#### Material and Energy Balances Prof.Vingesh Muthuvijayan Department of Biotechnology Indian Institute of Technology – Madras

#### Module No # 08 Lecture No # 36 Introduction to Energy Balances – Part 2

Welcome to today's lecture on energy balances in the last lecture we looked at open and closed systems for single components and we perform some basic energy balance calculations. Today we will continue with more fundamental aspect with energy balances and for that we will now start with discussing energy balances for multiple component processes.

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# Energy Balances on Multiple Component Processes

- Specific enthalpy of each component has to be determined
- Total enthalpy change is calculated from individual specific enthalpies
- For ideal gas and liquid mixtures with similar molecular structures, assume that specific enthalpy of the mixture component is the same as for the pure substance at the same T and P



When you have multiple component present in a process when the specific enthalpy of the process itself will depend on the specific enthalpy of each of the component the total specific enthalpy of the process or system will be the summation of the specific enthalpy of the individual and the enthalpy.

And the enthalpy can be calculated as the mass of the individual component times the enthalpy specific enthalpy of the individual component + the mass of the second component times specific enthalpy of the second component and so on. And based on this you would be able to calculate is

the total specific enthalpy or total enthalpy of the system. So this is measured and used for performing energy balance calculations in multiple component processes.

When we do this we are making an assumption and this assumption is valid for ideal gas and liquid mixtures which have similar molecules structures and that is because we are assumption ideal solutions or ideal mixtures so based on this assumption we have that the total enthalpy of system is equal to the summation of the enthalpy if individual components at the same temperature and pressure.

This is true only under ideal conditions if there is non- ideality whether can be interaction between the molecules which are present in the mixture this assumption will not be valid. So initially we will start with ideal mixtures and solutions to perform these calculations.

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## Example #1

 A gas stream containing 60.0 wt % ethane and 40.0 wt % butane is to be heated from 150 K to 250 K at a pressure of 5 bar. Calculate the required heat input per kg of the mixture, neglecting potential and kinetic energy changes, using the enthalpy data given for ethane and butane and assuming ideal gas behavior.

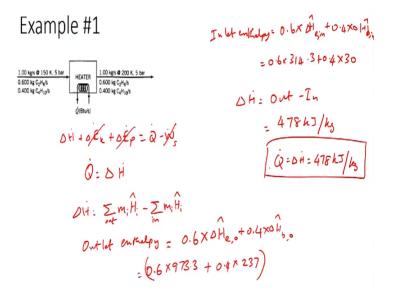
• 
$$\Delta \widehat{H}_{e|i}$$
 = 314.3 kJ/kg;  $\Delta \widehat{H}_{e|o}$  = 973.3 kJ/kg

• 
$$\Delta \hat{H}_{b|i}$$
 = 30 kJ/kg;  $\Delta \hat{H}_{b|o}$  = 237.0 kJ/kg;

Here is an example problem you have a gas stream containing 60% ethane in 40% butane this is to be heated from 150 kelvin to 250 kelvin at a pressure of 5 bar you are asked to calculate the heat input per kilogram of the mixture neglecting potential and kinetic energy changes using the enthalpy data that is given for ethane and butane and assuming ideal gas behavior.

So we have been given this specific enthalpy details for ethane and inlet conditions and outlet conditions and butane at inlet and outlet conditions

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Using this we have been asked to calculate the amount of heat that needs to fed to the system per kilogram of the mixture. For performing this calculation we have also been told to ignore kinetic and potential energies and using this we will start with our calculations. This system we have is our open system because you have mixture flowing in so we have been asked calculate the amount of heat that needs to be supplied per kilogram.

So we assume that the flow rate of the mixture which is entering into the heater is 1 kilogram per second. Using that basis we will perform the calculations we have been given that 60% is ethane and 40% is butane. So let us start performing the calculations so this is an open systems which means the energy balance for the system would be delta H dot + delta EK dot + delta EP dot = Q dot – WS dot.

So for this system we have been asked to ignore kinetic and potential energies so these two will go to 0 there are actually no moving parts in the system like a piston or (()) (04:12) so therefore the shaft work would also be equal to 0 this means the equation is simplified as Q dot equals delta H dot. So what we have is the amount of energy which needs to be supplied in the form of heat could be equal to the change in enthalpy which could be seen for the system.

So this delta H dot could be equal to sigma of MIHI cap in the outlet – sigma of MI HI cap in the inlet. Now let us calculate the outlet enthalpy outlet enthalpy would be equal to 0.6 kilograms of ethane times the delta H cap of ethane in the outlet + 0.4 kilograms of butane times delta H cap

of butane in the outlet. So this value would be 0.6 time 973.3 + 0.4 times 237 so this would be the outlet enthalpy.

Inlet enthalpy will be equal to 0.6 times delta H cap of ethane in the inlet + 0.4 times delta H cap of butane in the inlet. So this would be 0.6 times 314.3 + 0.4 times 30 so the difference between the outlet and the inlet enthalpies will be delta H dot which would be outlet – inlet which is 478 kilo joules per kilogram. So Q dot which is equal to delta H dot would also be equal to 478 kilojoules per kilogram.

So these would be the amount of heat which needs to be supplied to the system now that we have performed a simple energy balance calculation for a multiple component system. Let us move on to understanding a fundamental aspect which is required for performing energy balances which is thermodynamics tables.

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## Tables of Thermodynamic Data

- · Tables of enthalpies and other state properties
- Found in Appendix B5 B9 of Felder and Rousseau
- Perry's Chemical Engineering Handbook
- Lists values relative to a reference point
- · Reference point may or may not be listed
- It is not required to know the reference point for calculations

Thermodynamics information such as internal energy enthalpy specific volume can be provide in the form of tables in many (()) (06:59). So these tables are actually useful because you can get these values directly rather than having to calculate them every single time you perform these calculations. Such tables have been prepared for component which are very commonly used in chemical and biochemical industries.

So these tables show values such as enthalpies and other state properties and using a reference

state. So if you look at the appendix of B5 to B9 Felder and Rousseau is one of the prescribed

textbooks you would find such thermo dynamics tables. Perry's chemical engineering handbook

is another book which contains many such tables which provides all the thermodynamic data for

commonly used substances.

This tables these tables list values which are the enthalpy or internal energy values in reference

to our reference point. So these values as you remember cannot be calculated as absolute values

enthalpy an internal energy can be measured only as a relative value compared to a reference so

here some reference point would be used and the relative values would be given and since we are

always interested in finding the difference between one state to another so taking a difference

between the values from the table will eliminate the effect of such reference states that has been

taken.

So thereby we can use these values directly value perform these calculations even in the previous

example problem the enthalpy values which we have given for butane and ethane must have

been in reference to her reference point it would have been relative to reference point. So we did

not worry too much about what reference point was because it does not matter in the grand

scheme of things because we are only finding the different and not really looking at absolute

values.

So the reference point may or may not be listed in many of the tables in the previous example it

was not listed however if you were to refer to the tables in Perry's hand book or in Felder

Rousseau they usually have the reference states listed either directly or impressively. So you do

not need to know the performance point for performing the calculations.

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#### Example #2

 The following table gives the data for saturated methyl chloride.

	State	T (°F)	P (psia)	Specific volume (ft³/lb <sub>m</sub> )	Ĥ (Btu/lb <sub>m</sub> )
->	Liquid	-40	6.878	0.01553	0.000
	Vapor	0	18.90	4.969	196.23
	Vapor	50	51.99	1.920	202.28

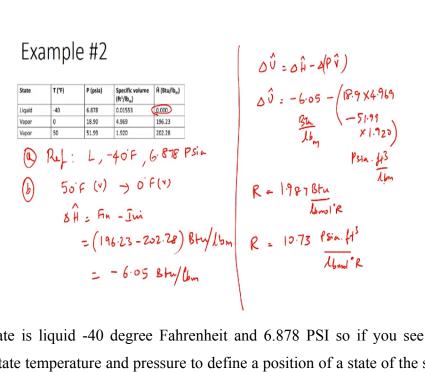
- · Can you identify the reference state?
- For the transition of saturated methyl chloride vapor from 50°F to 0°F, calculate
  - · Change in specific enthalpy
  - · Change in specific internal energy
- · What assumption was made in the previous section?

So here is the simple example problem to illustrate how such thermodynamics can be used. So this is the very concise table that has been presented in front of you let us try to use us to perform energy balance calculations. The following used the data for saturated methyl chloride you have the state of methyl chloride temperature of methyl chloride pressure specific volume and enthalpy all are listed in the table.

First step is for you to identify the reference state and the next test to identify the change in enthalpy and change in internal energy for specific process and the last one is to identify any assumptions if they reduced okay. Let us start with the identifying the reference state so look at the data you see that for liquid at -40 degree Fahrenheit and 6.878 PSI the specific volume is listed as 0.15553 feet cube per pound mass and the specific enthalpy is listed as 0.

So this implies that this particular condition would be the reference state used for this table so what we have is the specific enthalpy value of methyl chloride present as liquid at temperature at -40 degree Fahrenheit and pressure of 6.878 PSI relative to a reference point is 0 which mean these two values would have been equal implying these is the reference state. So the reference state for the system would be liquid -40 degree Fahrenheit and 6.878 PSI so that is the reference point.

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So reference state is liquid -40 degree Fahrenheit and 6.878 PSI so if you see I would have mentioned the state temperature and pressure to define a position of a state of the system. So this give you the complete of definition of in which the system can exist now moving on to the second part of the problem we have been asked to calculate the change in specific enthalpy for the transition of saturated methyl chloride vapor from 50 degree Fahrenheit to 0 degree Fahrenheit.

So the first part of the problem ask us to identify the reference sate in this table if you look at the first row it is liquid – 40 degree Fahrenheit 6.878 PSIA and for this articular condition you have a specific enthalpy value as 0. This implies that the specific enthalpy value entered here for this particular condition is relative to the reference state and that value is 0 implying this would be the reference.

So therefore the reference state would be liquid – 40 degree Fahrenheit and 6.878 PSIA so this identifies the first problem now the second part of the problem we would have to find the difference in specific enthalpy for the process where 50% Fahrenheit vapor is cooled to 0 degree Fahrenheit vapor. So this means the initial condition is 50% Fahrenheit vapor and the final condition is 0 degree Fahrenheit vapor.

So the difference in specific enthalpy delta H cap will be final minus initial so this would be 196.23 – 202.28 BTU per pound mass. So this gives you a value of -6.05 DTU per pound mass

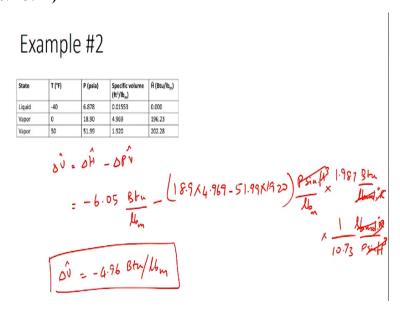
so this is the specific enthalpy for the process where the vapor is cooled from 50 degree Fahrenheit to 0 degree Fahrenheit we have been also asked to find the change in specific internal energy.

So this value is not directly available from the table however we can calculate specific internal energy as delta U cap could be equal to delta H cap – delta of PV cap. So using this let us calculate the delta U CAP as -6.05 which is the value for delta H cap which we calculated – PZV cap value for the final condition which would be 18.9 times 4.969 –initial which would be 51.99 times 1.920.

This particular term which is within the brackets would have the units of PSIA times feed cube per pound mass whereas the units for delta H cap were Btu per pound mass. So these units conversion needs to be done for doing this we can use the universal gas constants. The universal gas constants in terms of BTU is given as 1.987 BTU per pound degree Rankine.

Similarly universal gas strength is gas constant in PSIA can be given as 10.73 PSIA times feed cube divided by pound moles degree rankine. Now using these two values we can convert the value which we have is PSIA feed cube per pound mass into BTU per pound mass.

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Let us use these universal gas constant values to perform the calculation so delta U cap would be equal to delta H cap – delta PV cap which we wrote down as -6.05 BTU per pound mass -18.9

times 4.969 -51.99 times 1.920 the units being PSIA feed cube per pound mass. So now we are

converting this value into BTU using the universal gas constant which will be 1.987 BTU per

pound moles degree rankine divided by 10.73 into pound moles degree rankine divided by PSIA

feed cube.

So the PSIA feed cube gets cancelled pound mole degree rankine get cancelled so the units for

this terms now becomes BTU per pound. So using this you can get the final value for delta U cap

as -4.96 BTU per pound mass. So this is the change in the specific internal energy for the process

of cooling the vapor from -50 degree Fahrenheit from 50 degree Fahrenheit to 0 degree

Fahrenheit.

So the third part of the question is to identify the assumptions that has been made so we have

calculated the specific enthalpy values without actually knowing the pressure of the final

condition which means we have assumed that the change in specific enthalpy was independent of

pressure so this is a reasonable assumption to make for any small changes in pressure because it

is gas an assume ideal gas behavior.

Amongst thermodynamic tables one of the most common thermodynamic table which is used is

the stream tables. So stream tables are very commonly used because the stream is involved in

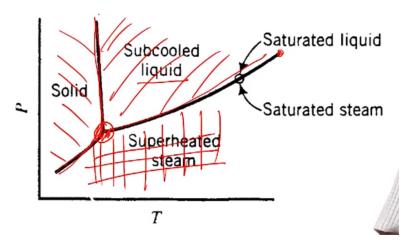
many chemical and biochemical processes and because it is so commonly used it is a waste of

time to actually perform calculation to identify the change in enthalpies every single time. So

people have already built table that can be used directly.

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#### Phase diagram of water



So what you see here the phase diagram of water so this is a pressure versus temperature graph. At low pressure and high temperatures water exist in the form of super heated steam or vapor at low temperatures and high pressures water exist as a solid and at temperature which are above a certain value and pressure which are above a certain value water exist in terms of liquid.

So that is what you see here so the graph you have here so this line that you see is the solid vapor equilibrium this line that you see is the liquid vapor equilibrium the vapor liquid equilibrium and this line you see is the solid liquid equilibrium. So water exist as liquid in this region and exist as solid in this region and here it exist as superheated steam. So this value you have here this particular value would be the critical point and this point is the state at which the different between liquid and vapor becomes in distinguishable.

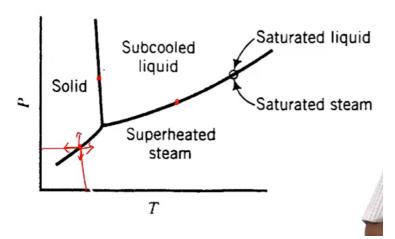
At condition above the critical point you would have a (())(19:54) mess which you cannot distinguish between a liquid and a vapor there is no definite change which actually converted it from liquid to vapor. And this particular point is called as the triple point so triple is the point in which you have all three states existing in equilibrium you can have solid liquid and vapor existing in equilibrium at this point is called as the triple point.

On this lines which I called as the solid vapor equilibrium or the vapor liquid equilibrium or the solid liquid equilibrium two cases can actually exist. So what would happen is if you even have

the slightest change in temperature or pressure water would move towards one particular point so let it be explain this in graph.

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#### Phase diagram of water



So let us take this point which is on the solid vapor equilibrium so here at this particular pressure and temperate you have water existing in the form of solid and vapor in equilibrium. So if you were to change the temperature so let us say if you increase the temperature it will move towards superheated steam whereas if you decrease the temperature it will move toward to a solid similarly if you increase the pressure it will move towards a solid phase and if you decrease a pressure it will move towards the vapor phase.

So what you see here is by even slight changes in temperature or pressure you can shift the equilibrium towards one direction. However at that particular point which lies on that equilibrium curve you would have both phases existing simultaneously you would have saturated solid and saturated vapor existing at this point similarly a point on this line would have a saturated liquid existing simultaneously.

Similarly here in this line you would have saturated solid and liquid simultaneously so these are the equilibrium curves on which two phases can exist and triple point is the equilibrium where three phases can exist. Now that we have some fundamental understanding of what a phase diagram is let us look how the steam tables are built.

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#### Saturated Steam Tables - Temperature

Table B.5 Properties of Saturated Steam: Temperature Table<sup>a</sup>

T(°C)	P(bar)	$\hat{V}(m^3/kg)$		$\hat{U}(kJ/kg)$		Ĥ(kJ/kg)		
		Water	Steam	Water	Steam	Water	Evaporation	Steam
0.01	0.00611	0.001000	206.2	zero	2375.6	+0.0	2501.6	2501.6
2	0.00705	0.001000	179.9	8.4	2378.3	8.4	2496.8	2505.2
4	0.00813	0.001000	157.3	16.8	2381.1	16.8	2492.1	2508.9

- Column 2 Pressure corresponding to the given temperature on the VLE curve, called the vapor pressure of water at the given temperature
- Columns 3 and 4 Specific volumes of saturated liquid water and saturated steam at the given temperature
- Columns 5 and 6 Specific internal energies of saturated liquid water and saturated steam at the given temperature relative to a reference state of liquid water at the triple point
- Columns 7-9 Specific enthalpies of saturated liquid water (Column 7) and saturated steam (Column 9) and the difference between these quantities called as heat of vaporization



Steam tables are actually built for saturated teams and for superheated steams saturated steam is the steam which exist in the vapor liquid equilibrium what you see here is the saturated steam which has been taken out of the Felder Rousseau. So what we have here is that temperature based table the first column that you see is the temperature.

So what is given there is the condition temperature condition in which vapor liquid equilibrium is exist the pressure is corresponding pressure to that particular temperature at which the vapor liquid equilibrium can exist. So let us take one particular example for a example if you were to take 2 degree Celsius and a pressure of 0.00705 bar in that particular condition you have a vapor liquid equilibrium where you have temperature at 2 degree Celsius and the pressure is the corresponding saturation pressure to that temperature.

So the first point which you see the first data point which you see is 0.01 degree and pressure of 0.00611 bar so this is the triple point. What you see is the specific internal energy and specific enthalpy for this particular point has been represented as 0. So this implies that the reference state that has been used is liquid water at triple point the values for steam at triple point has been given as non-zero values.

However the value for water at the triple point is given as 0 this means liquid at triple point as been used as reference state for this table so now let us look at each of these columns. Column 2 is the pressure which corresponds to the given temperature on given VLE for it is also called as

the vapor pressure of the water at given temperature. So column 3 represents the specific volume in terms of water exist in vapor liquid equilibrium and liquid water which exist.

And the steam which exist would give in the column 4 you have column 5 and 6 giving the specific internal energies instead of saturated liquid water and saturated steam at given temperatures these values are relative to the reference stage which is the liquid water at the triple point. Column 7 through 9 represent the specific enthalpies column 7 is specific enthalpy of saturated liquid water and column 9 specific enthalpy of saturated steam.

Column 8 is actually difference between the 2 representing the heat of vaporization at that particular condition. Once this particular amount of heat is supplied the water liquid will completely be converted to water vapor. So that is what this heat of vaporization evaporation or heat of vaporization represent.

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# Saturated Steam Tables – Pressure

Table B.6 Properties of Saturated Steam: Pressure Table\*

P(bar)	7(°C)	<i>Ŷ</i> (m³/kg)		$\hat{U}(kJ/kg)$		$\hat{H}(kJ/kg)$		
		Water	Steam	Water	Steam	Water	Evaporation	Steam
0.00611	0.01	0.001000	206.2	zero	2375.6	+0.0	2501.6	2501.6
0.008	3.8	0.001000	159.7	15.8	2380.7	15.8	2492.6	2508.5
0.010	7.0	0.001000	129.2	29.3	2385.2	29.3	2485.0	2514.4
0.012	9.7	0.001000	108.7	40.6	2388.9	40.6	2478.7	2519.3
0.014	12.0	0.001000	93.9	50.3	2392.0	50.3	2473.2	2523.5
0.016	14.0	0.001001	82.8	58.9	2394.8	58.9	2468.4	2527.3
0.018	15.9	0.001001	74.0	66.5	2397.4	66.5	2464.1	2530.6

You can also have a similar table existing in terms of pressure so what you see here is the first column is the pressure and for that particular pressure you have a corresponding temperature which is given and rest of the values are given to the similar table.

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#### Superheated Steam Tables

Table B.7 Properties of Superheated Steam<sup>e</sup> Temperature (°C) → 2689 2517 2584.8 2438.0 2880 2661 21.8 2977 2736 24.2 2588 19.5 2890 28.7 26.5 2878 2660 4.35 2979 2735 4.83 313.9 3177 2484.0 3.24 209.2 2675.4 2506.1 1.69 2676 2507 1.69 209.3 3176 2583 2658 2.17 2889 2.87 0.00103 2747.5 2560.2 0.375 419.4 2855 209.2 0.00101 313.8 418.8 631.6 0.00103 0.00104 210.1 3159 2876 0.282 419.7 632.5 313.7 418.7 631.4 0.194 0.00101 0.00103 0.00104 0.00109 211.0 315.5 420.5 633.1

Other than the saturated steam tables you can also something called as the superheated steam table this particular table which is actually been taken out of Felder Rousseau text book is a superheated steam table. What you have here is information about any temperature and pressure which means the water can actually exist either as liquid or vapor and does not have to be in the saturated condition.

So what you observe in this table is the first column which is given in the left hand side is the pressure and within the brackets below every pressure you have a temperature value which is given which is the boiling point of water at that particular pressure and then this next two column represents the saturated liquid and saturated steam where you have been given the specific enthalpy specific internal energy and specific volume for the saturated steam and water.

After the temperature which have been given are all different temperatures are not corresponding to the saturation temperature for example if you were to take the third data point for pressure which is 0.5 bar you have a saturation temperature or boiling point given as 81.3 degree Celsius so if you have 0.5 bar and 81.3 degree Celsius then you have a point on the vapor liquid equilibrium.

So the values for H cap U cap and V cap can be obtained from the saturated water and saturated steam values given in the column here. So these would be saturated steam and values. However

if you want it temperature other than the 81.3 degree Celsius then you can look up these table

where you have values for 50, 75, 100, 150 and so on.

So what you would have here is the value for the specific internal energy and enthalpy and

specific volume is given as 50 degree Celsius here where as you have 150 degree Celsius values

given here. What you would have observe is at 50 degree Celsius this water exist only as a liquid

it is not in any kind of equilibrium and that 25 degree Celsius will again exist only at liquid and

at 150 degree Celsius it will exist only as vapor.

So whatever condition in which water exist only as liquid which is covered in this step shape box

everything outside of the step shape box is a vapor condition. So within the box we have only

liquid exist it is either called a sub pool liquid or liquid and outside of it is called the superheated

steam. Where you have only steam it is not equilibrium with anything.

So now that we have looked at these tables let us see if we can use them to perform some

calculations I strongly recommend that you have access to these steam tables there are many

steam tables which are readily available for either for purchase or for even freely available on

online.

Please use this steam tables get familiarized with how to refer to this steam tables to identify

specific enthalpy specific internal energy specific volumes. So that we can make calculation in

volume steam in simple.

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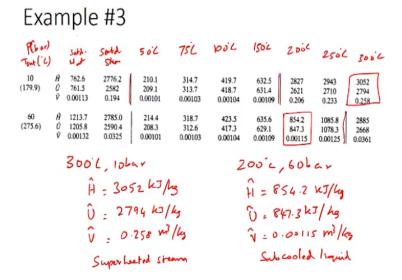
## Example #3

- Determine the following of water at 300°C and 10 bar relative to water at 200°C and 60 bar.
  - Specific volume
  - Specific enthalpy
  - Specific internal energy

Identify what phase the water is in for both states and find the dew point for the superheated state.

Here are some example problems which will help understand this better determine the following of water at 300 degree Celsius is at 10 bar relative to water at 200 degree Celsius 60 bar. Specific volume and specific enthalpy specific internal energy you have been asked identify what phase the water is in for both states and find the due point for the superheated state.

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What I have done here is taken out the relevant portion of the steam tables for performing the calculations the values we have here is pressure in bar and the saturation temperature in 10 degree Celsius this is saturated water values and this saturated steam values and this is for 50 degree Celsius 75 degree Celsius 100 degree Celsius 150 degree Celsius 200 degree Celsius 250 Celsius and 300 degree Celsius.

Now let us look at the values we have and we have a condition the final condition is 300 degree Celsius and 10 bar. So 300 so 10 bar is the value given here is 300 degree Celsius would be this particular column so we have for this H cap is given as 3052 kilo joules per kilogram and U cap is given as 2794 kilojoules per kilogram and V cap is given as 0.258 meter cube per kilogram. So these line you see here are actually the boundaries of the step shape box which we saw earlier.

So this particular point lies outside the step shape box indicating that this would be a superheated steam. So the condition here is superheated steam. So the other condition is the 200 degree Celsius and 60 bar. So this is the 60 bar column and we are trying to find the information for 200 degree Celsius which is here. So we have H cap value as 854.2 kilo joules per kilogram and U cap value is 847.3 kilojoules per kilogram and V cap value is 0.00115 meter cube per kilogram.

So here again this would be the boundary for the step shape box so this value lies within the step shape box indicating this to be a sub cooled liquid. So with this we have the information for specific internal energy and specific enthalpy for both these states. Now we need to find the difference between the two to actually calculate the specific enthalpy internal energy and specific volume relative to reference state.

So now let us go ahead and do the calculation but before that let us look at these values and try to get some physical meaning and understanding that what these value are if you look at the values for internal energy and enthalpy for 300 degree Celsius and 10 bar you would see that the difference between enthalpy and internal energy significantly large. However if you were to compare the internal energy and specific energy in enthalpy values for 200 degree Celsius in 60 bar the value difference is relatively small.

This is because for 200 degree Celsius in 60 bar you have water existing as a sub cooled liquid this mean the specific volume value is very small thereby here PV cap value is also small hence here internal energy and specific energy enthalpy value are not that very different the percentage difference is actually less than 1% however to look at the value difference in specific internal energy versus specific enthalpy for 300 degree Celsius and 10 bar.

It is quiet significant it is more than 10% difference so this indicates that the specific volume of steam which is much higher than the specific volume of liquid water influences the change in enthalpy so this is an aspect which we need to understand and which we can appreciate directly by looking at these value form the steam tables. Let us perform the calculation for finding the difference so that we will get the answer required by the problem.

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#### Example #3

Delta V cap would be equal to the difference between the specific volumes so that would be 0.258 which is the final condition – from here 0.00115 meter cube per kilogram giving you a value of 0.257 meter cube per kilogram so this would be the value. So we have delta U cap as 2794 – 847.3 kilojoules per kilogram giving you a value of 1496.7 kilojoules per kilogram and your delta H cap would be equal to 3452 -854.2 kilojoules per kilogram which is equal to 2197.8 kilojoules per kilogram.

In addition to all thee we also been asked to find the due point or the boiling point for the superheated steam. So due point would be the point at which the condensation happens so here the superheated stated state is 300 degree Celsius and 10 bar so going back to this values here you can find the boiling point as 179.9 degree Celsius which is also the due point or point at which condensation would happen.

With this we have identified all the values that are been asked for and we have come to the end of today's lecture on introduction to energy balances in the next lecture we will look at some

example problems and perform tutorial problems to strength fundamentals on how to perform energy balance calculations for simple systems that we have looked at till now until then thank you and good bye.