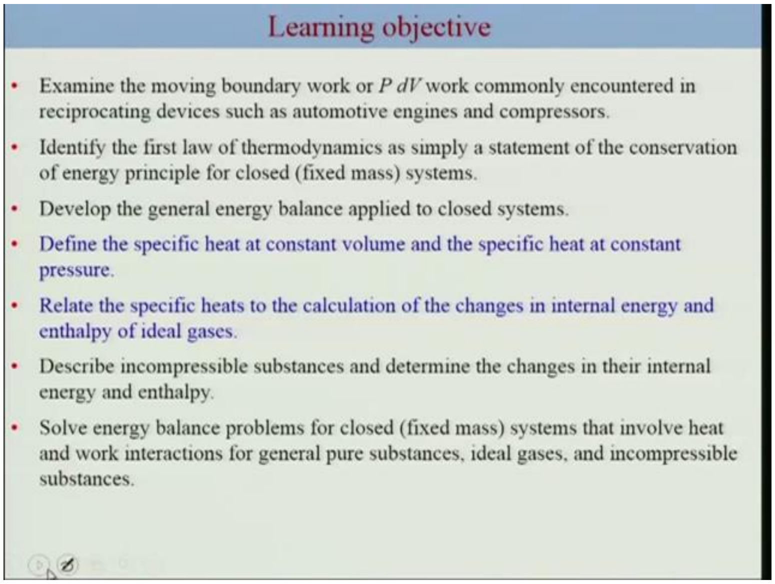
Engineering Thermodynamics
Professor Jayant K Singh
Department of Chemical Engineering
Indian Institute of Technology Kanpur
Lecture 18
Internal energy, enthalpy, and specific heats of ideal gas

(Refer Slide Time: 0:15)



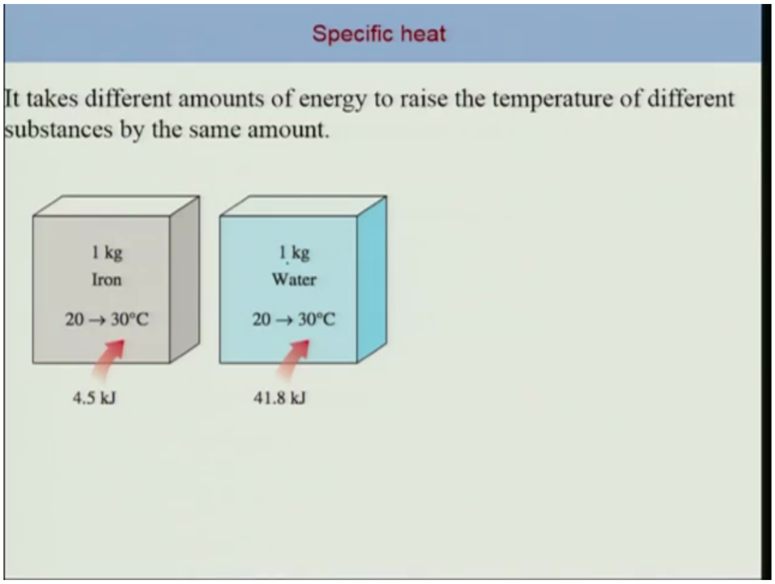
Learning objective

- Examine the moving boundary work or $P\,dV$ work commonly encountered in reciprocating devices such as automotive engines and compressors.
- Identify the first law of thermodynamics as simply a statement of the conservation of energy principle for closed (fixed mass) systems.
- Develop the general energy balance applied to closed systems.
- Define the specific heat at constant volume and the specific heat at constant pressure.
- Relate the specific heats to the calculation of the changes in internal energy and enthalpy of ideal gases.
- Describe incompressible substances and determine the changes in their internal energy and enthalpy.
- Solve energy balance problems for closed (fixed mass) systems that involve heat and work interactions for general pure substances, ideal gases, and incompressible substances.

Okay welcome back we are discussing energy analysis for closed system, so this is a part 4 of the model. So in this particular lecture we would be covering specific heat at constant volume and constant pressure and then we will try to relate this specific heat to the changes in the internal energy and enthalpy, specifically of ideal gases.

So what is specific heat? Okay so let us take a example for daily life we based on our experience we know that it takes different amount of energy to raise a similar amount of temperature for two different objects.

(Refer Slide Time: 0:53)

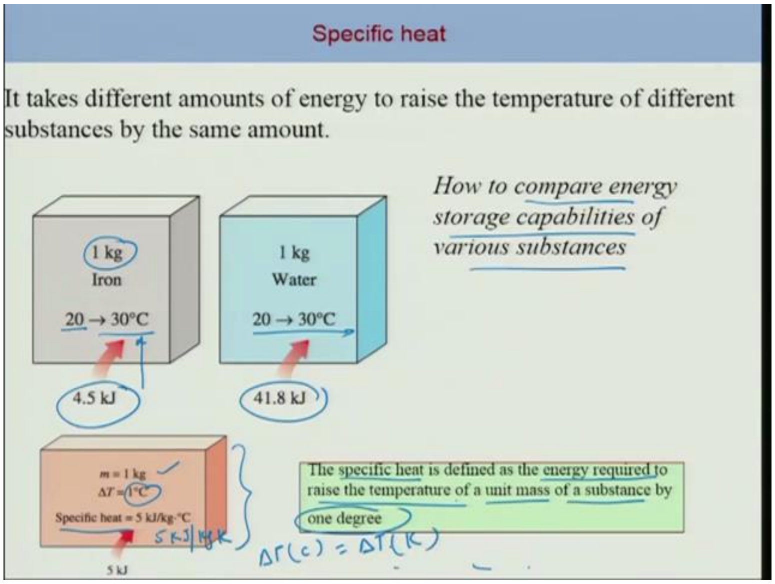


Specific heat

It takes different amounts of energy to raise the temperature of different substances by the same amount.

So just take an example of let us iron and water, so it takes around 4.5 kilo joules to raise temperature of iron from 20 degree to 30 degree Celsius, okay for 1 kg of iron the same mass that is 1 kg if we consider for water the amount of energy to change from 20 degree to 30 degree Celsius is 41.8 kilo joules which is quite low for the case of iron which takes which requires only 4.5 kilo joules to raise 10 degree Celsius for same amount of mass, okay. So it clearly we have same mass and same change in temperature but it requires different energy. So there is a different capacity to store energy and this capacity is reflected in (())(1:41) property which we call it as specific heat.

(Refer Slide Time: 1:50)



Specific heat

It takes different amounts of energy to raise the temperature of different substances by the same amount.

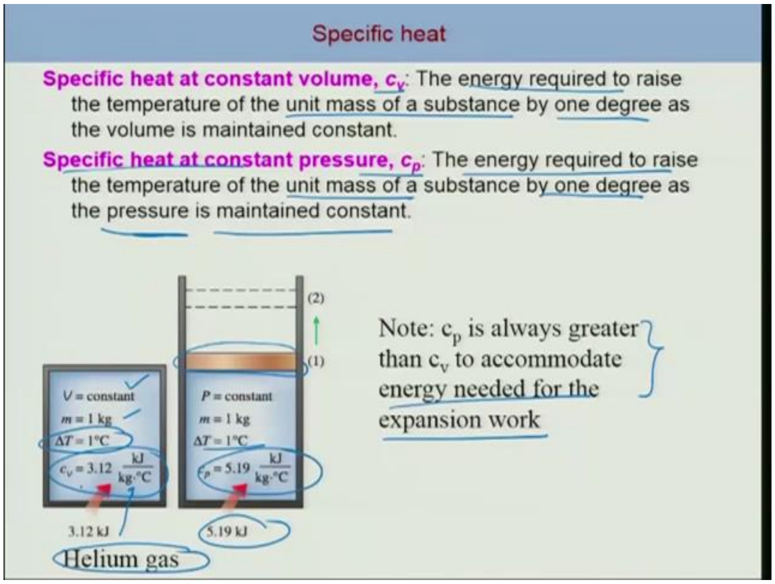
How to compare energy storage capabilities of various substances

The specific heat is defined as the energy required to raise the temperature of a unit mass of a substance by one degree

$\Delta T(c) = \Delta T(K)$

So how to compare energy storage capabilities of various substance, we define a term called specific heat which is a property which is defined as a energy required to raise a temperature of a unit mass of a substance by one degree, okay. So this is the illustration, so for example you have a 1 kg of this particular substance, it requires let say 5 kilo joules to raise 1 degree Celsius thus its specific heat is 5 kilo joules per kg degree Celsius. You can also write it in this form kelvin, because delta T for Celsius is same as delta T in kelvin.

(Refer Slide Time: 2:29)



Specific heat

Specific heat at constant volume, c_v: The energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant.

Specific heat at constant pressure, c_p: The energy required to raise the temperature of the unit mass of a substance by one degree as the pressure is maintained constant.

Note: c_p is always greater than c_v to accommodate energy needed for the expansion work

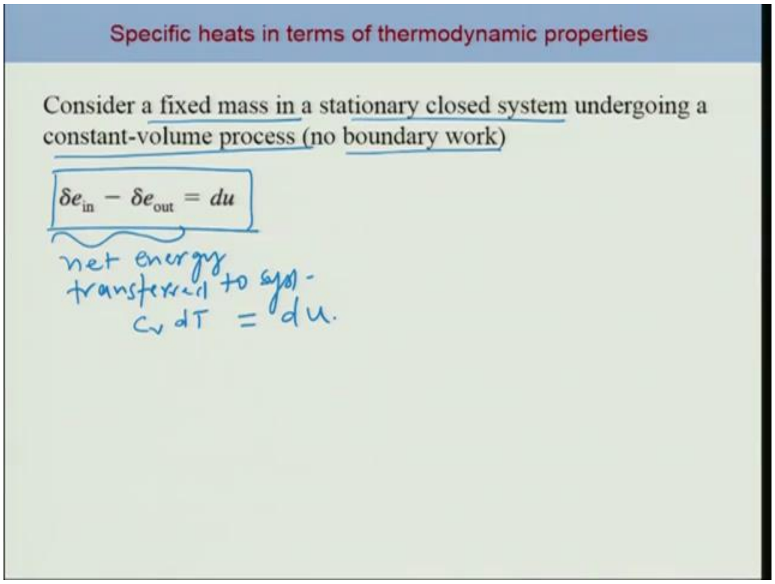
Now there are two specific heats depending on how the process is, one is called specific heat at constant volume and other is called as specific heat at constant pressure. Okay, so the way you define is Cv so that is a specific heat at constant volume which is the energy required to raise the temperature of a unit mass of a substance by one degree keeping the volume constant.

And similarly for the case of specific heat at constant pressure u is a energy required to raise the temperature of unit mass by one degree keeping the pressure constant. So this is by definition and it is universal it does not depend on particular which substance we talking about. Cp is always a greater than Cv to accommodate energy needed for expansion work.

So for example, in the case of a helium, okay you have a volume which is constant here, mass is 1 kg and the delta T again we are keeping it 1 degree Celsius because that is the change. It requires 3.12 kilo joules to raise 1 degree and that is why Cv is 3.12 kilo joules per kg degree Celsius.

On the other hand when you consider removable piston here which means the volume can change, you need more energy okay in order to accommodate expansion work and thus the more energy for changing the temperature to by 1 degree Celsius. And thus your Cp is higher than Cv, okay. So that is a typical behavior of Cp and a Cv okay, so Cp is usually greater than the Cv.

(Refer Slide Time: 4:06)



Specific heats in terms of thermodynamic properties

Consider a fixed mass in a stationary closed system undergoing a constant-volume process (no boundary work)

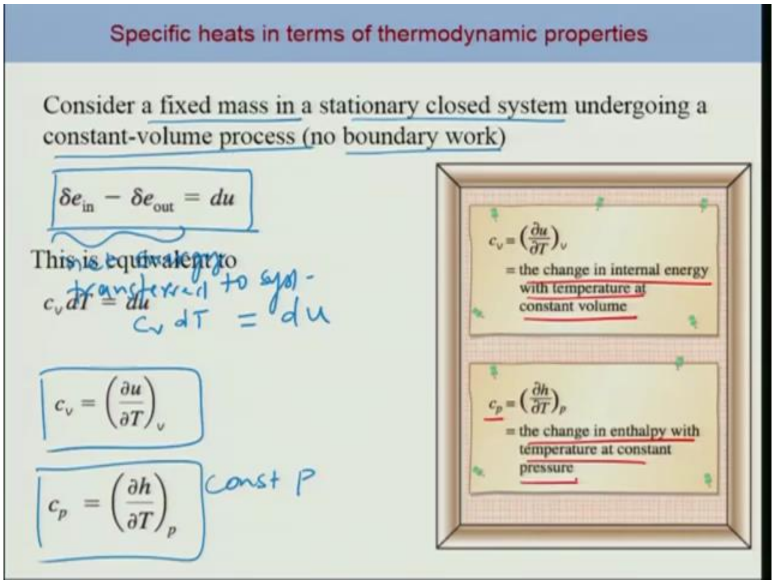
$$\boxed{\underbrace{\delta e_{\text{in}} - \delta e_{\text{out}}}_{\text{net energy transferred to sys.}} = du}$$

$$C_v\,dT = du.$$

So let us now try to connect this Cp and Cv in terms of thermodynamics parameters, so we can consider a fixed mass, okay in a stationary closed system undergoing a constant-volume process, okay. So which means there is no boundary work, so you can come up with the energy balance, so this is your energy balance. Now this is nothing but the net energy transferred to the system, okay.

So this is a net energy transferred to the system, so if we assuming this Cv which is defining is energy required to raise 1 degree is thus we can say that this by definition is going to be Cv times the change in energy or in terms of differential form is a dT. And this is by definition we are saying this to be equal to du.

(Refer Slide Time: 4:54)



Specific heats in terms of thermodynamic properties

Consider a fixed mass in a stationary closed system undergoing a constant-volume process (no boundary work)

$$\delta e_{in} - \delta e_{out} = du$$

This is equivalent to

$c_v dT = du$

this is energy transferred to sys -

$C_v dT = du$

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

const P

$c_v = \left(\frac{\partial u}{\partial T}\right)_v$ = the change in internal energy with temperature at constant volume

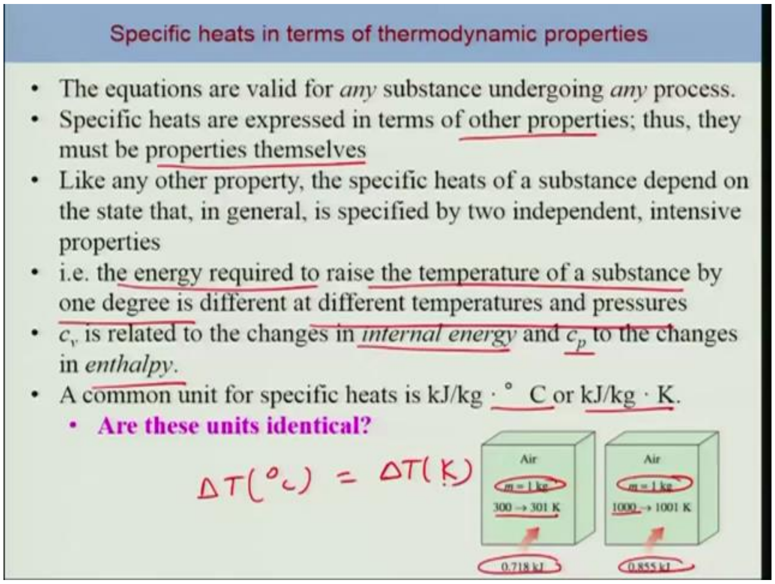
$c_p = \left(\frac{\partial h}{\partial T}\right)_p$ = the change in enthalpy with temperature at constant pressure

So this is at constant volume, thus if you consider in a differential form, this would be Cv is partial differentiation of u with respect to T at constant volume. Using similar analysis for a constant pressure, okay, where you are doing a expansion compression at constant pressure the expression for specific heat would be Cp and that would be related to your enthalpy, change in enthalpy with respect to the temperature at a constant pressure.

So the definition of Cv would be the change in internal energy with temperature at constant volume, okay. It is a partial derivative of internal energy with respect to temperature. And for the case of Cp is a change in enthalpy with temperature at constant pressure, okay.

So what about this equations which we have written the expression of Cv and Cp are they valid only for specific substance the answer is no, this equation are a valid for any substance undergoing any process, okay. Now you also notice that Cp and Cv are related to changes in the u and changes in the enthalpy which essentially means they are related to the properties and hence they are also itself properties.

(Refer Slide Time: 6:06)



Specific heats in terms of thermodynamic properties

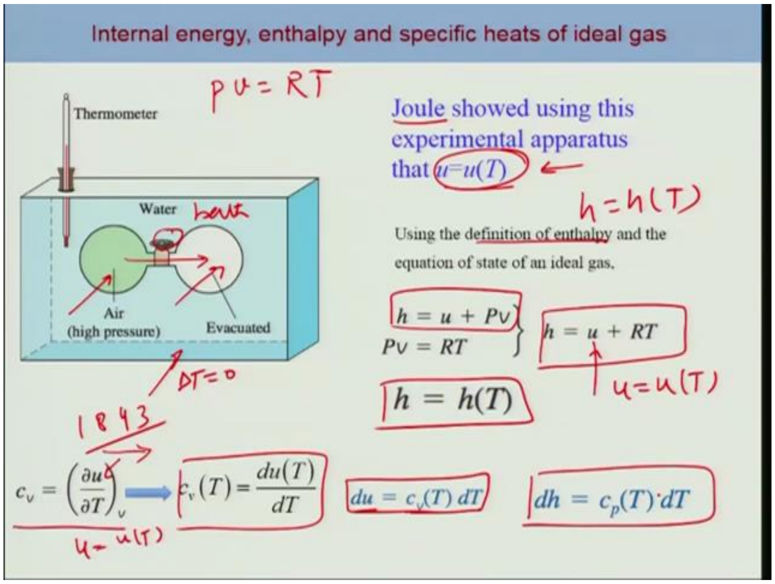
- The equations are valid for *any* substance undergoing *any* process.
- Specific heats are expressed in terms of other properties; thus, they must be properties themselves
- Like any other property, the specific heats of a substance depend on the state that, in general, is specified by two independent, intensive properties
- i.e. the energy required to raise the temperature of a substance by one degree is different at different temperatures and pressures
- c_v is related to the changes in *internal energy* and c_p to the changes in *enthalpy*.
- A common unit for specific heats is kJ/kg · ° C or kJ/kg · K.
  - **Are these units identical?**

$\Delta T(^\circ C) = \Delta T(K)$

So specific heat said is express in terms of other properties, hence they are properties themselves which essentially means you can define specific heat in terms of intensive variable temperature and pressure. So that is energy required to raise the temperature of a substance by 1 degree is different at different temperature and pressure. So they are variable as we already mentioned that they depend on intensive variable as they are just a property, hence they will also vary with temperature and pressure. With an example is for air, so for the case of air with mass of 1 kg change from 300 to 301 kelvin just 1 kelvin change the energy required is 0.718 kilo joules.

On the other hand, at a very high temperature they are changed from 1000 to 1001 kelvin the energy required is much higher. So that means it depends on the temperature and pressure and just to remind Cv is related to the variation in the internal energy Cp is related to the variation in enthalpy, okay. Now what are the units? The units are as I said is Celsius, units are kilo joules per kg per degree Celsius or kilo joules per kg per kelvin, okay are they same? The answer is yes, they are identical, the reason is delta T for degree Celsius is same as delta T for kelvin.

(Refer Slide Time: 7:27)



Internal energy, enthalpy and specific heats of ideal gas

$Pv = RT$

Joule showed using this experimental apparatus that $\boxed{u = u(T)}$ ←

$h = h(T)$

Using the definition of enthalpy and the equation of state of an ideal gas,

$$\left.\begin{array}{l} \boxed{h = u + Pv} \\ Pv = RT \end{array}\right\} \boxed{h = \underset{\underset{u = u(T)}{\uparrow}}{u} + RT}$$

$$\boxed{h = h(T)}$$

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \xrightarrow{\quad} \boxed{c_v(T) = \frac{du(T)}{dT}} \qquad \boxed{du = c_v(T)\,dT} \qquad \boxed{dh = c_p(T) \cdot dT}$$

$u = u(T)$

Okay, so now let us consider the case of ideal gas, so we know that ideal gas we can write Pv is equal to RT where R is a gas constant. Now what about the internal energy for such as system, so the idea is basically to come up with the expression of Cv and Cp. The internal energy apparently was shown by Joules that it depends on only temperature for the case of ideal gas. What he did is he took two tanks, one with high pressure air which is this okay and he connected with another tank which was evacuated at a 0 pressure connected with a pipe and with a valve.

He put these two tanks in a water bath at a certain temperature, allow it to thermal equilibrate and once the thermal equilibration was attained he opened the valve to let the air pass for one tank to another until the pressure equalize. Now Joule observed that there was no change in the temperature, so that means the delta T here it was 0, and he assumed that no heat was transferred from the air or to the air.

Since there was no work done due to the expansion against 0 pressure or it was a free expansion he concluded that the internal energy of the air did not change. So and thus he concluded that the in order to change internal energy of an ideal gas you need to change your temperature.

Thus, u depends only on the temperature, okay. So that was the classy experiment which he collected it in 1843 and concluded this property of ideal gas where u is depends only on temperature. Now we can take a definition of enthalpy, okay and also prove that if u depends on T for the case of ideal gas, h also depends on T.

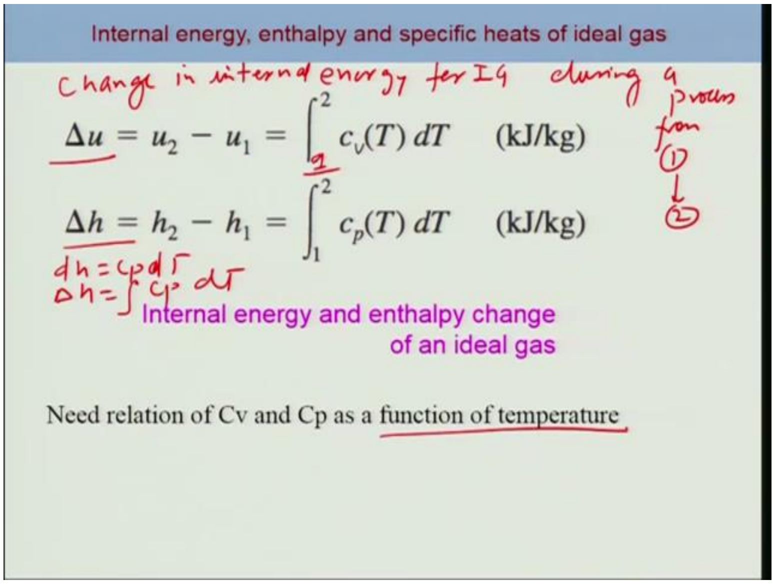
So this is definition of enthalpy where h is equal to u plus Pv and now you can make use of a ideal gas equation on state which is Pv is equal to RT plug in there. So what you get is h is equal to u plus RT, now given that u for ideal gas just depends on temperature and thus h also depends on temperature.

Okay so enthalpy depends only on the temperature. Joule also showed that there is a deviation from this particular expression for the case of gases which deviates from ideality. So for the non-ideal gases these expressions would not hold, okay.

Now if this is known that u and h depends on temperature, then you can take the definition of Cv, now this is represented in terms of partial derivative of internal energy with respect to temperature. So given that u is only function of temperature you can change from partial differentiation to ordinary differentiation which is this, okay.

And thus, you can write the du as simple Cv (T) multiplied by dT, okay. Similarly, you can also do the same exercise and you can write dh is equal to Cp multiplied by dT, so this is for ideal gas.

(Refer Slide Time: 10:41)



Internal energy, enthalpy and specific heats of ideal gas

Change in internal energy for IG during a process from ① ↓ ②

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T)\, dT \quad \text{(kJ/kg)}$$

$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T)\, dT \quad \text{(kJ/kg)}$$

$dh = c_p dT$

$\Delta h = \int c_p \, dT$

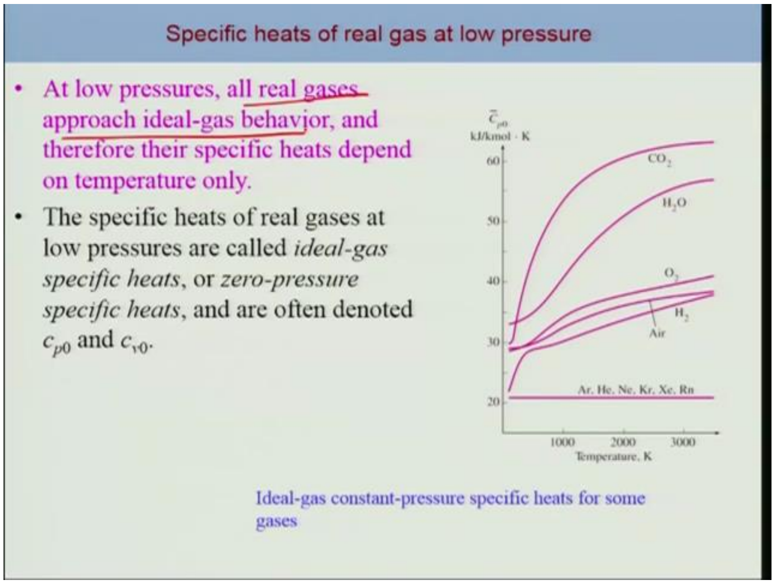
Internal energy and enthalpy change of an ideal gas

Need relation of Cv and Cp as a function of temperature

Okay, so now given that the expression you can easily integrate, so this will be your change in internal energy for ideal gas, ideal gas during a process from state 1 to state 2, okay. So this is going to be your expression for delta u, okay and this will be the expression for delta h, so you are just integrating nothing but dh is equal to Cp dt and thus u delta h is nothing but Cp delta T.

Okay, so this will be the change of the internal energy and enthalpy for ideal gas. Now in order to obtain the change, we need some relation of Cv and Cp as a function of temperature, because these are given here. So another important aspect in order to come up with the values.

(Refer Slide Time: 11:46)



Specific heats of real gas at low pressure

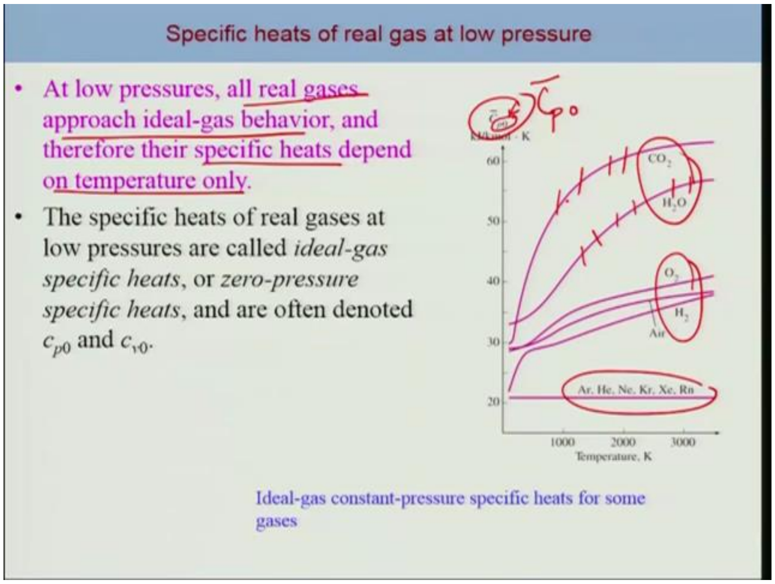
- At low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only.
- The specific heats of real gases at low pressures are called *ideal-gas specific heats*, or *zero-pressure specific heats*, and are often denoted c_{p0} and c_{v0}.

Ideal-gas constant-pressure specific heats for some gases

Now, let us look at what happens for this specific heats of real gases and that particularly at low pressure. So at low pressure all real gas is approaches ideal behavior, that we know that. Now at low pressure your gases turn out to be at low density or in a sense they are very far from each other and hence they do not experience each other’s presence.

So they do not get influenced and due to that their behavior can be approximated as an ideal gas behavior. And thus we are going to make use of low pressure approximation for the gases. We can make use of the specific heat values for the gases.

(Refer Slide Time: 12:22)



Specific heats of real gas at low pressure

- At low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only.
- The specific heats of real gases at low pressures are called *ideal-gas specific heats*, or *zero-pressure specific heats*, and are often denoted c_{p0} and c_{v0}.

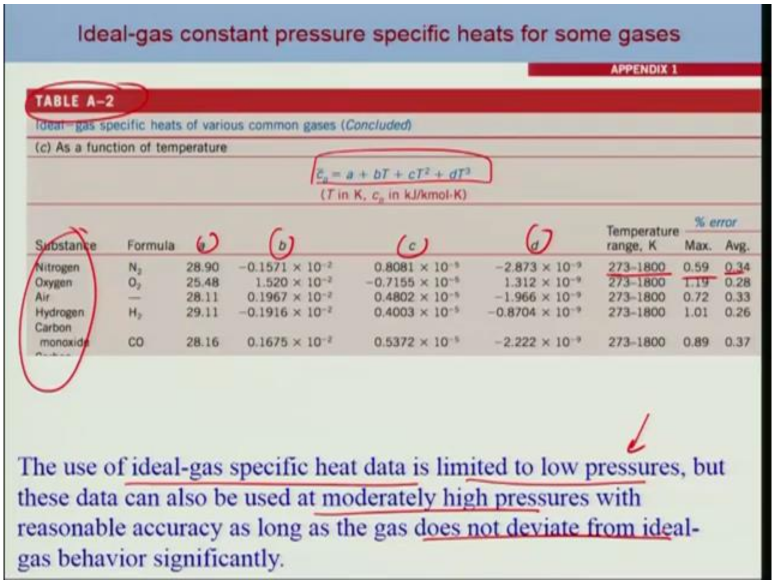
Ideal-gas constant-pressure specific heats for some gases

So just take a look at the real gas behavior at low pressure. So as I said the all real gases at low pressures approach ideal gas behavior and therefore once they do that their specific heat depends only on the temperature, as we have already mentioned that ideal gas specific heat depends only on the temperature.

So specific heat for real gases at low pressure are given in this particular temperature where we have plotted specific heat of real gases at zero pressure and this particular value is represent zero, again this is Cp which means is a zero pressure at constant pressure but extremely low value that why it is Cp. And the bar represent that it is a molar basis, so this is your typical specific heat for real gases this is a mono atomic gases, these are bi-atomic and this are the molecules. And you can clearly see that for mono atomic the specific heat at low pressure is almost constant for all the temperatures.

On the other hand this is almost linear nature and this has curvature but we can see that this is almost linear small range of temperatures, okay. So we can approximate different ranges and we can consider this to be a linear within that. So this particular plots or the behavior can be fitted to some analytical expression, for example you can put you can feed this expression into a cubic form or third polynomial. And this has something which we are going to make use of it, because at the end we have to make use it in order to find out changes in the internal energy or enthalpy.

(Refer Slide Time: 14:02)



Ideal-gas constant pressure specific heats for some gases

APPENDIX 1

TABLE A-2

Ideal-gas specific heats of various common gases (*Concluded*)

(*c*) As a function of temperature

$$\bar{c}_p = a + bT + cT^2 + dT^3$$

(T in K, c_p in kJ/kmol·K)

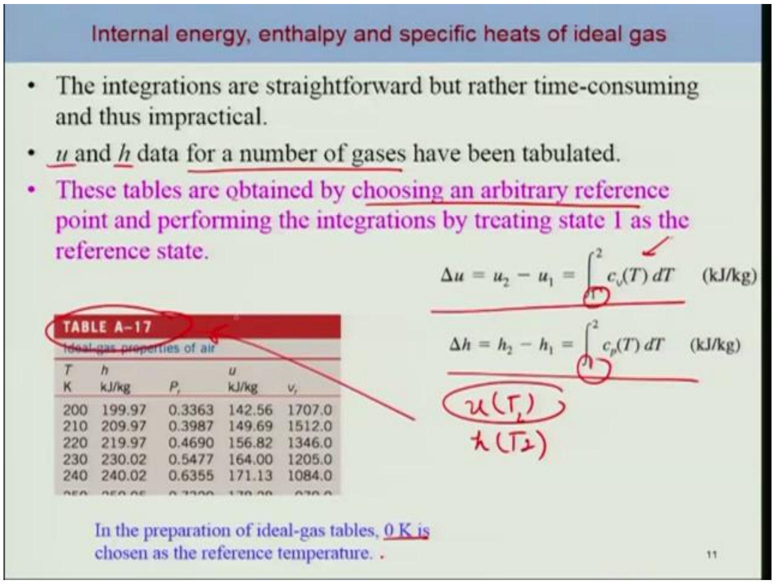
							% error	
Substance	Formula	a	b	c	d	Temperature range, K	Max.	Avg.
Nitrogen	N_2	28.90	-0.1571×10^{-2}	0.8081×10^{-5}	-2.873×10^{-9}	273-1800	0.59	0.34
Oxygen	O_2	25.48	1.520×10^{-2}	-0.7155×10^{-5}	1.312×10^{-9}	273-1800	1.19	0.28
Air	—	28.11	0.1967×10^{-2}	0.4802×10^{-5}	-1.966×10^{-9}	273-1800	0.72	0.33
Hydrogen	H_2	29.11	-0.1916×10^{-2}	0.4003×10^{-5}	-0.8704×10^{-9}	273-1800	1.01	0.26
Carbon monoxide	CO	28.16	0.1675×10^{-2}	0.5372×10^{-5}	-2.222×10^{-9}	273-1800	0.89	0.37

The use of ideal-gas specific heat data is limited to low pressures, but these data can also be used at moderately high pressures with reasonable accuracy as long as the gas does not deviate from ideal-gas behavior significantly.

Let us take a look what are the different ways to make use of specific heats. Okay this is one way to represent specific heats. The specific as I said you can feed this variations as a function of temperature by this third order polynomial, okay. So then these are tabulated in a table a2 for a certain substance, we have not given the complete list of substances so you can look at table a2 for the complete list. These are the values a, b, c, d and this is the temperature range where this particular approximation of fit to the real data is valid within certain error, okay.

So average is around 0.34 percentage which is really not bad very good in fact. So the use of ideal gas specific heat data okay as an approximation is limited only to low pressures, so you cannot make use of it at higher pressure okay remember that. But you can still make use of it at moderately moderate pressures, of course you can ask like what is a range for moderate pressure, but this depends on different gases, okay. So what we are going to use in this particular course will be approximation for at low pressures. Okay, so as long as the gases do not deviate from ideal gas behavior we can make use of this approximation.

(Refer Slide Time: 15:21)



Internal energy, enthalpy and specific heats of ideal gas

- The integrations are straightforward but rather time-consuming and thus impractical.
- u and h data for a number of gases have been tabulated.
- These tables are obtained by choosing an arbitrary reference point and performing the integrations by treating state 1 as the reference state.

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T)\,dT \quad \text{(kJ/kg)}$$

$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T)\,dT \quad \text{(kJ/kg)}$$

$u(T_1)$

$h(T_2)$

TABLE A-17

Ideal-gas properties of air

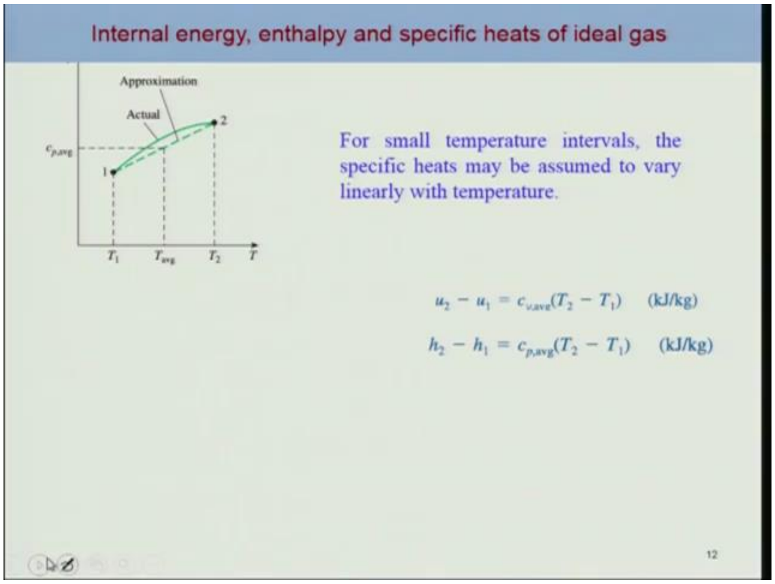
T K	h kJ/kg	P_r	u kJ/kg	v_r
200	199.97	0.3363	142.56	1707.0
210	209.97	0.3987	149.69	1512.0
220	219.97	0.4690	156.82	1346.0
230	230.02	0.5477	164.00	1205.0
240	240.02	0.6355	171.13	1084.0

In the preparation of ideal-gas tables, 0 K is chosen as the reference temperature. .

Okay so since we have to integrate if in order to find out the changes in the internal energy or enthalpy if you can make use of this third order polynomial it is going to be time consuming. So because you have to integrate a the series and then you have to put the values. So what we have done, it has been done that a values of u and h data for number of gases have been tabulated.

These tables are obtained by choosing a arbitrary reference points, so because you have to provide a reference point 1 and then if you let us say keep it a reference point where you can assume that Cp for that value is close to zero, then whatever the value would be u and h for specific temperature, okay. So in this case the table a17 is given to you in which 0 kelvin is chosen as a reference temperature, okay. So that is another way, so instead of integrating and making use of table a2 for a specific temperature you can directly make use of table a17. So that is another way of calculating the change.

(Refer Slide Time: 16:32)



Internal energy, enthalpy and specific heats of ideal gas

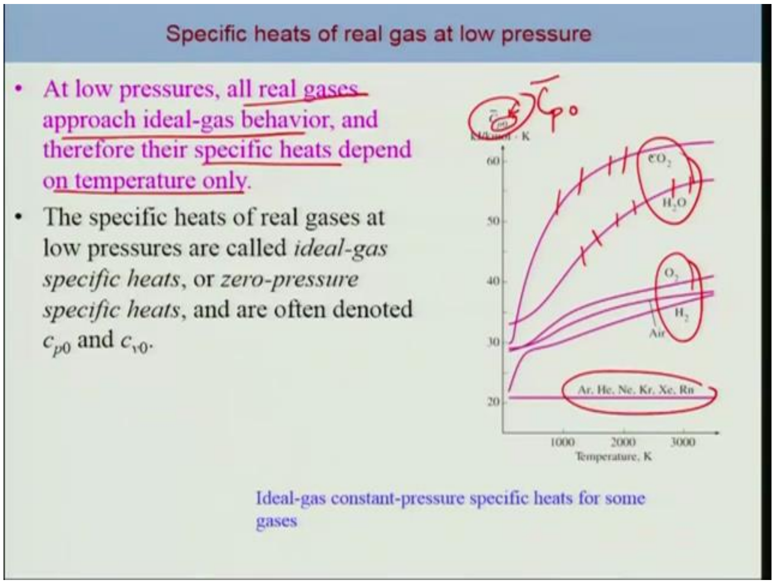
For small temperature intervals, the specific heats may be assumed to vary linearly with temperature.

$$u_2 - u_1 = c_{v,avg}(T_2 - T_1) \quad \text{(kJ/kg)}$$

$$h_2 - h_1 = c_{p,avg}(T_2 - T_1) \quad \text{(kJ/kg)}$$

Now the other possibility we can do is for the case of a small temperature intervals you can approximate also. So you can consider the variations (())(16:40) okay.

(Refer Slide Time: 16:47)



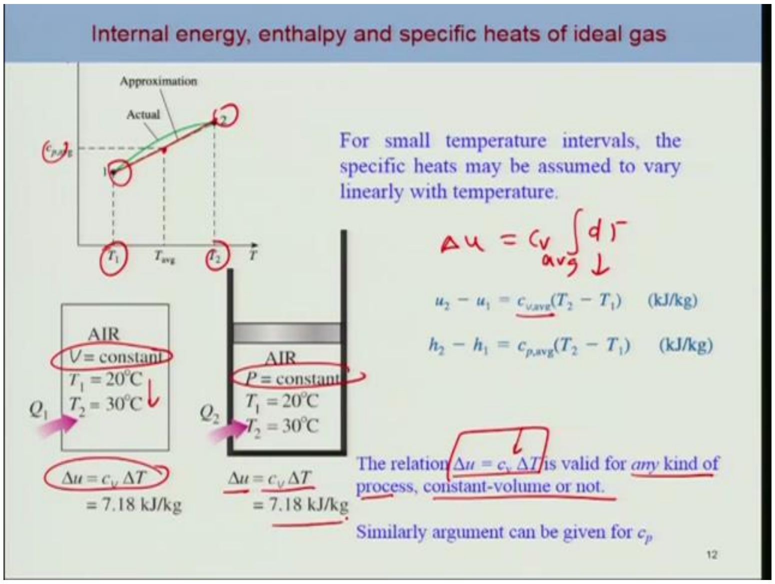
Specific heats of real gas at low pressure

- At low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only.
- The specific heats of real gases at low pressures are called *ideal-gas specific heats*, or *zero-pressure specific heats*, and are often denoted c_{p0} and c_{v0}.

Ideal-gas constant-pressure specific heats for some gases

So I was mentioning in that in this particular plot that this particular (())(16:44) there is a change in curvature although there is a variation which is significant the first small range you can always consider to be linear. So you can linearly approximate, okay so in that something which we can consider in this another possibilities to obtain the change or to obtain the values of Cv or Cp.

(Refer Slide Time: 17:03)



Internal energy, enthalpy and specific heats of ideal gas

For small temperature intervals, the specific heats may be assumed to vary linearly with temperature.

$$\Delta u = \underset{avg}{C_v} \int dT$$

$$u_2 - u_1 = c_{v,avg}(T_2 - T_1) \quad \text{(kJ/kg)}$$

$$h_2 - h_1 = c_{p,avg}(T_2 - T_1) \quad \text{(kJ/kg)}$$

$$\Delta u = c_V \Delta T = 7.18 \text{ kJ/kg}$$

$$\Delta u = c_V \Delta T = 7.18 \text{ kJ/kg}$$

The relation $\Delta u = c_v \Delta T$ is valid for *any* kind of process, constant-volume or not.

Similarly argument can be given for c_p

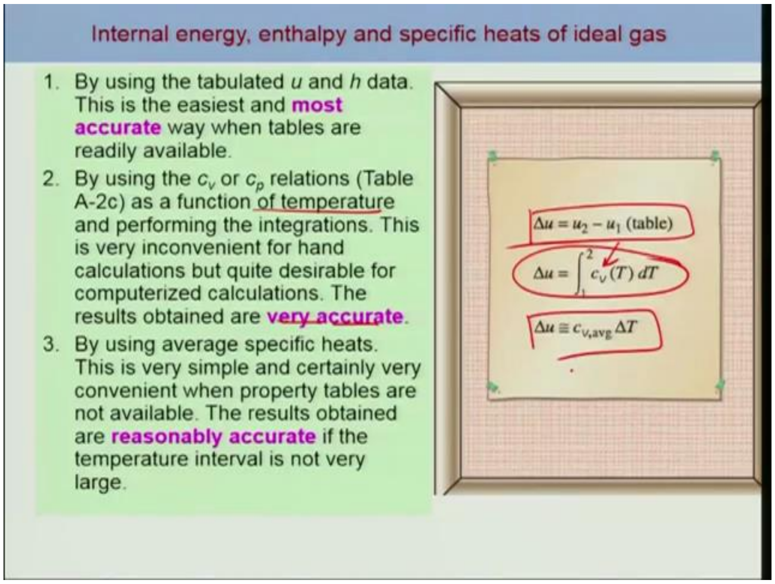
12

So this is an example here, so you have a T1 and T2 and what you can do is you can take the Cv for the complete rear process the process is occurring from 1 to 2, but you can consider Cp average or the average of specific heat at T average values. So and then you can directly use this as a constant and integrate only the dT part. So in this case u is Cv dT, okay so that gives you this things.

So this is another way or this is useful only for small temperature range, delta u equal to Cv delta T this relation is valid for any kind of process, it need not be constant volume. This expression requires that we use specific heat at constant volume, but this expression is true for whether the process is occurring at constant volume or process is occurring at constant pressure, okay.

So for example in this case you take volume as constant okay the temperatures are changing from T1 to T2 by providing some heat delta u in this case can be directly using Cv delta T, okay. On the other hand this is similar example here delta u can also be calculated by using the same expression, okay though the p is constant. So similar argument can be given for Cp, okay these expressions are true with respect to the process.

(Refer Slide Time: 18:33)



Internal energy, enthalpy and specific heats of ideal gas

1. By using the tabulated u and h data. This is the easiest and **most accurate** way when tables are readily available.
2. By using the c_v or c_p relations (Table A-2c) as a function of temperature and performing the integrations. This is very inconvenient for hand calculations but quite desirable for computerized calculations. The results obtained are **very accurate**.
3. By using average specific heats. This is very simple and certainly very convenient when property tables are not available. The results obtained are **reasonably accurate** if the temperature interval is not very large.

$$\Delta u = u_2 - u_1 \text{ (table)}$$

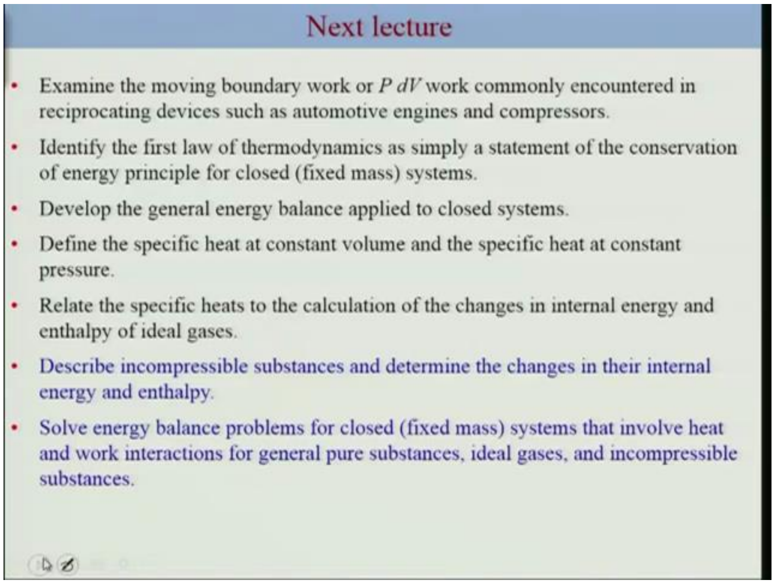
$$\Delta u = \int_1^2 c_v(T)\, dT$$

$$\Delta u \cong c_{v,\text{avg}} \Delta T$$

Okay, so let us summarize the different methods to obtain changes in the internal energy and enthalpy so as we discussed there are three possible ways, so let us try to summarize. One is (th) directly use the tables, okay which essentially is going to be much easier, okay it is one of the most accurate way. The other is you take the expression of Cv, okay as a function of temperature as we with the polynomial functions are used.

And then you make you integrate it is time consuming some time cumbersome but still very accurate, okay. So this is another way. Okay and the third is of course you consider an average Cv for specific temperature range and then you take that average and just multiply by delta T. Now this is acquired only or reasonable acquired only when the delta T or the range of the temperature which we are considering is not very large. So these are the three different ways we are going to make use of it in this particular course.

(Refer Slide Time: 19:32)



Next lecture

- Examine the moving boundary work or $P\,dV$ work commonly encountered in reciprocating devices such as automotive engines and compressors.
- Identify the first law of thermodynamics as simply a statement of the conservation of energy principle for closed (fixed mass) systems.
- Develop the general energy balance applied to closed systems.
- Define the specific heat at constant volume and the specific heat at constant pressure.
- Relate the specific heats to the calculation of the changes in internal energy and enthalpy of ideal gases.
- Describe incompressible substances and determine the changes in their internal energy and enthalpy.
- Solve energy balance problems for closed (fixed mass) systems that involve heat and work interactions for general pure substances, ideal gases, and incompressible substances.

So that will be the end of this lecture so in the next lecture we are going to talk about specific heat for incompressible substances and we will consider couple of examples before concluding this particular module, okay see you in the next lecture.