_T \approx 0$$

$$\left(\frac{\partial H}{\partial p}\right)_T \approx V$$

$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial p}\right)_T + V}$$

$= 0$ $\quad \equiv 0 \quad$ $-\cancel{V} + \cancel{V}$

12

Now, let us consider how this quantity what will be the value of this quantity for different system let us consider first an ideal gas. Now for an ideal gas we know that internal energy is a function of temperature only now since H is nothing, but U plus p v which is U plus R T for an ideal gas.

So, this right hand side is always a function of temperature because internal energy is a function of temperature and R T is of course, depending on temperature. So, del H del p T should be 0 because we are keeping the temperature constant. So, internal energy will not change R T will also be constant. So, their differential will be 0. So, del H del p T is 0 for an ideal gas you could also get it by a different way for an ideal gas this term is 0 as we already discussed.

Now you can carry out this quantity you just write v in terms of the pressure which will be n R T by p and then you can calculate this derivative and you will find that the answer will be minus v, this minus v cancels with this plus v and you will also get 0 if you follow this equation. So, either by following the logic that for ideal gas the internal energy is a function of temperature only we get del H del p T equal to 0 or just following the formula also we can get it 0.

Now for solids and liquids of a condensed phase what about the value of this del v del p T remember what is del v del p T it tells you the change in volume part change in part change in unit pressure keeping the temperature constant.

Now, solids and liquids are known as condensed phase where the intermolecular interactions are much more compared to gaseous phase. So, there the change in volume will be very little compared to pressure when we apply pressure, this term we can almost ignore for. So, far solids and liquids the value of del H del p T would be almost equal to v itself from this equation now let us try to understand what is the Joule Thomson experiment.

Now, already we discussed for ideal gas del H del P T is 0 similarly we saw earlier that del U del v T is also 0 and there was an experiment which we called as Joules experiment that also showed that del U del v T is zero; however, for real gases del U del v T or del H del P T is not 0. Now you may ask this question why then in Joules experiment we did not get any finite fellow for del U del a del v T which means actually why we did not see any drop in temperature.

So, the answer is that experiment was not one of the very refined experiment meaning the gas Joule used was already, diluted that it was behaving ideally.

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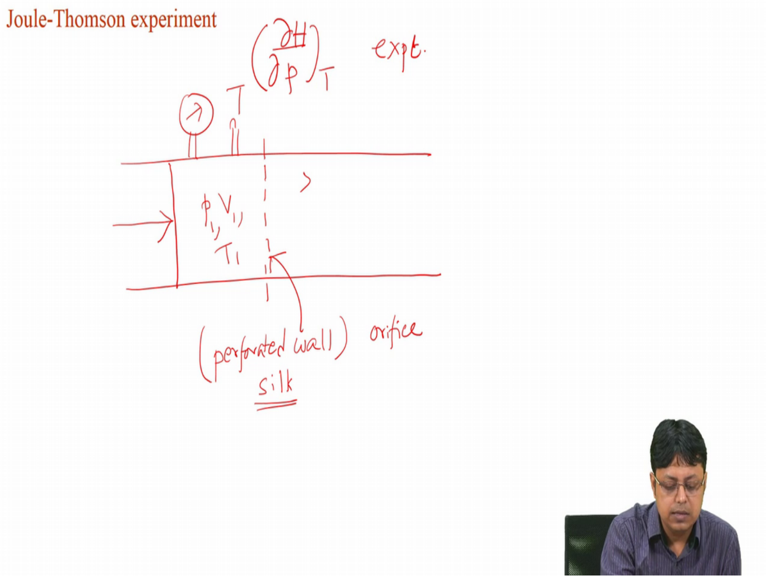

Joule-Thomson experiment

When Joule and Thomson carried out another experiment which is known as Joule Thomson experiment they figured out that there is a small, but finite change in that quantity del H del p t. So, Joule Thomson experiment discusses about measuring this quantity del H del p T experimentally. Now let us first describe what is the experiment, in this experiment Joule Thomson took a cell tube and inside the cell tube there was a wall which is a perforated wall.

What do you mean by that it is a wall through which the gas molecules can pass from one side to the other side in the original experiment they took wall made up of silk. So, it is a fine orifice or sieve kind of wall where the gas can pass through now initially they put a piston here and they applied pressure on this piston the pressure of the gas here was P 1 and the volume V1 and say that temperature was T 1 the pressure and the temperature were simultaneously measured by a pressure gauge and a thermometer.

Similarly, on the other side initially the piston was kept here very close to the wall.

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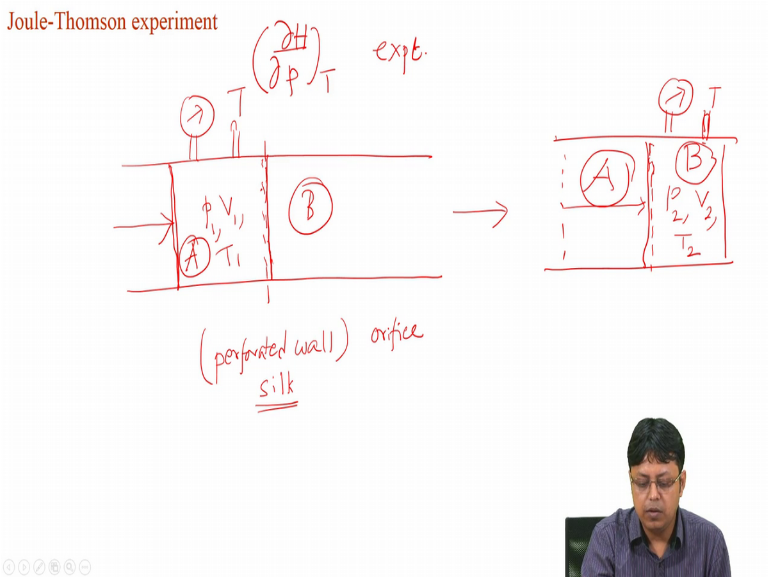

Joule-Thomson experiment

Now if you make a pressure from left to right what will happen is that eventually this piston will move from it is initial position to the wall which is a fine orifice and then the other piston will move to some distance because the gas molecules are passing through this fine orifice.

So, let us assume that the final pressure volume and temperature are P 2 V 2 T 2 for this chamber let us name this chamber as A and let us name this chamber as B and for this chamber also there was a pressure gauge and temperature and the thermometer which was measuring the temperature. So, we divided the system into 2 parts A and B which were divided by a fine orifice or a piece of silk and a piston from left to right collapsing the system A and then increasing the volume for system B that was the experiment.

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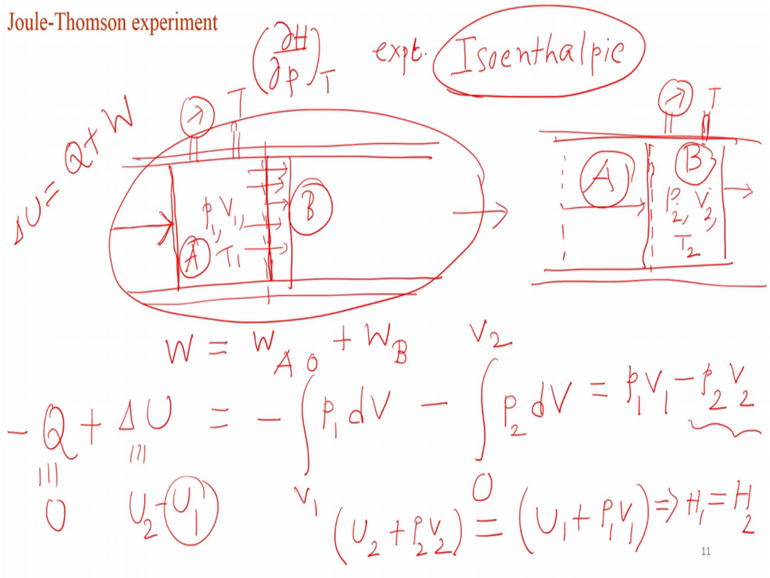

Joule-Thomson experiment

Now, initially; that means, the volume of system B was 0 and also after the experiment was done the volume of system A was 0. So, if we want to write down what was the work done in this process we can write the work done is nothing, but or the total work done is nothing, but the work done on the left hand side or we can just write it as W A and work done for the chamber B together.

Now, what was the work done for the chamber which is we denoted as chamber A. So, the expression for work done is minus P opposing into d v now what was P opposing in this case is P 1 because remember as we increase as we move the piston from left to right with some pressure the opposite pressure is always P1 because the gas molecules are living the chamber A and going to the chamber A and as a result the piston which was here initially the second piston that keeps on moving. So, the opposite pressure was P 1 times d V and the initial volume remember was V 1 but the final volume was 0 for chamber 1.

Similarly for the work done in the other chamber which is the chamber b is nothing, but P opposing into d v in this case the P opposing has to be P 2 because remember that the pressure was developed the final pressure was P 2, but it maintained the pressure so that the piston actually kept moving as we were trying to increase the pressure. So, for this chamber it is P 2 times d V the initial volume was 0 the final volume was V 2. Now we can easily rearrange it will rearrange to minus P 1 this is there is a change in volume is minus V 1, we will finally get P 1 V 1 minus P 2 V 2.

Now the work done according to the first law can be written as change in internal energy plus the associated heat change. So, remember the first law delta U is Q plus w. So, w is nothing, but delta U minus Q now in this case Q is 0 why because this entire tube was thermally insulated. So, there was no heat exchange with the surrounding.

So, we can write since U is a state function delta U as U 2 minus U 1 then we can arrange the terms what we got, we got U 2 and we can write this P 2 V 2 term together U 2 plus P 2 V 2 is nothing, but equal to we can take this U 1 on the right hand side U 1 plus P 1 field. So, what we got is that U plus P V is nothing, but the enthalpy which means H 1 is equal to H 2 in this process. So, in Joule Thomson experiment the process is called iso enthalpy because the enthalpy of the system did not change.

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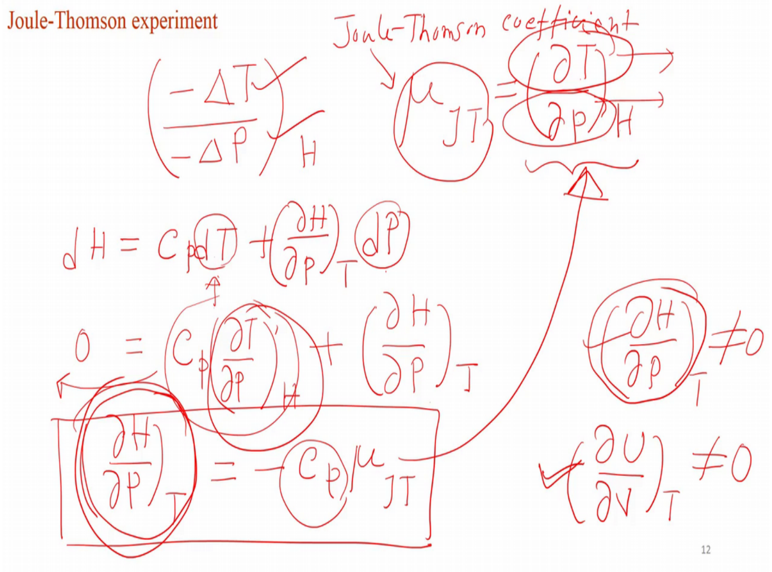

Joule-Thomson experiment

So, what joule and Thomson measured is the associated temperature drop which is minus delta T as a function of the associated drop in pressure at a constant enthalpy. So, they defined a term which they called as mu J T which is known as the Joule Thomson coefficient and defined it at the change in temperature as a function of pressure for a constant enthalpy process which was carried out in there or measured in their experiment now what will be the expression of del T del P H.

Now, remember since it is a partial derivative of enthalpy temperature with respect to pressure with keeping the enthalpy constant we can just start with the equation of enthalpy that d H is C p d T plus del H del P T d p. Now what we have to show here is this term, we can easily get it by taking by taking derivative del T del p means actually we have to divide both sides by d p and somehow write this term as del T del P for constant enthalpy if the enthalpy is constant the left hand side becomes 0 and if we divide both side by d p will get C p del T del P at constant enthalpy plus del H del P T.

So, we got a very interesting relationship del H del P T is nothing, but minus C p because we are moving this term on the left hand side and this term was already defined as mu J T. So, Joule and Thompson did this experiment where they measured mu J T by measuring the change in temperature as a function of pressure and they are measuring the temperature drop as a function of pressure drop as is shown here and C p was of course, known for a gas and then if you measure mu J T.

Then you can measure this quantity del H del P T, this del H del P T was found to be small, but a nonzero quantity for real gases similarly if one does a very defined experiment then one can also show that del U del v T for real gases is actually nonzero for ideal gas either del H del P T or del U del v T both are 0.

So, far what we have discussed is as follows we first discussed the statement of the first law and how the mechanical equivalence of work leads to the statement of first law as the for any cyclic process the work done must be equal to the heat return from that we got a very interesting concept which we termed as the energy or the internal energy of the system. Then we considered the change in volume for a process and we got a beautiful relation for the total differential of the internal energy connecting it with C v the heat capacity at constant volume.

Similarly, for a constant pressure process we define another quantity H which is U plus p v and just like the U or the internal energy it was also a state function and then we talked about the relationship between the total differential d H connecting it to C p which is heat capacity at constant pressure. Then using those relations we got a relationship between C p and C v what is the difference between heat capacity at constant pressure minus heat cost and heat capacity at constant volume we found for ideal gases for one mole of the ideal gas this will be the difference will be nothing, but equal to the molar gas constant and then we proceed it and try to figure out what is the value of this quantity del H del P T for ideal for a real gas for that we described what is known as Joule Thomson experiment which was basically carried out for a sealed tube which is thermally isolated and which is divided the 2 portions of the tube are divided as A and B by fine orifice or in this original experiment they used a piece of silk and then we discussed how movement of the piston from one side moves the piston on the other side and then how the associated drop in temperature and pressure can be measured to define a quantity which we called as Joule Thomson coefficient and then.

If one measure the Joule Thomson coefficient experimentally with Joule and Thomson did in their experiment then one can also measure del H del P T which is small for real gases similarly one could also measure del U del V T using joules experiment although joule did not find any noticeable change in temperature, but later on people found by refined experiment that del U del V T is also nonzero for real gases.