Advanced Thermodynamics and Combustion
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Module - 03
Thermodynamic Property Relations
Lecture - 11
Property Relations for Phase Change Processes

Dear learners, greetings from IIT Guwahati. We are in the course Advanced Thermodynamics and Combustion, module 3 that is Thermodynamic Property Relations.

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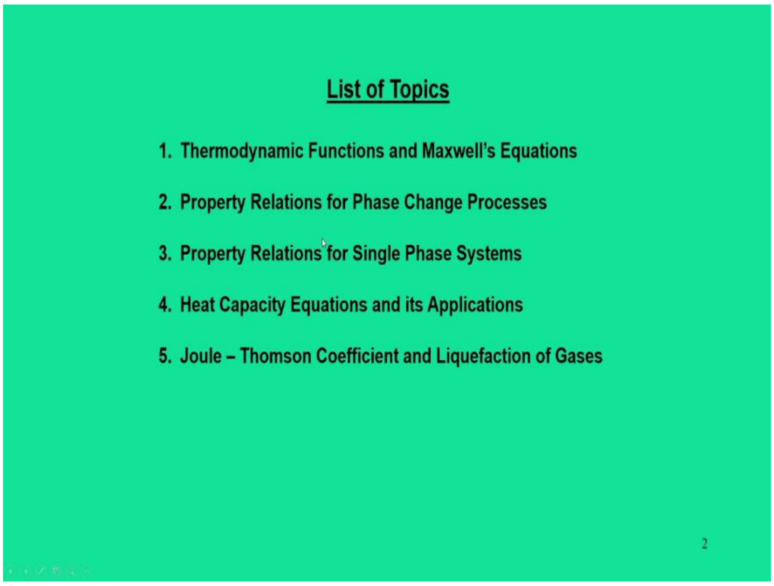

List of Topics

1. Thermodynamic Functions and Maxwell's Equations
2. Property Relations for Phase Change Processes
3. Property Relations for Single Phase Systems
4. Heat Capacity Equations and its Applications
5. Joule – Thomson Coefficient and Liquefaction of Gases

In total in this module, there are 5 lectures and already we have covered the first lecture that is thermodynamic functions and Maxwell's equations. In fact, we derived in the last class various thermodynamic functions and Maxwell equations based on the understanding of differential equations. And, that differential equations were in the form of ordinary or partial differential equations. We are now in the lecture number 2.

Here we are going to apply this Maxwell equations for thermodynamic processes. The first part of this is that we are going to derive the property relations for a phase change process.

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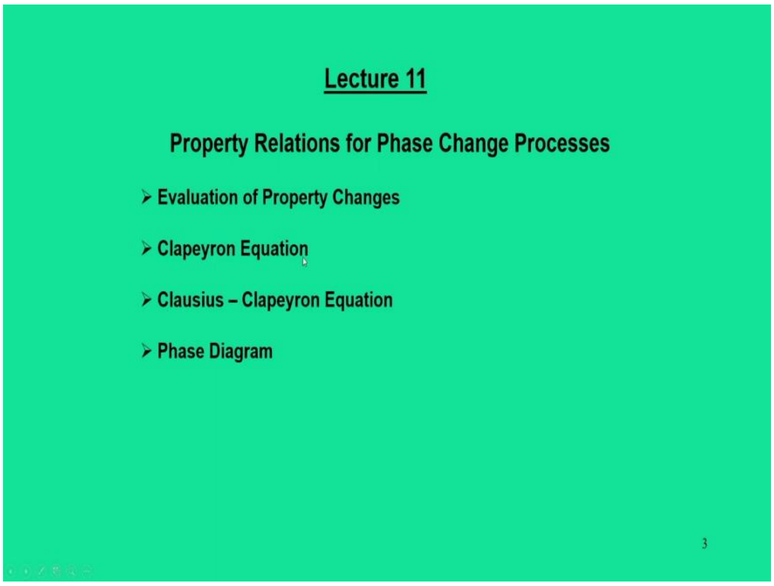

Lecture 11

Property Relations for Phase Change Processes

- Evaluation of Property Changes
- Clapeyron Equation
- Clausius – Clapeyron Equation
- Phase Diagram

So, in this lecture that is Property Relations for Phase Change Processes, these are the some contents. First of all, we will discuss what we derived in our last lectures. What are the different property changes that are associated in the form of Maxwell’s equations and other relations. And, for phase change processes, two important equations are predominantly used. One is Clapeyron equations, other is Clausius - Clapeyron equations.

In fact, both the equations are more or less same, but with certain approximations different concepts were developed. Now, after deriving this Clapeyron equations and Clausius Clapeyron equations, we will be discussing its applications with respect to phase diagrams. The phase diagrams normally refers to pressure, temperature projections where we distinctly decide about fusion curve, sublimation curve and in these curves, we will see how these two equations are applicable or vital.

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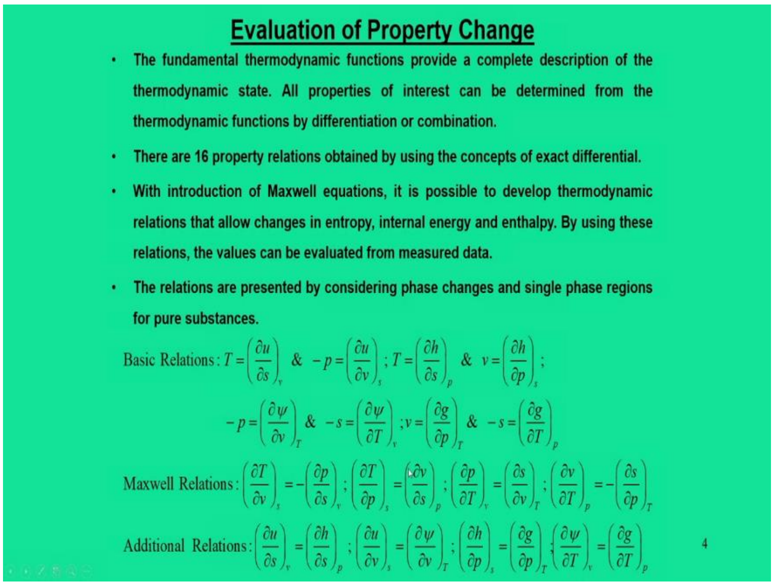

Evaluation of Property Change

- The fundamental thermodynamic functions provide a complete description of the thermodynamic state. All properties of interest can be determined from the thermodynamic functions by differentiation or combination.
- There are 16 property relations obtained by using the concepts of exact differential.
- With introduction of Maxwell equations, it is possible to develop thermodynamic relations that allow changes in entropy, internal energy and enthalpy. By using these relations, the values can be evaluated from measured data.
- The relations are presented by considering phase changes and single phase regions for pure substances.

Basic Relations: $T=\left(\frac{\partial u}{\partial s}\right)_v$ & $-p=\left(\frac{\partial u}{\partial v}\right)_s$; $T=\left(\frac{\partial h}{\partial s}\right)_p$ & $v=\left(\frac{\partial h}{\partial p}\right)_s$;

$-p=\left(\frac{\partial \psi}{\partial v}\right)_T$ & $-s=\left(\frac{\partial \psi}{\partial T}\right)_v$; $v=\left(\frac{\partial g}{\partial p}\right)_T$ & $-s=\left(\frac{\partial g}{\partial T}\right)_p$

Maxwell Relations: $\left(\frac{\partial T}{\partial v}\right)_s=-\left(\frac{\partial p}{\partial s}\right)_v$; $\left(\frac{\partial T}{\partial p}\right)_s=\left(\frac{\partial v}{\partial s}\right)_p$; $\left(\frac{\partial p}{\partial T}\right)_v=\left(\frac{\partial s}{\partial v}\right)_T$; $\left(\frac{\partial v}{\partial T}\right)_p=-\left(\frac{\partial s}{\partial p}\right)_T$

Additional Relations: $\left(\frac{\partial u}{\partial s}\right)_v=\left(\frac{\partial h}{\partial s}\right)_p$; $\left(\frac{\partial u}{\partial v}\right)_s=\left(\frac{\partial \psi}{\partial v}\right)_T$; $\left(\frac{\partial h}{\partial p}\right)_s=\left(\frac{\partial g}{\partial p}\right)_T$; $\left(\frac{\partial \psi}{\partial T}\right)_v=\left(\frac{\partial g}{\partial T}\right)_p$

Now, let us revisit our previous lectures, where we derived the thermodynamic property changes. In total there are 16 property relation, that were obtained by using the concept of exact differentials. Then, we introduced Maxwell’s equations and through this Maxwell equations it is possible to develop the relations to allow the changes in entropy, internal energy and enthalpy.

And in fact, these properties values can be measured or can be evaluated from the measured data, that is most important thing. Normally the measured datas are pressure, density and temperatures. Now, through this measured data, we are going to develop equations and that equation will give other property values such as changes in the entropy, internal energy and enthalpy.

Now, after having deriving these equations, we are now going to consider the phase changes processes and single phase regions. And, basically we are applying these equations in two situations. One is for phase change case, other is single phase case. The phase change case; it may be solid to vapour or solid to liquid or liquid to vapour and vice versa. And, single phase region means either it is in solid or it is in liquid or it is in the vapour.

So, in total there are 16 relations and to summarize these 16 lessons what we can say pressure, temperature and specific volume or density these are the measured data. And, properties that need to be evaluated are internal energy, enthalpy, then entropy and of course, the Gibbs function g and Helmholtz function ψ. In fact, through this basic relations, we have additionally Maxwell relations and some other relations as well. So in fact, these relations are very generic and mathematical in nature. And, since they are mathematical in nature, they are applicable to all kind of thermodynamic processes. But, only thing is that these equations need to be simplified based on the requirement.

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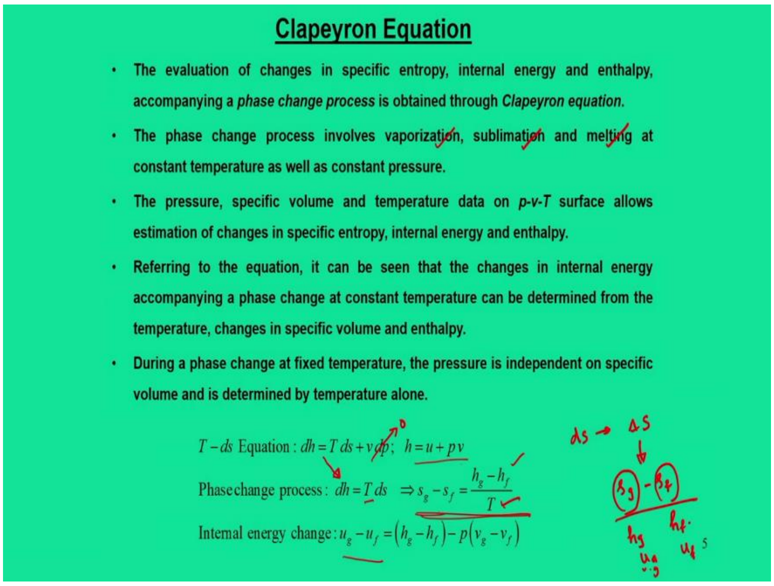

Clapeyron Equation

- The evaluation of changes in specific entropy, internal energy and enthalpy, accompanying a *phase change process* is obtained through *Clapeyron equation.*
- The phase change process involves vaporization, sublimation and melting at constant temperature as well as constant pressure.
- The pressure, specific volume and temperature data on *p-v-T* surface allows estimation of changes in specific entropy, internal energy and enthalpy.
- Referring to the equation, it can be seen that the changes in internal energy accompanying a phase change at constant temperature can be determined from the temperature, changes in specific volume and enthalpy.
- During a phase change at fixed temperature, the pressure is independent on specific volume and is determined by temperature alone.

$T-ds$ Equation : $dh = T\,ds + v\,dp$; $h = u + pv$

Phase change process : $dh = T\,ds \Rightarrow s_g - s_f = \dfrac{h_g - h_f}{T}$

Internal energy change : $u_g - u_f = (h_g - h_f) - p(v_g - v_f)$

Now, one such situations or requirement in our case is a phase change process. So, the most important equations that allows us; that means, which is derived from all 16 thermodynamic relations, one of them is the Clapeyron equations. And in fact, it is applicable for a phase change processes. And, we will see that how this Clapeyron equations help us in simplifying certain analysis.

Now, when I say phase change processes, it involves three things. One is vaporization, second one is sublimation, third in melting. So, solid melts to become liquid. Sublimation means the solid goes directly to vapour, vaporization means liquid goes to vapour. So, we are going to see that how this Clapeyron equations is useful for this phase change process. Even, I am repeatedly telling that the measured data are pressure, specific volume and temperature on a p-v-T surface.

And, the properties that needs to be calculated are typically entropy, specific entropy, internal energy and enthalpy. Now, if you look at these equations in fact, this is the Tds equations that is $dh = Tds + vdp$. We all known that all these numbers are properties; so, it is applicable for all the processes whether it is reversible or irreversible. And, if you are going to apply for a phase change processes; so, for a phase change processes we can say that $dh = Tds$; because in a phase processes normally temperature or pressure do not change.

So, the second term goes to 0. So, this equation now simplifies to $dh = Tds$. From this equation, since it is in differential form; so, with finite value we can write or simplify these equations taking ds close to Δs and Δs we are finding out from $s_g - s_f$. So, s_g stands for specific entropy in gas phase and s_f stands for specific entropy at the liquid phase and corresponding value of enthalpy would be h_g and h_f.

And, and since the phase change process happens at a constant temperature T; so, T remains constant. So, this expression helps us that from the enthalpy values one can calculate entropy values. And in fact, we all know that enthalpy is also $u + pv$. So, from this enthalpy value, one can also calculate the internal energy change $u_g - u_f = (h_g - h_f) - p(v_g - v_f)$. So, this is the significance of equations.

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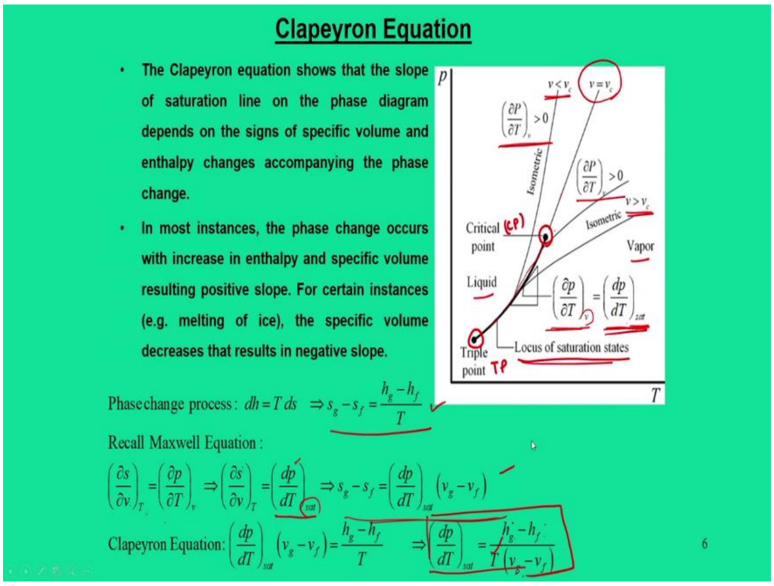

Clapeyron Equation

- The Clapeyron equation shows that the slope of saturation line on the phase diagram depends on the signs of specific volume and enthalpy changes accompanying the phase change.
- In most instances, the phase change occurs with increase in enthalpy and specific volume resulting positive slope. For certain instances (e.g. melting of ice), the specific volume decreases that results in negative slope.

Phase change process: $dh = T\,ds \Rightarrow s_g - s_f = \frac{h_g - h_f}{T}$

Recall Maxwell Equation:

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \Rightarrow \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{dp}{dT}\right)_{sat} \Rightarrow s_g - s_f = \left(\frac{dp}{dT}\right)_{sat}(v_g - v_f)$$

Clapeyron Equation: $\left(\frac{dp}{dT}\right)_{sat}(v_g - v_f) = \frac{h_g - h_f}{T} \Rightarrow \boxed{\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T(v_g - v_f)}}$

Now, let us see how we can come back to the Clapeyron equations. So, just refer to our figure that is pressure temperature plot for a pure substance. What we have here is that this plot talks about two important points. One is the triple point, we normally call this as a TP, other is the critical point; CP. So, there is a continuous curve and we call this as a locus of the saturation states. So, it means that across the line the state of the system is liquid and vapour.

Now, since it connects to triple point to critical point if you go along this line, we say we are now moving in the constant volume line and that is nothing but the critical volume. And, towards the left side of this curve your $v < v_c$ and towards the right side of the curve $v > v_c$. So, we are trying to find out here is that what happens to the slope of the curve.

So, on the saturation line we say this $\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{sat}$. Because, at this point there is no role of specific volume, because it is a saturation line. And, left side of this curve we say $\left(\frac{\partial p}{\partial T}\right)_v > 0$. So, basically the role of $\frac{dp}{dT}$ is very important in deriving this Clapeyron equations.

So, in our earlier relations we know that $s_g - s_f = \frac{h_g - h_f}{T}$. Now, we can recall one of the Maxwell equations $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$. Now, here we will apply the simplifications. Since, the specific volume has no role along this saturation line; so, we can write this partial differential equation $\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{sat}$. This is a ordinary differential equation of the saturated line.

Now, here the significant point is that if we can find the slope and this slope will give you the change in the entropy with respect to change in the specific volume. So, further this equation is simplified to this form in a finite part $s_g - s_f = \left(\frac{dp}{dT}\right)_{sat}\left(v_g - v_f\right)$. And, when you equate both these two equations, we get this Clapeyron equations like $\left(\frac{dp}{dT}\right)_{sat}\left(v_g - v_f\right) = \frac{h_g - h_f}{T}$.

And finally, we arrive at a very fundamental relations that is $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T(v_g - v_f)}$; that means, if you want to calculate this value on this particular curve; we can easily find out from the values of enthalpy changes and the gas phase and liquid phase and specific volume in the gas phase and liquid phase. And, since this phase change occurs at constant temperature, at that temperatures we have to take this value; that means, slope can be easily calculated.

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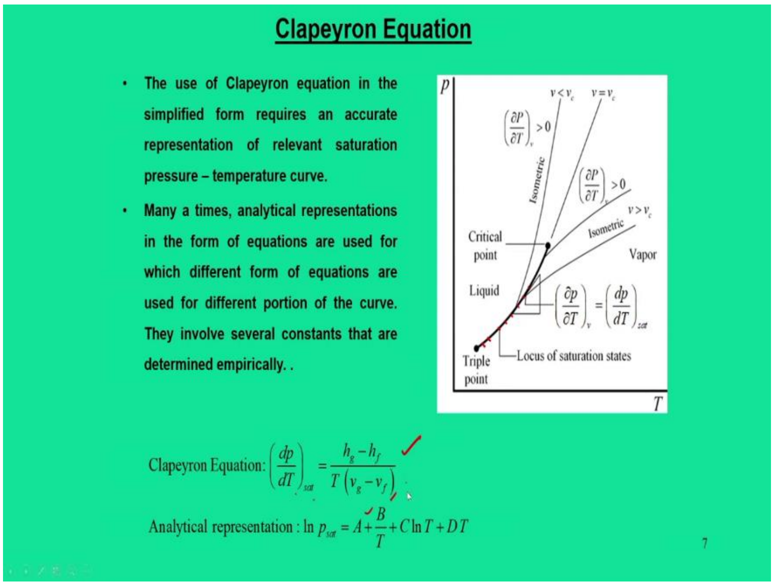

Clapeyron Equation

- The use of Clapeyron equation in the simplified form requires an accurate representation of relevant saturation pressure – temperature curve.
- Many a times, analytical representations in the form of equations are used for which different form of equations are used for different portion of the curve. They involve several constants that are determined empirically. .

Clapeyron Equation: $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\left(v_g - v_f\right)}$

Analytical representation : $\ln p_{sat} = A + \frac{B}{T} + C\ln T + DT$

And of course, this Clapeyron equations has a many significance. But, apart from that there are some other kind of analytical representations people have made correlations; that means, people have developed the analytical representations in a logarithmic form. That means, we have assumed that if you want to give more accurate results; that means, if you want to increase your accuracy level then you can involve multiple constants that is A, B, C, D.

And; that means, each stage we have to calculate these constant values and try to implicate what is the relation between saturated pressure and temperature regions. So, basically this involves the constants that need to be determined empirically. But however, we will stick to the Clapeyron equations for our study only by this calculations that is $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\left(v_g - v_f\right)}$

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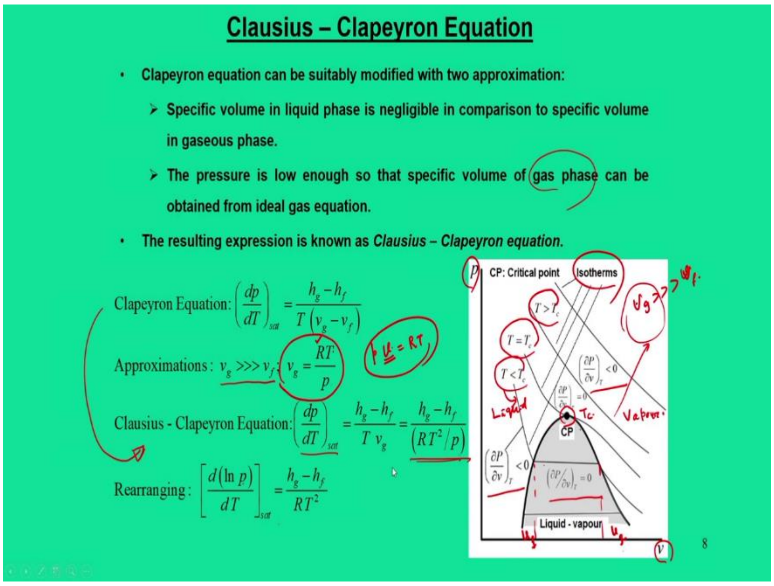

Clausius – Clapeyron Equation

- Clapeyron equation can be suitably modified with two approximation:
  - Specific volume in liquid phase is negligible in comparison to specific volume in gaseous phase.
  - The pressure is low enough so that specific volume of gas phase can be obtained from ideal gas equation.
- The resulting expression is known as *Clausius – Clapeyron equation.*

Clapeyron Equation: $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\left(v_g - v_f\right)}$

Approximations: $v_g >>> v_f$; $v_g = \frac{RT}{p}$

$pv = RT$

Clausius - Clapeyron Equation: $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\, v_g} = \frac{h_g - h_f}{\left(RT^2/p\right)}$

Rearranging: $\left[\frac{d(\ln p)}{dT}\right]_{sat} = \frac{h_g - h_f}{RT^2}$

Now, moving further we are now going to get more information; that means, if you want to include more approximations on to the Clapeyron equations, then how it is going to change. So, basically Clapeyron's equations was suitably modified with two approximations. First is specific volume in the liquid phase is negligible in comparison to specific volume in the gaseous phase.

In fact, if you recall our steam table data; that means, if you have solved at UG level the data from the steam table, you will find that; when you look at the data, we will see that gas phase has higher specific volume than the liquid phase. So, what this Clausius Clapeyron equation assumes that the specific volume on the liquid phase will be negligible.

And in fact, if you recall this pressure volume diagram for a pure substance and if you look at this particular dome and we have this critical point. And, here we have liquid region and we have vapour region and during phase change; that means, we are going inside the dome where both pressure and temperature is constants. And, along the line you do $\left(\frac{\partial p}{\partial v}\right)_T = 0$ and beyond this line, this value is less than 0.

So, what we are trying to say here is that if you go towards the higher pressure and in fact, these are the constant temperature line which you called as isotherms. So, if you are talking about $T = T_c \; or \; T < T_c \; or \; T > T_c$, these are the plots.

So, these are basically the isotherms. So in fact, what we have drawn is this constant temperature lines on a p-v diagram. And, accordingly the slopes also we can find out at the slope that is $\left(\frac{\partial p}{\partial v}\right)_T = 0$ at critical point and above that it is less than 0. Then, what this Clausius Clapeyron equation assumes that specific volume in the liquid phase is negligible.

So, basically if you drop a vertical and find out the value, we have v_f and we have v_g and it says that $v_g >>> v_f$. And, if you are going for higher pressure side; that means, if you are somewhere in this zone where $v_g >>> v_f$which means that we are approaching to a gas side.

So, whatever gas phase, now it can be approximated as an ideal gas model. So, when you have ideal gas model, we can write $pv = RT$. So, as if we are saying the specific volume we are getting in terms of v_g; that means, gas phase specific volume is represented in terms of temperature and pressures with an ideal gas constant value R. This R value has to be chosen for water vapour.

So, now when you make this approximations, we find the Clapeyron equations gets modified to a another expression. We call this as Clausius Clapeyron equations. We says that $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{Tv_g} = \frac{h_g - h_f}{\left(\frac{RT^2}{p}\right)}$. So, ultimately we get two expressions.

One is $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{Tv_g} = \frac{h_g - h_f}{\left(\frac{RT^2}{p}\right)}$. This is one expression. And, if you rearrange this equations then we can say $\left[\frac{d(\ln p)}{dT}\right]_{sat} = \frac{h_g - h_f}{RT^2}$. And, we have basically taken p to the other side. So, this is all about the Clausius Clapeyron equations.

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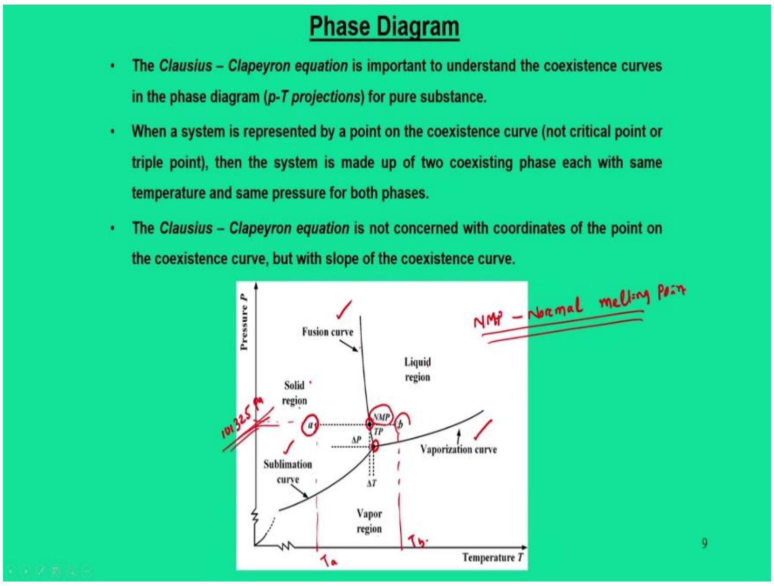

Phase Diagram

- The *Clausius – Clapeyron equation* is important to understand the coexistence curves in the phase diagram (*p-T projections*) for pure substance.
- When a system is represented by a point on the coexistence curve (not critical point or triple point), then the system is made up of two coexisting phase each with same temperature and same pressure for both phases.
- The *Clausius – Clapeyron equation* is not concerned with coordinates of the point on the coexistence curve, but with slope of the coexistence curve.

Now, let us see that how this Clausius Clapeyron equation will be useful to study the phase diagram. So, the name indicates the phase diagram means it is pressure temperature projections. And in this projections, we have two distinct line. One is fusion curve, other is vapourization curve, third is sublimation curve.

Fusion curve separates solid to liquid, sublimation curves separates solid to vapour and vapourization curve separates liquid to vapour. And, the most important point is the triple point. So, wherever all these curves meet at one particular point that point we called as a triple point. Now, let us see that how our Clapeyron equations is useful to study this phase diagram. So, let us first concentrate or locate point a on the solid regions and this curve is for water.

So, I can say we can imagine some kind of ice which exists at point a for which the temperature we can drop this point. And, now if you heat this piece of ice at constant pressure; that means, at constant pressure let us say I am doing heat at atmospheric pressure. So, 101325 Pa. So, if you keep on heating this ice at certain temperature Ta and keep on heating, slowly will be moving towards the fusion curve.

And, will arrive at a point which is called as a melting point and here I will refer as the NMP that is Normal Melting Point. So, why I am saying this as normal melting point, I will give its significance later. And, this normal melting part we means that this is at constant pressure. So, that is the word which is refer as normal melting point at constant pressure. So, basically when ice is heated, its temperature is increasing and this heating takes place at constant atmospheric pressure.

So, we reach this fusion curve and the further heat is added, the ice becomes liquid and when ice become liquid at that point of time there will be no change in the temperature. But, when the ice melts completely to liquid then the liquid with addition of heat, liquid temperature further increases and we move to the point b. So, the final point will be T_b. So, basically in one way I am saying that the constant pressure heating changes the state of the ice from point a to point b.

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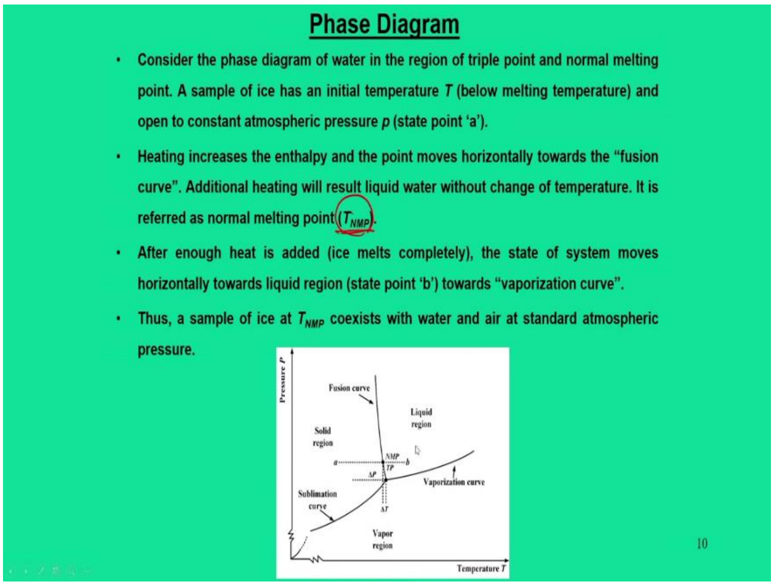

Phase Diagram

- Consider the phase diagram of water in the region of triple point and normal melting point. A sample of ice has an initial temperature *T* (below melting temperature) and open to constant atmospheric pressure *p* (state point 'a').
- Heating increases the enthalpy and the point moves horizontally towards the "fusion curve". Additional heating will result liquid water without change of temperature. It is referred as normal melting point (T_{NMP}).
- After enough heat is added (ice melts completely), the state of system moves horizontally towards liquid region (state point 'b') towards "vaporization curve".
- Thus, a sample of ice at T_{NMP} coexists with water and air at standard atmospheric pressure.

And at that point of time we say that we are reaching this normal melting point which is called as T NMP. And, ultimately what we can say is that when enough heat is added and ice melts completely, the state of the systems moves from fusion curve to the vaporization curve. In other words, we can say that this normal melting point whatever we have defined; that means, the sample of ice at normal melting point coexist with water which is in the liquid state, air which is at standard atmospheric pressure.

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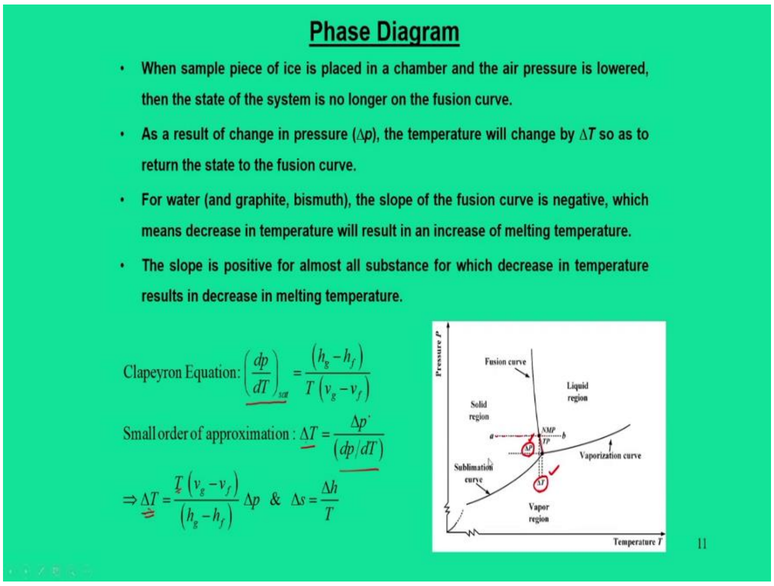

Phase Diagram

- When sample piece of ice is placed in a chamber and the air pressure is lowered, then the state of the system is no longer on the fusion curve.
- As a result of change in pressure (Δp), the temperature will change by ΔT so as to return the state to the fusion curve.
- For water (and graphite, bismuth), the slope of the fusion curve is negative, which means decrease in temperature will result in an increase of melting temperature.
- The slope is positive for almost all substance for which decrease in temperature results in decrease in melting temperature.

Clapeyron Equation: $\underline{\left(\frac{dp}{dT}\right)_{sat}} = \frac{(h_g - h_f)}{T(v_g - v_f)}$

Small order of approximation : $\underline{\Delta T} = \frac{\Delta p}{\underline{(dp/dT)}}$

$\Rightarrow \Delta T = \frac{T(v_g - v_f)}{(h_g - h_f)} \Delta p$ & $\Delta s = \frac{\Delta h}{T}$

Now, imagine a situation that I am doing heating with change of pressure as well. So, the same situation was modified little bit and try to see how we are going to show it in the phase diagram. That means, when a sample piece of ice is placed in a chamber and the air pressure is lowered; that means, that chamber is designed in such a way that we can control its pressure. And when the air pressure is lowered, the state of the system will no longer be fusion curve.

Ideally, point a would have gone towards the fusion curve, but since I am changing this pressure, so, not necessarily that I will be moving to that. So, basically as a result of the change in pressure, the temperature also will change by ΔT.

Δp is in our control and we can see that when there is a drop in pressure, the slope of the fusion curve will be negative. Because, the decrease in the temperature will result in the increase in the melting temperatures and the slope of the fusion curve is negative. This is specifically for water or substances like graphite and bismuth which expands during freezing.

But, for all other substances the slope is positive; that means, for which the decrease in temperature results in the decrease in the melting temperatures. So, although we know this fact in our earlier thermodynamics course, but here we try to link of that how this property relations helps to justify our stands or whatever you have observed that is true.

So, we can recall to study this Clapeyron equation here because all these things that we need is the change in the pressure and change in the temperatures and it is happening on the saturated line. So, we can use this Clapeyron equations $\left(\frac{dp}{dT}\right)_{sat} = \frac{(h_g - h_f)}{T(v_g - v_f)}$

So, we can also write $\Delta T = \frac{\Delta p}{\left(\frac{dp}{dT}\right)}$. $\Delta T = \frac{T(v_g - v_f)}{(h_g - h_f)} \Delta p$; $\Delta s = \frac{\Delta h}{T}$ And, this change in the temperature of ΔT which is a function of the specific volume difference and the enthalpy difference. And, this occurs at the temperature T because this phase change process is occurring at particular temperature.

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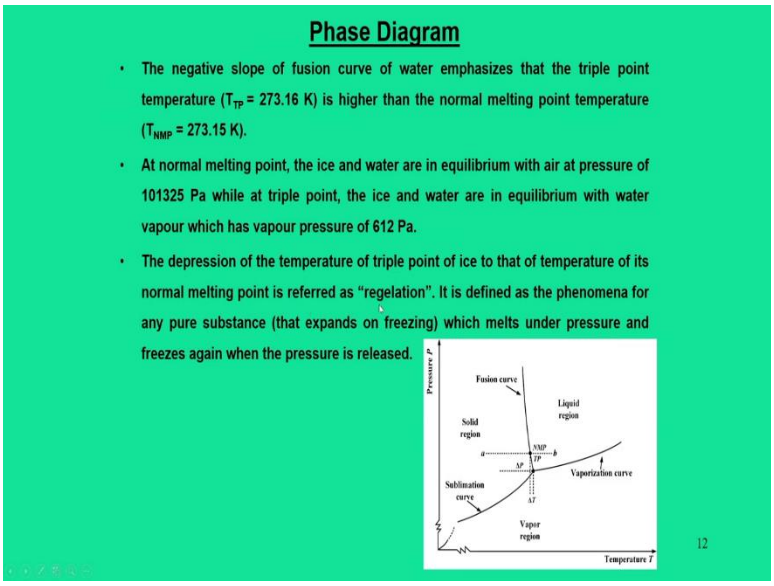

Phase Diagram

- The negative slope of fusion curve of water emphasizes that the triple point temperature (T_{TP} = 273.16 K) is higher than the normal melting point temperature (T_{NMP} = 273.15 K).
- At normal melting point, the ice and water are in equilibrium with air at pressure of 101325 Pa while at triple point, the ice and water are in equilibrium with water vapour which has vapour pressure of 612 Pa.
- The depression of the temperature of triple point of ice to that of temperature of its normal melting point is referred as "regelation". It is defined as the phenomena for any pure substance (that expands on freezing) which melts under pressure and freezes again when the pressure is released.

So, ultimately the conclusion that we derive from our analysis for a phase diagram is that the negative slope of the fusion curve of water emphasizes that the triple point of water which is 273.16 K is higher than the normal melting temperature that is 273.15 K. Now, what is the significance at normal melting point and triple point?

That normal melting point we say that ice, water are in equilibrium with air at pressure 101325 Pa. While, at triple point ice and water are in equilibrium with water vapour which has a vapour pressure of 612 Pa. So, you can see that how a drastic reduction of pressure happens at the triple point and because of this there is a depression in the triple point value.

So, we call this depression as a phenomena we call it as regelation, which means it is defined as the phenomena for any pure substance. In fact, with those pure substance that expands on freezing, this pure substance melts under pressure. So, these substances melt under pressures and freezes again when the pressure is released. So, as if they behave as an elastic situations where they melts first and again freezes again when the pressure is released. So, such a phenomena we call as regelation.

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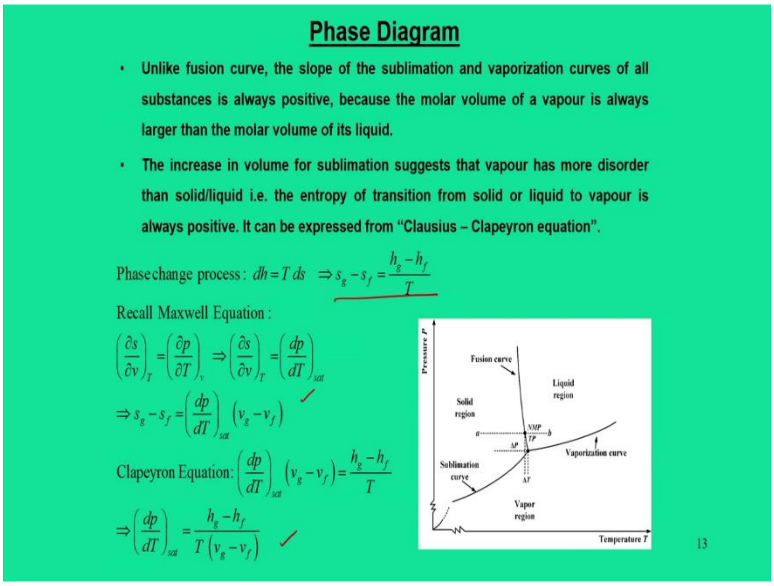

Phase Diagram

- **Unlike fusion curve, the slope of the sublimation and vaporization curves of all substances is always positive, because the molar volume of a vapour is always larger than the molar volume of its liquid.**
- **The increase in volume for sublimation suggests that vapour has more disorder than solid/liquid i.e. the entropy of transition from solid or liquid to vapour is always positive. It can be expressed from "Clausius – Clapeyron equation".**

Phase change process: $dh = T\,ds \quad \Rightarrow s_g - s_f = \dfrac{h_g - h_f}{T}$

Recall Maxwell Equation:

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \Rightarrow \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{dp}{dT}\right)_{sat}$$

$$\Rightarrow s_g - s_f = \left(\frac{dp}{dT}\right)_{sat} (v_g - v_f) \checkmark$$

Clapeyron Equation: $\left(\dfrac{dp}{dT}\right)_{sat} (v_g - v_f) = \dfrac{h_g - h_f}{T}$

$$\Rightarrow \left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\,(v_g - v_f)} \checkmark$$

Now, the other significant part for this pressure temperature diagram is nothing but we have this sublimation curve and vaporization curve. And, for both the curves the characteristic features are typically not complicated. So, here it is not like fusion curve and in this sublimation and vaporization curve, the slope is always positive because the molar volume of vapour is always larger than the molar volume of liquid.

And of course, we all know that increase in the volume of sublimation suggest that vapour has more disorder than the solid or liquid. So, means that entropy plays a role. So, the entropy transition from solid or liquid to vapour is always positive. And, this entropy calculations we can calculate from the Clausius Clapeyron equations which is derived earlier and through Maxwell equations and Clapeyron equations. So, this is all about the concept of phase diagrams based on the thermodynamic properties relations.

Now, with this background let us try to solve some numerical problems. And this numerical problem is nothing but we need to justify the property data from the pressure, specific volume and temperature data for pure substances. And, in particular we will recall with water. In the basic thermodynamic course the steam table datas has been exhaustively used. But, here we will try to link of how these data were generated.

And, when you say for a given pressure temperatures we find s_f, s_g, v_f, v_g, enthalpy, internal energy; how they are calculated? They are actually derived data. And in fact, thermodynamic property relations helps us to derive this data. Now, in this numerical problem we try to see that what is the significance or role of this thermodynamic relations in the formation of steam table in or any property data for pure substances.

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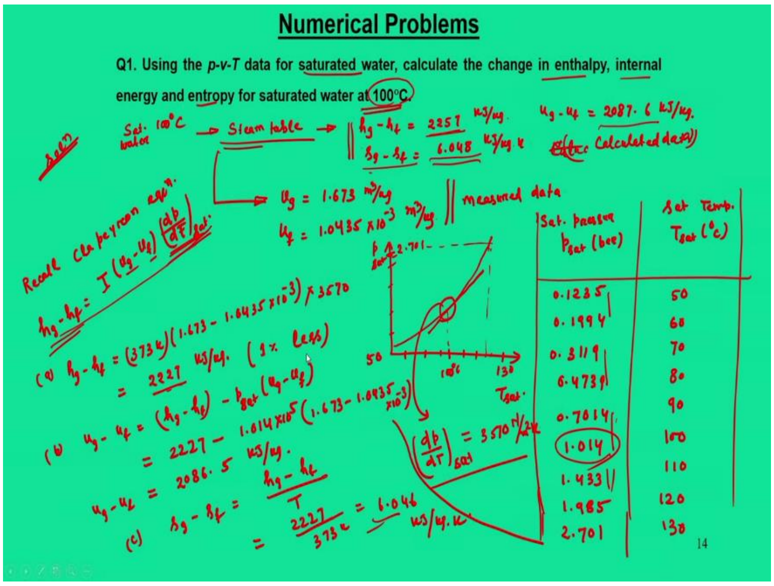

Numerical Problems

Q1. Using the *p-v-T* data for saturated water, calculate the change in enthalpy, internal energy and entropy for saturated water at 100°C.

Sol

Sat. water 100°C → Steam table → $h_g - h_f = 2257$ kJ/kg; $u_g - u_f = 2087.6$ kJ/kg; $s_g - s_f = 6.048$ kJ/kg K (Calculated data)

$v_g = 1.673$ m³/kg; $v_f = 1.0435 \times 10^{-3}$ m³/kg (measured data)

Recall Clapeyron eqn.

$h_g - h_f = T(v_g - v_f)\left(\frac{dp}{dT}\right)_{sat}$

(a) $h_g - h_f = (373\,K)(1.673 - 1.0435 \times 10^{-3}) \times 3570$

$= 2227$ kJ/kg. (1% less)

(b) $u_g - u_f = (h_g - h_f) - p_{sat}(v_g - v_f)$

$= 2227 - 1.014 \times 10^5 (1.673 - 1.0435 \times 10^{-3})$

$u_g - u_f = 2086.5$ kJ/kg.

(c) $s_g - s_f = \frac{h_g - h_f}{T}$

$= \frac{2227}{373\,K} = 6.046$ kJ/kg.K

$\left(\frac{dp}{dT}\right)_{sat} = 3570$ N/m²K

Sat. pressure p_{sat} (bar)	Sat Temp. T_{sat} (°C)
0.1235	50
0.1994	60
0.3119	70
0.4739	80
0.7014	90
1.014	100
1.433	110
1.985	120
2.701	130

So, with this background the first problem talks about the saturated water which is available at 100 C. Now, it is very clear that when we say saturated water at 100 C; so, we can use this steam table or the property data for water and from this we can easily find out the enthalpy, internal energy and entropy.

So, let us recall that these values at 100 C, we require the change in the enthalpy; that means, $h_g - h_f = 2257 \frac{kJ}{kg}; u_g - u_f = 2087.6 \frac{kJ}{kg}; s_g - s_f = 6.048 \frac{kJ}{kg-K}$. Nothing to worry because any steam table data will give you this value or any thermodynamic book will give this value.

There is nothing new in it. But, what is new in it is that whatever equations we have derived so far, how those equations can be used to find this value. And, here we will see one thing that we require information is these are actually the calculated data. And, the measured data we can say that we can also find out $v_g = 1.673 \frac{m^3}{kg}; v_f = 1.0435 \times 10^{-3} m^3/kg$.

Since, it is the specific volume, we can say it is a measured data. Why I say measured data? Because normally pressure, temperature, density or specific volume are considered as a measured data. Now, we need to recall this Clapeyron equation which says that $h_g - h_f = \left(\frac{dp}{dT}\right)_{sat} T\left(v_g - v_f\right)$. So, we do not know is $\left(\frac{dp}{dT}\right)_{sat}$, slope of this $\left(\frac{dp}{dT}\right)$ curve.

So, to do that we can take some data sheet like we can say saturated pressure and saturated temperature or I will say p saturated in bar, T saturated in degree centigrades. So, we can get the data or we can measure the data at different temperatures. Since, we require at 100 C, let us start some value from may be starting from 50 60 70 80 90 100 110 120 130. I think this would be sufficient to get a set of data.

And, corresponding pressure value we can again refer the steam table likefor 50C, we have 0.1235, then 60 degree centigrade we have 0.1994, 70 degree we have 0.3119, 80 degree 0.4739, 90 degree 0.7014, 100 degree we have 1.014, 110 degree we have 1.433 and 120 degree we have 1.985, 130 degree we have 2.701. So, basically dp by dT can be calculated from any these states. And, one way to do this is that we can plot it graphically, p saturated T saturated. We can start with maybe 50 and end with 130.

And, with different intervals 60 70 80 90 100 like this and accordingly we have pressure values. So, a plot can be done, upper limit of pressure is 2.701 and at 100 C somewhere here, if you drop a vertical it touches this curve and at that point we can draw a tangent. And, at this point we can find out $\left(\frac{dp}{dT}\right)_{sat}$ and from these calculations we can find out this number as $3570 \frac{N}{m^2K}$.

Now, once I know this and; obviously, we can go do calculation one by one that $h_g - h_f = 373(1.673 - 1.0435 \times 10^{-3}) \times 3570 = 2227\ kJ/kg$. So, we recall this is 2227 what actual value is steam table data is 2257. So that means, Clapeyron equation is accurate by 1 percent less.

And once you know enthalpy, we can find out internal energy $u_g - u_f = (h_g - h_f) - p(v_g - v_f) = 2227 - 1.014 \times 10^5(1.673 - 1.0435 \times 10^{-3}) = 2086.5\ kJ/kg.$ But, steam table data is 2087.6 kJ/kg and last part is entropy. $s_g - s_f = \frac{h_g - h_f}{T} = \frac{2227}{373} = \frac{6.046kJ}{kg-K}$

So, of course, this value is close to 6.408 from the steam table data. So, this demonstrates how this Clapeyron equation is useful to get the thermodynamic properties value. And, in particular we have validated it with respect to the steam table data.

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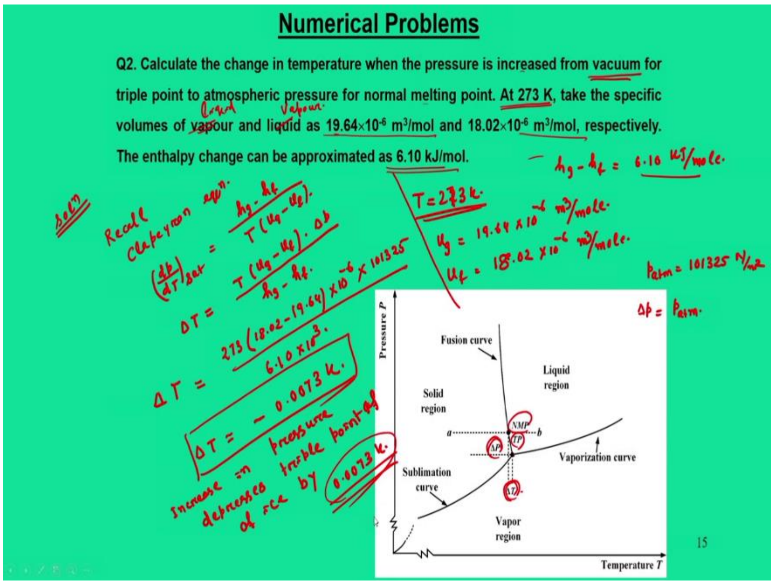

Numerical Problems

Q2. Calculate the change in temperature when the pressure is increased from vacuum for triple point to atmospheric pressure for normal melting point. At 273 K, take the specific volumes of ~~vapour~~ liquid and ~~liquid~~ vapour as 19.64×10^{-6} m³/mol and 18.02×10^{-6} m³/mol, respectively. The enthalpy change can be approximated as 6.10 kJ/mol.

Sol^n

Recall Clapeyron eq^n.

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T(v_g - v_f)}.$$

$$\Delta T = \frac{T(v_g - v_f)\cdot \Delta p}{h_g - h_f}.$$

$$\Delta T = \frac{273(18.02 - 19.64)\times 10^{-6} \times 101325}{6.10 \times 10^3}.$$

$$\boxed{\Delta T = -0.0073\ K.}$$

Increase in pressure depressed triple point of ice by 0.0073 K.

$h_g - h_f = 6.10$ kJ/mole.

T = 273 K.

$v_g = 19.64\times10^{-6}$ m³/mole.

$v_f = 18.02\times10^{-6}$ m³/mole.

$P_{atm} = 101325$ N/m²

$\Delta p = P_{atm}$.

Now, another important significant point that I need to emphasize in the second problem is the phase diagram. So, basically I have been talking about the change in the pressure Δp with respect to ΔT on a phase diagram, when we are moving along a fusion curve and the pressure and temperature changes simultaneously; then what happens?

So, calculate the change in the temperature when pressure is increased from vacuum, vacuum means it is initially at 0 pressure, for triple point to atmospheric pressure at normal melting point. So, data that is given is at 273 K, because 273 K is 0 C. The specific volumes of liquid and vapour are represented in m^3/mol and enthalpy changes are also noted down 6.1 $kJ/mol.$

So, just want to signify that if you recall the Clapeyron equation which says that $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T(v_g - v_f)}$. Now, here we will be trying to represent in terms of dp and dT. So, I will rewrite this equation as $\Delta T = \frac{T(v_g - v_f)}{(h_g - h_f)}\Delta p$. Now, data that is given the phase change occurs at 273K.

And, that point we have data $v_g = 19.64 \times 10^{-6}\frac{m^3}{mol}; v_f = 18.02 \times 10^{-6}\frac{m^3}{mol}$. And the enthalpy change $h_g - h_f = 6.10\frac{kJ}{mol}$. Now, this value would be liquid and this is vapour, there is a correction. So, I think since the slope is negative, I think that data was interpreted wrongly. So, $\Delta T = \frac{273(18.02-19.64)\times 10^{-6}\times 101325}{6.10\times 10^3} = -0.0073K$. So, what is the significance of this number, means that the increase in pressure depresses the triple point of ice by 0.0073 K.

And, this happens because, one is we have normal melting point and other is triple point. Ideally, it should have located at this point, but due to this pressure change, it is getting located little bit lower than the normal melting point this fusion curve. And, this difference is 0.0073 kelvin for this data. So, with this let us close this lecture today.

Thank you for your attention.