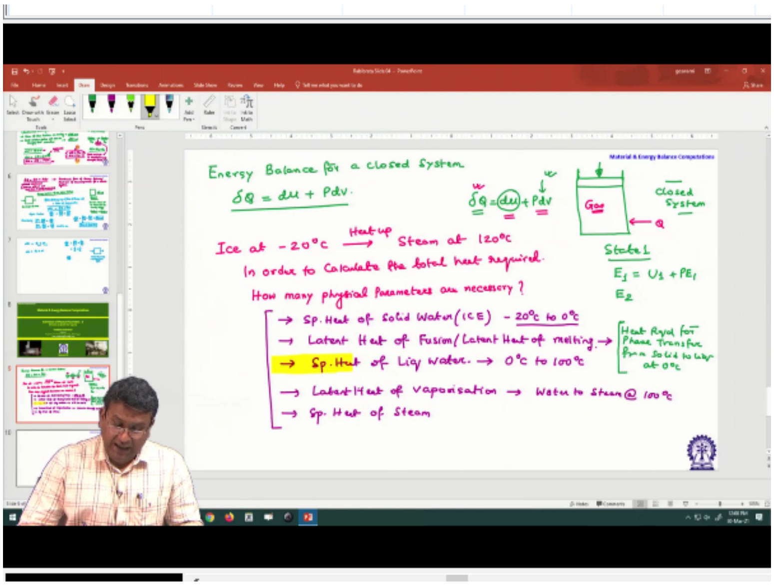
Material and Energy Balance Computations
Prof. Rabibrata Mukherjee
Department of Chemical Engineering
Indian Institute of Technology-Kharagpur

Lecture-42
Estimation of Physical Parameters-I

Welcome back. In the previous lecture we have studied finally the first law of thermodynamics. So, we now know what is the functional form of first law of thermodynamics. And, this is important for us because the name of the course is material energy balance computations. So, in order to do the computations, first we need to have the constitutive law. We took a lot of time to reach at the equation which could have been done in two classes but I hope now you understand all the nitty gritty issues associated with this equation and stuff like that.

(Refer Slide Time: 00:48)



Material & Energy Balance Computations

Energy Balance for a closed system

$\delta Q = du + Pdv$.

$\overset{w}{\delta Q} = \boxed{du} + \overset{w}{Pdv}$

State 1

$E_1 = U_1 + PE_1$

E_2

Ice at −20°C $\xrightarrow{\text{Heat up}}$ Steam at 120°C

In order to Calculate the total heat required.

How many physical Parameters are necessary?

- → Sp. Heat of Solid Water (ICE) − 20°C to 0°C
- → Latent Heat of Fusion/ Latent Heat of melting → Heat Reqd for Phase Transfer from Solid to Liqr at 0°C
- → Sp. Heat of Liq water. → 0°C to 100°C
- → Latent Heat of vaporisation → Water to Steam @ 100°C
- → Sp. Heat of Steam

So, what are the components that we have in the first law of thermodynamics? For a closed system, we have $\delta Q = du + Pdv$. So, what are the thing that can happen in a closed system? So, initially let us say the system is at state '1' and it is associated with some energy let us say $E_1 = U_1 + PE_1$.

Of course, it has some potential energy (PE_1) because whatever elevation it is at, it will certainly have some potential energy. Here, you can essentially have a piston cylinder system as described in the above slide with a piston at the top which can be compressed or pushed up. When the piston is pushed into the cylinder or the gas inside it is compressed, we are applying some energy from outside. So, in that case $dv \neq 0$;

This might lead to some heat generation or may not lead to heat generation depending on the condition you have because one of the problems we have looked into the work, you can undergo a process under isothermal condition or non isothermal condition.

So, in case the piston moves in a non isothermal condition then du even will be non-zero. So, you might be essentially required to change in the delta u and from there you find out E_2. The assumption is whatever you do, the potential energy does not change.

Or, what can be the other types of problem? The other type of problem can be like heat is supplied from outside. So, first thing is 'δQ' term will be non-zero and as a consequence of that two things can happen. If this boundary is flexible, so what will happen? This is a classical problem. Let us say you have a gas and you are supplying heat from outside. So, the temperature of the gas will go up but simultaneously its volume will also expand. So, in case you heat up a cylinder from outside, so what will happen the internal energy will go up as well as it will do some work. So, this might lead to increase or change in this as well as this. But in order to estimate how much amount of temperature goes up, or what is the amount of work done etcetera we will need to know the specific heat capacity of gases. So that we can essentially estimate the heat applied or temperature increased by a very simple formula like $mC_p\Delta T$.

So, let us say you have a block which weighs 50 kg whose specific heat capacity C_p is given and it is heated from 30°C to 70°C. So, the total heat required is $mC_p\Delta T$. However, you can only solve this problem because of the fact that the value of C p is given. But in real life, when you go to the field or go to the plant, you might encounter with a new compound or a new material whose C_p value is not there or other physical properties are not there. So, we are all very well trained to solve problems in the examination setting where all the physical parameters are given. But in real life in many cases the physical parameters themselves are not given. So, what will you say? Well I do not know the physical parameters and therefore I can't do any calculation!! Unfortunately, in engineering that is not accepted. Because we are all engineers and to engineers the fundamental approach that we have is something is better than nothing. So, we always will try to come up with some first guess or fast approximation of these physical parameters as well. And there are certain cases where some relatively good guesses or good first approximations can be done based on other properties.

So, let us try to focus on that. why at all we need to bother about these properties? So, now, let us also look into the whole heating problem. Let’s say we have ice at -20°C and you would like to heat it all the way to steam let us say at 120°C. And, this can very well be done in this particular piston cylinder set up.

So, you have some ice, and you heat from outside. So, in order to calculate the total heat required, you can all start guessing how many physical parameters I need. Well, essentially five physical parameters; if you think carefully five physical parameters will be necessary to fully define this problem or fully solve this problem. What are these? Number one is specific heat of solid water or ice.

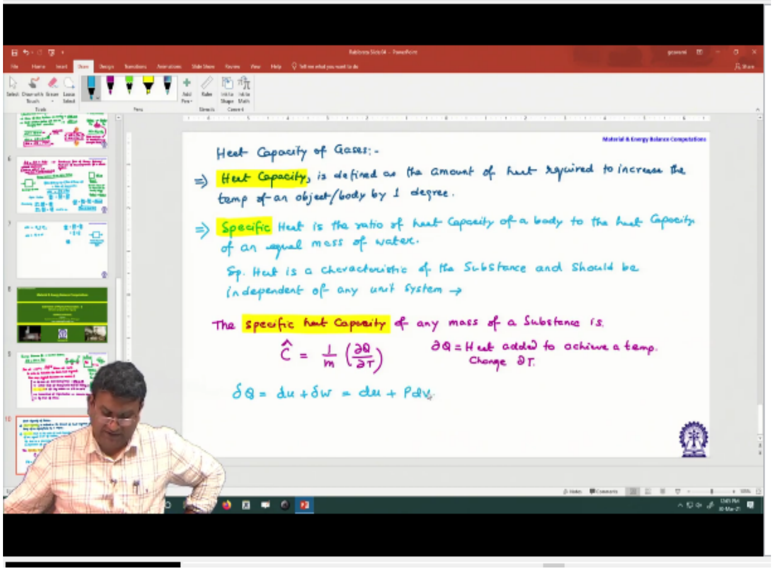
So, let’s say we do this whole experiment at 1 atm pressure. So, then for calculating the heat required for heating of ice from -20°C to 0°C, you essentially require first the latent heat of fusion or latent heat of melting, then you will be needing the specific heat of liquid water (if it is a constant value it is good, in most cases it is constant for water at least it is constant).

Essentially, what does it take care? So, this is for heating of liquid water from 0°C to 100°C, what does this thing take care about it? This thing takes care about the heat required or energy required for phase transition from solid to liquid at 0°C. And, next we will be needing the latent heat of vaporization. For water most of you know the value also, so this is again phase transition from liquid water to steam at 100°C and then you will be needing the specific heat of steam.

So, we have already talked about water but you might encounter the entire process or part of this process for a non reacting system. Of course you need to understand that though there is change of energy etcetera, etcetera. This is a non reacting system. There is no reaction going on. Because if there is reaction, all of you know that reactions can be of two types: exothermic and endothermic. So, that is also associated with some change in energy which we will talk after few lectures in this course only.

But as of now we are talking about non reacting system and for any other material you might be essentially looking into this type of a problem or part of this problem; maybe you can heat up let us say solid iron from 300°C to 700°C then there is no phase change. Then you are essentially looking only at this part of the problem for whatever material you are looking at. So, in this chapter quickly what I will try to give you is some rules of thumb or some empirical formula or some logical formula that exist for estimating these specific heat capacities or the latent heats etcetera.

(Refer Slide Time: 11:17)



Heat Capacity of Gases:-

⇒ Heat Capacity, is defined as the amount of heat required to increase the temp of an object/body by 1 degree.

⇒ Specific Heat is the ratio of heat Capacity of a body to the heat Capacity of an equal mass of water.

Sp. Heat is a characteristic of the Substance and Should be independent of any unit system →

The specific heat Capacity of any mass of a Substance is.

$$\hat{C} = \frac{1}{m}\left(\frac{\partial Q}{\partial T}\right)$$

∂Q = Heat added to achieve a temp. Change ∂T.

$$\delta Q = du + \delta w = du + Pdv$$

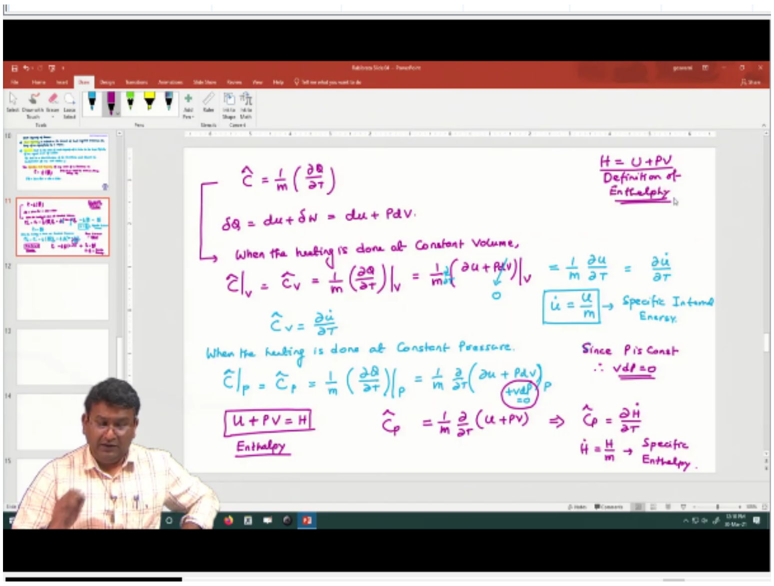
Now, in order to sort of make the discussion complete, let us quickly define what is meant by heat capacity of gases. So, heat capacity of gases is in general sense, heat capacity, this you all know, but I for the sake of completeness I am just writing it down, is defined as the amount of heat, this you have been doing from your high school science, amount of heat required to increase the temperature of an object or body by 1 degree.

So, these we all know, this is what is heat capacity. Now, the next thing is, what is specific heat? Specific heat is the ratio, this is important actually ratio of heat capacity of a body to the heat capacity of an equal mass of water. Specific heat is a characteristic of the substance and just like specific gravity the word ‘specific’ means that it should be independent of any unit system; though it might depend on temperature of the substance.

So, let us not talk about that. However, in most cases we actually write the heat capacity as the specific heat capacity and often it is mentioned as the specific heat. So, when we write C_p for example for a substance or C_v for a substance it actually comes with an unit. So, this C_p, C_v whatever these are though they are defined as the specific heat. In many cases we actually refer to the specific heat capacity.

So, the specific heat capacity of any mass of a substance is C^ = 1/m (δQ/ δT), where T is temperature. So, 'δQ' is the heat added to achieve a temperature change 'δT'. Now, we know that δQ = du + δW = du + Pdv (as explained in the following slide).

(Refer Slide Time: 16:44)



$$\hat{C} = \frac{1}{m}\left(\frac{\partial Q}{\partial T}\right)$$

$$\delta Q = du + \delta W = du + PdV.$$

When the heating is done at Constant Volume,

$$\hat{C}\Big|_V = \hat{C}_V = \frac{1}{m}\left(\frac{\partial Q}{\partial T}\right)\Big|_V = \frac{1}{m}\frac{\partial}{\partial T}\left(\partial u + \underset{0}{\cancel{PdV}}\right)\Big|_V = \frac{1}{m}\frac{\partial u}{\partial T} = \frac{\partial \dot{u}}{\partial T}$$

$$\boxed{\dot{u} = \frac{u}{m}} \rightarrow \text{Specific Internal Energy.}$$

$$\hat{C}_V = \frac{\partial \dot{u}}{\partial T}$$

When the heating is done at Constant Pressure.

$$\hat{C}\Big|_P = \hat{C}_P = \frac{1}{m}\left(\frac{\partial Q}{\partial T}\right)\Big|_P = \frac{1}{m}\frac{\partial}{\partial T}\left(\partial u + PdV \underset{=0}{+VdP}\right)_P$$

Since P is Const
$\therefore$ VdP = 0

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

Enthalpy

$$\hat{C}_P = \frac{1}{m}\frac{\partial}{\partial T}(u + PV) \Rightarrow \hat{C}_P = \frac{\partial \dot{H}}{\partial T}$$

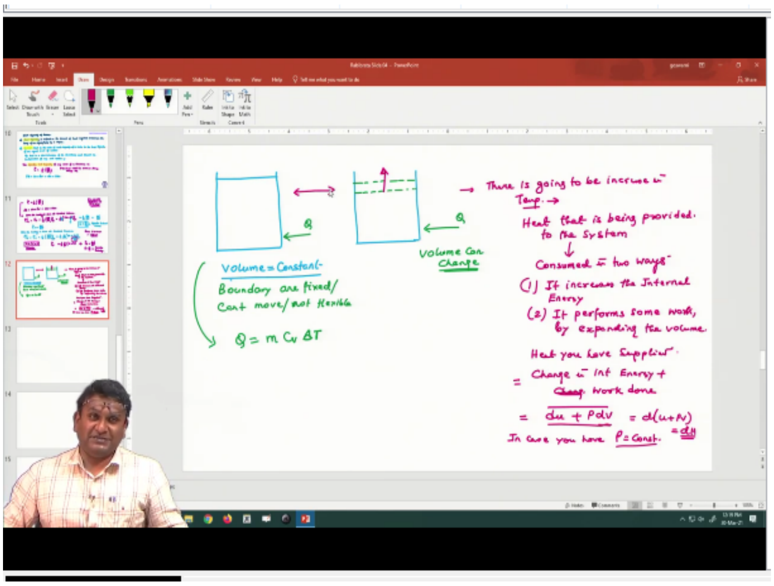
$$\dot{H} = \frac{H}{m} \rightarrow \text{Specific Enthalpy.}$$

H = U + PV
Definition of Enthalpy

So, here are the key formula that we need to have as shown in the above slide. Now, when the heating from this one at constant volume, then essentially we can write C at constant volume is C_v^ = 1/m(∂Q/∂T)$_{volume=cont}$ = 1/m (∂/∂t)(∂u+Pdv) = 1/m (∂/∂t) (∂u/∂T) as dv=0. When heating is done at constant pressure, the specific heat is defined as Cp^ as written in the above slide. Since, p is constant, therefore, vdp is actually zero. This term vdp equal to zero. Since, Therefore, we can actually write this term pdv as d(PV).

Now, this term u plus PV many of you know is an important parameter and which is collectively defined as the Enthalpy. So, I hope all of you understand that under what condition, so for some people this is like nothing. Since, pressure is constant, therefore vdp equal to zero and that allows you to essentially add to this expression du + pdv, a vdp and the moment you do that you essentially can convert pdv plus vdp as d(pv). And therefore, you are now left with C_p^ = dH'/dT where H' is (H/m) and it can be considered as 'specific enthalpy'. So, the important massage that emerges out from our discussion is H = PV or the definition of Enthalpy. Now, enthalpy is actually a very interesting parameter and you can understand its significance from a very simple example that we can talk about.

(Refer Slide Time: 21:50)



Volume = Constant

Boundary are fixed/
Can't move/not flexible

$Q = m\,C_v\,\Delta T$

Volume Can Change

→ There is going to be increase in Temp. →
Heat that is being provided to the System
↓
Consumed in two ways
(1) It increases the Internal Energy
(2) It performs some work, by expanding the volume.

Heat you have Supplied
= Change in Int Energy + ~~Chang~~ Work done
$= \overline{du + Pdv} = d(u+Pv)$
In case you have $\underline{P = Const.}$ $= \underline{\underline{dH}}$

Let’s say, we have two cylinders; for the first one, the volume is constant. Or, in other words one can argue that the boundaries are fixed, cannot move rigid or rigid is not the view context may not be flexible whatever. And, in the second one, volume can change as shown in the above slide. So, either you can have a piston cylinder or it can be a flexible boundary like a balloon or whatever volume can change.

And let’s say to both of this system you are supplying some heat δQ. So, here in the first case where the volume is constant what will this heat do? The heat that is coming from the surrounding is simply going to increase the temperature by only changing the internal energy because the boundaries are rigid. So, the heat, whatever heat comes in it increases the internal energy only and that is manifested as the increase in temperature.

So, what is the increase in temperature if one asks you? It is very simple now, the delta T is nothing but if the amount of heat that is given is known $mC_v\Delta T$. So, $Q= mC_v\Delta T$. So, if your mass of the system is known; C v is known; and amount of heat that is supplied is known or Q amount of heat is added in both the cases and you can calculate the change in the temperature.

Now in the second case, what is happening is the volume can change. So, when you apply some heat from outside what is going to happen? There is going to be increase in temperature but in addition to that we know that because of heating the volume will try to expand and as the volume expands it is going to push this cylinder piston. So, it performs some work.

So, of course you cannot directly apply $Q = mC_v\Delta T$ because in order for you to apply that it must be specified that the pressure is constant. So, the moment you have volume is not constant it does not allow you to actually use $C_p\Delta T$; because I must mention particularly for a gaseous process in order for you to apply $mC_p\Delta T$. it must be specifically mentioned that pressure is constant.

Forget about that for the time being. What you look into that this heat that you are providing, heat that is being provided to the system, is actually consumed in two ways; number one: it increases the internal energy and number two: it performs some work by expanding the volume and straight away unless you know what is the exchange in volume etcetera, etcetera. So, again some restriction is there like constant pressure, process etcetera, etcetera.

You do not know we how much fraction is consumed in increasing the internal energy and how much fraction has been consumed in performing the work. So, this you do not know, but what you know is that collectively whatever heat you have supplied has essentially been utilized for u + pdv. So, it is the change in the internal energy, so whatever heat you have supplied has been used for change in internal energy plus the work done.

So, here it is, its du + pdv. That's what it is done. Now, can you write that this is enthalpy? as of now? No, because $H = u + PV$ and what you have is du + pdv. Only, for the restrictive case that pressure is does not change. So, this is it. But what does it mean? What it means is a very interesting simplistic thought that you can come up.

So, whenever a gas molecule for example is heated, so what happens? What happens is that the molecules attain more kinetic energy. So, they are more free to move around. So, they are more free to move around. So, the pressure increases because as the molecules travel faster the number of collisions increase. So, the system, if the volume is constricted, if the boundaries are rigid the system cannot do anything, but if the boundary can be moved if the volume can increase.

Then what the system realizes, the molecules that I have they are now attending to have more kinetic energy and I must provide them more space to move around. So, let me spend some amount of energy that I am receiving in creating this excess volume where the molecules can move around. So, what is going to be the difference between the two systems? Here, the temperature rise will be maximum and pressure will also shoot up because the internal.

So, whatever heat comes in the temperature rises straight away, and as the temperature rises the number of collision increases and the pressure goes up. Now here what happens the rise in the temperature will be little less, because some amount of energy is consumed in creating this excess volume and as the rise in the temperature forget about any formula this is a qualitative understanding is a very important understanding and as some additional volume has been created the rise in the pressure is also going to be less.

So, the system knows that it might be dangerous actually to allow all the molecules to attain this much amount of high kinetic energy because the pressure will go up extremely high and therefore it might lead to an expression explosion. So, here it is better that whatever energy I am receiving I better spend some amount of energy for creating some extra volume where the molecules can roam around.

Of course, as I mentioned that some part of the energy is consumed in creating this extra volume, some part is consumed in increasing the kinetic energy and collectively what the system is doing if the pressure is constant the system's enthalpy is increasing. This is the significance of enthalpy. We are stopping here and from the next class I will start showing how we can estimate the values of C_p and C_v starting with an ideal gas. Thank you very much.