Chemical Engineering Thermodynamics
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Lec 09
First law of thermodynamics for closed system: Ideal gas behavior

Welcome back, in this lecture we are going to look at the first law of closed systems and discuss the ideal gas behaviour and equation and then will be trying to solve some two examples and basically to straight learning which we have till date.

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So, we have already discussed in last lecture the first law, now putting it in a formal way here.

$$\Delta E = Q + W$$

Now as we have already discussed this the Q and W are basically the interaction between the system and surrounding and that occurs at the boundary and that is why it is called boundary phenomena.

In the differential form one can write this same expression in this way: $dE = \delta Q + \delta W$

where dE is it exact differential whereas delta here is indicative of path function and this is indicative of straight function. So, this would your inexact differential which is basically due to the path functions of the terms, which are heat and work which are boundary phenomenon.

So, if you consider composite system and surrounding then in that case the change in universe, energy of the universe remains constant that is what is reflected here:

$$\Delta E_{system} + \Delta E_{surrounding} = 0$$

We already know that the work the way we have define the work done on the system is basically positive. $W_{system} = -W_{surrounding}$

Hence, $Q_{system} = -Q_{surrounding}$

Now let, I just review that ideal gas there is something which we have already done earlier. In the engineering thermodynamic course, but we are trying little bit to recall those concepts because we are going to use this in one of the examples. Now ideal gas typically occurs at where varies operation in fact at pressure approaching to 0 all the systems all the fluids starts behaving like ideal gas because the volume is infinitely large, particles are far apart, they density it is extremely small and they do not feel each other an essentially they behave like a non- interactive system.

So, if you want to do a simple experiment one can consider helium containing in this piston cylinder system where one can put the piston cylinder device at the different temperature and the temperature which we consider is that of boiling water or an ice it is observe that this two points fall on line approaching towards zero value. When we plot this point on a curve is molar volume as function of temperature.

If you change the pressure of the system by varying the piston weight other surrounding pressure even is kept in very low pressure we will see the slopes are different but all of them intersect at V is equal to 0 and T is equal to 0. So, this is basically the behaviour of ideal gas and occurs at extremely low pressure and any of this line can be an ideal gas which can be used for temperature based on the basic reflection of this observation.

One can make use of these two very simple expressions that is PV by T can be shown can be shown to be a constant. Now you can also vary the number of moles and you can show that PV by NT is nothing but again a constant which we call a gas constant. and this is basic relation of ideal gas law.

$$\frac{PV}{T} = constant$$

$$\frac{PV}{NT} = constant = R$$

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Or it is also called equation of state which is any equation that relates pressure temperature specific volume of a substance and the simplest as we already seen is the equation of state for the ideal gas that is the ideal gas equation. So, this equation predicts PVT behaviour of gas quite accurately within some properly selected region and this is somet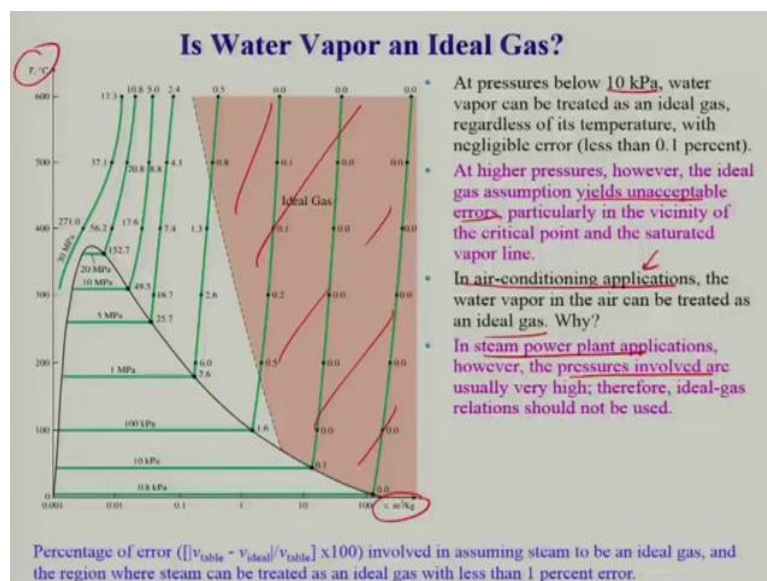hing which we are going to discuss that when then fluid starts behaving like an ideal gas but as per as ideal gas is concern you have very specific relation that is your ideal gas relation which is P, molar volume and RT.

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Now, you ask the question will that helium for nitrogen or for similar kind of molecule fluids or atomic fluids, they can be treated as ideal gas at normal conditions, normal temperature

pressure but what about the water, so if you consider particular plot which is the temperature against the specific volume then what is observed that at this region which is a shaded region, this is where the water vapour because is it supper heated vapour, this region can be consider or fluids within this condition behaves like an ideal gas.

So, at pressure below 10 kilo Pascal water vapour can be treated as ideal gas regardless of the pressure with a negligible error. So this is something which is clear and this is something which you can also try to prove it by considering simple PV RT and plugging the values of molar volume for a given pressure and temperature and comparing this with a steam data which you can take it from the steam table.

So this is quite illustrative also because it also tells you that at very low pressure because this is like 0.8 kilo Pascal, this is 10 kilo Pascal so at low pressure all the fluids are behaving like an ideal gas or extremely at high temperature which is here this temperatures are going to be extremely high, still it behaves like an ideal gas.

So, at high pressure however the ideal gas assumptions yield unacceptable here because at high pressure you essentially start looking at, if you compare the high pressures this would be the conditions of high pressure so what happens at that in this case the particles are close enough and they starts interacting and hence they cannot be represent as an ideal gas. So now that leads to another simple question that in air conditioning application the water vapour in air can be it is an ideal gas, based on this data you can say that will yes because usually this are at low pressure.

However, in stem power plant application you cannot consider because pressures involved very high and therefore the ideal gas relationship for water are not use and that is the reason that you have to consider steam tables more carefully for the use for the application of steam power plant based problems.

In order to find out the deviation from the ideal gas a common terminology or common factor which is a use or the variables which is use compressibility factor and this is something which is one can see here, so this is nothing but Z which is ratio of PV by RT, so for an ideal gas this is going to be 1, for real gases it can be less than 1 or greater than one. Z basically anything away from Z is equal to 1 indicates deviation from ideal gas behaviour so, as I said gases behaves as an ideal gas at low density which is low pressure high temperature.

$$Z = \frac{PV}{RT}$$

$$Z = \frac{V_{actual}}{V_{ideal}}$$

So, the question is what the definition is lower and the high pressure and temperature ok how do you define low and high is always relative because even an 300 kelvin may be very high for CO2 or N2 but will be very low for polymer, in order to behave as a the gas, so it is always relative to something and that relative is nothing but the critical point so the pressure or temperature of a gas is high or low relative to it is critical point, that is something which one should remember.

So, as I was mentioning earlier the real gas, any real gas starts behaving like an ideal gas as the pressure, pressure towards 0 and basically what happens the particles at this condition are very

far from each other and hence, they do not effect this properties that can be consider as non-interactive system which is nothing but ideal gas.
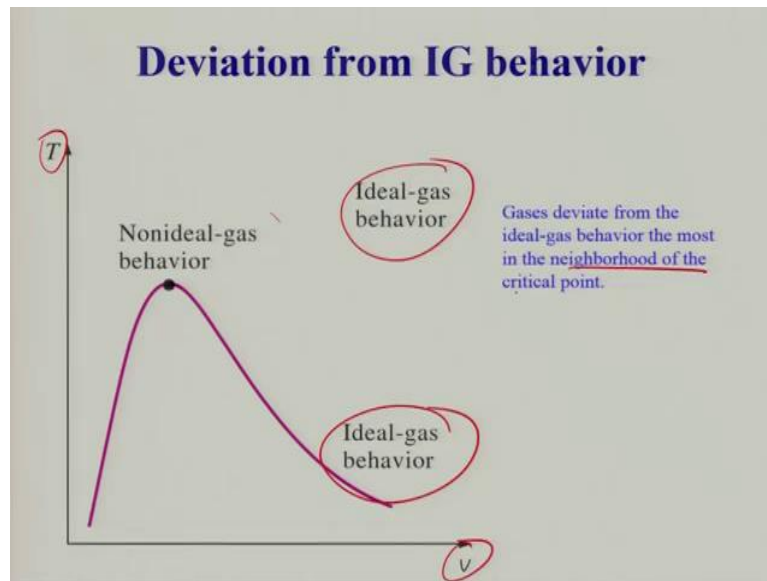
So, this is what you can describe the behaviour of the fluids in a simple schematic form, this is temperature against specific volume, typical ideal gas behaviour will be here and here as well but certainly not here because in this region you have high pressures are very high, ok, and the temperature and pressure with respect to the critical point is very high. So, whereas this is very low as per as the condition are concern with respect to the temperature or with respect to the critical temperature or pressure. So the gases deviate from ideal gas mostly in the neighbourhood of the critical point.

So let us now get to the little bit making of this understanding to solve some problem. Let us write down the basic thing again so, we have the equation of state PV is equal to NRT we know R is nothing but the 8.314 joule per mole kelvin. Now mainly we do not use most of the time in terms of absolute value of internal energy in general properties, we use the usually then the molar form or specific form.

So that is what we are going to use that but before we move to that point I would like to make a statement here that for ideal gas the energy or enthalpy is just a functional temperature because the temperature brings a kinetic energy and since they are not interacting anything so only the kinetic energy changes so internal energy is nothing but simply the kinetic energy of the molecules here.

If it is a monoatomic molecule, if it is of course vibration and other things are there, you have to worry about that as well. Now so, that why it is just a function of temperature, now you can consider this U in terms of molar form, so, $U^{IG} = Nu^{IG}(T); \ u^{IG}(T) = U(T)$

So, let me read this as well because this is something I mentioned that ideal gas molecules do not have interaction energy, that means they do not have potential energy as well as molecule potential energy they do not interact and that is why they do not feel each other, if you bring two ideal gas they pass through each other without feeling it and thus, the total energy nothing but the sum of individual energy molecules which is intermolecular energy that includes the translation rotational vibration and so forth.

Now, consider an ideal gas in rigid container. If you consider a simple ideal gas here and this is a rigid so whatever the change in energy of the system will be whatever the delta Q been provided to the system because being rigid the delta W is going to be 0. So, if you consider del dU this is going to be del Q and this dU is now defined as the we are going to introduce new thing new variable is here that is N number of mole multiply by heat capacity multiply by DT.
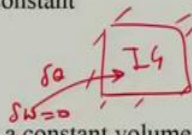
$$dU^{IG} = \delta Q = NC_V^{IG} dT$$

So, we are introducing a new quantity heat capacity, this is at constant volume that is the example which we are considering. So, $C_v^{IG} = \frac{dU^{IG}}{NdT} = \frac{dU^{IG}}{dT}$

So, you can measure this heat capacity experimentally as well as theoretically. Now each degree of freedom contributes R/2 to heat capacity, so for simply monoatomic ideal gas, $C_v^{IG} = \frac{3R}{2}$ only three translation degree of freedom for monoatomic gas because it can only translate so, X, Y, Z, you have and hence every dimensions, every dimension leads to R by 2 contribution to heat capacity.

But if you have a complex molecule the rotational vibrational and it also contribute to heat capacity. Now, as we say that the gases behave as ideal gas as low density so as the density increases molecule starts feeling the presence of other molecule, so internal energy is not anymore dependent only on temperature but also a density. So, this is for real gas the internal energy is not just dependent on temperature but also on density, but in general one can write CV as definition assembly a partial derivative of U with respect to T.
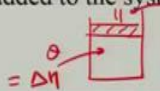
$$C_v = \left(\frac{dU}{dT} \right)_V$$

Not the complete derivation but simply this is only for ideal gas but for the K for the fact that CV is not just the dependent on T for the real gases but also another variable that is density you have to consider partial derivative with respect to T as a definition of CV in general. So, as I said we can measure the heat capacity directly from experiment one can think of simple experiment and then measure the volumetric property as a function of pressure and temperature.

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The Ideal Gas: heat capacity at constant P

Consider a Piston-Cylinder system, heat being added to the system such that piston volume increase by ΔV

$dU = \delta Q + \delta W$ $-pdv$

$= \Delta H$

Here work is done by the system

$\Delta U = Q - P\Delta V$

$Q = \Delta U + P\Delta V = \Delta H$

So, at constant P, heat capacity of an IG is defined as

$C_p^{IG} = \dfrac{dH^{IG}}{dT}$

$C_p^{IG} = C_v^{IG} + R$

In general : $C_p = \left(\dfrac{\partial H}{\partial T}\right)_P$

At non-ideal consider, the relationship is more complex

We will come back to this again but let us first consider the case where we are allow the volume to change but keeping the pressure constant so this is going to be again piston cylinder system where heat is being added, where heat is being added to the system so that the piston volume increases by delta V in that case you can make use of first law here and here dU is equal to del Q plus del W, once you provide the heat the piston moves upward.

Because of the expansion of the gas and hence work is done by the system so, in that case del W is nothing but minus PDV. So, if you consider increment by delta V this expression will be Del U is equal to Q minus P delta V. So you can rearrange and you can write:

$Q = \Delta U + P\Delta V = \Delta H$

So, at a constant pressure, this is a constant pressure which essentially means you keeping outside pressure constant and the weight of the piston of course can be massless or with certain mass, it does not matter as long as the pressure is constant. So at a constant pressure the heat

capacity can be shown or at constant pressure heat capacity is defined as nothing but the differential of a molar enthalpy with respect to T.
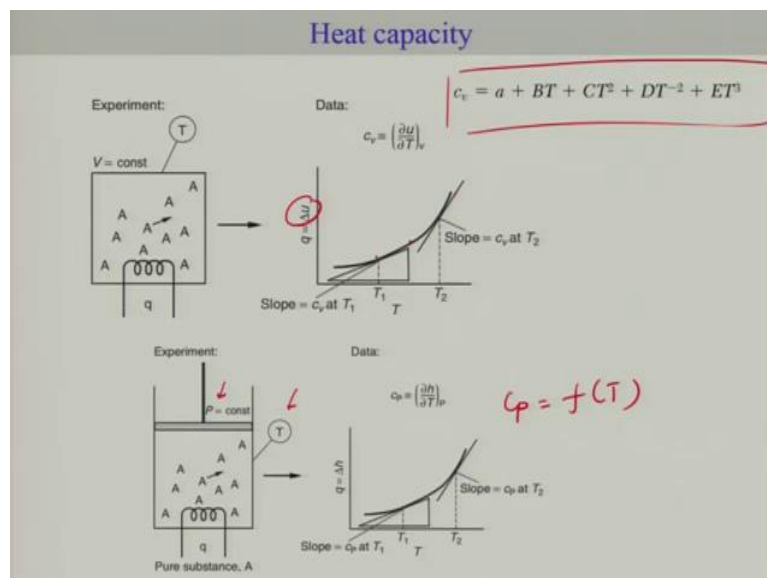
$$C_p^{IG} = \frac{dH^{IG}}{dT}$$

$$C_p^{IG} = C_V^{IG} + R$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

The partial derivative with respect to T at a constant volume so, considering the molar properties here.

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Alright so, as a I said we can do next experiment, so we can try little bit of here to understand how to do that, so in the case of CV you are providing heat at constant volume, we are measuring temperature, so, in this case whatever Q we are providing is nothing but the change in internal energy so, we plot that as function of the temperature which we try to measure the temperature and then we can observe this this may appear to be this kind of curve.

Now CV is nothing but slope at each different point so, you have one particular CV here at this temperature one is here and so far. So, in reality CV is not only constant is going to vary as temperature vary and hence you have something like this polynomial expressions which

usually is used and is plugged in form of table so, you every steam table or thermodynamic property table will have CV values for different gases as will.

$$c_v = a + BT + CT^2 + DT^{-2} + ET^3$$

Similarly, you can also do that for similar kind of experiment for to calculate CP so, here you have providing heat and then you have a piston, pressure is constant so again you have sense of temperature and in this case what you measuring is Q is nothing but directly delta A so, whatever Q you are providing you can simply plot that as a function of temperature by measuring T and again you get some kind of curve.

Here again you can measure take a slope at each point and you can get a this as a function of temperature and again you can come up with the expression like this, so again where is different polynomial expression are being calculated for different gases and those are part of table which are widely available.

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Now, let us consider an example of ideal gas particularly adiabatic expnasion. We would be coming with an expression relevant for such a case. So, here what we are considering is a adiabatic expansion with a constant and the reason why we are doing this because it leads to very useful expression and for many different physical systems where one can approximate the process of adiabatic expansion so, let us consider dU as we know from the first law.

$$dU = \delta W = -pdV$$

$$Nc_v dT = -pdV$$

Ideal gas equation of state, $V = \frac{NRT}{P}$

$$C_V dT = -pd\left(\frac{RT}{p}\right) = -RdT + \frac{RT}{P}dp$$

$$(C_V + R)dT = \frac{RT}{P}dp$$

Since, $C_P + C_V = R$

$$\frac{dT}{T} = \frac{R}{C_P}\frac{dP}{P}$$

Now, one can integrate this so from T_0 to T, and corresponding value for P is from P_0 to P, we

get: $\quad \dfrac{T}{T_0} = \left(\dfrac{P}{P_0}\right)^{\frac{R}{C_P}}$

We define, $\dfrac{C_P}{C_V} = \gamma;\ thus,\ \dfrac{R}{C_p} = \dfrac{\gamma-1}{\gamma}$

Hence, $\dfrac{T}{T_0} = \left(\dfrac{P}{P_0}\right)^{\frac{\gamma-1}{\gamma}}$

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Ideal Gas: Adiabatic expansion

Now, if we eliminate pressure,

$$dU = NC_V dT = -PdV = -\frac{NRT}{V}dV$$

$$\frac{dT}{T} = -\frac{R}{C_V}\frac{dV}{V}$$

$$\frac{T}{T_o} = \left(\frac{V}{V_o}\right)^{-\left(\frac{R}{C_V}\right)} = \left(\frac{V}{V_o}\right)^{1-\gamma}$$

Now, if you note that this is something which you are not using molar and this is go volume, so this further can be shown to this to be molar volume also or you can use specific volume both will work in this case. So, that was an example or rather making use of an ideal gas expression particularly for adiabatic expansion. So, we can continue with another example but I will stop here and will continue in the next lecture with another example particularly some engineering examples, which is this one and we will stop here and continue this with the next class.