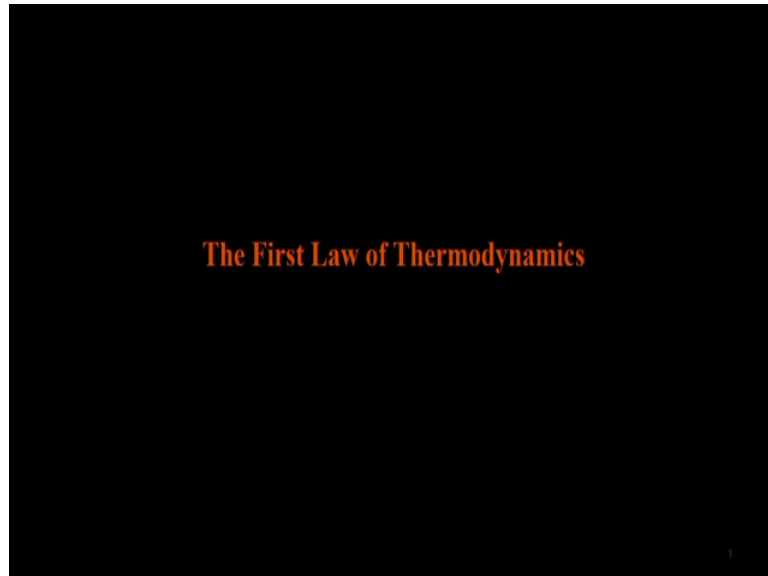


Chemical Engineering Thermodynamics
Prof. Sasidhar Gumma
Department of Chemical Engineering
Indian Institute of Technology Guwahati

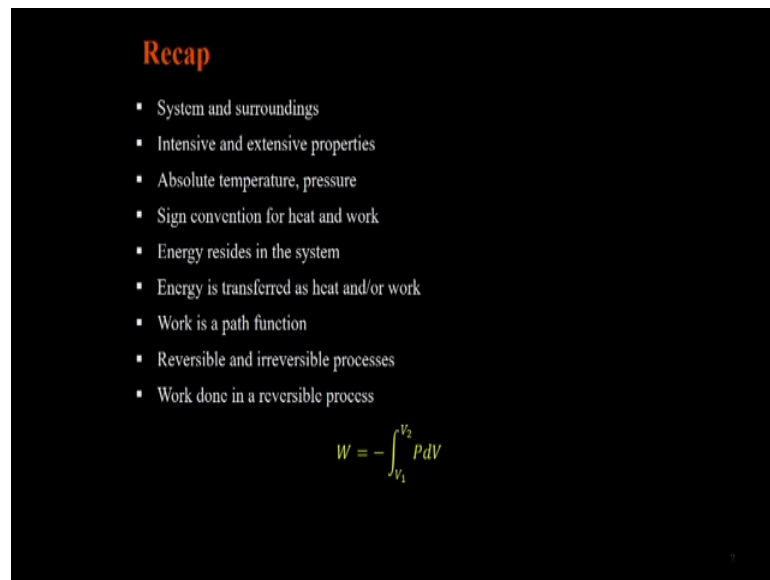
Lecture - 02
The First Law of Thermodynamics

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Hello and welcome back to the online course on Chemical Engineering Thermodynamics. Today we will be looking at the first law of thermodynamics in particular for closed systems.

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Recap

- System and surroundings
- Intensive and extensive properties
- Absolute temperature, pressure
- Sign convention for heat and work
- Energy resides in the system
- Energy is transferred as heat and/or work
- Work is a path function
- Reversible and irreversible processes
- Work done in a reversible process

$$W = - \int_{V_1}^{V_2} P dV$$

In the previous lecture we looked at a variety of things such as what we mean by a system in thermodynamics, what we mean by surroundings, the intensive and extensive properties, we talked about the absolute temperature which comes out from the ideal gas law. Then we talked about the pressure, and the relation between gauge pressures and absolute pressures. We also looked at design conventions for heat and work, the heat added to the system is positive, the work done on the system is positive according to our sign convention. We said that the energy that is transferred to the system is going to reside in the system and it is transferred as heat or work.

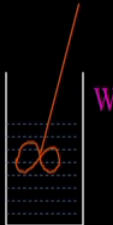
We looked at the nature of work and we said that work is a path function, it is going to depend on the path we take to go from one state to another state. Then we looked at a variety of processes which we called as reversible processes and irreversible processes. And in case of a reversible process we said the work done is going to be the integral of P dV.

We will extend these concepts or will base our discussion today on the concepts we have discussed in the previous lecture and try to extend it to a closed system and derive the first law of thermodynamics.

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Internal Energy

- Energy Stored in fluid
- Does NOT include macroscopic K.E and P.E
- Energy of molecules internal to the substances
- Total internal energy U^t (SI Unit: J) U^t
- Molar internal energy $U = \frac{U^t}{n}$ (SI Unit: J mol⁻¹) *specific $U = J\ kg^{-1}$
 $U = U^t/m$*
- U is an intensive property, U^t is an extensive property



The first law of thermodynamics involves a quantity which we call as internal energy for a system. Essentially if you recall the earlier discussion on using a stirrer, to stir a fluid in a vessel then we are doing some work on the fluid and if we stir long enough the temperature of the fluid is going to rise. This rise in temperature is essentially due to the energy that is transferred through the stirring. And once this energy is transferred, we have convert the temperature has risen we have converted work effectively into heat.

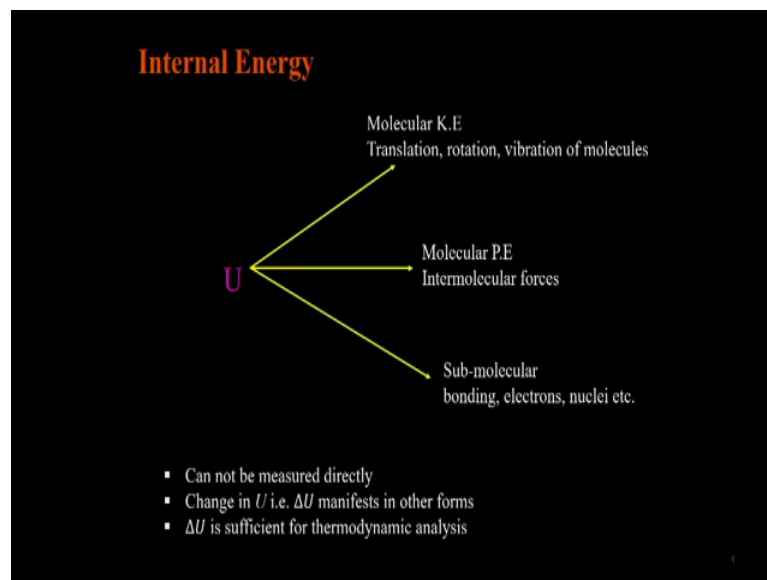
Now, after this process I can put a cooling jacket around this vessel and extract the heat I have transferred to this fluid out, which means in between these two states the initial state where the work has been done on the fluid and the later state where I am extracting heat out of the fluid in between these two states the energy is stored in the fluid somehow.

Now, notice that this fluid is after I stop studying the fluid is not moving there is no kinetic energy visible, macroscopic kinetic energy to this fluid, neither there is a change in the physical location of the fluid, so the potential energy has not changed. So, where is this energy residing? This energy is internal to the fluid, right and it actually relates to the energy of the molecules inside the fluid. We call such energy as the internal energy of the fluid. The total internal energy is indicated by the variable U and is superscript t to denote that it is the total internal energy of the system. The units are Joules. And as opposed to the total internal energy I can define an intensive internal energy, if we divide

the total internal energy with the number of moles then I get the intensive internal energy of the system which is simply denoted by U . So, the units for this molar internal energy are going to be Joules per mol.

I can also write a specific internal energy instead of the molar internal energy. So, the units are going to be Joules per kilogram and to be able to get the specific internal energy all I need to do is divide U or the total internal energy with the mass of the system. So, either of these two quantities, either the molar internal energy or the specific internal energy are going to be the intensive variables and the total internal energy is an extensive variable.

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When we say it is internal to the molecules, what do we mean? The internal energy can be due to the molecular kinetic energy, molecular level it is not macroscopic, but it is microscopic or at the level of the molecules. It is may be due to the molecular level kinetic energy that is due to translation, rotation or vibration of the molecules present in the system. It can be due to the molecular level potential energy due to the intermolecular forces that are always present inside the fluid or it can be sub molecular energy such as the energy due to the bonding, energy of the electrons, the nuclei, etcetera. All of these together make the internal energy of the system.

Because it is a microscopic quantity, we cannot measure it directly there is no device which I can put in and measure the internal energy of a system. However, the change in

the internal energy is going to manifest in some other form either as heat or work or in some other very a quantity which can be measured. And remember in the first lecture during introduction we said that the goal of thermodynamics is always to be able to relate the quantities that cannot be measured to the quantities that can be measured.

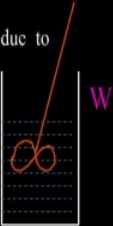
So, what I am interested in is how this ΔU or the change in internal energy manifests in other forms and we are going to try to use that concept to be able to quantify this change in internal energy, and that alone is enough for our thermodynamic analysis.

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Conservation of energy

- Recall the example of conversion of work to heat due to stirring
- Energy disappearing in one form appears in another
- Total of all energies is constant

$\Delta \text{Energy of system} + \Delta \text{Energy of surroundings} = \text{constant}$

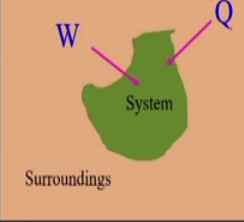
A diagram of a beaker with a stirrer. The stirrer is a red line that enters the beaker from the top right, loops around twice, and exits at the top right. To the right of the beaker is a purple letter 'W'. The beaker is filled with a liquid, indicated by horizontal dashed lines.

Before we move on to the first law let us talk about conservation of energy. Recall the example we discussed for stirring a fluid and where work is converted to heat due to this stirring. If you think about this example the energy that is disappearing in one form appears in another form or in other words according to the conservation of energy the change in energy of the system plus the change in energy of the surroundings is going to be equal to 0.

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First Law for Closed System

- **Closed system:** No transfer of matter across the boundary
- Energy transfers as heat or work
- Q = heat added to the system
- W = work done on the system
- $\Delta \text{Energy of system} = Q + W$
- $\Delta \text{Energy of surroundings} = -Q - W$



Now, let us try to take this idea of conservation of energy between the system and surroundings and extend it to develop the first law. We are going to focus today's lecture on very specific type of systems which are called as closed systems. By a closed system what we mean is that there is no transfer of matter or mass through the system boundary. What the system can exchange with the surroundings is only heat and work, the mass cannot cross the system boundary, right. So, I can add or remove heat from the system, I can add or remove work from the system. So, let these quantities be denoted by Q and W as is the usual notation, the positive sign is heat added to the system and work done on the system.

Now, the sum total of the energy that is delivered to the system to this closed system is going to be the sum of the heat added and the work done which is Q plus W , right. This is the energy that we are adding to the system, there is no transfer of mass so there is no other energy stream coming in to the system. Now, because of conservation of energy the delta energy for the surroundings is going to be negative of this quantity which is essentially negative Q minus W . So, once we add these two it goes to 0.

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First Law for Closed System

For a closed system,

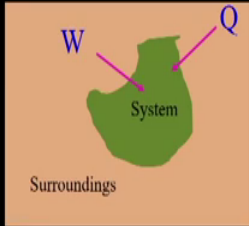
$\Delta \text{Energy of system} = Q + W$

BUT, $\Delta \text{Energy of system} = \Delta U^t$

$dU^t = dQ + dW$

$d(nU) = dQ + dW$

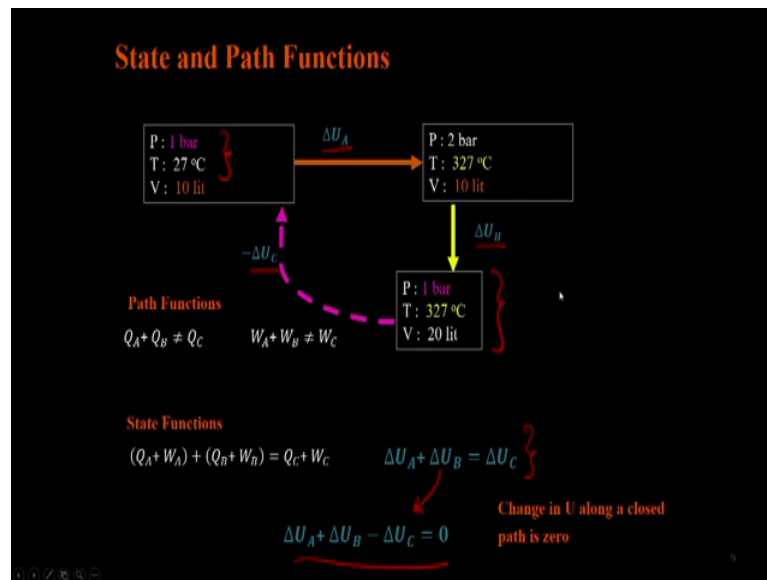
$d(mU) = dQ + dW$



So, now I have a quantity Q plus W which is energy that is added to the system. But where is this energy going to reside? It is going to reside as the internal energy or the change in internal energy of the system. Once I put this energy into the system it has to be residing in the system as the internal energy because that is the change in energy of the system itself.

So, now I can equate these two quantities or in the differential form the change in the internal energy total internal energy which is dU^t will be equal to dQ plus dW , the differential amounts of work and heat that are transferred to the system. And if we want to write it in terms of the intensive variables, intensive internal energy, let us say molar internal energy then we write instead of U^t we write n times U . The number of moles times the molar internal energy or if we are writing in terms of specific internal energy then the mass in kilograms times the internal energy is Joules per kilogram etcetera. So, we multiply with appropriate quantity and we can rewrite this equation in terms of the intensive properties, either molar or specific. This is the differential form of the first law of thermodynamics for closed systems.

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We said that work and heat are path functions, let us see what happens to internal energy. Let us take an example to demonstrate this idea let us say I have a fluid at 1 bar, a gas at 1 bar 27 degree centigrade and it occupies a volume of 10 liters whatever may be the number of moles. I take this gas and subject it to a isochoric process and by an isochoric process we mean that the volume is held constant and what I am changing is the other two variables, the pressure and the temperature. The temperature has gone up from 27 degrees centigrade to 327 degrees centigrade, and the pressure has gone up from 1 bar to 2 bar accordingly. And to achieve this process I have added some amount of heat and work to the system Q_A and W_A .

Then I take this gas and subject it to an isothermal process, right. In an isothermal process the temperature is held constant, this time right the temperature is held constant. Let us take it different color, temperature is 327 in both cases. The pressure is reduced to half the original value 2 bar to 1 bar, and accordingly the volume went up to 20 liters so. Maybe we can draw a bigger size of the vessel just to indicate that it is double the original size.

So, now, we have taken the initial gas and subjected it to two steps. Instead of these two steps I could have also gone from the first stage or the first state to the final state in a single step, and notice that what is same in the initial and the final states is 1 bar pressure, the temperature and volume are changing and because the pressure is same we

call such a process as an isobaric process, right. And it is a single step process instead of two steps involving an isochoric process and isothermal process. I achieved the same objective at the end the final temperature pressure and volume are 1 bar 327 degree centigrade and 20 liters.

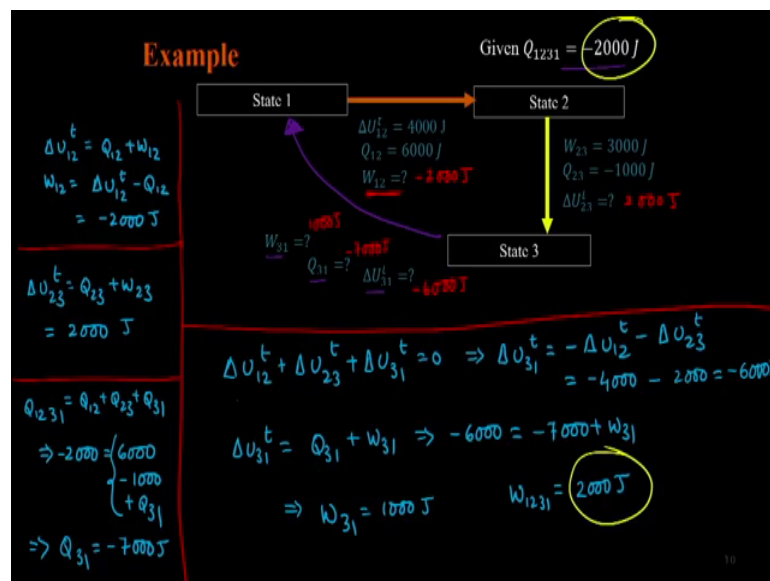
Now, because we have seen earlier that work and heat are path functions the sum of the work done in the first and second steps Q_A plus Q_B or I am sorry these sum of work done in the first and second steps that is W_A plus W_B is not going to be equal to the work done in the third step which is W_C . Although in both cases whether I go like this from step 1 to step 2 to step 3 or directly from step 1 to step 3, I am sorry state 1 to state 3, we are always achieving the final same change in the states in both cases, the some of the work done. So, the total work done in the first scenario in a two-step process is different from the work done in a single step process because work is dependent on path. Same is the case for heat exchanged.

However, it has been observed that the some of the work done and heat exchanged in the two-step process is exactly equal to the sum of the work done and heat exchange in a single step process that is Q_A plus W_A plus Q_B plus W_B is exactly equal to Q_C plus W_C . This is applicable always, and remember from the first law we call this as ΔU_A , this as ΔU_B , this will be equal to ΔU_C , which means the change in internal energy is independent of the path. I can go in a two-step process or in a single step process the difference between the internal energies of the state 1 here and state 3 here is exactly same irrespective of which path I choose to go from state 1 to state 2.

What it also means is this, I can reverse the direction of the last step, instead of stores going from state 1 to state 3 I can go from state 3 to state 1 in that case the change in internal energy is going to be negative of ΔU_C . ΔU_C is in the forward direction, now because I reverse the direction the change in internal energy let us say is negative U_C . And because we already said that this is true the change in internal energy in the step A and step B is equal to the change in internal energy in step C when I rewrite this expression it turns out the change in internal energy ΔU_A plus the change in internal energy ΔU_B minus ΔU_C is going to be equal to 0. This follows directly from this equation.

What it means is that once I complete the cycle going from the initial state to the second state to the third state and coming back to the initial state once I complete that cycle the total change in the internal energy is 0, which means the internal energy itself does not care what paths I have followed. All it cares about is the state in which it is in, once I am in the same state the internal energy is always going to be the same. So, internal energy is a state function.

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Let us look at a quick example how we can extend these concepts to solve a problem. Let us say I have a fluid in three states state 1, state 2 and state 3. To go from state 1 to state 2 there is a certain amount of change in internal energy and heat requirement we want to know what the work requirement yes, we want to calculate this quantity. Let us pick a different color, so that it is easy on our eyes.

So and similarly going from state 2 to state 3 we have to calculate some other quantity, going from state 3 to state 1 we need to calculate another quantity. We will come back there later, but first let us look at the first step going from state 1 to state 2. If I apply the first law it says delta U 12 total is Q 12 plus W 12. And what I am interested in is W 12, so I can rewrite this equation and this will turn out to be delta U 12 minus Q 12 which will be 4000 minus 6000 that is negative 2000 Joules.

Now, for the second step going from state 2 to state 3 we do not know delta U, we know W and Q its again pretty straightforward delta U 23 total is going to be Q 23 plus W 23

according to the first law. So, that will be 3000 minus 8000 which will be 2000 Joules. And finally, we also need to calculate going from state 3 to state 1 what the numbers are W_{31} , Q_{31} and ΔU_{31} . So, let us draw that step first to indicate this change, so and let us pick a different color here. So, one it is less confusing. Let us pick that color. And I am going from state 3 to state 1. What I am interested in is these quantities W_{31} , Q_{31} and ΔU_{31} I have to calculate all the three quantities I do not know any one of them.

So, what is given to us though is that Q for the whole cycle going from 1 to 2 to 3 back to 1 is negative 2000 Joules, right. I know Q going from 1 to 2 and 2 to 3. So, I can easily calculate Q going from 3 to 1. So, Q_{1231} is essentially $Q_{1 \rightarrow 2}$ plus $Q_{2 \rightarrow 3}$ plus $Q_{3 \rightarrow 1}$. This implies negative 2000 is $Q_{1 \rightarrow 2}$ is 6000; $Q_{2 \rightarrow 3}$ is a negative 1000 plus $Q_{3 \rightarrow 1}$. So, $Q_{3 \rightarrow 1}$ is going to be negative 7000 Joules.

Now, I know Q_{31} , but I still do not know two variables W_{31} ΔU_{31} . How do I calculate them? Well, I know that U is a state function and if I complete the whole cycle ΔU has to be 0 which means $\Delta U_{1 \rightarrow 2}$ plus $\Delta U_{2 \rightarrow 3}$ plus $\Delta U_{3 \rightarrow 1}$ has to be equal to 0. I know the first two quantities so $\Delta U_{3 \rightarrow 1}$ can be easily calculated it is negative $\Delta U_{1 \rightarrow 2}$ negative $\Delta U_{2 \rightarrow 3}$. So, that will be negative 4000 and negative 2000 which is negative 6000 Joules, right.

So, now, I can go back and use the first law for the third step what is going from state 3 to state 1. $\Delta U_{3 \rightarrow 1}$ is $Q_{3 \rightarrow 1}$ plus $W_{3 \rightarrow 1}$. I already know $Q_{3 \rightarrow 1}$, so negative 6000 is going to be negative 7000 plus $W_{3 \rightarrow 1}$ which implies $W_{3 \rightarrow 1}$ is a 1000 Joules.

Also notice, so now, I have solved my problem I know all the quantities whatever are the missing quantities. Also notice that W_{1231} is going to be equal to 2000 Joules. And when you compare this quantity with this quantity Q_{1231} they are exactly opposite in sign. Once you add them they are equal to 0, which should be the case because when you add them it is the internal energy you are calculating and in a cyclic process the internal energy will be 0 or change in internal energy will be 0. So, that solves our problem of applying first law to a simple case where some quantities from heat work and internal energy are missing, we can easily calculate them applying the first law.

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Example

2 moles of steam in a closed vessel undergo a state change from 50 kPa and 200 °C to 100 kPa and 250 °C. Calculate the change in the molar internal energy change of the steam between these two states.

Steam
P: 50 kPa
T: 200 °C

$\Delta U_A = ?$

Steam
P: 100 kPa
T: 250 °C

$Q_A = 2000 \text{ J}$
 $W_A = 880 \text{ J}$

$$\Delta U_A^t = Q_A + W_A = 2880 \text{ J}$$
$$\Delta U_A = \frac{2880}{2} = 1440 \text{ J mol}^{-1}$$

Now, let us take another example we applied first law in the previous case and most of these applications we have used in the previous case for for the total internal energy calculation. But we are probably also interested in calculating a molar value of the internal energy as we will see later on in the course.

So, let us solve a quick example of how to convert between the molar and total quantities and apply first law. So, let us say I have two moles of steam in a closed vessel that undergoes a change of state from 50 kilopascal and 200 degrees centigrade to 100 kilopascals and 250 degrees centigrade, both pressure and temperature is changing. And to accomplish this change we are adding some heat and work to the system, 2000 Joules of heat and 880 Joules of work. The question is what is the change in the molar internal energy for the steam due to this process. What is the change in the molar quantity?

We want to apply the first law right and the first law says this is very important we often tend to forget; the first law says delta U is going to be equal to Q plus W. So, that will be 2880 Joules when you add these two quantities. The total internal energy change in the process is 2880 Joules. If I am interested in calculating the molar change then I should remember to divide this quantity with the number of moles. So, delta U is going to be 2880 over 2 or 1440 Joules for mol. So, as you can see both these numbers are different, I am still applying first law, but the first slice applicable only for the total

internal energy change we have to subsequently convert it into the molar quantity as required.

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The Phase Rule

- Variables such as U, ρ are state properties
- How many variables are needed to define “the state” of a system?
State refers to a set of thermodynamic properties such as T, P, V, U etc.
- Can you find the molar volume of a gas at a given T (273.15 K)?
- Can you find it given T (273.15 K) and P (1 atm.)?

22.4 liters/mol

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Now, we said in the discussion earlier quantities such as density or for that matter internal energy are state properties they are going to depend only on the state of the system. The question is how many variables do I really need to define the state of a system. When we mean or when we say the state of a system what we mean is a set of thermodynamic properties it might be temperature, pressure, molar volume, molar internal energy whatever we can think of, a set of thermodynamic quantities that are needed to define the particular state of a system.

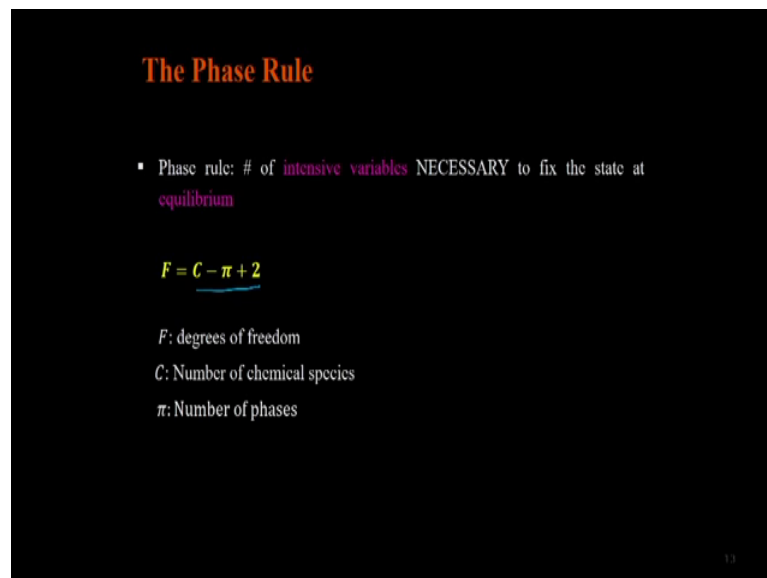
So, for example, let me elaborate. If I say what is the molar volume of a gas at a given temperature, let us say the temperature is 273 Kelvin 0 degree centigrade, 273.15 Kelvin. At this temperature if I say I have a gas, can you tell me the molar volume of the gas? Obviously, the answer is no, because we also need to know the pressure of the gas to be able to answer this question. I do not know what the pressure is. So, at each pressure it will have a different molar volume. So, having just one, defining one variable the temperature is not sufficient to tell the state of the system or to fix as we call it the state of the system.

On the other hand, if I say well can you tell me the molar volume of a gas at 273 Kelvin and one atmosphere? The answer is yes, for an ideal gas. This is a pretty straightforward

answer this is a standard temperature and pressure the molar volume is 22.4 liters per mole, right. So, once you tell me both the temperature and pressure and if I think that if I can assume that it is an ideal gas then the molar volume is known, I can fix the state of a system.

So, the question is how many variables do I need to define the state of a system. It turns out in this case I need two variables, a temperature and a pressure, and you can tell me the molar volume. It can be the other way around I could have defined the temperature and the molar volume which is 22.4 liters, and then the other parameter, thermodynamic variables such as pressure etcetera. In fact, internal energy all of them are going to be fixed.

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The Phase Rule

- Phase rule: # of intensive variables NECESSARY to fix the state at equilibrium

$$F = C - \pi + 2$$

F : degrees of freedom
 C : Number of chemical species
 π : Number of phases

So, the way we answer this question although we are going to derive it later on in the course, for now it is necessary to help us solve problems based on the first law. So, let us define what we call as the phase rule in thermodynamics. It tells us the number of intensive variables so that word needs to be highlighted; it is a number of intensive variables that are necessary to fix the state of a system at equilibrium. And this number of intensive variables is often also called as degrees of freedom F and this is given by the formula C minus π plus 2, where C is the number of chemical species in the system and π is the number of phases. The other thing we want to highlight is that it is applicable

only at equilibrium condition, right. So, number of degrees of freedom is $C - \pi + 2$.

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What is a phase?

- Phase: Part of the system where ALL physical properties are uniform throughout
- Air although a mixture of two chemical species has same properties (density, mole-fraction, specific heat, thermal conductivity etc.) throughout
One phase
- Liquid mixture of water and methanol
One phase
- A closed container containing liquid water in equilibrium with a mixture of water vapor and air
Two phases: Vapor phase and liquid phase, each have different physical properties
- A liquid mixture of water and oil
Two phases: Oil phase and water phase, each have different physical properties

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When we say number of phases what exactly is a phase? Phase is that part of the system with all the physical properties are uniform throughout. Physical properties such as density, mole fraction, thermal conductivity, viscosity whatever physical properties that might come to your mind all of them; it is not exclusive, we have to have it is exhaustive list all the physical properties need to be uniform throughout the part of the system we are calling as a single phase.

Now, a is a mixture of two chemical species predominantly nitrogen and oxygen, but then the mole fraction if I take a rene a container the mole fraction, the density, the mole fraction, the specific heat whatever part of that container I choose are going to be uniform throughout the container. So, although it is a mixture of two chemical species it is still considered to be a single phase. Similarly, a mixture of two liquids such as water and methanol they can mix very well and we still form a single phase of water and methanol.

On the other hand, if I have a closed container, containing liquid water at the bottom and then water vapor and air above it, it is at equilibrium the water vapor is the air is saturated with water vapor everything is at equilibrium. But then if I look at this container, I have two distinct phases, one is the liquid phase which is only water maybe a

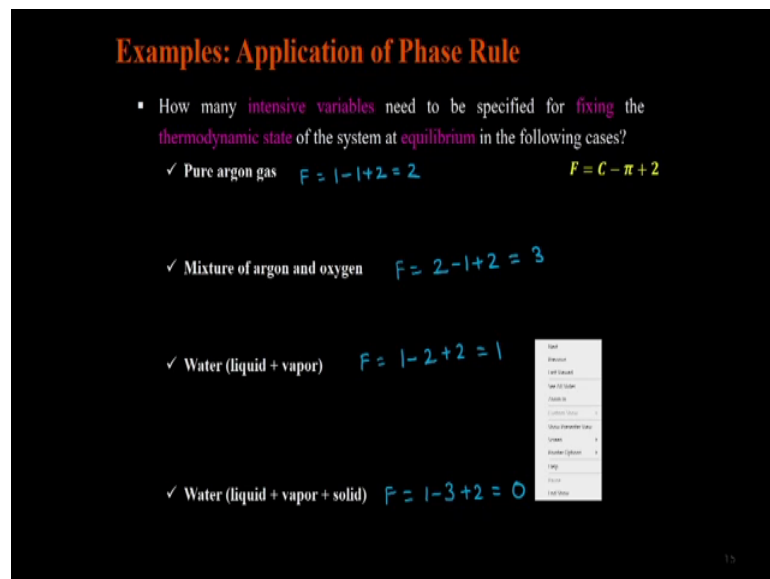
little bit of air dissolve water, but it is still liquid phase it has a very high density other physical properties such as viscosity thermal conductivity are also different whereas, the vapor phase is predominantly air and water vapor. And some amount of water vapor depending on the temperature of course, or the vapor pressure of that water.

But then the density of the vapor phase is much lower than that of the liquid phase, it will have different other physical properties such as viscosity, thermal conductivity etcetera. So, in this container then I have two phases a liquid phase and a vapor phase. Similarly, if I have a liquid mixture of water and oil how many phases do I have? Water and oil, they are immiscible liquids, right. So, there are pockets in that container although everything is in the liquid state, there are pockets in that container which are rich in oil, there are pockets in that container which are rich in water both of them have different physical properties. So, it will be a two-phase mixture not a single-phase mixture.

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Examples: Application of Phase Rule

- How many intensive variables need to be specified for fixing the thermodynamic state of the system at equilibrium in the following cases?
 - ✓ Pure argon gas $F = 1 - 1 + 2 = 2$ $F = C - \pi + 2$
 - ✓ Mixture of argon and oxygen $F = 2 - 1 + 2 = 3$
 - ✓ Water (liquid + vapor) $F = 1 - 2 + 2 = 1$
 - ✓ Water (liquid + vapor + solid) $F = 1 - 3 + 2 = 0$



Now, keeping these ideas in mind, let us answer or try to apply phase rule to a variety of systems. The first system we are looking at is a pure argon gas, how many intensive variables need to be fixed or need to be specified for fixing the thermodynamic state of the system at equilibrium. So, we are interested in calculating the degrees of freedom remember F is C minus of π plus 2; for pure argon gas then F is going to be the number of chemical species which is 1, number of phases which also happens to be 1 plus 2, so the degrees of freedom is 2 for this case.

If I have a mixture of argon and oxygen then F is going to be number of chemical species is 2, number of phases is still 2 plus 2, so F is going to be 3. So, I might have to also specify the mole fraction in addition to temperature and pressure to fix the state of the system.

In the next case if I have water in two phases liquid and vapor then the degrees of freedom is going to be two, sorry one chemical species minus 2 phases plus 2, so there is only one degree of freedom in this case if I have water in both liquid and vapor phases. And finally, if I have water in the three phases in all the three phases at equilibrium the solid, liquid and the vapor phase we call such a state as a triple point for in this case water. And in this at this triple point where all the three phases coexist, I have 1 chemical species 3 phases plus 2, so the degrees of freedom is 0. So, I do not have to specify anything, if I say distribute point of water that can occur only at a particular temperature pressure. So, the degrees of freedom is 0.

So, we have seen demonstration of how I can apply phase rule to a variety of cases. So, we know how many intensive variables need to be fixed, to define the state of the system. The one other small thing we did not talk about is what exactly do I mean by equilibrium, right. We said it is the degrees of freedom is defined for the state of, to fix the state of a system at equilibrium. What exactly do we mean by this word equilibrium?

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Equilibrium and Steady State

- Equilibrium : Absence of change and tendency to change
- How is it different from steady-state?
- What happens when you isolate it from the surroundings?

100 °C 40 °C

100 °C $t = 0$ 40 °C

$t = \infty$

$\sim 70^\circ\text{C}$

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Now, in most textbooks when we define equilibrium, we say that it is absence of change and the tendency to change. The question we ask is how different is this from a steady state condition, how is equilibrium different from steady state. The easiest way to answer this question is to take an example. For example, if I have an iron rod in contact with a hard surface one end of this hard surface is at high temperature, let us say 100 degree centigrade, the other end is open to is exposed to atmosphere, so it is at a lower temperature 40 degree centigrade, right.

And if there is a continuous supply of heat from the surface in which it is contact in where that there is some loss to the atmosphere eventually things will reach a steady state, so at any given location in this rod there is no change in temperature with time, right. So, there is no change. It is absence of change with time irrespective of how long you wait as long as there is a constant supply coming from this end to the rod for heat, and then there is some loss to the surroundings right, then everything will be nice and be at steady state do.

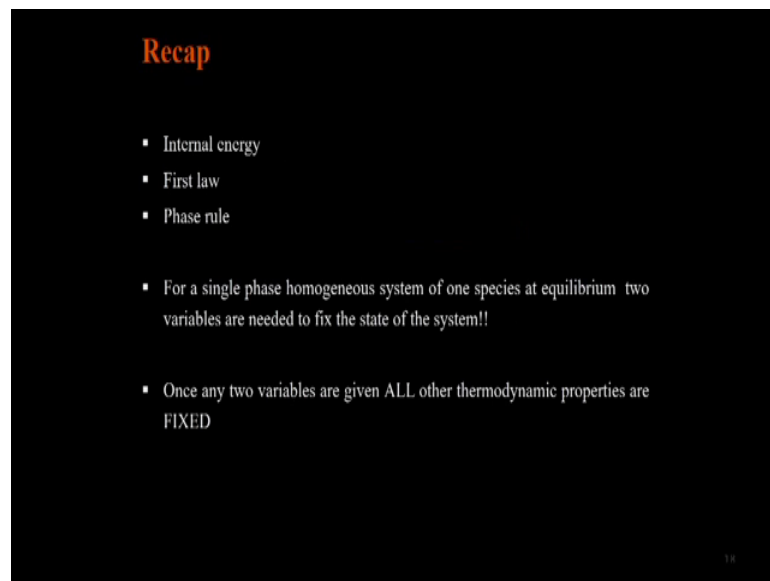
We call such a thing as equilibrium, why do not we call it as actual equilibrium if there is an absence of change. The key word there is its just for equilibrium we just do not need absolute having absence of change itself is not enough, we also need to have we should not have any tendency for change as well. Well, what exactly do we mean by tendency of to change? Just way to answer the question is to look at the system we have in this case let us look at the system at steady state the iron rod we talked about which was at steady state. And if I isolate this system from the surroundings, if I put a nice insulation around this ice a nice insulation around this iron rod and isolate it from the surroundings as we have shown here, what happens?

The moment we isolate it from the surroundings it will not get any more heat or it will not lose any more heat to the surroundings, it will not get any more heat from the hot surface it was in contact with because it was I it is isolated now. And once we do this isolation the temperature at various locations in the rod is going to change, the hotter surface is going to get a little colder, the colder surface is going to get a little hotter and eventually the whole rod is going to reach a constant temperature maybe let us say around 70 degree centigrade. Temperature of the rod is going to be uniform throughout because it is isolated. But then notice what has happened, things have changed they went from what they were at steady state condition is markedly different from what it is after

isolate, what it will be at after isolation. So, there is a tendency to change once we isolate from the surroundings and that should not be present if it is at equilibrium.

So, this is how we distinguish equilibrium from steady state condition. It should be both absence as well have changed as well as, you should not have any tendency or absence of tendency to change also if it is at equilibrium.

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Recap

- Internal energy
- First law
- Phase rule

- For a single phase homogeneous system of one species at equilibrium two variables are needed to fix the state of the system!!

- Once any two variables are given ALL other thermodynamic properties are FIXED

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So, so far we talked about what we call as the internal energy of a system, the first law we use the phase rule for a variety of systems and we looked at how we can apply phase rule to a variety of systems.

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Reversible constant volume process

- Work done in a reversible constant volume process

P_1, T_1, V_1 → P_2, T_2, V_1

$dW = -PdV = 0$ $dU = dQ + dW = dQ$

The next thing we are going to talk about is apply the first law in a closed system to a few simple processes. The first process we look at is a constant volume process, so the total volume is not changing, but the temperature and pressure are changing. What would be the work done for such a reversible process? We know that dW for a reversible process is negative PdV and because dV is 0 the work requirement for this process, for a reversible constant volume process also is going to be 0, and because the work done is 0 dU is going to be equal to dQ in a reversible constant volume process.

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Reversible isobaric process

- Work done in a reversible constant pressure process

P_1, T_1, V_1 → P_2, T_2, V_2

$dW = -PdV = -d(PV)$

$dU = dQ + dW = dQ - d(PV)$

$\Rightarrow dQ = dU + d(PV) = d(U + PV)$

$dQ = d(U + PV)$

*Const. P
dQ = dU + PdV*

Now, if I talk about another process, now an isobaric process the volume is changing the temperature is changing, but the pressure is constant. What is the work done in such a process? Process is still reversible dW is negative $p dV$ right and because the pressure is constant, I can take it into the derivative here so that it becomes negative $d(PV)$, and dU is going to be dQ plus dW so that will be dQ negative $d(PV)$, right. And if I rewrite this equation for dQ what I get is dQ is d of U plus PV both of the all of them are total quantities U and PV . So, dQ is going to be d of U plus PV .

Remember in the previous case in a reversible constant volume process dQ was dU in this case it is d of U plus PV . That is the essential difference between the two processes.

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Enthalpy

- Work done in a reversible constant pressure process

$P_1, T_1, V_1^i \longrightarrow P_2, T_2, V_2^i$

$dQ = d(U + PV)$

H^i
 $H^i = U^i + PV^i$

$dQ = dH^i$ (const. P process)

These processes are so important that we tend to give a particular, we assign a particular variable to this quantity U plus PV , we call it as enthalpy H right or in this case the total enthalpy H , so U plus PV is often represented by the variable H or enthalpy. And in case of a constant pressure process then of course dQ is going to be equal to dH . And this quantity H will also have the same units as internal energy, so it will be in Joules.

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Enthalpy

- Total enthalpy: $H^t = U^t + PV^t$
 - Extensive property
 - SI Units: Energy, J
- Molar enthalpy: $H = U + PV$
 - Intensive property
 - SI Units: Energy, $J mol^{-1}$
- Does enthalpy depend on path?

I can write a molar internal energy. So, instead of the total internal energy I can write the molar quantities H and then it will be related to the molar internal energy U and the molar volume V. So, instead of the total volume and total internal energy, if I write the expression for molar enthalpy it will be in terms of molar internal energy and the molar volume the units accordingly are going to be Joules per mole.

Next question we asked is does this quantity enthalpy depend on the path, that is very easy to answer we already demonstrated that internal energy does not depend on the path. We know that the volume molar volume does not depend on the path. So, H which is U plus PV also will not depend on the path, it just depends on the state of the system.

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Heat Capacity at constant pressure

- Consider a **constant pressure** process (closed system, n is constant)

- $C_p = \lim_{\Delta T \rightarrow 0} \frac{H_2 - H_1}{\Delta T}$
- $C_p = \left. \frac{\partial H}{\partial T} \right|_P \quad dH = C_p dT \quad \Rightarrow \quad \Delta H = \int_{T_1}^{T_2} C_p dT \quad (\text{const. } P)$
- SI Units: $J \text{ mol}^{-1} K^{-1}$

Now, we will go to define two other important quantities in thermodynamics, one is what we call as heat capacity at constant volume. Now, consider this process it is a closed system and I am going from a temperature T and volume V_1 to a temperature of T_1 plus ΔT , but the volume is still constant which is V_1 . The derivative of the internal energy with respect to temperature in such a process or if I take the limit as ΔT goes to 0, the change in internal energy to the change in temperature we call this derivative as the quantity C_v which is known as the heat capacity at constant volume. So, that subscript v here stands for a constant volume process. And in terms of derivatives we write it as derivative of U the molar value of internal energy with respect to the temperature at constant volume. So, after the derivative we put a vertical line and a subscript v to indicate that it is a constant volume process.

Now, I can integrate this expression or sorry I can rewrite this expression in terms of dU it will be $C_v dT$, but then of course, it has to be a constant volume process. I can integrate it from temperature T_1 to T_2 . So, ΔU is going to be $C_v dT$ integral of that quantity between T_1 and T_2 . Now, notice that C_v is derivative of internal energy molar internal energy which is Joules per mole with respect to temperature, so the units for C_v are going to be Joules per mole per Kelvin.

Now, similar to the heat capacity at constant volume I can define another quantity which is often called as heat capacity at constant pressure. So, for that I take a constant pressure

process the pressure p is same, but then I change the temperature from T_1 to $T_1 + \Delta T$. Now, if I take the derivative in this case for the enthalpy then what I get is a quantity known as C_p or the heat capacity at constant pressure because it is a constant pressure process.

Similar to the previous expression in the derivative form C_p is going to be derivative of the molar internal energy U , the sorry molar enthalpy H with respect to temperature or dH/dT at constant pressure. And in the integral form this will be ΔH is going to be integral of T_1 to $T_2 C_p dT$ and it is in a constant pressure process; again because it is a derivative of enthalpy with respect to temperature molar enthalpy with respect to temperature the units are same as that of C_v it is Joules per mole per Kelvin.

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Example

- 1 mole of gas initially at 300 K and 1000 kPa undergoes a change to 350 K and 500 kPa. Calculate the changes in internal energy and enthalpy for this process. Assume that the gas is ideal and that $C_p = \frac{7}{2}R$ and $C_v = \frac{5}{2}R$

State 1: 300 K, 1000 kPa, $2.49 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$

State 2: 350 K, 500 kPa, $5.82 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$

$\Delta U_A = ?$, $\Delta H_A = ?$

$V_1 = \frac{RT_1}{P_1} = \frac{8.314 \times 300}{1000 \times 10^3}$

$V_2 = \frac{RT_2}{P_2} = \frac{8.314 \times 350}{500 \times 10^3}$

Now, what we are going to do next is try to solve a simple example based on these ideas of heat capacities internal energies and enthalpies. The question says one I have 1 mole of a gas initially at 300 Kelvin and 1000 kilo pascals that undergoes a change to 350 Kelvin and 500 kilopascals. We want to calculate the changes in the internal energy and enthalpy for this process, and we are given the values of C_p and C_v as $7/2 R$ and $5/2 R$. So, let me draw a quick schematic for this process, this is what I am looking at, going from state 1 to state 2 I want to calculate ΔU_A and ΔH_A .

Now, the problem is I cannot calculate them right away because it is neither a constant temperature a constant pressure process or a constant volume process. I only know how

to calculate delta H and delta U for these two processes using the C_p and C_v is given, but I do not know this process is not any one of them. So, what we do is a very simple trick, we will employ an alternate path which will have either a constant volume step or a constant pressure step. So, that I can calculate either delta H or delta U and use that information for calculating the change in the process I am looking at.

So, to be able to employ a constant volume or a constant pressure step we are given temperatures and pressures, we are not given the volumes. What I will do is first quickly calculate the volumes initial and the final volumes. And what we do is we apply ideal gas law. So, for example, at this condition V₁ is going to be the molar volume is going to be R T₁ by P₁. So, that will be 8.314 Joules per mole per Kelvin times 300 Kelvin over the pressure which is 1000 kilo pascals, 1000 into 10 cube pascals and that will give me the value you see there, 2.49 10 power minus 3 meter cube per mole. That is the molar value of the volume at the initial condition.

Now, at state 2 I can similarly calculate the molar volume it will be R T₂ over P₂. So, that is 8.314 times 350 over 500 times 10 cube, so that will give me the value I have here which is 5.82 to 10 power negative 3. So, I calculated the molar values for the volumes at the initial and the final conditions. Once we get that out of the way, now we can go about constructing an alternate path where I can calculate the changes in the internal energy and the enthalpy.

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Example

- 1 mole of gas initially at 300 K and 1000 kPa undergoes a change to 350 K and 500 kPa. Calculate the changes in internal energy and enthalpy for this process. Assume that the gas is ideal and that $C_p = \frac{7}{2}R$ and $C_v = \frac{5}{2}R$

State 1: 300 K, 1000 kPa, $2.49 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$

State 2: 350 K, 500 kPa, $5.82 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$

State 3: 500 kPa, $2.49 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, $T_3 = 150 \text{ K}$

Process 1 → 2: $\Delta U_A = ?$, $\Delta H_A = ?$

Process 1 → 3: $\Delta U_B = \int_{T_1}^{T_3} C_v dT$

Process 3 → 2: $\Delta H_C = \int_{T_3}^{T_2} C_p dT$

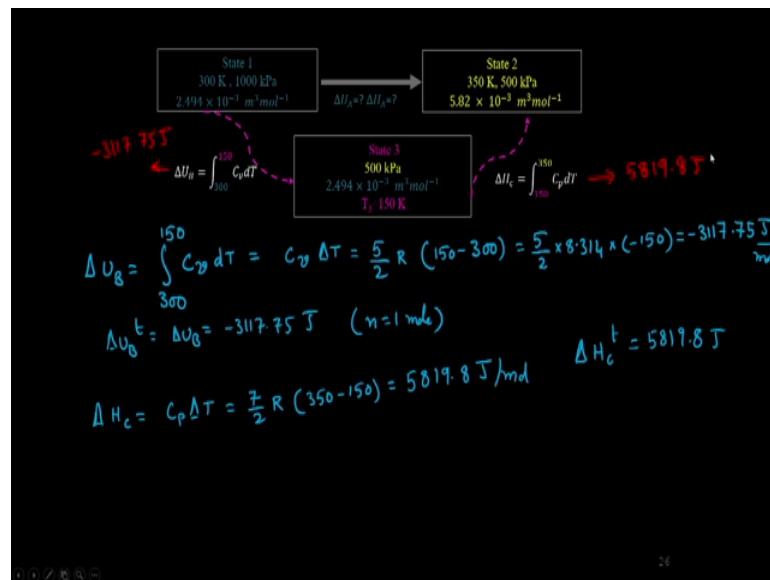
Handwritten calculation: $T_3 = \frac{P_3 V_3}{R} = \frac{500 \times 10^3 \times 2.49 \times 10^{-3}}{8.314}$

So, what I will do next is construct an alternate path. And to be able to do that in the I choose a state such that the volume is same as the initial volume here, these two numbers are same the volumes here and here, and the pressure to be same as the final pressure such that both of them are 500 Pascals kilo Pascals right, here and here. So, I go from now I will construct an alternate path to my original process using this state 3.

So, initially I will go from state 1 to state 3 and then I will go from state 3 to state 2, and if you notice the transition from state 1 to state 3 is a constant volume process and the transition from state 3 to state 2 is a constant pressure process. And because they are either a constant volume or a constant pressure processes, in the first case I can calculate ΔU I can calculate the internal energy change using the C_v value and in the second case I can calculate ΔH going from state 3 to state 2 I can use the C_p value to calculate the enthalpy change. One of them is constant volume process and the other one is a constant pressure process.

So, once we agree on that then because I want to integrate and get the value of temperature and I want to get the value of ΔU or ΔH , I have to integrate it from T_1 to T_3 in the first case and T_3 to T_2 in the second case which means I am interested in this quantity temperature. And how do I get this temperature? I know the pressure and volume in state 3 already we agreed on using 500 kilo pascals and 2.49×10^{-3} meter cube per mole. Once I know the volume and pressure I can go back and use the ideal gas law as I have done earlier, right. In this case T_3 is going to be $\frac{P_3 V_3}{R}$, so that will be 500×10^3 times 2.49×10^{-3} divided by 8.314 and that is how I get this quantity 150 Kelvin.

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So, at state 3, once I choose the temperature pressure and volume, the temperature I can calculate to be a 150 Kelvin. So, now, I have all the steps sorted out, I also know the temperatures, I can write the expressions for delta U B and delta H c the temperatures are known, I just have to calculate the integral values.

And I can do that very quickly. Let us run through one example delta U B is going to be integral of 300 which is the initial temperature to the final temperature which is 150 C v dT all right. And C v is given to be 5 by 2 R and it is constant with temperature so it will be C v times delta T. Once you integrate this that will be 5 by 2 R and then 150 minus 300, so that will be 5 by 2, 8.314 times negative 150. If you solve this numerical value it will be 3117.75 Joules per mole and I have 1 mole of gas. So, delta U B total will be equal to delta U B which is negative 3117.75 Joules because n is 1 mole.

Similarly, I can calculate delta H c, in this case it will be C p delta T that will be 7 by 2 R 350 minus 150, and if I simplify this what I get is 5819.8 Joules per mole, and again it is 1 mole of gas, so delta H c total is going to be 5819.8 Joules. So, these two integrals can be solved very easily. So, let me get rid of the math here so that I can write the numbers. So, delta U B is negative 3117.75 Joules delta H c is 5819.8 Joules. So, I can use the C p and C v values to calculate these two numbers.

So, I am going to get rid of these calculations here so that we can proceed to calculate what else is missing from. Now, once I have delta H c and delta U B that is other thing I

have to calculate is how much is delta H B, how much is the enthalpy change in this step and how much is the internal energy change in this step.

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State 1: 300 K, 1000 kPa, $2.494 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$

State 2: 350 K, 500 kPa, $5.82 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$

State 3: 500 kPa, $2.494 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, $T_3 = 150 \text{ K}$

$\Delta U_B = \int_{300}^{350} C_p dT \rightarrow -3117.75 \text{ J}$

$\Delta H_B = ? \rightarrow -4364.7 \text{ J}$

$\Delta U_C = ? \rightarrow 4154.6 \text{ J}$

$\Delta H_C = ? \rightarrow 5819.8 \text{ J}$

$\Delta H_B = \Delta U_B + \Delta(PV)_B$ [$H = U + PV$]

$= -3117.75 \text{ J} + (P_3 V_3 - P_1 V_1) = -3117.75 + (500 \times 10^3 \times 2.494 \times 10^{-3} - 1000 \times 10^3 \times 2.494 \times 10^{-3})$

$= -4364.7 \text{ J}$

$\Delta U_C = \Delta H_C - \Delta(PV)_C = \Delta H_C - (P_2 V_2 - P_3 V_3)$

$= 4154.6 \text{ J}$

Until I have these two numbers I cannot go back and put the add them to get delta U A and delta H A. So, calculate delta H B for example, the way we do that is we write it as delta U B plus delta of the PV term for this step. Remember that H is U plus PV, right. So, delta of H is going to be delta of U plus delta of the PV the product delta of the whole product for step B.

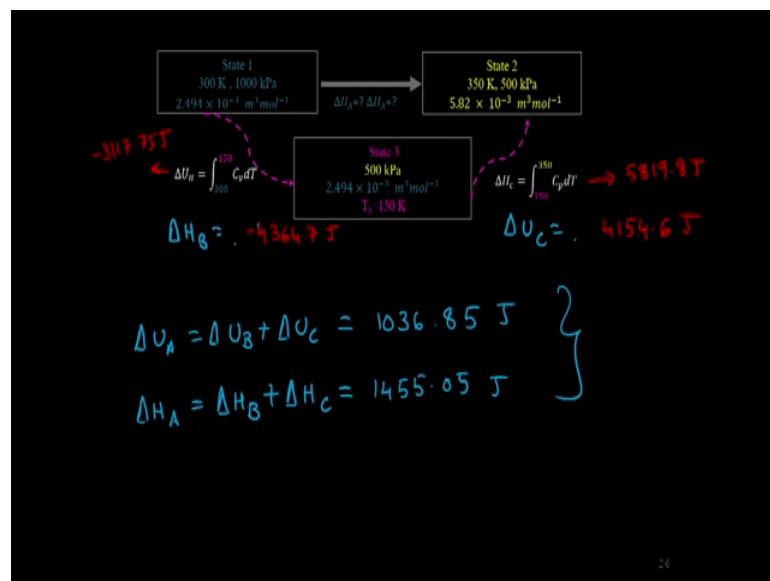
Delta U B we have already calculated, it is negative 3117.75 Joules plus delta of PV for step B is going to be P 3 V 3, the product final product in state 3 minus the product in state 1. This is step b right going from 1 to 3. So, the delta is going to be P 3 V 3 minus P 1 V 1. I can simplify these numbers, I can substitute all the values we have, so it will be 3117.75 plus P 3 V 3 is 500 times 10 cube times 2.494 times 10 power negative 3 minus P 1 V 1 is a 1000 kilo Pascal's 10 cube times 2.494 10 power negative 3.

And once I simplify all the math this value will turn out to be negative 4364.5 Joules. Similarly, I can calculate delta U C, in this case it will be delta H C minus delta of PV for this third step. So, this will be delta of H c which I already know minus P 2 V 2, P 3 V 3 we are going from state 3 to state 2 so that will be P 2 V 2 minus P 3 V 3. We can do the numerical calculation this turns out to be 4154.6 Joules, that will be delta U C.

So, what I will do is I will write these numbers here so that I can get rid of the calculation, delta H B is negative, let us write it in a different color negative 4364.7 and delta U C is 4154.6 Joules. So, with that I am going to get rid of these.

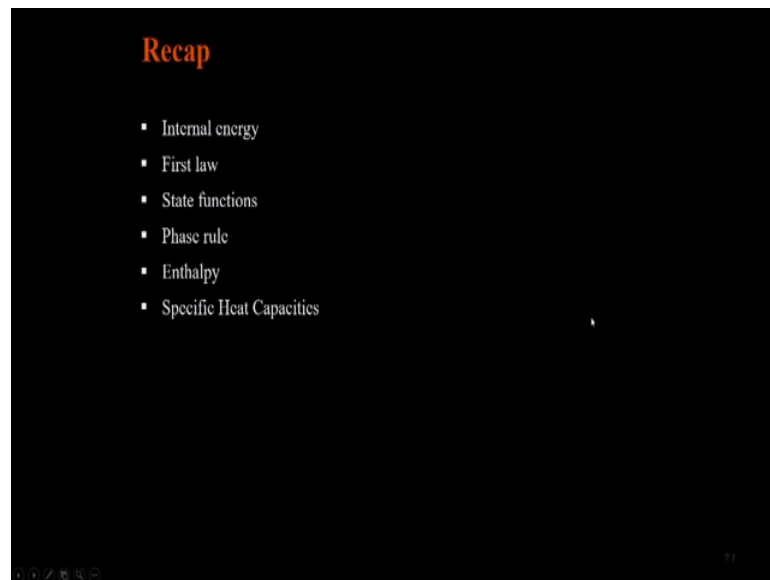
So, now, we found a way to construct an alternate path either a constant, using either a constant pressure or a constant volume process we calculate the appropriate quantity using C p or C v, either delta H or delta U and from the PV information we can calculate the other quantity. Once we have that we have everything we need. We have delta U B and delta U C and because U is a state property delta U A is going to be delta U B plus delta U C and I know both these quantities delta U B and delta U C. So, delta U A will be readily calculated to be 1036.85 Joules. And similarly, delta H A is going to be delta H B plus delta H C so that will be 1455.05 Joules in this case.

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So, the trick then for these processes is to be able to come up with a path which can actually change the existing path to ones involving either a constant pressure or a constant volume process, so that I can use the information on C p and C v and calculate the necessary quantities. So, that is a quick demonstration of how I can use the specific heat capacity values for simple cases. With that we end today's lecture.

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We talked about internal energy, we talked about the first law, talked about the state functions and specific heat capacities today.

Thank you for enjoying this lecture so far. I will see you in the next one.