# Chemical Engineering Thermodynamics
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## Lecture – 11
## Thermodynamic Diagrams and Tables

Hello and welcome back. In this lecture, we are going to look at using Thermodynamic Diagrams and thermodynamic Tables for calculating the property changes. Before we do that let us quickly recap what we have done earlier.

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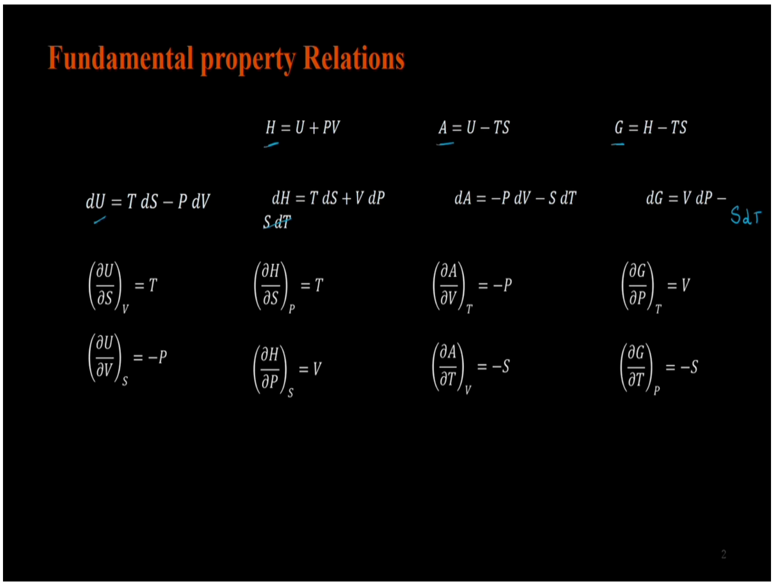

Fundamental property Relations

$H = U + PV$  $A = U - TS$  $G = H - TS$

$dU = T\,dS - P\,dV$  $dH = T\,dS + V\,dP$ $\cancel{S\,dT}$  $dA = -P\,dV - S\,dT$  $dG = V\,dP -$ $S\,dT$

$\left(\frac{\partial U}{\partial S}\right)_V = T$  $\left(\frac{\partial H}{\partial S}\right)_P = T$  $\left(\frac{\partial A}{\partial V}\right)_T = -P$  $\left(\frac{\partial G}{\partial P}\right)_T = V$

$\left(\frac{\partial U}{\partial V}\right)_S = -P$  $\left(\frac{\partial H}{\partial P}\right)_S = V$  $\left(\frac{\partial A}{\partial T}\right)_V = -S$  $\left(\frac{\partial G}{\partial T}\right)_P = -S$

In addition to the enthalpy and internal energy, we have defined two other thermodynamic quantities Helmholtz free energy and Gibbs free energy. And we have used these thermodynamic quantities or we have used these definitions to write the fundamental property relations for change in these thermodynamic quantities dU dH dA and dG, so, this is minus S d T there.

And by using these fundamental relations, we can define what the changes in these properties are going to be as partial derivatives, like I have shown here for each of these expressions.

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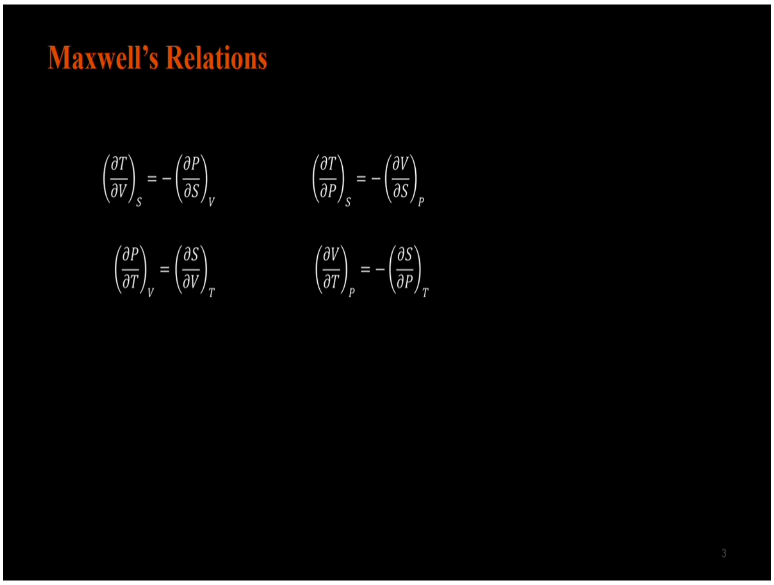

### Maxwell's Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

We can use the fact that the second derivatives are going to be same irrespective of the order of differentiation. So, we derive what are known as Maxwell's Relation and the importance of Maxwell's relation is that on one side we have quantities or variables that I cannot directly measure. On the other side, it is in terms of volume temperature and pressure things I can measure in the lab.

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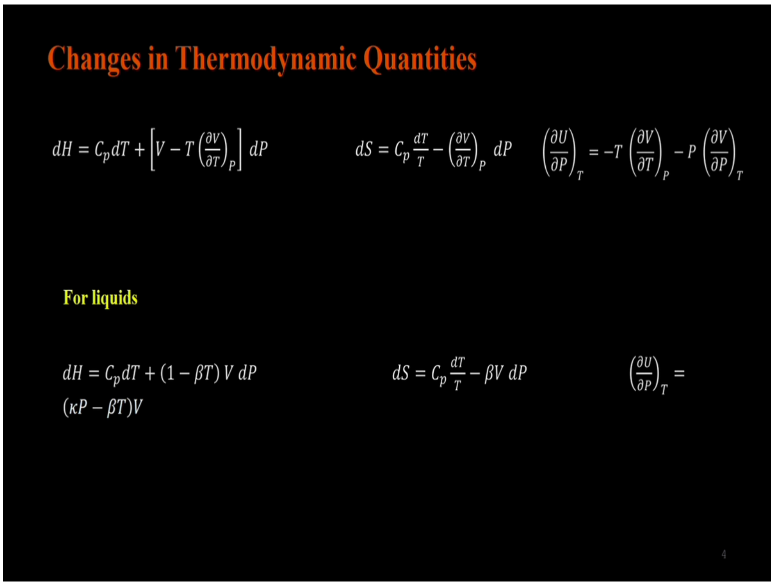

### Changes in Thermodynamic Quantities

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \qquad dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

**For liquids**

$$dH = C_p dT + (1 - \beta T)\, V\, dP \qquad dS = C_p \frac{dT}{T} - \beta V\, dP \qquad \left(\frac{\partial U}{\partial P}\right)_T =$$

$$(\kappa P - \beta T)V$$

So, they come handy when I try to write expressions for these variables. We have used this idea and written down expressions for d H d S and d U, and also for special cases, as in case of liquids what would be d H and d d S in terms of the isothermal compressibility and volume expensivity etcetera. We have solved one problem for liquids in the earlier class. What we are going to do now is look at what are known as thermodynamic diagrams first. This is a typical example of a thermodynamic diagram for a refrigerant known as R 134 a and it has a wealth of information in it which is useful. This particular diagram is what we call as a P H diagram, the pressure is on the y axis here and enthalpy or specific enthalpy is on the x axis there. So, we call this as a PH diagram.

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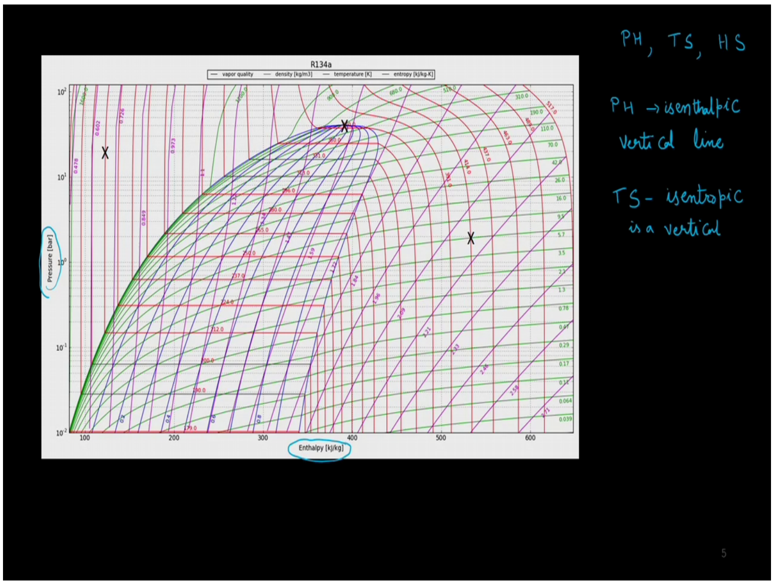

PH, TS, HS

PH → isenthalpic
vertical line

TS - isentropic
is a vertical

There are other types of diagrams such as a T and S diagram or a H S diagram. And depending on the type of process, we are looking at each of these diagrams is going to come in handy, but otherwise it is more or less the same information that is stored in each of these diagrams. For example, if the process is isenthalpic, in a PH diagram an isenthalpic process and we say isenthalpic process, we mean that the process occurs at constant enthalpy. And on a PH diagram, because the enthalpy is constant that process is going to follow a vertical line, because the value of X is same. So, it is going to follow a vertical line on a PH diagram, right.

Similarly, an isentropic process on a T S diagram and we say it is an isentropic process. We mean that the entropy is constant throughout the process on a T S diagram, isentropic process is a vertical line, etcetera. So, as I said each of these diagrams is going to be handy for solving for handling one process or the other, depending on what type of process we have, it is convenient to choose an appropriate thermodynamic diagram.

Now, let us focus our attention then for the time being on this P H diagram, right. So, on this diagram the enthalpies on the X axis and the pressure is on the Y axis.

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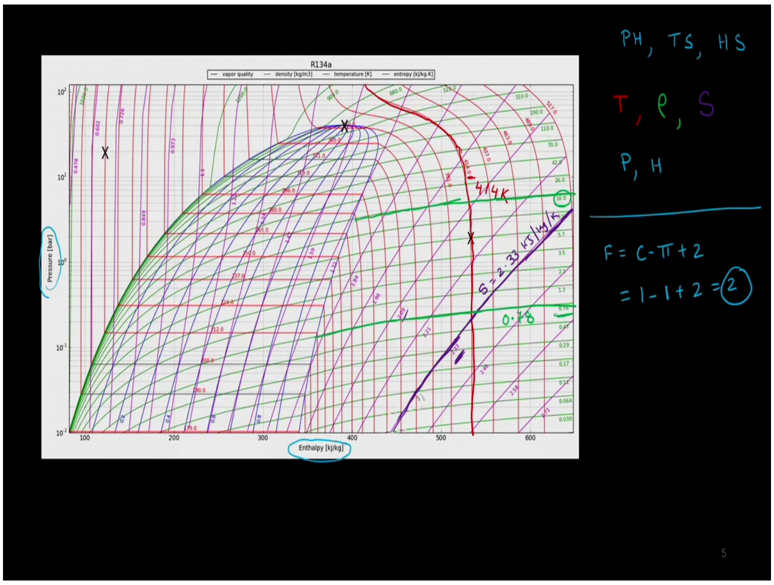

In addition, there are also several other thermodynamic properties that are shown. For example, the red curves, you see on this diagram, let me pick a red curve they are not horizontal or vertical, but then they have a constant thermodynamic property. The curve I am drawing here, right now is a curve along a constant temperature, that temperature is shown here, it is 414 Kelvin.

So, this red curve, I have highlighted is at a constant temperature of 414 Kelvin. Similarly, the purple lines you see here like this one for example, is a line that fall or a curve that follows a constant entropy process. The entropy at any point on this curve is 2.33 value there kilo joule per kg per Kelvin, right at any point on that curve. Similarly, the curve here this curve for example, would have a constant entropy of 2.09 kilo joule per kg per Kelvin and so on.

So, in addition to P and H there is entropy information on this curve and there is of course, a temperature information. We also have the density or molar volume inverse of density is going to be molar volume. So, we have the density information on this curve not molar volume. And sorry, it should be the specific volume, we have either the specific density or specific volume on this curve which are shown by those green lines.

So, for example, this green curve here follows a constant density or a constant volume condition of.78 kg per meter cube. Similarly, this curve here follows a constant volume condition of 16 kg per meter cube and so on. So, what I have done on this diagram are the temperature, then I have the density, we also have the entropy information in the right in addition to of course, P and H, this is for a single refrigerant. So, if you recall our discussion on the phase rule, the degrees of freedom are C minus of pi plus 2, it is a one component system if there is a single phase, then the degrees of freedom is 2.

So, I need to specify two conditions out of any of these. I can specify the pressure and enthalpy or I can specify the temperature and pressure or I can specify density and pressure things like any combination of these five variables. And we should be able to use this diagram to get the other three variables. So, we just need to fix two variables, if there is a single phase in the system, we will come back to what if there is more than one phase in a minute.

So, given any two properties, I should be able to tell what the other three properties are using this particular diagram. Let us, take one quick example and see how I can read all the information. All choose a point on this curve let us say the, let us get rid of what we have done earlier, let us say the pressure and enthalpy for a temperature and pressure are given.

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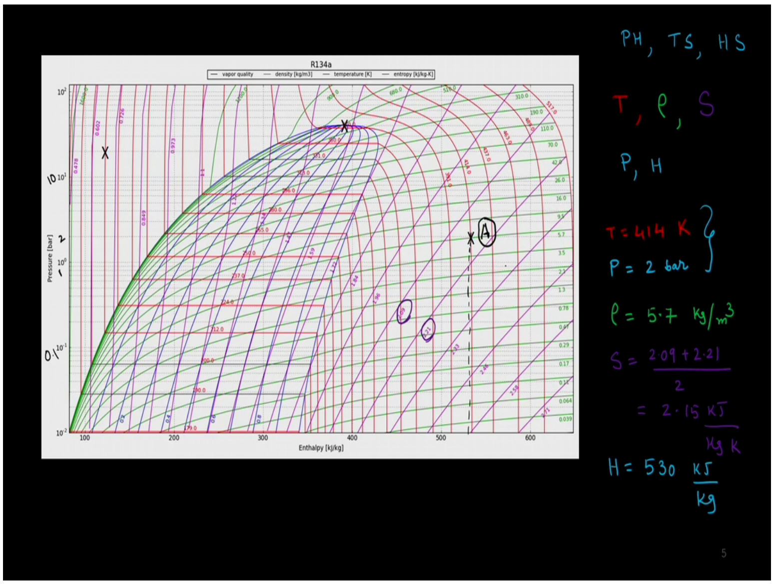

PH, TS, HS

T, ρ, S

P, H

T = 414 K

P = 2 bar

$\rho = 5.7 \ kg/m^3$

$S = \frac{2.09 + 2.21}{2} = 2.15 \ \frac{kJ}{kg \, K}$

$H = 530 \ \frac{kJ}{kg}$

So, I give the temperature and pressure and we want to find what the other three properties are on this curve, let us pick one point. So, if I tell you the temperature is 414 Kelvin and that the pressure is 2 bar. So, this is the given condition the temperature and pressure and we want to find density entropy and enthalpy at this condition, right.

So, the first thing is to locate the point which corresponds to 414 Kelvin and 2 bar on this curve and that occurs at this point shown with a cross mark, that is not a very nice convenient color to use. Let us see if, I have something better yeah, let us use that; let us call that point corresponding to the cross mark as A. And as you can see that falls on the temperature corresponding on the red curve which corresponds to 414 Kelvin which is the temperature of our interest. And it also corresponds to a pressure this is in a logarithmic scale, this pressure is 1 bar, this is 0.1 bar and this is 10 bar.

So, this is 1 so, this is 2 bar, right there. So, if I extend that line, as you can see it falls on the cross mark I have put there. So, that point A then corresponds to the temperature and pressure of our interest which is 414 Kelvin and 2 bar. At this condition I am interested in finding the other three thermodynamic variables, right which is pretty easy to read once, we get hold of what each of these curves represents. And the density as you can see at this condition is 5.7 and the units are kilogram per meter cube, kilogram per meter cube. If I want the volume, I can invert this value to get meter cube per kg. The entropy, well there is no curve passing through this particular point for entropy, but it falls in between two values at2.21 and 2.09 and it is fairly in between halfway in between these two.

So, I am just going to take an average of these two numbers that might be a good approximation. It is about halfway between these two curves that cross I have put. So, I am going to average this and that particular value turns out to be 2.15 kilo joule per kg Kelvin that would be the value for entropy. And finally, for enthalpy, I just need to read the value of the X axis and that particular value, if I can extend this curve all the way down to the X axis.

Let us see, if I can do that something like that and it is about one-third of the way to 600, so that might be around 530 or there about so I will just call it as 530 kilo joule per, per kg. So, once the two values, any two values in this case temperature and pressure are given, I can calculate all the three variables that are not known, right. This is one condition.

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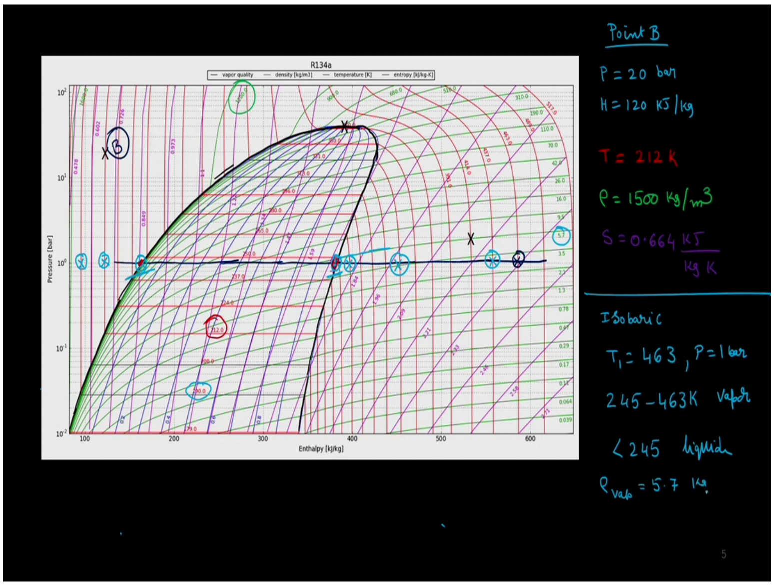

Point B

P = 20 bar

H = 120 KJ/kg

T = 212 K

$\rho$ = 1500 kg/m³

S = 0.664 $\frac{KJ}{kg\ K}$

Isobaric

$T_1$ = 463 , P = 1 bar

245 – 463 K vapor

< 245 liquid

$\rho_{vap}$ = 5.7 kg

We have identified how to get the coordinates for point A, it is pretty straight forward. Now, the next question we ask is what are the conditions for this point A, is it in a vapor phase, is it in a liquid phase, etcetera. That can be answered by actually understanding looking more closely at this diagram. If you look at it we have a region in this diagram, underneath this dome shaped curve. So, this dome shaped curve actually represents a two phase region. So, everything underneath this black dome I have just created is a two phase region. Within this two phase region, we have both liquid as well as the vapor that coexist. Anything to the right of this dome is a vapor phase to the left is a liquid phase, right.

So, in that sense A is going to be a vapor phase region for us. If we have this, we could, if we pick a point in the liquid phase for example, let us say point B, then just like we have done for the vapor phase. I can do an exercise and obtain all the thermodynamic information for this point B. Let us say what we are given is the pressure of 20 bar and an enthalpy of 120 kilo joules per kg, this corresponds to point B. So, once these information is given, I can obtain point B and then I can also obtain what the other thermodynamic variables at this condition are the temperature, then is going to be along the red curve. If you follow this red curve going through point B as you can see the temperature is 212 Kelvin.

So, this 212 Kelvin temperature starts here and then goes all the way like this and then follows that line there. The volume or the density at this condition is going to be somewhere in between 1200 and 1600 kilograms per meter cube more close to 1600 let us say somewhere around 1500 kg per meter cube. And the entropy similarly is going to be in between these two numbers 0.726 and 0.602. So, let us say the entropy has a value of about 0.664 kilo joules per kg Kelvin.

So, essentially almost the same way, we have obtained point A, given the values for any two thermodynamic properties; I can get the other three properties from this diagram. Now let us focus a little bit more on this two phase region and see what happens if I decrease the temperature, right. So, let us say I pick a pressure of 1 bar, right which is going to be along this curve here, along this horizontal line. I am going to do a isobaric process, but I am going to decrease the temperature.

I start with the temperature of corresponding to this which is 463 Kelvin and start decreasing the temperature, alright. So, the pressure is constant. So, let us get rid of this was point B, let us retain it for the time being. Now I am going to do a constant pressure process or an isobaric process starting at 463 Kelvin, at 463 Kelvin so that corresponds to this point here. And then I decrease the temperature when the condition reaches 437 Kelvin, I am going to be at this point when the temperature reaches this, which is 331

Kelvin, I am going to be at this point and so on. And when the temperature reaches 265 Kelvin, I am going to be here.

So, I gradually decrease the temperature, I keep moving to the left the temperature is decreasing. So, the density keeps increasing, right I had a density in between 2.1 and 3.5 here. By the time I come here, it is in between 3.1 and 5.7, etcetera the vapor density is increasing. And then once I hit this point on the dome at this pressure, I enter the two phase region, right. And everything under the dome at constant pressure is the two phase region where we will have a mixture of both liquid and vapor at equilibrium with one another. And along within the dome the temperature is constant as you can see, the isothermal lines within the dome are horizontal, because the two phase, the phase change occurs at constant temperature.

So, you see that the temperature is going to be or the isothermal process will be a horizontal line within the dome. And once, we come out of the dome at this point I can keep decreasing the temperature, but then now I am in the liquid phase region, I entered a single phase region. Again this is a liquid phase region and as I keep decreasing the temperature even further I travel to the left of this dome and I enter a completely liquid phase region. For example, at this point which corresponds to about a 190 Kelvin, I am completely in the liquid phase region at 1 bar.

So, as you have seen, we started in a completely vapor phase region at 463 Kelvin and 1 bar transited through the two phase region and finally, entered a liquid phase region 1 bar and a lower temperature this time at a 190 Kelvin. During this transition between 463 Kelvin and a temperature corresponding to this point which is roughly 245 Kelvin. 245 to 463 Kelvin, I am in the vapor phase region. At 245 Kelvin, I start in the two phase region in a completely vapor state and end up in a completely liquid state when I travel to the left over there. And below this temperature, I would be in a liquid phase region, right.

So as you can see, when I enter the vapor phase region the density is along this curve here about 5.7 kg per meter cube.