Engineering Thermodynamics
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Lecture 19
Internal energy, enthalpy, and specific heats of solids and liquids

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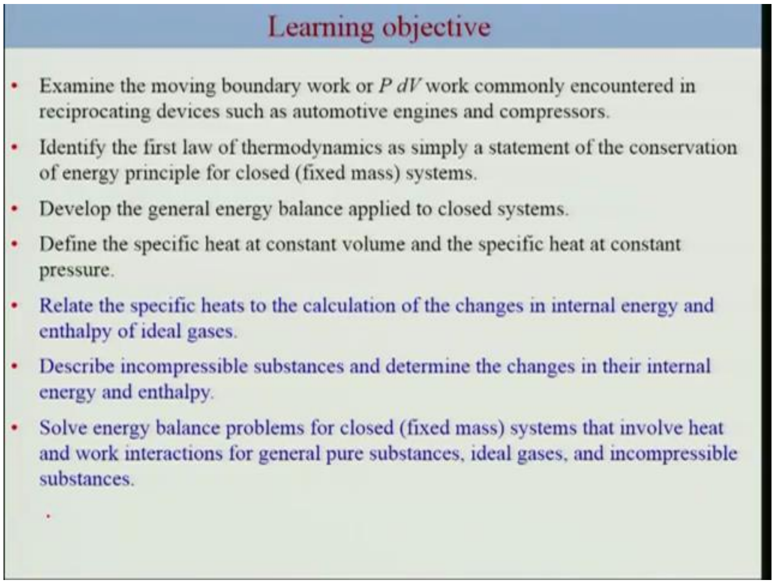

Learning objective

- 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.

Welcome back to the energy analysis of closed systems which we were discussing, this is the last part of this particular module. So we were discussing the specific heat of ideal gas, ok. And this particular module we are going to discuss a bit more and then we will discuss the incompressible part and followed by some example, ok.

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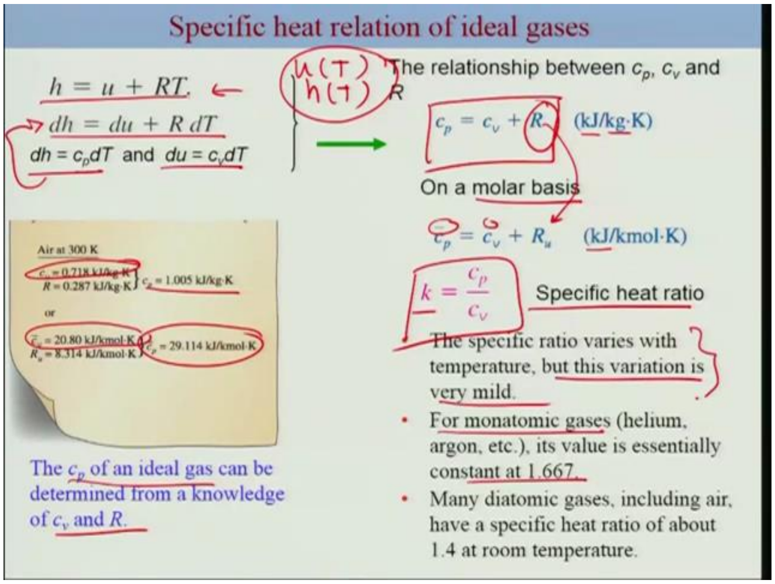

Specific heat relation of ideal gases

$h = u + RT$

$dh = du + R\,dT$

$dh = c_p dT$ and $du = c_v dT$

u(T)
h(T)

The relationship between c_p, c_v and R

$$c_p = c_v + R \quad \text{(kJ/kg·K)}$$

On a molar basis

$$\bar{c}_p = \bar{c}_v + R_u \quad \text{(kJ/kmol·K)}$$

$$k = \frac{c_p}{c_v}$$ Specific heat ratio

- The specific ratio varies with temperature, but this variation is very mild.
- For monatomic gases (helium, argon, etc.), its value is essentially constant at 1.667.
- Many diatomic gases, including air, have a specific heat ratio of about 1.4 at room temperature.

Air at 300 K

$c_v = 0.718$ kJ/kg·K
$R = 0.287$ kJ/kg·K $\}$ $c_p = 1.005$ kJ/kg·K

or

$\bar{c}_v = 20.80$ kJ/kmol·K
$R_u = 8.314$ kJ/kmol·K $\}$ $\bar{c}_p = 29.114$ kJ/kmol·K

The c_p of an ideal gas can be determined from a knowledge of c_v and R.

So let me summarize that what we have learned about a specific heat relation for the ideal gas. We know from the definition that H is equal to u+RT, we already defined that for ideal gas u is a function all the T, and h is a function of all the T. So if you take a derivate of h or this particular expression, you obtained this expression which is dh is equal to du+RdT.

Now considering the fact that u is just a functional temperature and h is a functional temperature, you can replace dh by simply cpdT, so this is just an ordinary differentiation, ok. The partial differentiation gets replaced by ordinary differentiation because of the fact that u and h is constant. Thus you can obtain a relation between cp and cv, ok by plugging this here so what you get is relation of cp and cv so you can obtain cv and from there also you can get cp, but these are related by the gas constant.

Now this you can write also in a molar basis, ok. This is kilojoules per kg kelvin and hence if you convert R to universal gas constant you get kilojoules per kilo mole and this represent molar gases. If you have the information of cv you can obtain cp, or the same thing if you have the information of molar specific heat at constant volume you can also get molar specific at constant pressure.

So cp of an ideal gas can be determined from knowledge of cv and R. There is an important parameter which is commonly used to analyze gases is the ratio of this specific heat that is called k, ok so specific heat ratio is k is equal to cp by cv, ok. And this is interesting because if you look at this ratio for many gases it is constant, for example for monatomic gas its value is essentially constant.

So you can relate this to the original picture or the graph which we have used in the last lecture where we showed that for monatomic gas the cp at very low pressure is almost constant with temperature. But otherwise the variation is very mild, ok for other gases, ok for the case of diatomic gases such as air, the specific ratio is around 1.4.

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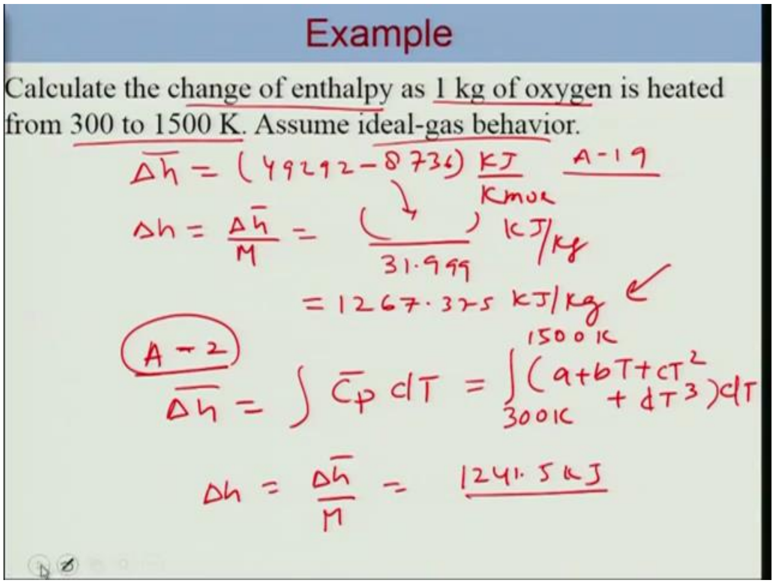

Example

Calculate the change of enthalpy as 1 kg of oxygen is heated from 300 to 1500 K. Assume ideal-gas behavior.

$$\Delta\bar{h} = (49292-8736)\,\frac{kJ}{kmol} \qquad \underline{A-19}$$

$$\Delta h = \frac{\Delta\bar{h}}{M} = \frac{(\quad)}{31.999}\,kJ/kg$$

$$= 1267.375\ kJ/kg$$

$$\boxed{A-2}$$

$$\Delta\bar{h} = \int \bar{C}_p\,dT = \int_{300K}^{1500K} (a+bT+cT^2+dT^3)\,dT$$

$$\Delta h = \frac{\Delta\bar{h}}{M} = \underline{1241.5\,kJ}$$

So let us do some example here, ok. And let us make use of the last lecture summary the way which we different ways to calculate the change in internal energy enthalpy. So this is the example to calculate change of enthalpy, for 1 kg of oxygen, which is heated from and what we have to assume is ideal gas behavior, ok.

So as I said there are different ways calculate so we will try two ways here, one is calculating directly delta h from the table. Now for the case of oxygen the table which is relevant is A-19 and this table the h is given on molar basis.

So delta h for the case of this 300 to 1500, is will be on a molar basis based on the table A-19 and the values are (49292-8736) kilojoules/kilomole. If you want to convert this into mass basis then essentially you can divide by the molar mass which for the case of oxygen is so this is the value divided by 31.999 this becomes kilojoules per kg. So this value turns out to be 1267.375 kilojoules per kg, or so this is one way to obtain the change in enthalpy we have directly made use of the table.

So again we are going to calculate delta h, ok so here what we are going to do is we are going to make use of A-2 table where the values are given in terms of polynomial functions and you can evaluate cp value, ok. So cp is given in terms of polynomial function but in terms of molar basis. So this is the second way of calculating delta h, we are going to make use of A-2 and delta h bar is given as cpdT as I said, we want to make use of table tables is mainly written in this form so irrespective to which ever textbook you pick up you find this kind of (())(5:16) for the cp values.

So this temperature is from 300 kelvin to 1500 kelvin and so without showing the details of the calculation it turns out that delta h, ok is around 1241.5 kilojoules. So this is much more the first, method is much more accurate ant this is not so but still it is very accurate compare if you look at the differences extremely small.

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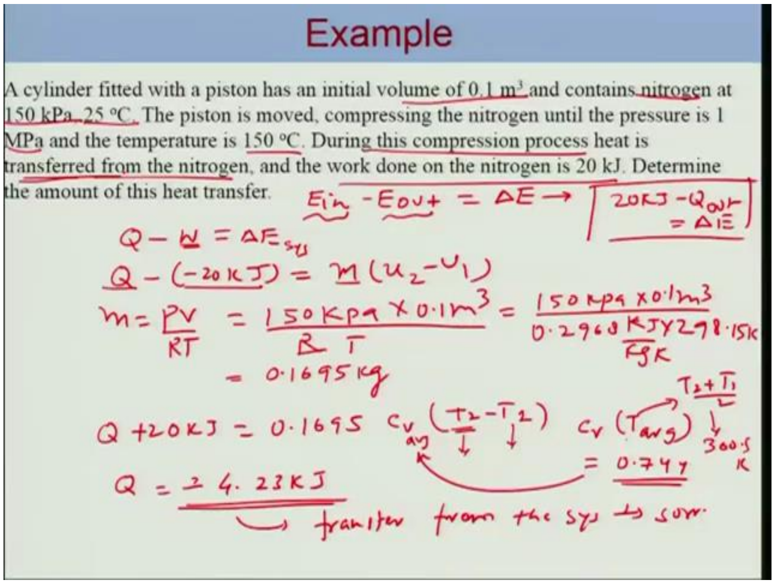

Example

A cylinder fitted with a piston has an initial volume of 0.1 m³ and contains nitrogen at 150 kPa, 25 °C. The piston is moved, compressing the nitrogen until the pressure is 1 MPa and the temperature is 150 °C. During this compression process heat is transferred from the nitrogen, and the work done on the nitrogen is 20 kJ. Determine the amount of this heat transfer.

$E_{in} - E_{out} = \Delta E \rightarrow \boxed{20\,kJ - Q_{out} = \Delta E}$

$Q - W = \Delta E_{sys}$

$Q - (-20\,kJ) = m(u_2 - u_1)$

$m = \frac{PV}{RT} = \frac{150\,kPa \times 0.1\,m^3}{R\ T} = \frac{150\,kpa \times 0.1\,m^3}{0.2968\,\frac{kJ}{kgK} \times 298.15\,K}$

$= 0.1695\,kg$

$Q + 20\,kJ = 0.1695\ c_{v_{avg}} (T_2 - T_1)$ $\quad c_v(T_{avg}) \rightarrow \frac{T_2+T_1}{2} \downarrow 300.5\,K$

$= 0.744$

$Q = 24.23\,kJ$

$\hookrightarrow$ transfer from the sys to surr.

So these are the different ways to solve problems, we will take another example this is a cylinder fitted with a piston which has an initial volume of 0.1 meter cube which contain nitrogen, ok which is at 150 kilopascal and is 25 degree Celsius, ok. The piston is moved compressing the nitrogen until the pressure is 1megapascal and the temperature is 150 degree Celsius.

So essentially it is being compressed such that the temperature is increased and as well as pressure. Now during this compression process heat is transferred from the nitrogen and the work done on this nitrogen is 20 kilojoule. So what we have to find out is the amount of this heat transfer. There are two ways to do this problem, one is of course you can simply write Ein minus Eout ok equal to delta E, ok. So this is one way where we know the net energy provided to the system and net energy which is transfer out of the system, ok.

So all the other way we can make use of a standard sign dimension where you say that Q minus W is your delta E and in this case the work is done on a system so essentially Q minus (20 kilojoules) because this definition is Q which is applied to the system minus work which is done by the system on the surrounding should be equal to change in energy of the system, ok. So this should be equal to m (u2-u1) considering the all other terms like such as kinetic energy and potential energies are 0. So this is one way of putting in.

So if I use those I would be using Ein which is work done on the nitrogen that is 20 kilojoules minus Qout, ok is equal to delta E. So this is one way where we just write because we know the sign of it, ok. But otherwise we can make use of a visualize form where Q is what is being supplied to the system minus work which is done by the system on the surrounding which is minus 20 kilojoules because the system here in this case solving does work on a system that is why it should be minus.

Now we assuming Q is supplied to the system that is why we put Q here, so we know with the sign. So what about my mass, what is the mass here and so we can calculate the mass here, m is simply PV by RT, ok we assuming nitrogen to be aduro gas ok so this is initial mass so the mass will be fix we have the information of 150 kilopascal into volume which is 0.1 initial volume, ok and R and T, R you can obtain R from the tables, so R is a gas constant so you can look at A1 and from there you can obtain 150 kilopascal into 0.1 meter cube and 0.2968 kilojoules per kg kelvin into 298.15 kelvin, ok.

So this is R value from the table and based on that the value comes out to be 0.1695 kg. So mass you know. Now the next thing is how to find the change in internal energy so we can write Q plus 20 kilojoules is equal to 0.1695 and delta u can be written as cv some average considering the difference here we will take an average here. So some average let us say T2 minus T1, ok.

So what we can do is we can look at the tables and first we find out cv at a specific T average, which is going to be T2+T1 divided by 2 and from the table this value comes out to be 0.744 so T2 plus T1 by 2 is nothing but 360.5 kelvin, ok. So this is the value which we are going to make use of it and from here you plug, this value of T2 is your 150 degree Celsius and this one is 25 degree Celsius you can convert this into kelvin but being difference between two temperature this is not going to make any difference.

So the key value turns out to be minus 4.23 kilojoules which essentially means there is a transfer from the system, ok to surrounding, ok as of course the question was mentioned. So without taking the direction from the question if we solve it the answer turns out to reflect the direction of the heat transfer, this was an example we made use of the fact that cv average can be calculated by taking the temperature average of the final (())(11:08) values.

So if the values are not dramatically does not change with temperature so this approximation is ok. So this was the example of that.

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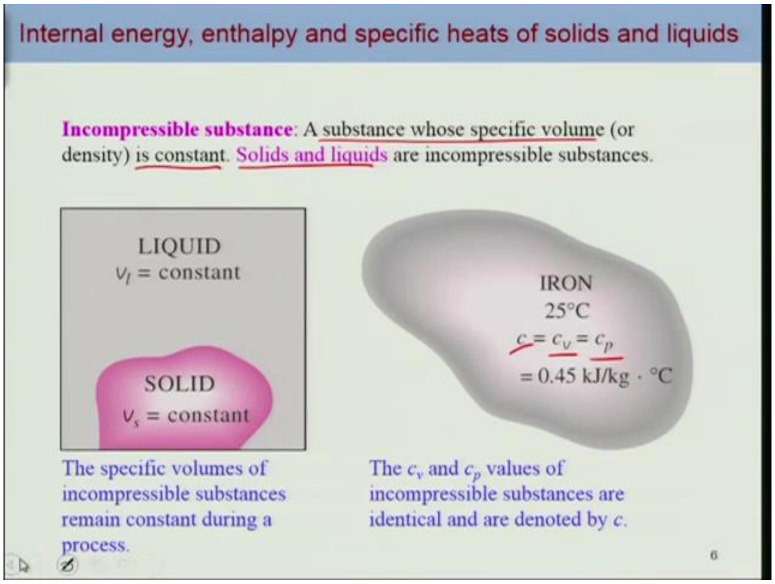

Internal energy, enthalpy and specific heats of solids and liquids

Incompressible substance: A substance whose specific volume (or density) is constant. Solids and liquids are incompressible substances.

The specific volumes of incompressible substances remain constant during a process.

The c_v and c_p values of incompressible substances are identical and are denoted by c.

Now let us pay attention to different system here we are able to consider substances which are incompressible or which means the substance whose specific volume is constant. And these are examples are solids and liquids, so that for such system one can show mathematically that specific heats are constant which mention means cv is same as cp, we are just going to denote by c for the case of solids and liquids.

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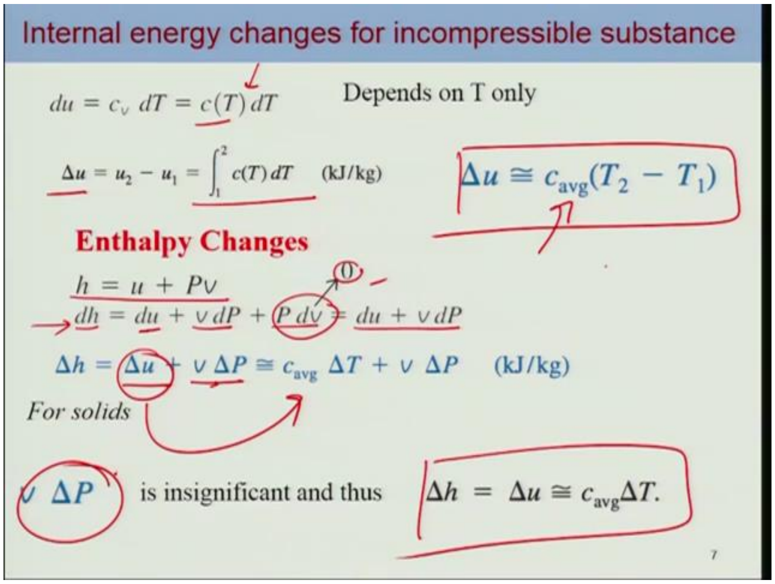

Internal energy changes for incompressible substance

$du = c_v\, dT = c(T)\, dT$ Depends on T only

$\Delta u = u_2 - u_1 = \int_1^2 c(T)\, dT$ (kJ/kg)

$\boxed{\Delta u \cong c_{avg}(T_2 - T_1)}$

Enthalpy Changes

$h = u + Pv$

$dh = du + v\,dP + \overset{0}{P\,dv} = du + v\,dP$

$\Delta h = \Delta u + v\,\Delta P \cong c_{avg}\,\Delta T + v\,\Delta P$ (kJ/kg)

For solids

$v\,\Delta P$ is insignificant and thus $\boxed{\Delta h = \Delta u \cong c_{avg}\Delta T.}$

So considering the fact that c and cv are same, one can also show that for the case of such system just like aduro gas your c only depends on temperature. So thus you can find out the change in internal energy by simply integrating c over a temperature (())(12:02) from state one to state two, ok. Or you can approximate again as we have done for the gases in this form, ok where you can approximate c average over the temperature range, ok.

So let us look at specifically enthalpy changes for the case of incompressible substance. As we know h is equal to you plus Pv that is a definition, so you can differentiate and so it will be dh is equal to du then it will be there will be two terms because you can differentiate first V and then later P. Now considering incompressible substance this part is going to be 0, ok so what remains is Duracell plus VdP.

Now you can integrate this and get your du to get your delta u and vdp, now vdP will talk about vdP later but delta u you can replace by c average delta T as an approximation. So this would be your enthalpy change for incompressible substance, ok for solid it turns out that this term is extremely small so this is specific volume it typically is very small, this was also listed it here in terms of that so this is typically very small that is your delta h is simply your c average delta T.

But this term is not may not be very small for the liquids so let us look at this change in enthalpy for liquids.

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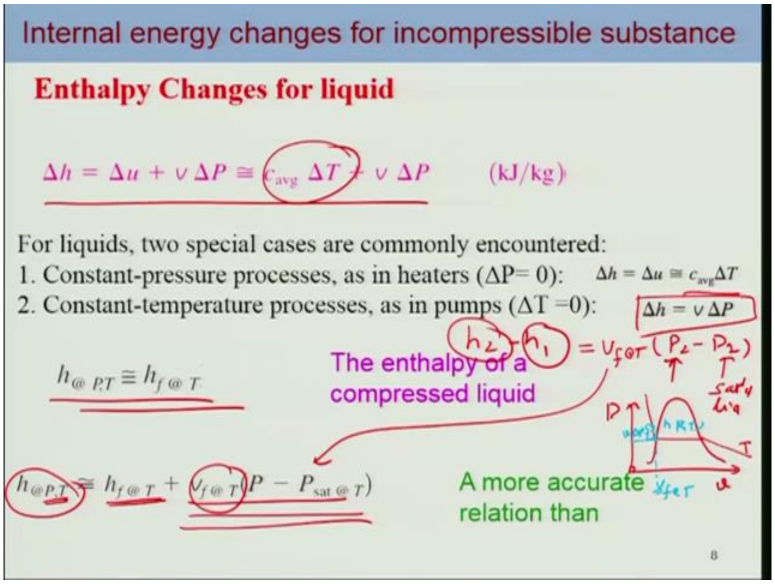

Internal energy changes for incompressible substance

Enthalpy Changes for liquid

$$\Delta h = \Delta u + v\,\Delta P \cong c_{avg}\,\Delta T + v\,\Delta P \qquad (\mathrm{kJ/kg})$$

For liquids, two special cases are commonly encountered:
1. Constant-pressure processes, as in heaters ($\Delta P = 0$): $\Delta h = \Delta u \cong c_{avg}\Delta T$
2. Constant-temperature processes, as in pumps ($\Delta T = 0$): $\boxed{\Delta h = v\,\Delta P}$

$h_2 - h_1 = v_{f@T}(P_2 - P_2)$

$h_{@P,T} \cong h_{f@T}$

The enthalpy of a compressed liquid

$$h_{@P,T} \cong h_{f@T} + v_{f@T}(P - P_{sat@T})$$

A more accurate relation than

So again we start with the same expression ok, now the two specific cases, ok. The first case we are going to consider a constant pressure process, ok where we can consider delta P to be 0, in that case you change in enthalpy is simply your c average delta T.

The other case we are going to consider where your temperature is constant that means your delta T is 0, which means the first term is going to be 0 and delta h is going to v delta P. Now if you recall earlier we approximated for a compress liquid the change in enthalpy to its saturated liquid values, ok at a given temperature.

So that was the early approximation, ok. But if you consider this the information that delta h can be related to v delta P and you say this simply as Vf at T and this will be your (P2 minus P1), ok. And your 1 could be your saturated liquid, ok and this could be your compressed liquid. So this will be your fP P1, ok a saturated condition.

So you can make use of this and plug in here to obtain your h at specific P, ok. So this is nothing but your h2 minus h1, h1 is your saturated liquid values and h2 is your specific compressed liquid so thus you can write in this form. This is your compressed liquid, this can be approximated, now that this is nothing but the values at saturated liquid plus this term which is going to be the values which we are considering volume, specific volume to be constant and the change in the ratio.

So this you can understand from a PU diagram, ok. So this is your pure substance and this is at a constant temperature, it so liquid and it evaporates as a constant temperature, ok when you reduce the pressure. So what we are assuming that is that you for a specific PT which is let us say this ok this is the (())(15:37) in this particular enthalpy at this P and T, you are assuming that this can be approximated by this value plus the change in the pressure, ok delta P multiplied by corresponding V for the specific T here which is this, ok.

So this is the reason being is that you can look at the slope here is very high assuming that the volume is not changing upon increasing the pressure by delta P. So this is a more accurate relation which we are going to use for the further in case of liquid.

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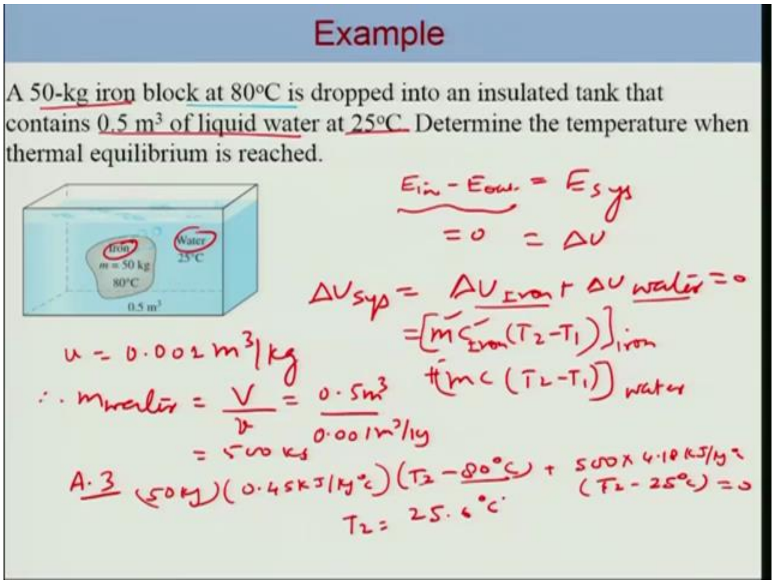

Example

A 50-kg iron block at 80°C is dropped into an insulated tank that contains 0.5 m³ of liquid water at 25°C. Determine the temperature when thermal equilibrium is reached.

$\underbrace{E_{in} - E_{out.}}_{=0} = E_{sys} = \Delta U$

$\Delta U_{sys} = \Delta U_{Iron} + \Delta U_{water} = 0$

$= [m c_{Iron} (T_2 - T_1)]_{iron} + [m c (T_2 - T_1)]_{water}$

$\nu = 0.002\ m^3/kg$

$\therefore m_{water} = \frac{V}{\nu} = \frac{0.5 m^3}{0.001 m^3/kg} = 500\ kg$

A.3 $(50 kg)(0.45 kJ/kg°C)(T_2 - 80°C) + 500 \times 4.18 kJ/kg°C (T_2 - 25°C) = 0$

$T_2 = 25.6°C$

So let us take a look of an example try to finish this module with an example, so this is in the example of 50 kg iron block at 80 degree Celsius which is dropped in an insulated tank and which contains 0.5 meter cube of liquid water at 25 degree Celsius, ok.

So this iron block is being placed in water which is at high temperature and it is the whole tank is insulated and then you have to find out the final temperature of the system, ok. So let us look at how we are going to solve, so we will take the generalize energy balance here Ein minus Eout is equal to E system.

Now upon dropping the iron block the system is insulated so after that of course there is no change in the energy which is being provided to the system or there is no transformed energy from the system thus your Ein should be 0 and as well as Eout should be 0 because once it is insulated the system is not getting any energy from the out surrounding as well as system is not transferring any energy to the surrounding.

So thus this must be 0 and what remains is nothing but delta u we are ofcourse ignoring other terms so delta u is 0, ok. Which means the change in internal energy of the system should remain 0, u should be constant. So what is u, u is an extensive property, so delta u system contains there two pieces here or two components one is iron and one is water, so it should be your delta u for iron plus delta u for water, ok so that should be 0, this is a solid and this is ofcourse liquid so we are going to make use of specific heat can be written as mc for iron and (T2 minus T1), ok for specific iron.

So let us say this is for iron plus mc (T2 minus T1), ok this is for water. So this T2 and T1 are respective temperatures of initial and a final state for iron and water, c is basically the respective specific heat for iron and water, ok. Now you need these values in order to solve the problem you also need the mass here we know the mass of iron, but what about the mass for water? We know the density of the water, we can make use of that and obtain the specific volume, so what is the specific volume for water would be 0.001 meter cube by kg, ok.

Thus your mass for water is going to be volume divided by specific volume which is going to be 0.5 meter cube by 0.001 meter cube by kg. So this is going to be 500 kg. Now the next thing which we are going to use is a table to obtain the specific heat for iron and water. So the table which contains this is A3 and then you plug in these values because now we know the mass of iron, c of iron from table 3.

So let me write it down here 50 kg and the value from table for the case of iron for specific heat is 0.45 (T2 minus 80) initially the iron was 80, what is the final temperature that let us say T2 plus 500 into 4.18 kilojoules per kg specific heat for water and this is going to be (T2 minus 25 degree Celsius), ok and this should be 0.

So if you solve this T2 turns out to be 25.6 degree Celsius. So that is how we are going to solve such a problem making use the specific heat, ok.

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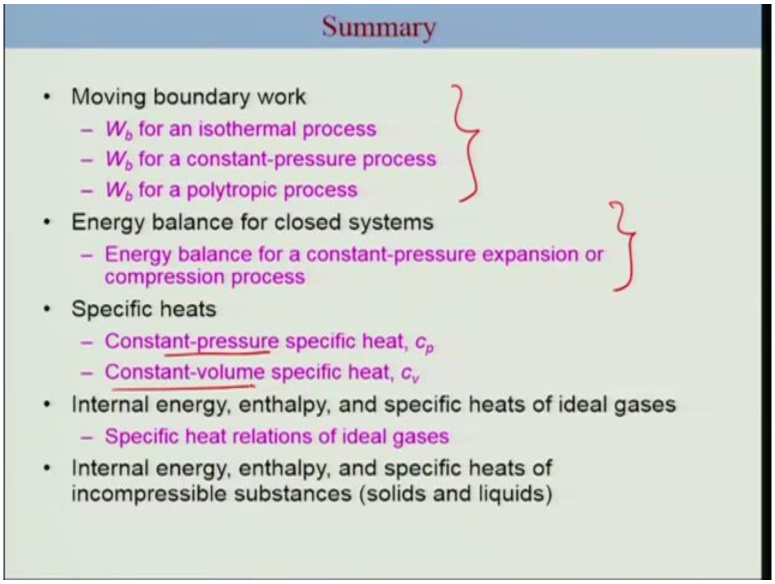

Summary

- Moving boundary work
  - W_b for an isothermal process
  - W_b for a constant-pressure process
  - W_b for a polytropic process
- Energy balance for closed systems
  - Energy balance for a constant-pressure expansion or compression process
- Specific heats
  - Constant-pressure specific heat, c_p
  - Constant-volume specific heat, c_v
- Internal energy, enthalpy, and specific heats of ideal gases
  - Specific heat relations of ideal gases
- Internal energy, enthalpy, and specific heats of incompressible substances (solids and liquids)

So let me summarize this particular module so we describe the boundary work for different processes that was an initial part of this particular module. Then we looked into the energy balance for closed systems. Then we describe specific heat for ideal gas for different and specific heat, one as cos temperature, one at constant volume, ok.

And then we relate this cp and cv values in terms of relation for ideal gas. Then we mention that cp and cv is constant for incompressible substance and later we solved an example so that will be the end of this particular module so we will continue with the new chapter. So see you in the next lecture.