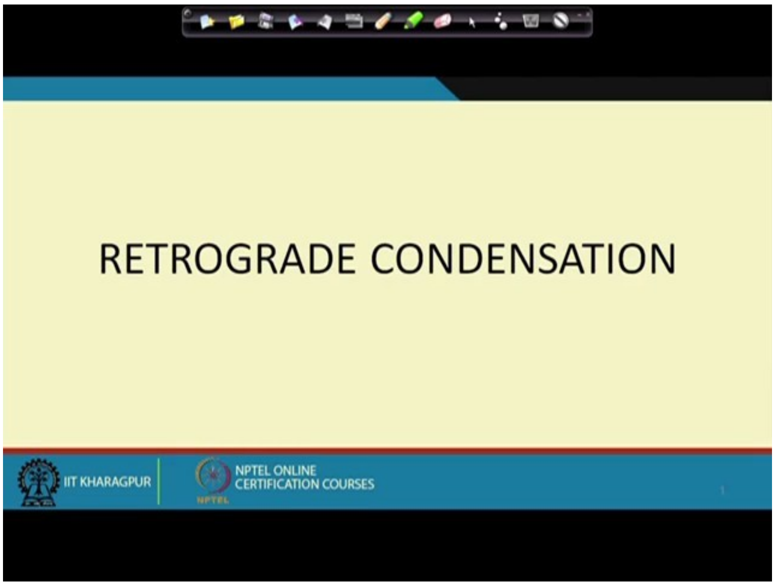
Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture No 49
Retrograde condensation

Well, so we have come to the almost the end of your nonideal solutions and there is just one part which there is one very interesting thing which I would like to discuss before we go on to our next topic on partially miscible and completely miscible systems. Now we have already discussed when we were discussing miscible systems we have already discussed Pxy diagrams Txy diagrams and xy diagrams.

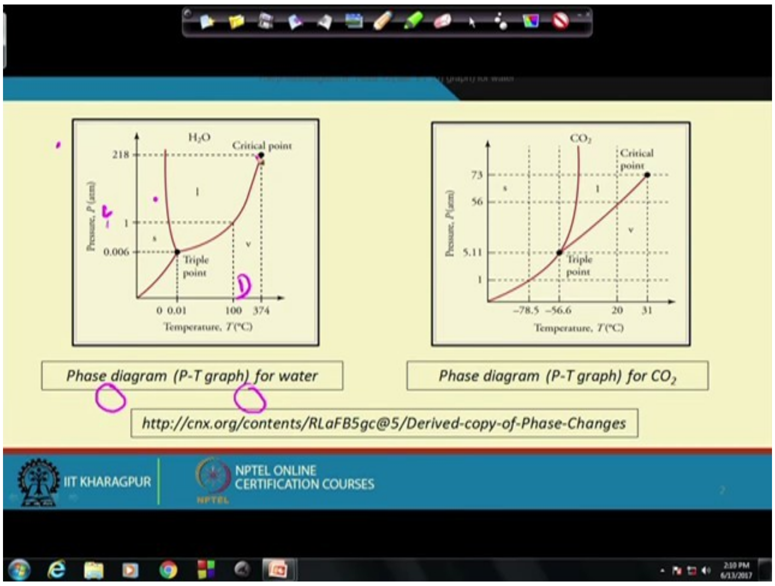
(Refer Slide Time: 0:48)



RETROGRADE CONDENSATION

Let us see what happens or rather what are the characteristics of pressure temperature diagrams under constant quality conditions.

(Refer Slide Time: 1:01)



Phase diagram (P-T graph) for water

Phase diagram (P-T graph) for CO$_2$

http://cnx.org/contents/RLaFB5gc@5/Derived-copy-of-Phase-Changes

For pure substances if you see we find that the pressure versus temperature curve particularly on the liquid vapor coexistence liquid vapor coexistence curve we find that it increases the pressure increases monotonically with temperature and the curve finally ends at the at the critical point as we have discussed quite a number of times and we know that this critical point it is the point of highest temperature and pressure where the 2 phases can coexist and beyond the beyond this particular condition the 2 phases they become indistinguishable.

And I have shown the typical PT the curve for a single phase or rather for a single component system for both water and carbon dioxide; we find that for both the cases the characteristics of the liquid vapor coexistence curve is the same.

(Refer Slide Time: 2:12)

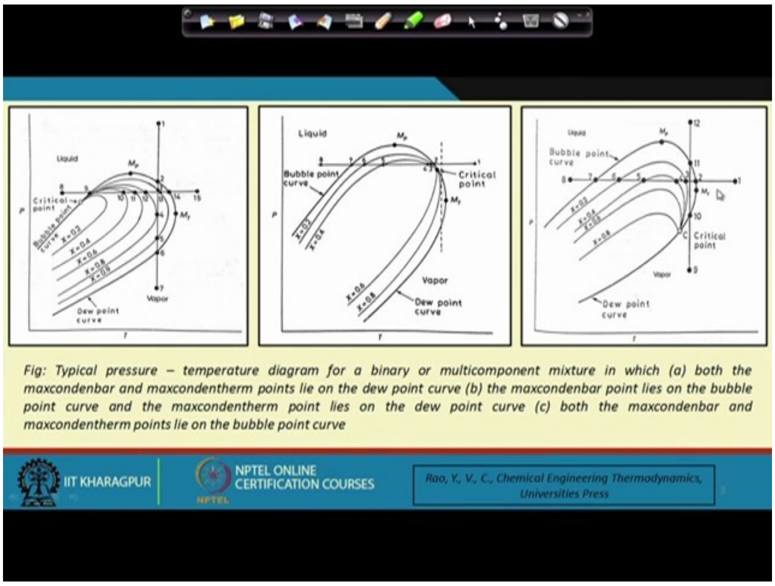


Fig: Typical pressure – temperature diagram for a binary or multicomponent mixture in which (a) both the maxcondenbar and maxcondentherm points lie on the dew point curve (b) the maxcondenbar point lies on the bubble point curve and the maxcondentherm point lies on the dew point curve (c) both the maxcondenbar and maxcondentherm points lie on the bubble point curve

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

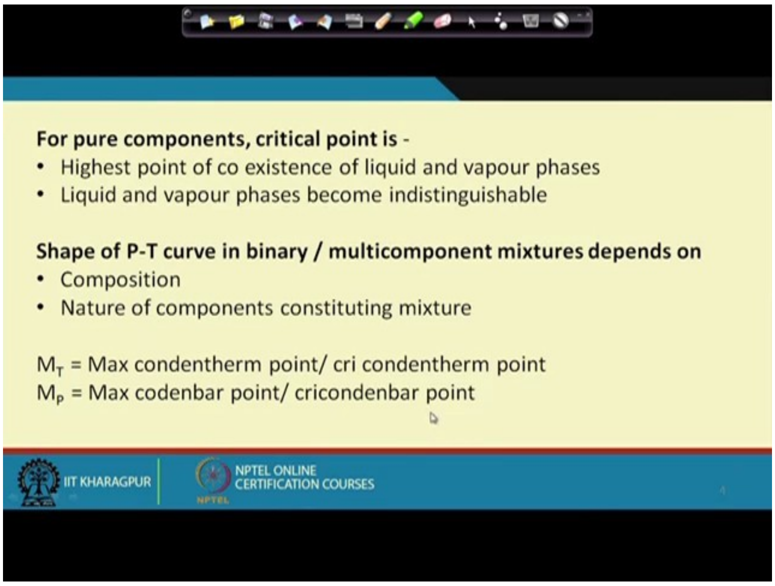
Rao, Y. V. C., Chemical Engineering Thermodynamics, Universities Press

Now let us take up the case for a simple binary mixture. Let us take up the case of a simple binary mixture this case if you observe a typical pressure temperature diagram, what do we find? We find that at a fixed composition each curve it is marked by a bubble point curve it is marked by a it is enclosed by a Dew point curve and the bubble point curve and the dew point curve they meet at the critical point. We find that the bubble point curve it comprises of only liquid phase dew point curve it comprises of fully vapor phase and in between there are a large number of curves which are actually constant quality lines, right?

Now if you closely observe we find that while we were discussing pure components we found out that the liquid and vapor can coexist under equilibrium conditions at the highest point of the critical point but if you observe the 3 diagrams which I have given here you can very well find out that the liquid and vapor they can coexist at temperatures higher than the critical point at pressures higher than the critical point.

So therefore the critical point for the case of a mixture is not necessarily the highest point with respect to temperature and pressure the liquid and vapor may coexist at temperatures and pressures higher than the critical point.

(Refer Slide Time: 4:08)



For pure components, critical point is -
- Highest point of co existence of liquid and vapour phases
- Liquid and vapour phases become indistinguishable

Shape of P-T curve in binary / multicomponent mixtures depends on
- Composition
- Nature of components constituting mixture

M_T = Max condentherm point/ cri condentherm point
M_P = Max codenbar point/ cricondenbar point

And the point of existence of liquid and vapor at the highest pressures this particular pressure is known as the maxcondenbar pressure or the cricondenbar pressure. In the similar way we find that the highest temperature at which the liquid and vapor can coexist, it is known as the max condentherm temperature of the cri condentherm temperature. So therefore we find that unlike single phases definitely the bubble point curve and the dew point curve they intersect at the critical point the single phases, the bubble point curve and the dew point curve they are the same and therefore the critical point is a point of highest pressure and temperature conditions under which the liquid and the vapor can coexist.

In this case also the critical point is the point of intersection of the bubble point curve and the dew point curve but it does not signify the highest temperature and pressure condition under which the liquid and vapor can coexist. They can coexist at temperatures and pressures higher than the critical point the highest temperature at which the liquid and vapor can coexist is known as the cricondentherm or the maxcondentherm temperature the highest pressure at which liquid and vapor can coexist is known as the maxcondenbar pressure or the criconden bar pressure.

And there are some very interesting things which happen in this particular region which is bounded by the critical point the maxcondenbar point and the maxcondentherm point. We find that there are 2 or 3 ways by which we can locate the MP and MT with respect to the critical point, one is both of them can be either on the bubble Pt curve which is the case in this case this is not very common case both of them can exist on the beyond the critical point on the dew point curve which is quite a common case and the third one is while Mp lies on the bubble Pt curve Mt lies on the dew point curve.

(Refer Slide Time: 6:51)

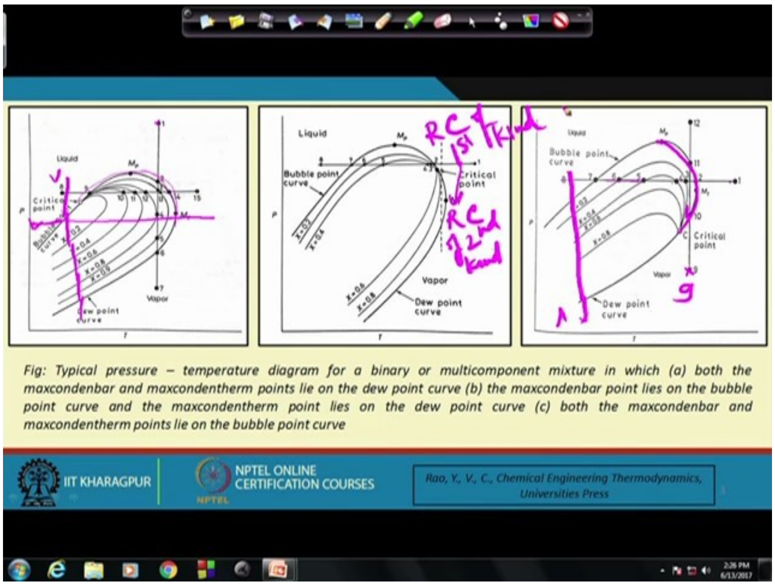


Fig: Typical pressure – temperature diagram for a binary or multicomponent mixture in which (a) both the maxcondenbar and maxcondentherm points lie on the dew point curve (b) the maxcondenbar point lies on the bubble point curve and the maxcondentherm point lies on the dew point curve (c) both the maxcondenbar and maxcondentherm points lie on the bubble point curve

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

So therefore MP and Mt they can be located with respect to the critical point or they can replace with respect to the critical point in 3 ways one is both lying on the bubble Pt 1 is both lying on the dew point and the third is one lying on the bubble Pt while the other lies at the dew point. Now very curious and peculiar phenomena occurs in the region which is bounded by MP critical point and the MP, Mt and the critical point, what happens under this particular condition let us see?

Now suppose we deal at a much lower temperature pressure conditions, what do we find? We have already discussed it suppose we start with the vapor phase and we start compressing the vapor at constant temperature, so therefore what happens the vapor it follows this particular vertical line and we find as the vapor gas gets compressed at one point it reaches the dew point curve, when it reaches the dew point curve the first dew appears.

Now if you continue this particular compression process we find that greater and greater amount of liquid is formed and finally when we reached the bubble Pt curve the last drop of vapor it disappears and then we have entered a single phase liquid region this is true for all the different phase diagrams that I have shown but suppose we deal at the condition or rather under a condition which is bounded by a critical point Mp and Mt there we find that the counterintuitive phenomena occurs.

What happens? Suppose we take up the vapor phase at State one say and we start expanding the vapor phase under isothermal conditions naturally when temperature is constant and we start expanding it follows this particular vertical line. So as we continue this particular expansion we find that the vapor it first reaches the point 2 which lies on the dew point curve. So naturally under this condition the first dew is formed. If we continue this expansion process we find that the proportion of liquid it keeps on increasing as we move from point 2 to point 3. If you observe we have shifted from a higher to a lower quality line. We continue this expansion process and we reach point 4 again the proportion of liquid increases just the thing which had happened under this condition.

But if we again continue the expansion process we find that from 4 to point 5 actually the proportion of liquid has decreased. If you observe closely you will find that from point 4 to point 5 you have actually moved from a lower quality to a higher quality line and if you continue this at point 6 you again reach the dew point curve and beyond that when you continue this expansion process you result again in the vapor phase.

So we find that for conditions where the constant temperature line it crosses the dew point curve not once but twice and never touches the bubble Pt curve under this condition we find that if we expand the vapor phase then we do result in a liquid phase but at the end we again land up in a vapor phase, counterintuitive phenomena which does not occur at lower temperature pressure conditions this particular phenomena is known as retrograde condensation and here it is known as retrograde dew formation at constant temperature this is what that has happened here.

The same thing can not only happen by expanding the gas but it can also happen by cooling the gas suppose for example that we start from point 8 and in this case also we ensure that the point where we have started that is again bounded by the dew point curve Mp, Mt suppose the point 8 is at a much lower pressure conditions where it is not bounded by this zone. In this case suppose we start heating the, in this case we have a liquid phase if we start heating the liquid phase we find that the first bubble forms and then if we continue this heating process finally we end up in a vapor phase.

Now for example instead of starting at this point we start at a higher pressure temperature condition the condition which is bound or which is beyond the critical point. So therefore under this condition since it is beyond the critical point naturally we do not have a liquid phase like this we have a vapor phase in this particular case. We start heating the vapor phase what happens? We first come and touch the dew point curve moment we touch the dew point curve the first dew appears.

Now if you continue this particular heating process the isobaric heating process we find that the proportion of liquid first increases and then it decreases finally the system it again touches the dew point curve and then it goes into the single phase vapor region, so therefore this is known as retrograde dew formation at constant pressure. Now in this particular situation or in this particular system where both the Mp and the Mt they lie on the dew point curve under this condition we have retrograde dew formation at constant pressure, retrograde dew formation at constant temperature and these are known as retrograde condensation of the first kind.

Just the reverse thing happens if instead of on the dew point both Mp and Mt they lie on the bubble Pt curve. In this case also suppose we are operating at lower temperature pressure conditions we find that we take a vapor we start heating the vapor at constant pressure the first dew appears when it touches this point and then if we continue we find the proportion of liquid increases and finally we have entered the single phase liquid region but suppose we are operating under this particular condition.

So for this particular condition what do we have? Again it was not heating it was compressing, anyhow we have compressed vapor and we have come to the liquid phase I was wrong in telling, anyhow. And if we continue this compression process say instead of starting from say point A we have started from point 9 and we continue the compression process at constant temperature.

What happens? We find as we keep on compressing we reach the dew point the first dew appears it continue with the compression process the proportion of liquid first increases then decreases finally the vapor is reformed when we reached point 12. Same thing can be observed when we continue isobaric cooling of the vapor phase. If we continue isobaric cooling under some other condition we find that you can keep on cooling the vapor phase finally from the vapor we can come to the liquid after traversing all the constant quality lines and we go in the direction of decreasing constant quality lines.

If suppose we start at point 1, right? Which again forms in the zone bounded by Mp M(t) and the critical point C, what do we do? We start cooling the vapor we continue the cooling till we reach the dew point curve the first dew appears then we continue the cooling process the proportion of liquid increases this continues till we come to state 4 and then if we still continue the cooling process we find that again from state 5 we are shifting towards higher quality lines and finally at point 7 the last drop of liquid disappears and we have entered into a single phase vapor zone.

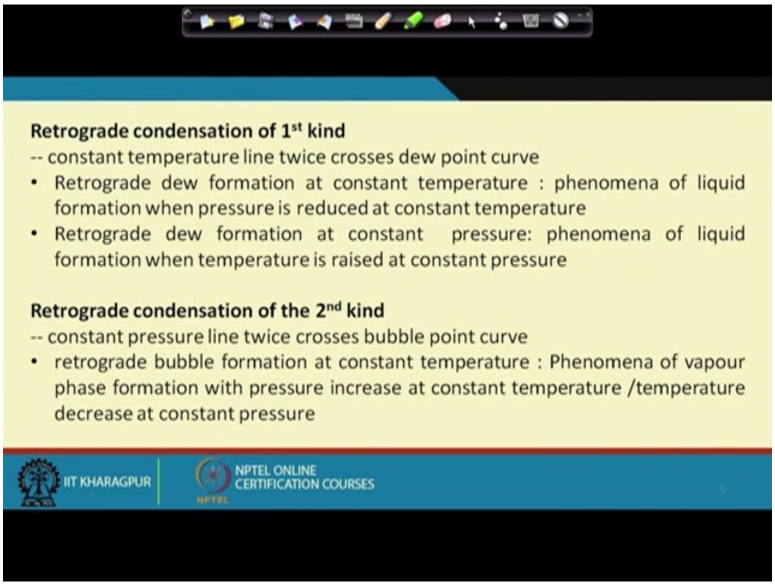
Now this particular phenomena which was just the reverse of the other this is known as the retrograde condensation of the second kind where we get retrograde bubble formation at constant pressure or we can also obtain retrograde bubble formation at constant temperature. So the first kind retrograde condensation of the first kind occurs when both Mp and M(t) lie on the dew point curve and the retrograde condensation of the second kind occurs when both of them are lying on the bubble Pt curve and very interestingly when we find that Mp lies on the bubble Pt curve and Mt lies on the dew point curve we find that for this particular situation we can get the retrograde condensation of the first kind as well as the retrograde condensation of the second kind.

For example if you in this case, if you start you're cooling the vapor from state one, what do you find? That if you start cooling the vapor from state one and to continue the cooling we it first touches the dew point curve the proportion of liquid increases and then after awhile the horizontal line it starts going from a lower quality to a high quality line and finally the vapor is reformed here.

So therefore this particular horizontal line this suggests retrograde condensation of second kind where the similar to what we have seen in this figure and if we follow this isothermal compression at constant temperature then under this condition we find that initially with the vapor phase we get the first drop of liquid the proportion of liquid increases and then it decreases and finally we land up into the single phase vapor region.

So therefore while this path refers to retrograde condensation of the second kind this vertical part refers to retrograde condensation of the first kind. So therefore when the Mp and Mt are 2 sides of the critical point we find that both the types of condensation can be obtained this particular case.

(Refer Slide Time: 17:47)



Retrograde condensation of 1st kind

-- constant temperature line twice crosses dew point curve

- Retrograde dew formation at constant temperature : phenomena of liquid formation when pressure is reduced at constant temperature
- Retrograde dew formation at constant pressure: phenomena of liquid formation when temperature is raised at constant pressure

Retrograde condensation of the 2nd kind

-- constant pressure line twice crosses bubble point curve

- retrograde bubble formation at constant temperature : Phenomena of vapour phase formation with pressure increase at constant temperature /temperature decrease at constant pressure

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

(Refer Slide Time: 18:14)

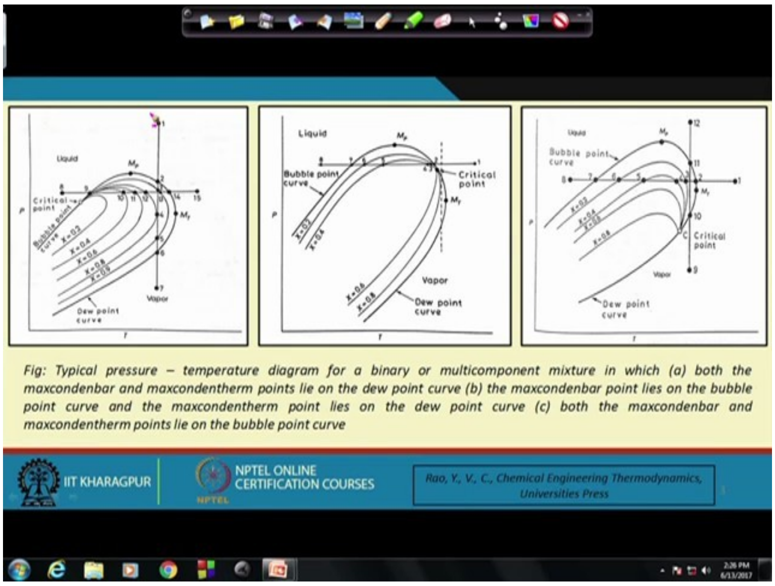


Fig: Typical pressure – temperature diagram for a binary or multicomponent mixture in which (a) both the maxcondenbar and maxcondentherm points lie on the dew point curve (b) the maxcondenbar point lies on the bubble point curve and the maxcondentherm point lies on the dew point curve (c) both the maxcondenbar and maxcondentherm points lie on the bubble point curve

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

Well, what was the need of discussing this entire thing? The need of discussing these entire phenomena was because it is of great importance in natural gas wells, natural gas wells as we know they are very high temperature and very high pressure and for such a case we find that suppose we are dealing with usually the conditions are at point 1, okay. So therefore if we are dealing with high pressure and temperature conditions under at point 1 and we keep on drawing the natural gas from it we find that the pressure keeps on decreasing but the temperature remains constant.

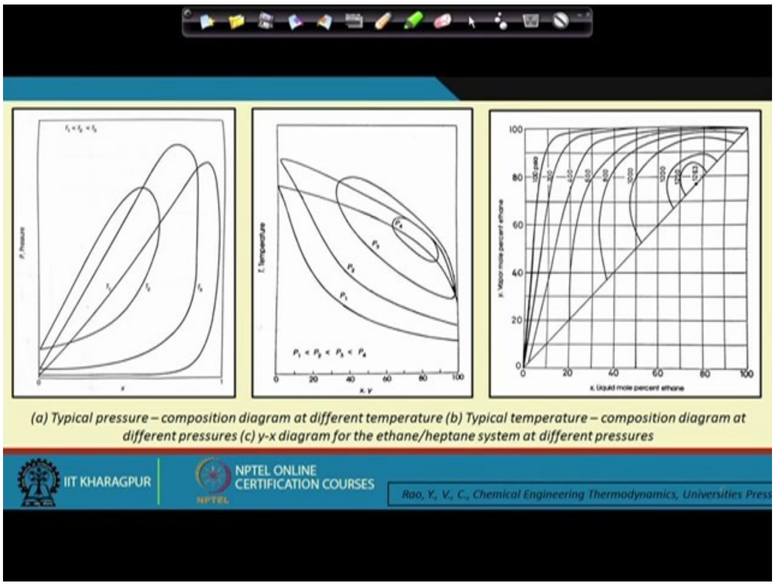
So what is basically happening in the natural gas wells? You basically the gas inside the well it is following this vertical path 1, 2 as long as it lies above point 2 we have no problems but moment in the process of drawing out the vapor suppose we reached point 2 then what happens liquid starts forming when liquid starts forming this liquid it seeps into the underground strata and it gets lost we cannot recover this liquid, number 1.

Number 2 when there is a presence of liquid near the bore pipe it reduces the gas flow rate therefore naturally the output of the gas decreases and the third important thing is when we have both the vapor as well as a liquid phase inside the reservoir, naturally they would like to be in a state of equilibrium and therefore the vapor which is being withdrawn from the bore pipe it is in equilibrium with the liquid phase inside the reservoir therefore the composition of the output gas from the well it keeps on changing continuously with time and therefore to overcome this disadvantage it is essential to maintain the pressure at the well at a value which is greater than the dew point value corresponding to point 2 here.

So therefore we would always prefer to operate natural gas well along this particular vertical line but above point 2. So it is very important to know the dew point pressure corresponding to point 2 and ensure that that we are operating well above the point in order to alleviate the disadvantages and the limitations which I have already mentioned when liquid appears in the well.

Well, apart from this there is also another very interesting situation where we can get retrograde condensation and that happens under constant temperature and pressure conditions. Let us see when it happens? We have already discussed Pxy, Txy and xy diagrams at low pressure for completely miscible systems. So suppose we would like to generate the Txy, xy diagrams at higher pressure let us see what happens?

(Refer Slide Time: 20:18)



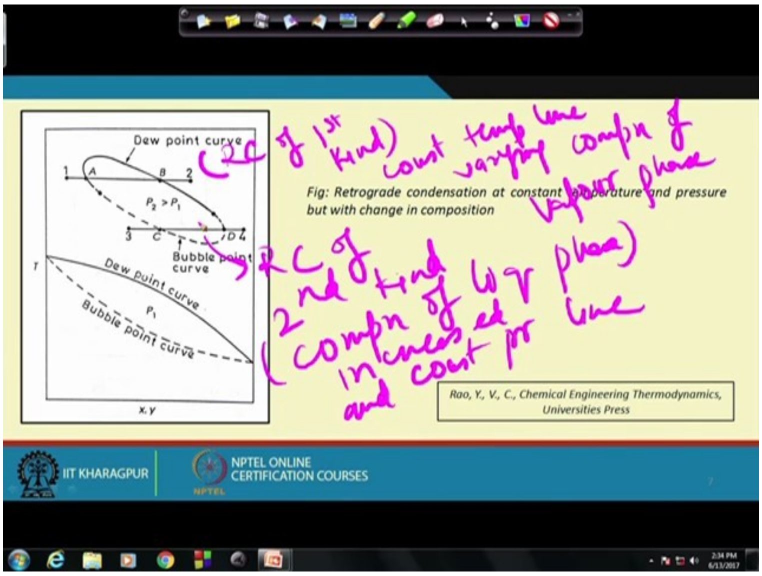
(a) Typical pressure – composition diagram at different temperature (b) Typical temperature – composition diagram at different pressures (c) y-x diagram for the ethane/heptane system at different pressures

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

If you observe this particular phase diagrams you will see that as you go for higher and higher pressure the zone of existence of 2 phase that decreases and this is of great concern to the designers of distillation columns because moment zone of two-phase decreases it is very difficult or rather it is impossible to separate any particular mixture into 2 components. We would again land up in separating it in into 2 particular liquid mixtures.

Now under this condition suppose we concentrate on the phase diagram at P1 and the phase diagram at P4. Let us see if you observe them more closely what do we get?

(Refer Slide Time: 21:35)



(RC of 1st kind) const temp line varying compn of vapour phase

Fig: Retrograde condensation at constant temperature and pressure but with change in composition

RC of 2nd kind (compn of liq phase increased and const pr line)

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

Suppose we observe these more closely then we find that at high pressure what do we get? At higher pressure if you observe we find that suppose we have taken up a constant temperature line here we have we have taken the line such that it does not cross the bubble Pt curve but it crosses the dew point curve twice, right? So therefore under this condition if we if we keep the temperature and pressure constant and vary the vapor phase composition we have started with a vapor phase and then some amount of liquid form and the vapor gets reformed at B and we get pure rather we get only vapor at state 2.

So therefore path 1, 2 this definitely denotes retrograde condensation of the first kind. Since it is crossing the dew point twice and this is happening when we are dealing with a constant temperature line and we are varying the composition of vapor phase. We can also get a similar situation if we are operating again along isothermal conditions at a slightly different temperature and pressure such that in this particular case instead of crossing the dew point twice, we in the process of isothermal in the isothermal process we are crossing the bubble Pt curve twice.

So in this case what we do? We are crossing the bubble Pt twice by varying the liquid phase composition and by this process we are able to get retrograde condensation of the second kind where we have achieved this by varying the composition of the liquid phase or rather by increasing the composition of the liquid phase and travelling along a constant pressure line. We need to remember that the vertical lines they are constant temperature and pressure lines because this curve has been generated at constant pressure and the horizontal lines denote constant temperature lines.

So therefore we find that although at lower pressures, at lower pressure conditions say at pressure P1 it was not possible to obtain any such sort of retrograde condensation but keeping everything constant if we just increase the pressure we find since the 2 phase region has decreased here. So in this case we could demonstrate the retrograde condensation of both the first kind as well as the second kind. The first kind could be demonstrated when we were traversing a horizontal path along 1, 2.

In this case the condensation was achieved by varying the vapor phase and we were traversing the constant temperature line and also since the line it crossed the dew point twice and the bubble Pt never. Also the same thing happen if we just vary the temperature at the same pressure conditions in this particular case retrograde condensation can be achieved by increasing the liquid phase composition and traversing the constant pressure horizontal line in this case such that the line it traverses the bubble curve twice and the dew point curve never.

So this is one particular interesting thing which we can obtain if we are dealing with high pressure vapor liquid equilibrium for completely miscible systems, thank you very much.