Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application

Prof. M K Panigrahi
Department of Geology and Geophysics
Indian Institute of Technology, Kharagpur

Lecture - 09

Microthermometry : Principles (Contd.)

Welcome to today's lecture on fluid inclusions in minerals, we are in the middle of the second module, where we have been discussing about the principles of micro thermometry of fluid inclusions.

Because micro thermometry is the very basic source of information by using microscopic heating freezing system, like the once we described. They give us the bulk of the fluid inclusion data and the only source of data by which we can constrain, the thermal regime of the fluid that we are interested in, through our study of fluid inclusions in minerals.

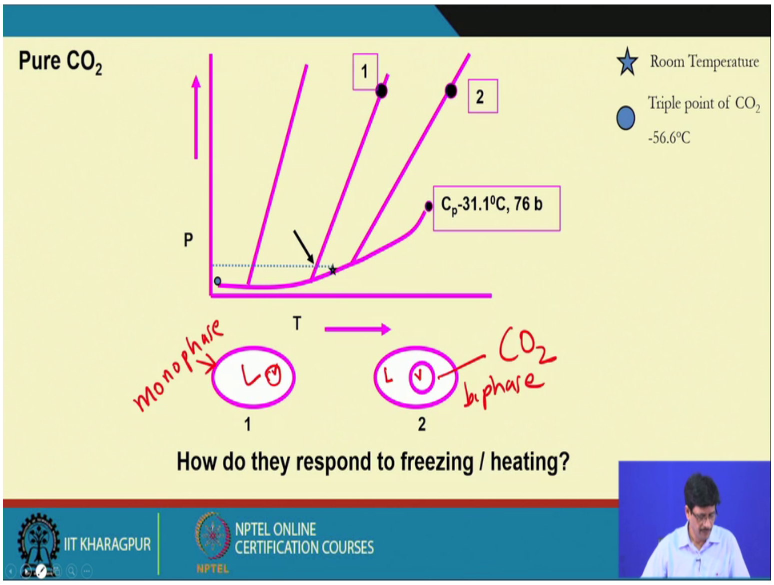
So, in the last class we were trying to just visualize the situation in which, aqueous inclusions what we see them in room temperature as either aqueous biphase with the liquid plus vapor combination, or aqueous polyphase the liquid plus vapor plus dotted crystal, which is a product of the is a product of post entrapment change in the inclusion cavity, when the inclusions have behaved like a closed system.

Without addition or subtraction of component to the surrounding, exchange of component of the surrounding and, we at this point of time we can we have some basic idea as to the entrapment process.

So, that provides the basis for the micro thermometric of the fluid inclusions. The other common type which we discussed we discuss three types the aqueous biphase aqueous, polyphase and the two liquid plus vapor type of inclusions.

And where the other so, it is essentially is as the fluid the original fluid was a mixture of water plus non electrolytes species like carbon dioxide, we are not taking any other non electrolytes species to consideration right now, when we will be we are dealing with very simple cases. We very commonly observed fluid inclusions, which have got an aqueous liquid plus a carbonic liquid and a carbonic vapor combination at room temperature.

(Refer Slide Time: 02:39)



Pure CO_2

How do they respond to freezing / heating?

And we also please do please note that we also do see inclusion which have mono phase at room temperature, you just looking like a liquid or vapor mono phase. And such kind of mono phase inclusions under some special conditions could be aqueous inclusions, because of certain situation which will again will discuss later, could be a situation in which the vapor phase has not been able to be nucleated, or the entrapment process to place its such low temperature, that the vapor phase inside inclusion could not could not nucleate we will discuss such cases later.

But the coming to the situation in which the liquid that we are talking about a homogenous liquid, or homogenous vapor is carbon dioxide, which is very possible and is abandoned in anywhere in the crystal segment depending on the environment we can get carbon dioxide in the liquid state, or a vapor state and such kind of liquid carbon dioxide, or vapor carbon dioxide inclusions get entrapped in the minerals which are either, primarily going for recrystallizing at any other point of time.

So, diagram here is shows almost analogous or identical to the kind of diagram which you saw before for pure water. This diagram is a diagram for pure carbon dioxide, just as we as we have seen before in case of water. This is the liquid vapor coexistence of carbon dioxide a carbon dioxide, triple point occurs at minus 56.6 degree Celsius. And the critical point occurs at 31 it is not minus it is just the dash plus 31.1, 76 bars and this takes place in minus 56.6.

Now, with the help of this diagram let us try to explain how pure carbonic inclusions could be could be occurring in minerals, that we see in the room temperature in the laboratory and what possible situations what are the two possible situation. Let us say that that exactly as if we have understood it properly so, here this is the one phase liquid carbon dioxide field. And any point on this liquid the density is uniquely fixed and, also the values of density at or the identical points on the density till the point that it insects with boiling curve is also uniquely define.

And this also is an isochore for a carbon dioxide liquid. And similarly this 3 isochore, which has shown here are the isochores with decreasing density. And which we can represent as a rho its gram per C in its unit. And let us say that we had two situations corresponding to in situation 1 and situation 2, where the situation two is correspond is representing a liquid for the density is little lower and it was trapped here. If it was trapped here, it is followed the isochore and is intersected the boiling curve over here. And further the since it was it was happened to be conditions higher than the conditions prevailing at room temperature pressure.

So, the star represents the point at which has this star represents the room temperature pressure condition. So, this in this fluid which was trapped to is likely to be present, in the form of liquid plus vapor liquid plus vapor, both a solve its carbon dioxide only carbon dioxide liquid and vapor. In contrast to that so, the inclusion which has a little higher and its density and was trapped at a point corresponding to here at 1.

So, that will that was also following the isochore, but the point which is the pressure and temperature condition which is here, is corresponding to this particular point that we can see. So, now, this particular inclusion has not been able to intersect the boiling curve.

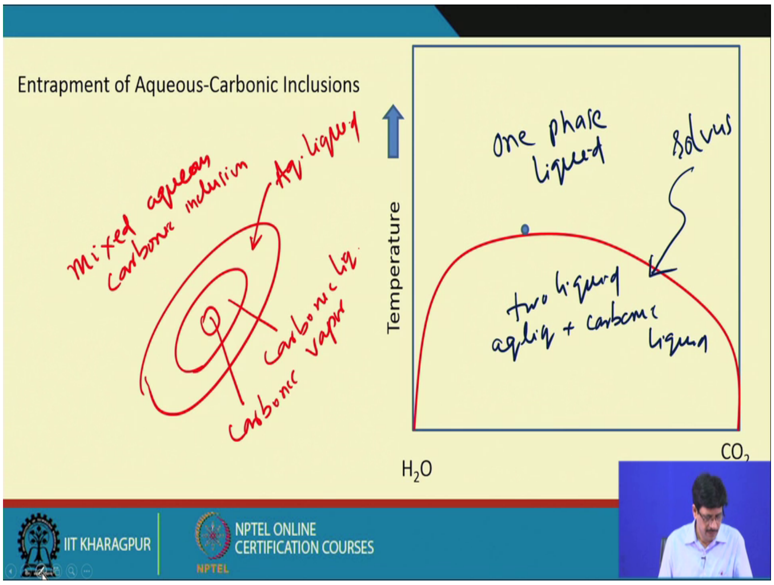
So, this will remain as liquid this will remain only as a liquid and it will be monophase, here this is a biphase remember of is condition. Now, what will happen here if you see this when we see this inclusion at this particular point is monophase and if we decrease the temperature, because if we are using if it is put into the heating freezing stage, where the temperature could be lower below the room temperature a slight lowering of the temperature and can make it change from a monophase to a biphase condition.

So, a vapor bubble will nucleate as and when we decrease the temperature from room temperature by a few degrees, it could be how much or how much we should lower that will depend on what is the density of the original originally trapped carbonic liquid walls.

So, this explains the occurrence of pure carbonic inclusions, either in monophase, or biphase condition and also its it would be worth noting here, that such kind of situation which is very common and most of the cases there pure carbon dioxide, but in many cases in many instances this particular carbonic of the carbon dioxide liquid is not pure.

But sometimes is mixed with variable proportion of other gases which is such as methane, with which it is miscible in all proportions and which does not and, they do not have any non ideality. And we can see that so, similarly we can also look at how to have an idea about the composition ok.

(Refer Slide Time: 09:49)


Entrapment of Aqueous-Carbonic Inclusions

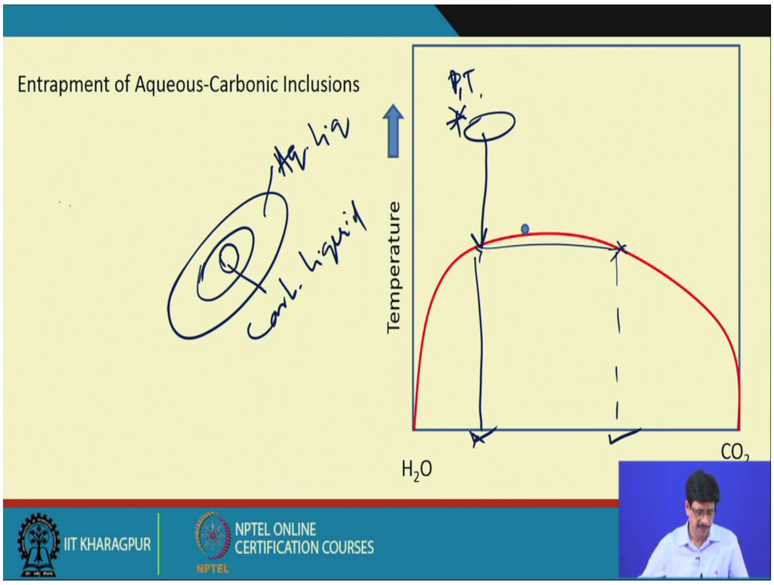
So, now come to the situation that we discussed before is the mixed aqueous carbon inclusions means, we will have an aqueous liquid a carbonic liquid and a carbonic vapor. So, we have to explain that how such kind of thing can happen. Similarly we are in the sub crystal condition and, we also go by a basic assumption that the fluid is in one phase condition. A since it is a mixture we can always represented as a binary of as a binary diagram you go it is presented here between water and carbon dioxide.

This curve is as we all know this is actually is something which you can call you just solvus, this is curve is a solvus. So, solvus means it separates the fields, where it will be a one phase liquid field and in this case it is two liquid, means it is an aqueous liquid plus a carbonic liquid.

So, whether the carbon dioxide part will be liquid, or vapor will be depending on the conditions corresponding to the liquid vapor equilibrium curve for the carbon dioxide vapor the timing. We can look at the simple situation where it is a solvus separates the one phase liquid to the two phases liquid.

Now, similarly we can always talk about a situation where the entrapment. So, this represents this field a vast field in which a one phase fluid will be present, even though it is a mixture of carbon dioxide and water it will be one phase, and either it will be the supercritical gas fluid, or it could be a liquid depending on so, what is shown here is the critical point critical point for this particular mixture and so, if we have if we have a inclusion.

(Refer Slide Time: 13:23)



Entrapment of Aqueous-Carbonic Inclusions

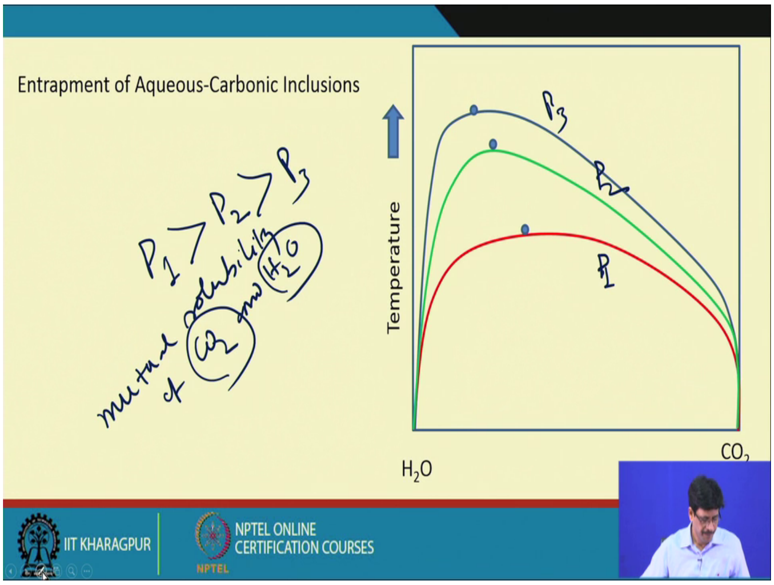
If we consider the situation somewhere here, corresponding to a pressure temperature P 1 and T 1 and, if there is a there is an inclusion which is trapped here and, we are decreasing the temperature, if the temperature is decreased. Then exactly following the rule that, we generally have for splitting of this particular liquid into two components here and here.

So, this particular inclusion which was the inclusion fluid, which was encapsulated in the host mineral as a homogenous aqueous carbonic fluid, after its entrapment with decrease in temperature, when will come to pressure later on. A decrease in temperature will intersect the solvus and, as it intersects the solvus it gets splited up into two components and aqueous liquid and the carbonic liquid. And it will be present exactly the way we are presenting that it will be an aqueous liquid and this will be carbonic liquid.

Now this carbonic liquid, so exactly after the entrapment process; since the pressure and temperature is decreasing and, also the differential contraction of the liquid with respective compared to that of these host solid. There will be still so, a vapor bubble will nucleate and vapor bubble will be a carbon dioxide vapor instead of a aqueous vapor, because the its basically the separation of the carbon dioxide vapor which will accommodate the string in the volume and it is always a carbon dioxide vapor.

So, this explains the entrapment condition of a homogenous fluid which is what are those carbon dioxide to the post entrapment change and giving rise to aqueous carbonic inclusion.

(Refer Slide Time: 15:43)



Entrapment of Aqueous-Carbonic Inclusions

$P_1 > P_2 > P_3$

mutual solubility of CO_2 and H_2O

Now, the solvus represented by red line, say it suppose it correspondence to a pressure which is P 1 just P 1. The one which represent the green line is P 2. And we can see that P 2 has a much larger immiscible region under it, field of immiscibility this, this field we can call we can always say that is the immiscible region and this the on above it is miscible region. And the orange one is corresponding to pressure as P 1 and the green one as p 2 and a third one this blue one is P 3. So, as it happens the phase behavior that the way we have studied.

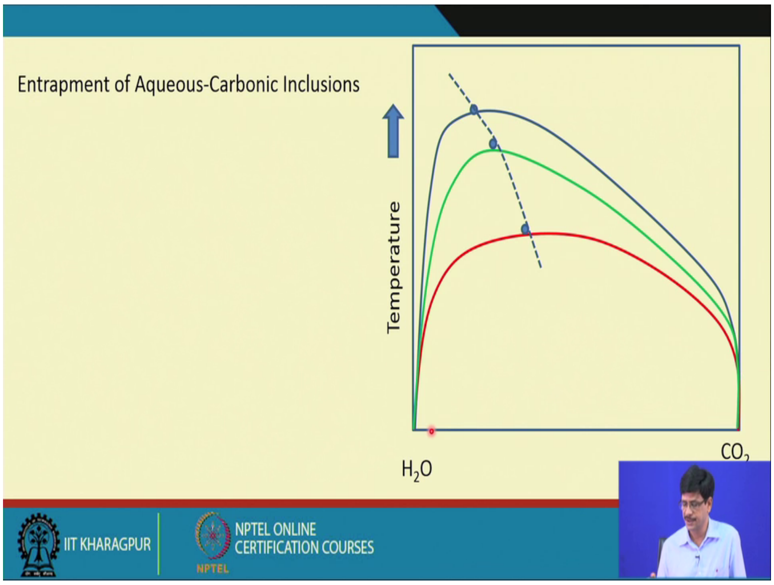
So, P 1 will be greater than P 2 is greater than P 3, means this solvus which gives rise to the splitting of a originally homogenous aqueous carbonic fluid will be will always be much easier, or this the immiscibility will be will be achieved at a much higher temperature.

If the pressure is low means in the pressure is higher and higher than the one phase region is expanding the one phase region is more dominant, or the reverse that the immiscible region expands with decrease in pressure. And as we know, the solubility because is essentially be coming out from the mutual solubility of carbon dioxide and water; because water is a polar molecule carbon dioxide is non polar molecule and, there is a lot of high degree of non ideality in the mixture. And their miscibility's very restricted and lower is the pressure higher is the immiscibility.

So, this will be so, on the basis of this a entrapment of a entrapment of a homogenous aqueous carbonic fluid and, the change in the post entrapment change in bringing about the phase separation is explainable on this basis of this diagram.

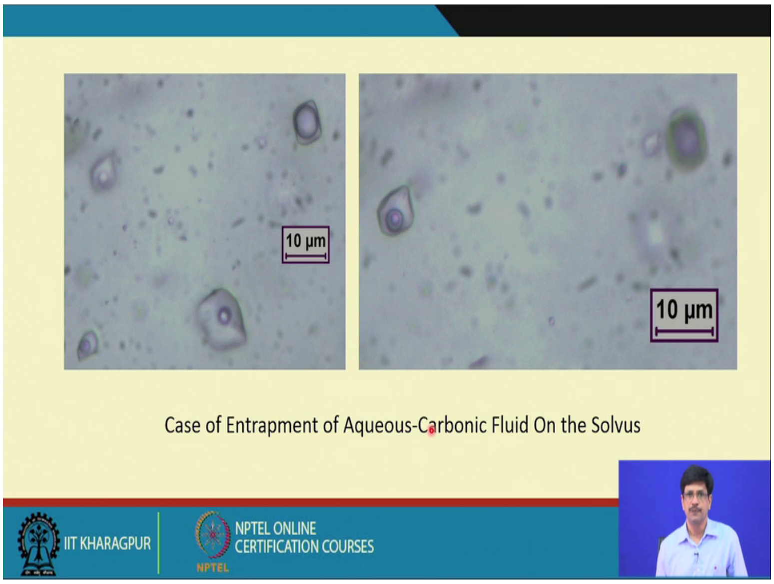
It is also possible that as you have said that, we are not considering any of the conditions corresponding to heterogeneity in the fluid during the time of the crystal growth, which always is possible in case of the pure aqueous system, in which you have a boiling curve on which liquid and vapor coexist so, heterogeneity is possible. Similarly in this case the heterogeneity is also possible on those on those solvus the discrete solvus, which you have shown at different pressure.

(Refer Slide Time: 19:05)


Entrapment of Aqueous-Carbonic Inclusions

So, this actually defines the change the critical point, with decreasing increasing with increasing pressure and, this dotted line (Refer Time: 19:14) of it is the trajectory of the critical point. And this solvus is inherently asymmetric and you see that the mutual solubility of the carbon dioxide solubility in water is a little bit more than that of the reverse that is the water solubility in carbon dioxide in the two extreme ends.

(Refer Slide Time: 19:44)



Case of Entrapment of Aqueous-Carbonic Fluid On the Solvus

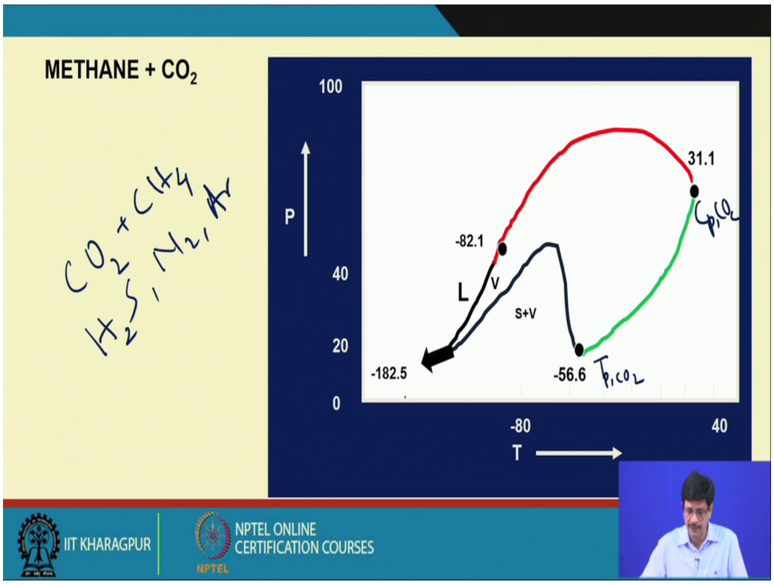
Well these photographs actually are showing the situation, on the left side photograph. We see that this is an inclusion aqueous carbonic inclusion; it is occurring in its two phase condition is the liquid carbon dioxide at the liquid water. And as you could see here the one which is here is out of focus, or the next on this diagram to the right, this inclusion is out of focus, and this inclusion is on focus.

Now, if we see these two which are very much in the host a crystal within the part of the occurring is a part of the random three dimensional network, you could clearly see that the proportion of carbon dioxide in this particular case, is perceptible more than that even the taking into the uncertainty of the third dimension into consideration. Still we can say that this particular inclusion represents, a higher proportion of carbon dioxide compared to the one which is here, which is occurring in a try phase condition. We can clearly see the look liquid water liquid carbon dioxide and the carbon dioxide vapor.

So, it can be explained on the basis of this diagram, depending on the where if the competition is on the carbon dioxide on the waterich side or on the carbon dioxide which side, if it is on the carbon dioxide its right, then decrease in temperature will give rise to the splitting, where there will be a this could be all calculated by using this standard lever rule, as we follow in case of binary diagrams.

And depending on the composition being either somewhere here, or somewhere here, then they are going to give rise to inclusions which will be which will be aqueous carbon inclusion, showing the typical they can also be called as in way of polyphase means liquid two liquid and plus or minus vapor, such kind of entrapment processor very much possible and can be explainable on the basis of simple phase diagram. And we are still sticking to very simple situations and will discuss the more complicated once later.

(Refer Slide Time: 22:05)



METHANE + CO_2

Well as a just going a little further from a pure carbon dioxide, we also can take into consideration the fluid being charged with methane. So, it will be essentially carbon dioxide plus methane. And also with the same time so, the previous diagram was in respect of the entrapment conditions which is at higher temperature, again we will also be talking about the compositional characteristic.

So, we talk about a pure carbonic phase we talk about composition in terms of what other gases could be possible. So, it is in most of the cases this CO 2 and CH 4 are the dominant ones, one can also have situation like that could be some amount of H 2 S sulfurs species could be nitrogen could be argon. So, these are the kind of gases species which are detected by analytical equipment and, sometimes also can be studied by phase behavior in the fluid micro thermometric experiments.

This is also one example that I am showing here, what is what is shown here is exactly the triple point of carbon dioxide, which is minus 56.6 and is green curve which is hand written and this not to the scale and, this is the critical point ok.

So, this is the critical point C p of carbon dioxide, this is a triple point of carbon dioxide. And as we know that the liquid vapor coexistence takes place, anyhow anywhere in this pressure temperature condition, this is this correspond to about 76 bars and this still a lower pressure, and here the orange one ok. So, this one the black one is also similar curve for methane.

So, methane actually is a gas whose triple point is about minus 182.5. So, as you can imagine when we are using devices, where the temperature can be brought down to only level of minus 1 196, it is not possible for reasons which I will explain later, it is not possible to obtain the critical sorry the triple point of methane the mostly is very hardly, it is possible to observe where as the critical point of methane is minus 82.1, which is easily observable means any kind of a liquid vapor homogenizations.

So, here on this a pure methane, if you considered a fluid which could be a pure methane, then the pure methane liquid vapor homogenization, or the coming to one phase is possible up to up to minus 82.1, after which to be a supercritical gas as we all know in case. So, all this individual species such kind of phase diagrams can be constructed, critical because this critical density of carbon dioxide is about 0.4 gram per C C and it can also have a critical isochore, for the carbon dioxide as well as the critical isochore for methane.

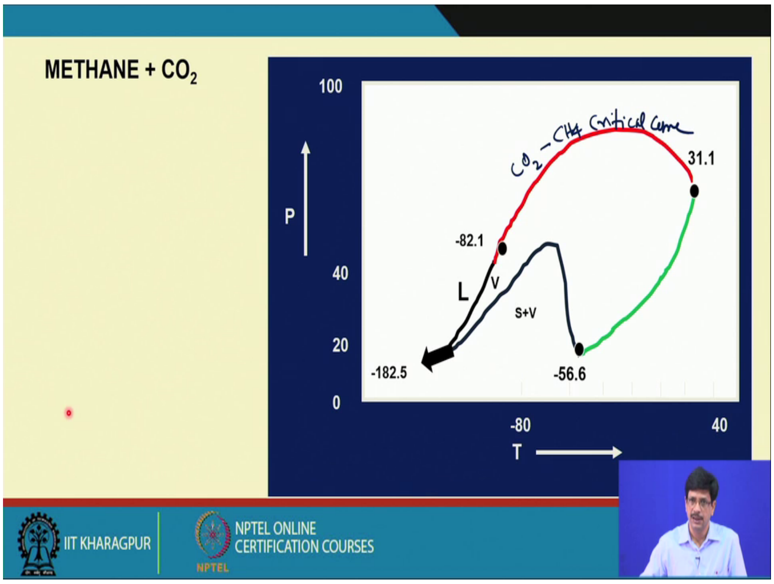
So, now why this diagram this diagram only tells that well, if carbon dioxiode if the fluid is mixed with methane if the carbon dioxide so; that means, whenever we get a carbon pure carbon dioxide liquid inclusions. If we are decreasing the temperature going to below temperature, which is minus 56.6, then we know that the carbon dioxide is pure. If the temperature so; that means, exactly here what is going to happen since the triple point triple point is solid liquid and vapor coexistence.

So, if you increase the temperature than solid is going to melt and will only be getting liquid plus vapor. So, now, since if we get the melting taking place exactly at 56.6 that we know that there is no other gas which is mix with it, where as if it is mixed with some amount of methane, then this triple point of carbon dioxide is going to get depressed, two variable value during it theoretically can go up to minus 182.5.

Similarly if we have that particular carbon dioxide inclusion, which is present is a liquid plus vapor inclusion and, its it happens to it shows critical homogenization; that means, which will also discuss later on what exactly critical homogenization is, but for the timing we can consider that the density of the carbonic fluid was such, that is exactly corresponding to the critical density.

And then under that kind of situation, if you find that the temperature of homogenization of the carbonic liquid is lower, then exactly what the way we have we saw for water and sodium chloride having a continuous critical curve.

(Refer Slide Time: 27:45)

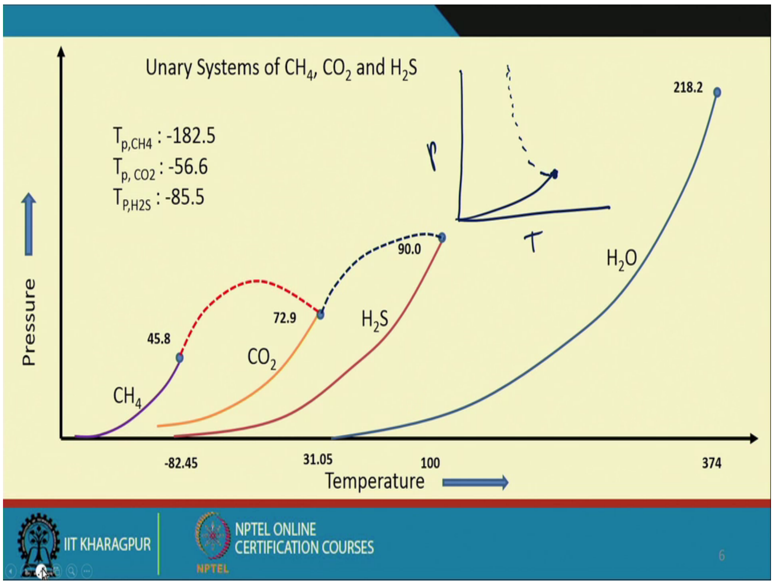


METHANE + CO_2

So, this also can be say as a CO 2 CH 4 critical curve. Hence even if it is not a critical homogenization, if the homogenization happens to be if it is happen, if it happens to be a fluid where it mixed with carbon methane carbon dioxide fluid which is mixed with methane.

It is temperature of homogenization is also going to be depressed, corresponding to compare to what it would happen, if the carbon dioxide good have been pure one. So, this kind of diagram give us some insight, to understand the behavior the response of the inclusion fluid to heating and freezing, are for understanding there compositional characteristic.

(Refer Slide Time: 28:41)



Unary Systems of CH_4, CO_2 and H_2S

$T_{p,CH4}$: -182.5

$T_{p,CO2}$: -56.6

$T_{P,H2S}$: -85.5

So, this diagram is kind of a combined unary methane carbon dioxide water and H 2 S so, it is possible that with the way it has been drawn here, so, this is methane is minus a methane is minus 182 degree Celsius the triple point.

And this is a critical point of methane corresponding to minus 82.45 degree Celsius temperature and, 45.8 bars pressure. And this one as we discussed just now this is the methane carbon dioxide critical curve, carbon dioxide critical point is a 72.9 bars and thirty 1.05 degree Celsius, we have a continuous critical curve for carbon dioxide methane.

And it is possible to calculate the concentration of methane in terms of more percent, from such kind of depression in the critical temperature of carbon dioxide, or even the change, or the depression in the homogenization temperature of carbon dioxide liquid, if it contains methane. And this one interestingly is for H 2 S H 2 S has a triple point, which is lower than that of carbon dioxide, it has a critical temperature which is about 100 degree Celsius and 90 bars and this is carbon dioxide.

So, even carbon dioxide and H 2 S are also miscible and there is no non ideality, there is no immiscibility in there in the phase relation. And you can also have a continuous H 2 S and carbon dioxide critical curve. So, sometimes when we find that the critical temperature. So, that the significance of this diagram is that, if the carbon dioxide is mixed with methane, then there is the pressure and its temperature of homogenization, or the critical homogenization whatever the case may be.

In case of it curve charged with H 2 S, then the then there is an elevation, or the increase in the temperature of critical homogenization, or the homogenization temperature of sometimes it is reported that a critical homogenization of carbon dioxide is more than what it is what should have been appear 1 so, at that point of time one can suspect that they could possibly be some amount of mix H 2 S which is mixed with it. And for your reference here the boiling curve for water is also plotted, here is the critical point of pure water, which is 218.2 bars 374 Celsius.

But since we have a lot of immiscibility in the carbon dioxide and water system, we are not there is no much of significance in seeing critical, there is no continues critical curve, but sometimes we do C such kind of relation this is temperature and pressure. If this is the temperature this the critical point of water which is 374 with increasing carbon dioxide, we find that we can trace the critical curve up to a certain percentage certain value of the concentration of carbon dioxide in the water.

So, it only so, this these are the so, this phase simple phase relations without getting into much more of the analysis of them any rigorous thermodynamic analysis, this simple phase relations are in the back of your mind, when we are doing studying fluid inclusions doing micro thermometric experiments recording observations and different types of phase changes that we see in the fluid inclusions during freezing and as well as heating.

So, heating done generally will be conducted to obtain the condition corresponding to homogenous fluid, because abiding by our confirm into the very basic assumption of homogenous entrapment. So, we conclude the discussion today here;

Thank you very much; we will continue discussing in the next class.