Concepts of Thermodynamics

Prof. Suman Chakraborty
Department of Mechanical Engineering
Indian Institution of Technology, Kharagpur

Lecture – 15
Enthalpy and Specific Heats

In the previous lecture, we were discussing about the statement of 1st law of thermodynamics for a cyclic process undergone by a control mass system and for any general process undergone by a control mass system. Now, in the process, we learned about a property called as internal energy. So, we will learn one more property and that one more property we will learn through a particular example.

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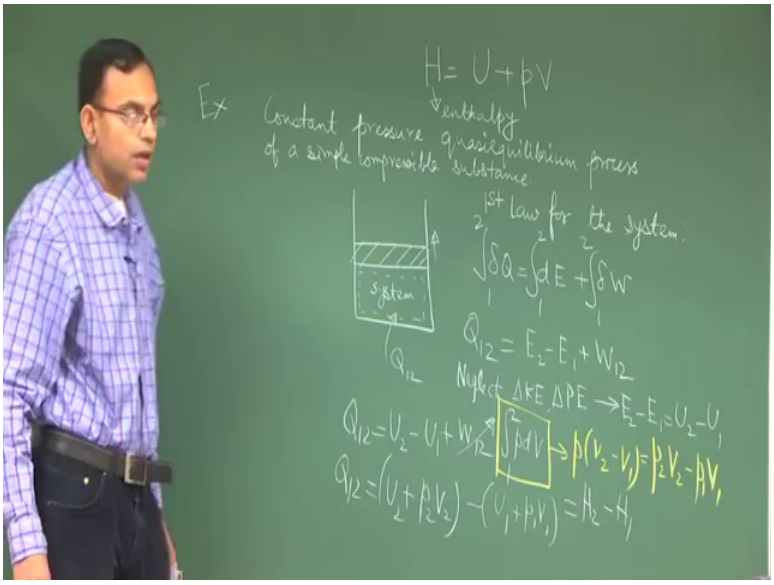

So, let us take an example of a constant pressure quasi equilibrium process. So, this is a very common example encountered in thermodynamics, where you have say a piston cylinder arrangement. There is a system here and this piston moves maybe because of heat transferred to the system Q 12, the piston moves slowly so that the pressure inside remains the same.

Why, if it moves slowly the pressure inside will remain the same, the resistance pressure also remains the same. The resistance pressure is nothing but the atmospheric pressure plus the pressure equivalent pressure due to the load of the piston, because the resistance pressure does not change. So, the inside pressure also will not change if this is moving in a quasi equilibrium process, so that kind of process we are considering.

So, let us write the 1st law for the system. So, it is basically the integration of delta Q is equal to d E plus delta W, you integrate it from 1 to 2. So, this we call as Q 12 not Q 2 minus Q 1, because this is not a property, this is the total heat transfer during the process 1 to 2, but this is the difference in property E 2 minus E 1 plus W 12.

So, if you neglect changes in kinetic energy and potential energy, then E 2 minus E 1 is as good as U 2 minus U 1 so Q 12. This is let us say that the system is a simple compressible substance so, if it is a simple compressible substance then the work done due to this moving boundaries integral p dV from 1 to 2.

So, constant pressure quasi equilibrium process let us qualify this a little bit by saying that of a simple compressible substance; otherwise p dV may not be the only form of work. There may be other forms of work as well. So, the p dV in this case, because pressure is a constant this is as good as p into V 2 minus V 1 and because p 1 and p 2 are the same, this is as good as p 2 V 2 minus p 1 V 1.

So, you can write Q 12 is equal to U 2 plus p 2 V 2 we can combine this together minus U 1 plus p 1 V 1. So, this U plus p V is a property, why, U is a property, p is a property, V is a property. Therefore, their combination is also a property and that property U plus p V this is defined as enthalpy.

So, enthalpy is defined as a property although we have introduced it through this example never get confused by thinking that it is valid only for a constant pressure quasi equilibrium process not like that. This is an example where the heat transfer comes directly as a difference of enthalpy. This is a consequence of the 1st law of thermodynamics, but enthalpy is a property, which is valid at any state point, because any state point will have a pressure volume and internal energy. Therefore, their combination will exist for any state point no matter what kind of process that has taken place to arrive at that state point. So, this will become H 2 minus H 1.

So, with this background, we have come across two properties. And these two properties internal energy and enthalpy, they are tabulated in property tables. Sometimes internal energy is not separately tabulated, but if enthalpy and pressure and volume are tabulated, you can calculate internal energy by H equal to U plus p V, so U equal to H minus p V.

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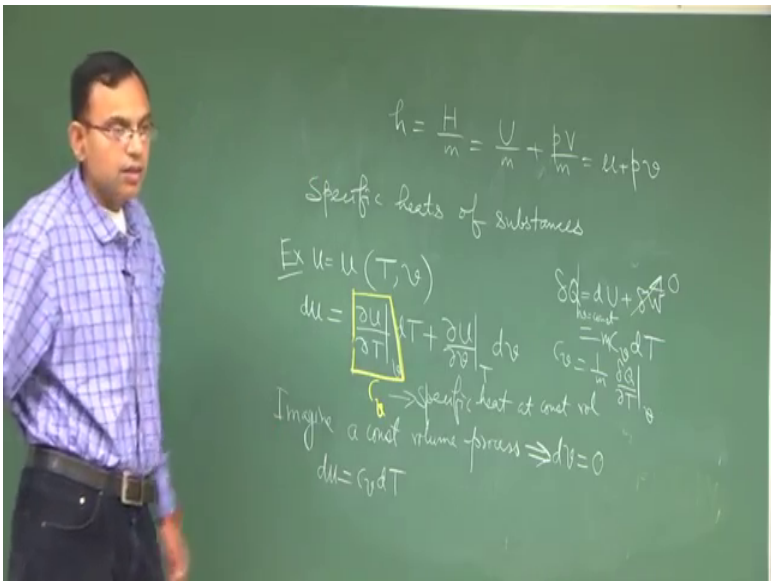

So, just like specific internal energy specific enthalpy H is capital H by m so this is U by m plus p V by m. So, this is small u plus p into small v. So, in the table, it may not be that H and U are both given any one of them is given, but you can calculate it from the other if pressure and specific volume are known.

The next set of property is which we will learn in the context of 1st law not that they are directly outcomes of 1st law as such that is the specific heats of substances ok. So, now when we say specific heats of substances, we will start with an example a very abstract algebraic example. And we will bring out the physics, as we go along with the example.

So, let us consider internal energy as a property. So, how do you estimate a property? You estimate a property when you identify the state point, because the property is a unique function of the state point. The state point can be ascertained if you specify two independent intensive thermodynamic properties for a simple compressible pure substance. This is called as a state postulate.

So, state postulate means that how do you specify the state of a system thermodynamic system. For a simple compressible pure substance, you require two independent intensive properties. So, in this case, let us take temperature and specific volume as two independent properties. You could also take temperature and pressure or if they are at all independent, but in this case just for convenience let us take any two. So, these two is good enough, because these two if they are independent they will specify the state and then u is a unique function of the state, so that is the meaning of this functional dependence.

So, when you write this u as a function of T and v, so you can write d u, which we will write as a partial combination of partial derivatives ok, so the total the total differential is sum of the partial differential that is what this is the basic rule of differential calculus. We have not brought any physics here except for writing this as a function of two independent thermodynamic properties.

So, then we just give a definition, this we define as C v specific heat at constant volume. And why do we call this as specific heat at constant volume, we will be very clear if we do a few additional steps, but the definition is not governed by the physics. The definition is governed by the simple mathematical expression, and this simple mathematical expression is a property. Why, it is a property, because it is a partial derivative of one property with respect to another property, given another property remaining fixed, so that is also a property. So, this C v is called as specific heat at constant volume. Question is why?

So, let us imagine a constant volume process although see C v is defined for all processes. The way in which it is calculated is that u is varied with T given v as constant, but once this property is evaluated, because it is a property this property does not depend on the process, so that means, that if you have a state point where you have a temperature and specific volume at that state point, you have a unique C v.

So, how that state point is arrived, whether it is arrived at a constant volume process or not is not important, this physical sense you have to develop. Although the property is defined in this way it is just for the sake of evaluation of the property. But once the property is evaluated, this can be applied to any process right. It is not just restricted to constant volume process.

But imagine why it is called as specific heat at constant volume; imagine a constant volume process. If you imagine a constant volume process, then d v is 0, right so then du is C v d T. So, in that case if you apply the 1 st law with negligible changes in kinetic energy and potential energy, you have this one right.

See, I will not specify the assumption again and again, but for a few times I have already iterated, because some of the students take this as granted, but you know, but you have to keep this in mind that this is not granted provided I mean this is true only if there is negligible change in kinetic and potential energy that must be remembered. Although every time, we may not write it explicitly and tell it explicitly, but whenever we are writing this it means that kinetic and potential energy changes are negligible.

So, now, for a constant volume process, there is no work done right. So, this dU since del Q for constant volume process is c v this is mass this is capital U so, this is mass into small u. So, mass into C v into change in small u is this one. So, you can also write C v is 1 by m this one right.

So, recall the school level definition of specific heat, the heat required to increase the unit mass u of a substance by a unit temperature. Here it is also like that it is this del Q it is what? So, C v is what the heat required to increase, if m is equal to 1 and this is equal to 1, then C v is the heat transfer. That means, the heat transfer required to increase, the unit mass of substance temperature by unity given that C v is kept constant during the heat transfer process, so that is why it is called as specific heat at constant volume that is the physical meaning, but keeping this physical meaning abstract you can come with this definition of C v without relating it to this. Similarly, so this is called as specific heat at constant volume.

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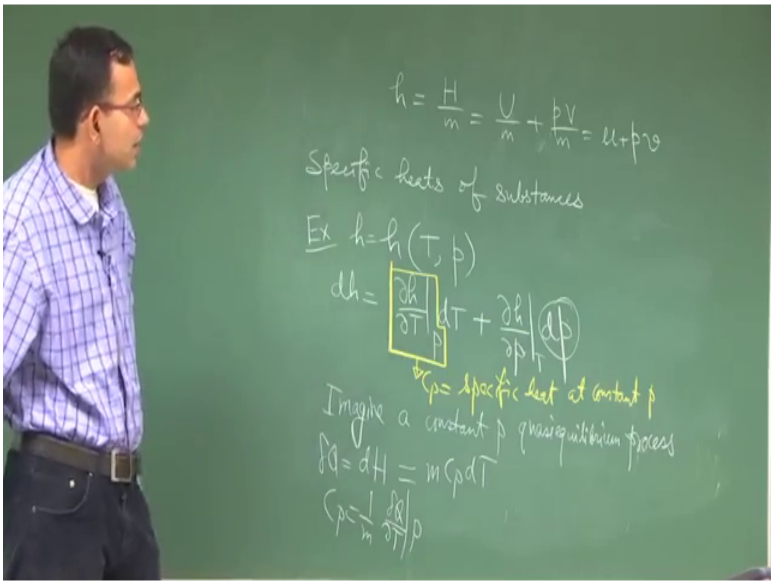

Next we will learn the definition of specific heat at constant pressure. So, let us take an example say enthalpy as a property. So, just as we wrote U as a function of T and v, we can write h as also as a function of p and v. But here for our purpose of defining the property that we want we take h as a function of T and p, assuming T and p are independent.

For example, you cannot write h as a function of T and p. When the substance is changing its phase, because when the substance is changing, it is phase T and p are dependent on each other. The saturation pressure is a function of saturation temperature. So, they are no more independent parameters ok, but in case they are independent you can write this.

So, then d h this is what we write exactly in the same way as we wrote for dU. This we define at C p specific heat at constant pressure. Again why such a name let us consider imagine a constant pressure quasi equilibrium process, the example with which we started this lecture.

So, if you imagine a constant pressure quasi equilibrium process, again for defining this property such a process may not be necessary, but this is to give a physical interpretation to the property. So, we have just seen that in that case, the heat transfer is the change in enthalpy, the first example that we did today. So, then in place of this so, because it is a constant pressure process in that case dH is C p d T. So, this is m C p d T, because for constant pressure process this is 0.

So, you can write C p is 1 by m. So, this gives a physical interpretation to C p that is the heat transfer required bar for by unit mass of a substance for unit change in temperature given that the heat transfer is taking place at constant pressure that is a physical interpretation to C p just analogous to C v.

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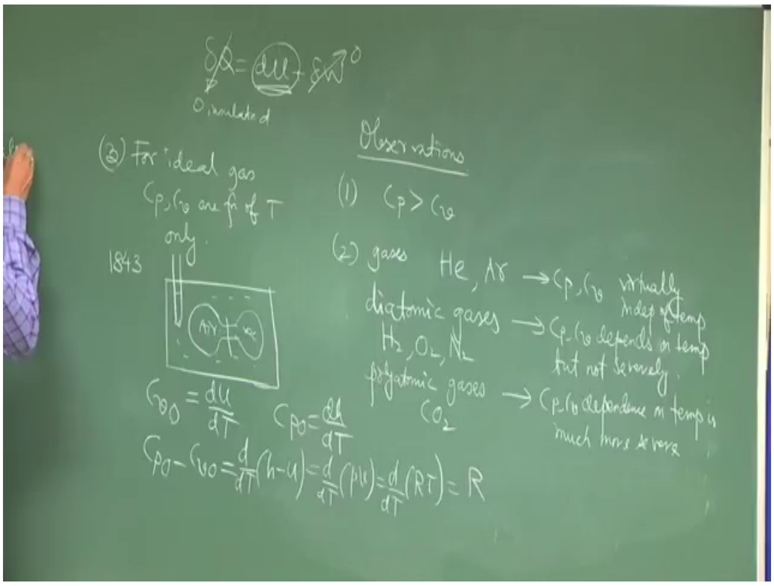

Now, without getting into any mathematical argument, of course by mathematical argument we can show this it is we can make this observations 1st observation is C p greater than C v. So, why it is so, see physically when you are supplying heat at constant pressure you also keep a provision of change in volume. And that equivalent energy must be supplied to achieve that change in volume. Whereas, when you are supplying heat at constant volume, you do not need to keep a provision of any heat energy transfer to accommodate change in volume. So, this under identical changes of temperature, this will require constant pressure process will require a more greater supply of heat and that means, C p is greater than C v.

Then imagine the molecular origin of this C p, C v and all these. So, these are all associated with sudden derivatives temperature derivatives of internal energy so that means, they are intrinsically associated with intermolecular forms of energy, they are the translational modes, the vibrational modes, the rotational modes all the modes of the molecular motion.

So, now, when we think of monoatomic gases as an example, so let us think of gases for monoatomic gases you have that translational modes only right. So, other modes are not relevant like vibrational, rotational these modes are not important. So, what are these monoatomic gases like helium, argon, mono atomic hydrogen like this. So, if you have nascent hydrogen for example, so, but typically we say this types of gases, because hydrogen will normally be there in H 2 form rather than H form.

So, if you have these gases, so they do not have these modes of energy beyond the translational. So, for them C p or C v are virtually independent of temperature, because they will remain constant over a wide range of temperature without being dictated by the changes in the vibrational modes of kinetic, the vibrational modes of energy with changes in temperature.

Now, if you have diatomic gases, those modes will be there. So, for diatomic gases, those modes are there, but the dependants of C p, C v which temperature is not that high as that for polyatomic gases. So, if you have more and more number of atoms added in a molecule, you will have the more severe dependence on C p and C v with temperature. So, C p, C v depends with depends on temperature, but not severely.

So, diatomic gases like H 2, O 2 these kinds of thing N 2. Polyatomic gases like C O 2 for example, there C p, C v dependence on temperature is much more severe. So, when we talk about C p, C v dependence on temperature, we must keep in mind that why we are bothered so much about C p, C v dependence of temperature we are bothered. So, much about this because for gases of course, C p, C v will depend on temperature and pressure or specific volume, but that dependence on temperature is primary. In fact, it is shown it can be shown that for a ideal gases C p, C v depend on temperature only.

So, this is the third point for ideal gas C p and C v are functions of temperature only. So, in fact this can be mathematically shown but in 1843 joule did a very classical experiment. So, what he did is I am briefly explaining the experiment, there is a water bath in which these 2 bulbs were connected this is water, and here it is air and here it is vacuum So, there is a stop cock here which prevents these two from mixing and there is hot water bath here.

So, he in stepped up the thermometer inserted to measure the temperature. And when this stop cock was opened this air occupied the entire volume. In this process there was no work done, because it was a free expansion. So, the entire heat transfer was due to the change in internal energy.

So, if you write for example, if the work is 0, then the heat transfer is this. So, now if this system is insulated, then this del Q is also 0 and then there is no change in internal energy. And joule measured that the temperature also remained the same. So, the internal energy for in this case where air was approximated as an ideal gas was supposed to be only a function of temperature. Of course, this is not a proof, but rigorously through thermodynamic property relationships it can be shown that for a ideal gases internal energy is a function of temperature only.

So, then you can write du so C v for ideal gas for ideal gas we give this 0 as a subscript this is simply du d T right, because u is a function of T only, because u is a function of T only, its derivative is also a function of T only, therefore C v is a function of T only. Similarly C p is d h d T. Interestingly, C p minus C v for an ideal gas 0 for ideal gas is d d T of h minus u h minus u is p v and for ideal gas p v equal to R T. So, this shows that C p minus C v is equal to R for an ideal gas.

Finally, I would like to conclude with a very important definition which is called as perfect gas. There is a difference between ideal gas and perfect gas. For a ideal gas C p, C v is a function of temperature, but for perfect gas or calorically perfect gas the C p, C v is considered to be a constant, so that temperature dependence is no more considered to be important. So, for an ideal gas C p and C v are functions of temperature only; for perfect gas or calorically perfect gas, there was a special case of ideal gas where C p, C v are constants.

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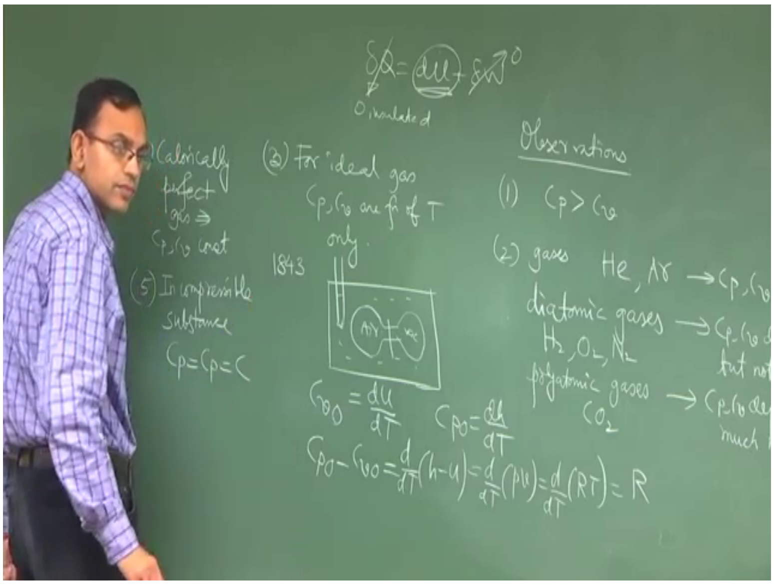

So, calorically perfect gas C p, C v constants. And finally, for incompressible substance, see the specific volume at sorry specific heat at constant pressure or constant volume, this distinction gets lost when it is an incompressible substance, constant volume, constant pressure all these things do not matter. So, in that case you can write C p is equal to C v equal to C ok. So, this is a unique specific heat where the distinction between C p and C v is completely lost.

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C p is equal to C v equal to C. So, with this little bit of background on the specific heats, we stop here today and we will continue with some problems in the next lecture.

Thank you.