

**Material and Energy Balances**  
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**Module No # 07**  
**Lecture No # 34**  
**Energy Balance Terminologies and Concepts**

Hello everybody welcome to today's lecture for the material and energy balances course until now we have performed calculations related to material balances we have covered all the fundamentals associated with material balances. We discussed single unit single units, multiple units system with recycle bypass purge combustion and biochemical reactions and so on. With that we have come to the conclusion for the material balances today we will start with energy balances.

The second part of the course would be about energy balances this concept of energy balances is built upon law of conservation of energy and we will perform calculations similar to what we have done for material balances and here you will try to account for how much energy is required for processes to function.

So before we start performing energy balance calculations it is important for us to learn some of the terminologies and also recollect some of the terms which we have already learnt and see how would have applied towards energy balance systems.

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## Terminologies – A review

- System – Region chosen for study enclosed by a boundary
- Surroundings – Everything outside a system boundary
- Boundary – Surface that separates system and surroundings
- Open system – Mass flow with surroundings
- Closed system – No mass flow. Heat and work can be exchanged

Let us first start with a review of terminologies that we have already looked at system is a region which is chosen for study and it is enclosed by an arbitrary boundary which we choose. The surrounding is everything that is outside this system boundary. Boundary is the surface that is drawn to separate this system and a surrounding. Open systems are systems where you have mass crossing the system boundary therefore there is mass flowing from the system to the surrounding or vice versa.

You can have closed systems which have no mass exchange between the system and the surrounding however heat and energy can be actually transferred between the system and its surrounding for a closed system. Hence when we perform material balance calculations we would not have looked at closed systems but now that we are going to look at energy balance calculations we have to consider closed systems also because energy is being transferred between the system and its surroundings in a closed system.

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## Terminologies – A review

- Property – Observable characteristic of the system
- Steady state – Accumulation is zero
- Unsteady state – Not in steady state
- Equilibrium – Thermal, mechanical, phase and chemical properties of the system are invariant
- Phase – Physically distinct

Property is any observable characteristic of a systems it could be temperature pressure volume mass and so on. So all these are the properties of the systems steady state is a process where the terminologies are there in the properties are not changing with respect to time. Unsteady state is when the system is not in steady state and there is accumulation happening.

The system can also exist in equilibrium which is basically thermal, chemical, mechanical and phase properties of the system being in variant with respect to time. Phase is basically any physically distinct components so this could be solids liquids and gases until now when we perform material balance calculations we were only looking at each component based on it is chemical identity.

So the water was distinguish between water liquid versus water vapor however when we perform energy balance calculations it is important for us to distinguish between water liquid and water vapor because there is energy associated with phase change. Hence phases of the components which are involved in the process have to be looked at carefully when we perform energy balance calculations.

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# Energy balance terminologies

- Adiabatic system – A system that doesn't exchange heat with the surroundings during a process (perfectly insulated)
- Isothermal system – A system in which temperature doesn't change during a process
- Isobaric system – A system in which pressure doesn't change during a process
- Isochoric system – A system in which volume doesn't change during a process

Let us look at some of the energy balance terminologies which you might you already been aware of but it is important for us to understand and remember these concepts to apply for calculating energy balance equations. Adiabatic system is a system that does not exchange with the surroundings during a process. So this is a perfectly insulated system so we would assume that heat transferred between system and the surrounding is 0 or any adiabatic process.

You can also have an isothermal system where the system temperature is maintained as the constant throughout the process. Here heat exchange the probably be happening between heat and it is surroundings to maintain the temperature of a system. You can also have isobaric systems where the system pressure does not change during the process and you have an isochoric systems where the system volume does not change with respect to time during the process.

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# Energy balance terminologies

- State variable

- A variable that depends only on the state of the system and not on how the process occurred
- State function or point function
- Ex. Internal energy



- Path variable

- A variable that depends on how the process takes place
- Path function
- Ex. Heat and work



The variables which we look at while we perform in energy balance calculations can be classified as state variables and path variables. State variables are basically variables that depend on the state of system and not how the process actually occurs. Example would be internal energy these are also called as function or point functions. Internal energy will depend on the temperature and pressure and composition of a system and does not depend on how the system gets to that particular point.

Hence it is state or a point function path variable is a variable which depends on the process actually takes place it is also called as a path function we can actually make assumptions about the reference state which can be used for performing calculations. You will get into the detail of that when we perform energy balance calculations. When we talk about the path variable the path taken the process which happens is crucial for the magnitude of this value.

So let us take this simple example if I were to move an object from point A to point B through a straight line there would be some amount of work which would be done on the object for it to be moved. However instead of moving it in straight line between A to B if I were to move it to a point C and then to a point D and then to point E and then back to a point B so now I have taken a much longer path and this would require much more work to be done on this object for it to be moved from point A to point B.

So the path or the process which had happened for moving this object point A to point B determined the magnitude of work which is one on the system. So these types of processes the variables are called as path variables or path functions.

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## Types of Properties

- Intensive
  - Physical property of a system that doesn't depend on the size
  - Ex. Temperature, density, viscosity
- Extensive
  - Property of a system that is directly proportional to the size of the system
  - Ex. Mass, volume
- Specific property
  - Intensive property that is obtained by dividing an extensive property by the total amount of the process material
  - E.g. – specific volume, specific growth rate

What are the different type of properties which are there when we talk about energy balance calculations. We can have intensive properties these are the physical properties of the system which do not change with respect to size so they do not depend on the size of the system. Example would be temperature density viscosity etc., You also have extensive properties which change directly with size of the system with directly proportional to the size of the system.

Example to be mass or volume you can convert extensive property is into intensive properties using something call it is specific property. Specific property is an intensive property obtained by dividing and extensive property by the total amount or mass of the total material. Example would be specific volume and specific growth rate if you remember when we discussed bio-chemicals reactions with cell culture we were talking about growth rate and specific growth rate.

Specific growth rate is obtained by dividing growth with the biomass concentration or the biomass number. So this gives us specific property which is an intensive property. Specific volume is also the same volume which is an extensive property depends on the size of the system when you divide the volume by the biomass then you get specific volume which is a specific property that is intensive property.

So specific volume is actually the inverse of density as a density is intensive property you would be have specific volume also being an intensive property.

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## Forms of Energy

- For a closed system, energy can be transferred between the system and the surroundings in two ways
- Heat – Energy transfer due to temperature difference between system and surroundings. Heat is positive when it is transferred to the system from the surroundings.
- Work – Energy transfer due to anything except temperature difference, such as force, torque or voltage. Work is positive when it is done by the system. This convention is arbitrary and some texts follow the opposite.

When we talk about energy balances there are different forms of energy which we have to look at. The energy can be exchanged between the system and its surroundings using two different forms. The first one is heat energy which is transferred due to temperature difference between the system and its surroundings it is called as heat. Conventionally we will be using heat as positive when it is transferred to the system from the surroundings.

Work is the other form in which the system and the surrounding exchange in it energy transferred that happens other than anything temperature difference. It could be because of force or torque or voltage is called as work. Work is positive when it is done by the system and it will be considered to the negative when it is on the system. So this convention which we are going to be using for the calculations for the respect of the course is actually arbitrary.

Different text books use different conventions it does not matter which convention you use as long as with consistent you are using the same convention throughout your calculations.

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# Forms of Energy

- For a closed system, energy can be transferred between the system and the surroundings in two ways
- Heat – Energy transfer due to temperature difference between system and surroundings. Heat is positive when it is transferred to the system from the surroundings.
- Work – Energy transfer due to anything except temperature difference, such as force, torque or voltage. Work is positive when it is done by the system. This convention is arbitrary and some texts follow the opposite.

What is work? Work is as I said energy which is transferred due to anything other than temperature difference which means there could be different types of work that can be done by the system or on the system. You can have a mechanical work you can have mechanical work which is the work that occurs due to a mechanical force that moves the boundary of the system. This is calculated as  $\int \mathbf{F} \cdot d\mathbf{s}$  where  $\mathbf{F}$  is force  $d\mathbf{s}$  is change in its state.

You can have an electrical work which is the work which is done when an electrical current passes through a resistant and this would create some amount of work so this is a type of which we will not look at for our course because we will be looking at chemical bio chemical processes where this is usually this is not a factor. We can also have shaft work which occurs when a force is acting on a shaft to turn against the mechanical resistance.

So this would be the shaft work you also flow work which is the work performed on the system when a fluid is pushed into the system by the surrounding so this is called as flow work.

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## Calculation of mechanical work

- An ideal gas at 300 K and 200 kPa is enclosed in a cylinder by a frictionless piston, and the gas slowly forces the piston so that the volume of the gas expands from 0.1 to 0.2 m<sup>3</sup>. Calculate the work done by the gas on the piston if two different paths are used.
  - Isobaric
  - Isothermal

So these are the different type of work and let us now look at how we calculate mechanical work. Here is the simple example problem and ideal gas at 30 kelvin and 200 kilopascals is enclosed in a cylinder bio-friction less pistol and the gas slowly forces the friction that the volume of the gas expands from 0.1 to 0.2 meter cube. Calculate the work done by the gas on the pistol if two different paths are used isobaric process and isothermal process.

Here the actual process itself is the same the path is different so the path is basically expansion of this ideal gas from 0.1 meter cube to 0.2 meter cube. However the path taken either isothermal or isobaric we will look at these two different paths and see how the work actually varies when two different paths are been taken.

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## Calculation of mechanical work

• Isobaric

$$\begin{aligned}
 P &= \text{constant} \\
 W &= \int_{V_i}^{V_f} P \, dV \\
 &= P \int_{V_i}^{V_f} dV \\
 &= P (V_f - V_i) \\
 &= 200 \times 10^3 (0.2 - 0.1) \\
 &= 20 \times 10^3 \text{ J} \\
 &= \boxed{20 \text{ kJ}}
 \end{aligned}$$

• Isothermal

$$\begin{aligned}
 T &= \text{const.} \\
 W &= \int_{V_i}^{V_f} P \, dV \\
 PV &= nRT \\
 \Rightarrow P &= \frac{nRT}{V} \\
 W &= \int_{V_i}^{V_f} \frac{nRT}{V} \, dV \\
 &= nRT \int_{V_i}^{V_f} \frac{dV}{V}
 \end{aligned}$$

$$\begin{aligned}
 W &= nRT \ln\left(\frac{V_f}{V_i}\right) \\
 n &= \frac{PV_i}{RT} = \frac{200 \times 10^3 \times 0.1}{8.314 \times 300} \\
 n &= 0.00802 \text{ kmol} \\
 W &= 0.00802 \times 8.314 \times 300 \times \ln\left(\frac{0.2}{0.1}\right) \\
 &= \boxed{13.86 \text{ kJ}}
 \end{aligned}$$

First let us look at an isobaric process for an isobaric process we know that pressure remains the constant. So let us try to calculate with which should be integral PDV where you have initial volume to final volume. Now pressure being a constant can be taken out of integral and it becomes P integral P initial to final DV so this is PV final – V initial. The problem statement gives us that the pressure is 200 kilopascal the volume is 0.2 as the final volume and the initial volume is 0.1 meter cube.

So solve you would get 20 times 10 power joules just equal to 20 kilo joules so 20kilo joules is the work that is done. Now let us look at an isothermal process. For an isothermal process temperature remains at constant so work equation is still integral V initial to V final PDV but pressure is not being a constant so we need to convert this pressure in a way that we can actually represent the volume term also.

We have been given that the gas present in system is an ideal gas so using that ideal gas law is PV = NRT. So this implies pressure is actually nothing but NRT divided by V so substituting that your W term integral V initial 2V final NRT divided by VDV. So temperature is a constant number of moles is not changing there is not reaction which is happening here. R is the universal gas constant is also a constant so this equation then becomes NRT times integral initial to V final DV divided by V.

So this can be then solved as  $NRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$  so integrating applying the limit we get this equation. Now let us substitute the values for each of these things so we do not know the values for the number of moles over we can calculate it using the ideal gas law for the initial condition  $NRT = PV$  it is  $N = PV / RT$  using the initial pressure volume so we assume this to be initial pressure and volume so we can calculate  $N$ .

So initial pressure is 200 kilopascal 200 times  $10^3$  Pascals times initial volume is 0.1 meter cube divided by  $R$  in SI units is 8.314 times temperature for initial conditions is 300 kelvin. So using this we can calculate  $N$  as 0.00802 kilo moles so now that we have  $N$  we can calculate the value for  $W$  already know the value for  $R$  we know the value for  $T$  300 kelvin and  $V_{\text{f}}$  and  $V_{\text{i}}$  is 0.1. So we basically calculate it as 0.00802 times 8.314 times 300 times  $\ln$  of 0.2 divided by 0.1.

Solving this we calculate  $W$  as 13.86 kilo joules so for isothermal process the work which is done is 13.86 kilo joules compared to an isobaric process where the work done is 20 kilo joules. This example clearly shows that work is a path function and all though process itself was the same where ideal gas expanded from 0.1 to 0.2 meter cube because of the process and the path which is taken from the process the values for  $W$  were actually different for an isobaric process we got 20 kilojoules versus and isothermal process we got 13.86 kilojoules.

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## Forms of Energy

- Total energy of a system has three components
- Kinetic energy ( $E_K$ ) – Energy due to translational motion of the system as a whole relative to some frame of reference

$$E_K = \frac{1}{2}mv^2$$

- Specific kinetic energy – Kinetic energy/mass

Let us move on to the next concept other than the two forms of energy heat and work which energy is transferred between the system and its surrounding they can actually be 3 different forms of energies which are inherently process by the system itself. The first type of energy would be the kinetic energy. Kinetic energy is the energy possessed by a system due to translation motion of the system as a whole relative to some frame of reference.

This can be calculated as half MV square where M is the mass is the system and V is the velocity which it is travelling. You can convert this term which is an extensive property into an intensive property where the specific kinetic energy by dividing kinetic energy W by the mass of the system.

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## Forms of Energy

- Potential energy ( $E_p$ ) – Energy due to the position of the system in a potential field

$$E_p = mgh$$

- Specific potential energy – Potential energy/mass
- Internal energy – All energy possessed by the system other than the kinetic and potential energy
- Specific internal energy – Internal energy/mass

Other than kinetic energy you can also have potential energy for the system which is the energy for the system possess by the system due to the possession of the system in the potential field. So this is calculated as MGH M is the mass G is the acceleration due to gravity and H is the height in which it is placed and the processional feed. So you can convert it potential energy to a specific property by dividing it by the mass of the system giving you potential energy.

Other than kinetic and potential energy the system also possess something called as internal energy all the energy that is possessed by the system which is not explained by the kinetic and potential energy is called is the internal this is the thermo dynamic energy of the system. Specific internal energy can also be calculated as the internal energy divided by mass.

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## Kinetic Energy: Example

- Water flows in to a process through a 2-cm inner diameter pipe at 2.00 m<sup>3</sup>/h. Calculate the kinetic energy for the system in J/s.

$$\begin{aligned} E_k &= \frac{1}{2} m v^2 \\ m &=? \\ v &=? \\ F &= 2 \text{ m}^3/\text{h} \\ \Rightarrow \dot{m} &= F \rho \\ &= 2000 \text{ kg/h} \end{aligned}$$
$$\begin{aligned} \dot{m} &= \frac{2000 \text{ kg}}{\text{h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \\ \dot{m} &= 0.556 \text{ kg/s} \\ v &=? \\ v &= \frac{F}{A} = \frac{2 \text{ m}^3/\text{h}}{\pi (0.02)^2} \times \frac{1 \text{ h}}{3600 \text{ s}} = 1.77 \text{ m/s} \\ E_k &= \frac{1}{2} \times 0.556 \times (1.77)^2 = 0.870 \text{ J/s} \end{aligned}$$

Problem adapted from Felder and Rousseau, Elementary Principles of Chemical Processes, 3rd edition, Wiley-India

So let us look at a couple of example problems where we try to look at kinetics and potential energies. Here is the example problem for kinetic energy water flows into a process through a centimeter inner diameter pipe at 2 meter cube per hour calculate the kinetic energy of the system in joules per second. So let us perform these calculations we know that kinetic energy is calculated as  $E_k = \frac{1}{2} M V^2$ .

We have to find what the value for M is and what the value for V is so that we can calculate kinetic energy so M would have to be calculate the volumetric flow rate so here we have M dot or mass flow rate which we can calculate from the volumetric flow rate. We know that the volumetric flow rate F is 2 meter cube per hour this implies mass flow rate would be volumetric flow rate density.

So density of water is 1000 kilograms per meter cube so you get 200 kilo grams per hour however the question ask us to calculate kinetic energy in terms of joules per second so this hour term would have to converted to second thereby our mass flow rate becomes 2000 kilograms per hour times 1 hour contains 3600 seconds giving you a value of 0.556 kilograms per seconds. So this is your mass flow rate.

Now we need to calculate the velocity if you remember in one of the earlier lectures I had described how to describe linear velocity from volumetric flow rate what we need to do is divide

volumetric flow rate by cross sectional area to get the linear velocity. So we will do that velocity = volumetric flow rate divided by cross sectional area. The cross sectional area of a pipe with a inner diameter of two centimeters would be  $\pi R^2$  where R is 0.01 meters.

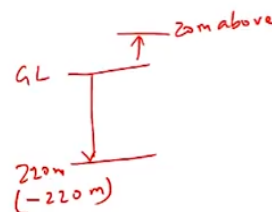
So diameter is 2 centimeters which is 0.02 meters so radius is 0.01 meters so you get the cross sectional area as  $\pi R^2$  volumetric flow rate is 2 meter cube per hour. So from here we can get the value for velocity in terms of meters per hour we still have to convert it meters per second. So we will convert that as one over divided by 3600 seconds giving us a velocity of 1.77 meters per second.

Now that we have the velocity for the water flowing we can calculate the kinetic energy as half times 0.556 times 1.77 squared giving us a final value of 0.870 joules per second so this is the kinetic energy of the system so we will move to the next example problem where try to calculate the potential energy.

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## Potential Energy: Example

- Crude oil is pumped at a rate of 15 kg/s from a point 220 m below the ground to 20 m above ground level. Calculate the rate of increase in potential energy.



$$\begin{aligned} \Delta E_p &= mg \Delta h \\ &= 15 \frac{\text{kg}}{\text{s}} \times 9.81 \frac{\text{m}}{\text{s}^2} \times (20 - (-220)) \text{m} \\ &= \boxed{35.3 \text{ kJ/s}} \end{aligned}$$

Problem adapted from Felder and Rousseau, Elementary Principles of Chemical Processes, 3rd edition, Wiley-India

According to the problem given crude oil which is 220 meters below the ground which is being pumped to it 20 meter about the ground level. So let us assume this is the ground level so from here we go all the way down to 220 meters below the ground level and this is being pumped to a level where you reach 20 meters above the ground level. So this would be used as -220 meters and this would be given as positive 220 meters.

Let us now calculate the change in potential energy which is  $\Delta EP = MZG \Delta H$  so this value would be 15 kilograms per second times acceleration due to gravity which should be 9.81 meters per second square times  $\Delta H$  which is from the final value of 20 meters and initial value of 220 meters below the ground level we get it as 240 meters difference. So finally we can calculate this value to get 35.3 kilo joules per second as the change in potential energy during this process.

With this we have performed examples problem which are simple and enough where we can calculate kinetic and potential energies. Let us now move on to the third type of energy which is possessed by us the system it is called the internal energy.

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## Internal Energy

- Point or state variable
- Macroscopic concept that accounts for all the molecular, atomic and subatomic energies
- All forms follow microscopic laws of conservation for dynamic systems
- Calculated based on pressure, temperature, volume, and composition

Internal energy is a point or state variable which I already mentioned so this is a important property which you will exploit when we perform energy balance calculations throughout the course it is the macro scoping concept that accounts for all the molecular and subatomic energies. All forms so this energy will follow the microscopic laws of equation for dynamic system this internal energy is calculated based on pressure temperature volume and composition of the system.

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## Specific Internal Energy – Single Phase, Single Component

$$\hat{U} = \hat{U}(T, \hat{V})$$

$$d\hat{U} = \left( \frac{\partial \hat{U}}{\partial T} \right)_{\hat{V}} dT + \left( \frac{\partial \hat{U}}{\partial \hat{V}} \right)_T d\hat{V}$$

$$\left( \frac{\partial \hat{U}}{\partial T} \right)_{\hat{V}} = \text{Heat capacity (specific heat) at constant volume, } c_v$$

$$\left( \frac{\partial \hat{U}}{\partial \hat{V}} \right)_T = \text{Negligible}$$



As I already mentioned internal energy which is an extensive property can be converted to an intensive property called as specific internal energy when you have system which is in a single phase with single components this specific internal energy is actually a function of temperature of specific problem. When you differentiate this equation what you would end up with this is differential of  $\hat{U}$  which is the specific internal energy could be equal to  $c_v dT + \left( \frac{\partial \hat{U}}{\partial \hat{V}} \right)_T d\hat{V}$ .

So here in the first term you are assuming specific volume to a concept but in the second term we are assuming temperature to be a constant. The term  $\left( \frac{\partial \hat{U}}{\partial T} \right)_{\hat{V}}$  at constant volume is called the heat capacity or the specific heat capacity at constant volume. So this term is used when we calculate change in internal energy.

The second term which is  $\left( \frac{\partial \hat{U}}{\partial \hat{V}} \right)_T$  is usually negligible because change in internal energy is almost 0 when the process is isothermal so for this reason the second term can be eliminated and the equation can be simplified to  $d\hat{U} = c_v dT$ .

As I already mentioned internal energy which is an extensive property can be converted to an intensive property called as specific internal energy when you have system which is in a single phase with single components this specific internal energy is actually a function of temperature of specific problem. When you differentiate this equation what you would end up with this is



differential of  $U$  cap which is the specific internal energy could be equal to though  $U$  cap  $DO T$  times  $DT + DO U$  cap  $V$  cap times  $DV$  cap.

So here in the first term you are assuming specific volume to a concept but in the second term we are assuming temperature to be a constant. The term  $DO U$  cap  $DO T$  at constant volume is called the heat capacity or the specific heat capacity at constant volume. So this term is used when we calculate change in internal energy.

The second term which is  $DO U$  cap  $DO V$  cap is usually negligible because change in internal energy is almost 0 when the process is isothermal so for this reason the second term can be eliminated and the equation can be simplified to  $DU$  cap =  $DVDT$ .

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## Calculating changes in internal energy

- Changes in specific internal energy can be calculated by integrating the previous equation

$$\Delta \hat{U} = \hat{U}_2 - \hat{U}_1 = \int_{\hat{U}_1}^{\hat{U}_2} d\hat{U} = \int_{T_1}^{T_2} C_V dT$$

- Only difference can be calculated, not absolute values
- Internal energy relative to a reference point can be calculated
- Integral equation is not valid if there is phase change



From this differential equation which we got we can calculate the change in specific internal energy. So to changes in specific internal energy will be obtained by integrating the equation we had so which would be integral of  $DU$  cap giving you  $\Delta U$  cap which is  $U_2 - U_1$  will be equal to integral of  $CVDT$  where you move from temperature  $T_1$  to  $T_2$ . So now we need to understand that internal energy is not an absolute value you cannot calculate the absolute value for internal energy.

You would only be able to calculate the difference in internal energy so from state 1 to state 2 where the difference in internal energy can be measured up calculating we cannot identify the

absolute values. So when we perform calculations or when to look up tables the value which are given for internal energy are a usually with reference point and it is given to a values of reference point.

Integral equation which we have given here will not be valid when phase change happens so what happens here is when particular system we have assumed as a single phase system and therefore we use this equation only when there is no phase change. If we have phase change there is an inherent change in internal energy associated with phase change and that needs to be accounted for separately and it cannot be brought into this integration.

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## Calculating changes in internal energy

- What is the change in internal energy for a constant volume system if 1 kg of water at 100 kPa was heated from 0°C to 100°C and then cooled back to 0°C and 100 kPa?
- For ideal gases, U is a function of T only
- Total internal energy of a system containing 'n' components

$$U_{tot} = \sum_{i=1}^n m_i \hat{U}_i$$



So when we talk about specific internal energy let us see a simple example problem which will help us understanding let us see if we can identify the change in specific internal energy for this simple system. Can you tell what the change in internal energy would be for a constant volume system if 1 kilogram of water at 100 kilopascals where heated from 0 degree Celsius to 100 degree and then cool back to 0 degree Celsius and 100 Pascals 100 kilopascals.

Think for seconds you do not need to do any calculations what I had told you earlier is internal energy is a point function or state function. It depends on a state at which is present so for this process you start from initial point go to intermediary point and then you come back to the initial point which means the total change in internal energy would be 0 for this process. For ideal gases

internal energy is the function of temperature only it does not depend on any other property pressure will not affect internal energy.

Total internal energy of a system which contains N components can be calculated as  $U_{\text{total}} = \sum M_i U_{\text{cap } i}$  where  $U_{\text{cap}}$  is the specific internal energy and  $M$  is the mass of that component and the multiplication product of mass times specific internal energy of that component will give you the total internal energy of that particular component. And summation of all the internal energies of different components will give you the total internal energy of the system.

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## Example

- What is the change in internal energy when 10 kmol of air is cooled from 60°C to 30°C in a constant volume process?  $c_v = 2.1 \times 10^4$  J/(kmol)(°C)

$$\begin{aligned}\Delta U &= \int_{T_1}^{T_2} c_v dT \\ &= \int_{60}^{30} (2.1 \times 10^4) dT \\ &= 2.1 \times 10^4 (30 - 60) \\ \Delta U &= -6.3 \times 10^6 \text{ J}\end{aligned}$$

Problem adapted from Himmelblau and Riggs, Basic Principles and Calculations in Chemical Engineering, 7th Edition, Prentice Hall India

Let us look at example problem it is simple example problem to calculate change internal energy what is the change in internal when 10 kilo moles of air is cooled from 60 degree Celsius in a constant volume process you have been given that CV for air is 2.1 times N power 4 joules per kilo mole degree Celsius. From the integral equation we got  $\Delta U = \int_{T_1}^{T_2} C_v dT$  integration happens from  $T_1$  to  $T_2$ .

So here initial temperature is 60 degree Celsius and final temperature is 30 degree Celsius you CV value is given as 2.1 times 10 power 4 DT. So this is calculated as 2.0 times 10 power 4 and this would be 30 – 60 giving you  $\Delta U = -6.3$  times 10 power 6 joules. So this is the change in

internal energy what you observe here is the delta U is negative so this because the system is actually being cooled from 60 degree Celsius to 30 degree Celsius.

When temperature difference is negative you would end up with an internal energy which is change in internal energy also being negative.

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### Specific Enthalpy – Single Phase, Single Component

$$\hat{H} = \hat{H}(T, P)$$

$$d\hat{H} = \left( \frac{\partial \hat{H}}{\partial T} \right)_P dT + \left( \frac{\partial \hat{H}}{\partial P} \right)_T dP$$

$$\left( \frac{\partial \hat{H}}{\partial T} \right)_P = \text{Heat capacity (specific heat) at constant pressure, } c_p$$

$$\left( \frac{\partial \hat{H}}{\partial P} \right)_T = \text{Negligible at lower pressures}$$



So let us move on to the next concept which would be the enthalpy enthalpy is measure of total energy of a thermodynamic system it includes the internal energy and also the energy which is required for making room of the system by displacing the environment so that it can establish its volume and its pressure.

So this enthalpy is also called as thermodynamics potential and is also a state function however it is also an extensive quantity which can be converted into a intensive quantity by dividing it with mass to get specific enthalpy. So enthalpy is given as  $U + PV$  where  $U$  is the internal energy  $P$  is the pressure  $V$  is the volume as I already said specific enthalpy which is the intensive property can be calculated as  $H \text{ cap} = U \text{ cap} + PC \text{ cap}$ .

Let us consider a system which is single phase single component system this specific enthalpy which we looked at would be a function of temperature and pressure. So if you were to differentiate this equation you would get  $dH \text{ cap} = dU \text{ cap} + d(P \text{ cap}) = dU \text{ cap} + P dT + T dP + dP \text{ cap}$ .

So this term which is there in the first part of the equation which is  $\int_{T_1}^{T_2} C_p dT$  at constant pressure is called as the heat capacity of the specific heat capacity at constant pressure which is also represented as  $C_p$ . The second term  $\int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_T dP$  at constant pressure is usually negligible when pressure difference is small. At lower pressure this term can be removed for all process.

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## Enthalpy

- Only difference can be calculated, not absolute values
- Enthalpy relative to a reference point can be calculated
- Total enthalpy of a system containing more than one component

$$H_{tot} = \sum_{i=1}^n m_i \hat{H}_i$$

When we are calculating changes in enthalpy we need to remember that we can integrate this equation to get the difference in enthalpy which would be  $\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_p dT = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_T dP$  where the integration is done between temperature 1 to temperature 2. Integral equation again will not be valid when there is phase change just like we had the specific internal energy specific enthalpy also changes with respect to phase 2.

So when there is phase change we cannot directly use this integration equation that has been given. At high pressures the  $\int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_T dP$  term which we looked at is not negligible so this would also be a factor that also be accountable for. This value of  $\int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_T dP$  at constant temperature is actually evaluated from experimental value.

So it cannot actually be calculated using some equations for ideal gases enthalpy is a function temperature only there by the second term which  $\int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_T dP$  at constant temperature goes

to 0. So the equation which we have integral CPDT is valid for ideal gases as long as there is no phase change.

So when we talk about calculating enthalpy we need to understand only differences can be calculated not the absolute values. Just like internal energy when you look at value is given in tables and values you find in text books these are usually in reference to reference point it is not the absolute value. So you should also understand that total enthalpy of the system which contains more than one component would be the summation of the enthalpy of the individual components.

So the enthalpy of individual component can be calculated as the mass of component times the specific enthalpy of that particular component. And the summation of all these enthalpies will give us the total enthalpy of the system.

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### Example

- The air you breathe is immediately warmed up from ambient temperature to 37°C before entering into your lungs. Calculate the specific enthalpy change when the temperature of air is raised from 20°C to 37°C. Assume that air is bone-dry. (Given:  $C_p$  of air =  $28.94 + 0.4147 \times 10^{-2} T + 0.3191 \times 10^{-5} T^2 - 1.965 \times 10^{-9} T^3$  J/mol.°C)

$$\begin{aligned} \Delta \hat{h} &= \int_{T_1}^{T_2} C_p dT \\ &= \int_{20}^{37} \left( 28.94 + 0.4147 \times 10^{-2} T + 0.3191 \times 10^{-5} T^2 - 1.965 \times 10^{-9} T^3 \right) dT \\ \Delta \hat{h} &= 494 \text{ J/mol} \end{aligned}$$

Problem adapted from Saterbak, McIntire, and San, Bioengineering Fundamentals, 1st Edition, Pearson

Here is one simple example problem which will help us understand how to calculate enthalpy for a system the air you breath is immediately formed up from ambient temperature to 37 degree Celsius before entering into your lungs. Calculate the specific enthalpy change when the temperature of air is raised from 20 degree Celsius to 30 degree Celsius. Assume that air is bone-dry and the value for CP of air is also given.

So what you see here is a polynomial with respect to temperature given as the value for CP. So we know that we can calculate  $\Delta H_{cap}$  as  $\int CP \, DT$  from temperature 1 to temperature 2. So initial temperature is 20 degree Celsius and final temperature is 37 degree Celsius we have been given the CP value as  $28.94 + 0.4147 \times 10^{-2} T + 0.3191 \times 10^{-5} T^2 - 1.965 \times 10^{-9} T^3$  times DT.

By performing this integration and applying the limit we would be able to calculate  $\Delta H_{cap}$  as 494 joules per mole with this calculation we have come to the understanding of how to calculate the specific enthalpy change for system. Now that we have learnt the fundamental and some terminologies associated with energy balances.

Let us move on to the next lecture where we talk about energy balance calculation and you will get some introduction on how to perform energy balance calculations and what is the principle behind energy balance calculations until then thank you can good bye.