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

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Lecture- 12
Aqueous Fluid Inclusions (Contd.)

Welcome to today's lecture, we just have started to discuss the response of fluid inclusions to micro thermometric experiments to freezing and heating cycles.

We discussed about the aqueous bipahse inclusions, approximating them to be belonging to water plus NaCl competition so, binary system of water NaCl.

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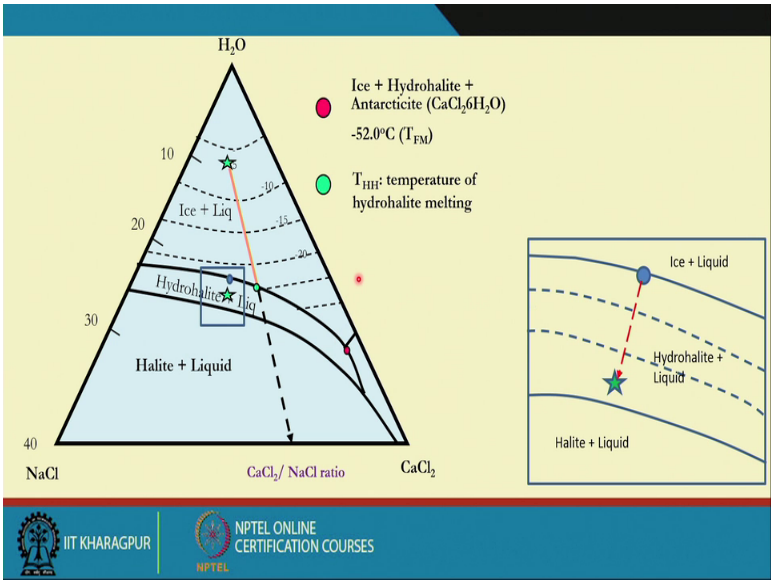

● Ice + Hydrohalite + Antarcticite ($CaCl_2 6H_2O$) -52.0°C (T_{FM})

● T_{HH}: temperature of hydrohalite melting

However, we know that the crystal fluids a natural fluid are complex mixtures containing many more electrolytes species and in a reality, we should possibly be considering such kind of multi component complex brines.

But since the concentration of the other species would always be much less or negligible compared to some of the dominant chloride species like; sodium chloride, calcium chloride and potassium chloride. So, I it will be worthwhile to look at the ternary system which is water; water sodium chloride and calcium chloride.

And from the phase relations at lower temperature to understand the, what will happen to a fluid inclusion aqueous fluid inclusion which is an aqueous biphase inclusion like what we have been considering before what will be the behaviour to freezing cycle?

So, here we see that this is a part of the ternary; this is the about 40 weight percent NaCl and also 40 weight percent CaCl 2 like curve here. Now on this ternary we are seeing the isotherms going up to this is from minus 10, minus 15, minus 20 and so, on; going to this is waterich region of the ternary in this region it is beyond concentration of sodium chloride above this the compared to the saturation value. So, here we will have the halite plus liquid and vision as we know this small region will be having the stability of hydro halite plus liquid.

Now, what is going to happen and kindly do recall that, we had listed the values corresponding to ternary eutectic so, some of the systems. And recall the ternary eutectic in the system NaCl CaCl 2 and water is minus 52 around minus 52 degree Celsius. So, if we have an inclusion which can be which is approximated or it has calcium chloride also in addition to sodium chloride; then if we freeze it decrease the temperature.

Then it is theoretically supposed to become completely frozen at minus 52, which we know is much lower than the binary eutectic of sodium chloride in water. So, you would expect the inclusion to remain in the liquid form till the temperature is lowered substantially or to negative values. And also at the effect of super cooling to it such kind of inclusion, which become frozen at temperatures much lower corresponding to sometimes minus 70, minus 80 or so, degree Celsius.

So, now what exactly happens? Like before suppose this star corresponds to the composition of the inclusion that we begin with; it is an, it is a waterich inclusion contain sodium chloride which is less than 10 weight percent and also contain sodium calcium chloride which will be of course, will be even less than that.

So, suppose we freeze this particular inclusion now what is going to happen we have super cooled it. And after the super cooling when we are gradually warming the temperature as and when the temperature of minus 50 is reached; it corresponds to this particular rate point is corresponding to the sodium chloride, calcium chloride, water ternary.

So, here this particular the inclusion when we raise the temperature from anything like minus 80 or minus 70; when we slowly warm up, then we were we would expect to see the (Refer Time: 04:44) liquid like the one, like the way we explained in the previous case. The (Refer Time: 04:50) liquid to form at this particular temperature, which we will record is the ternary eutectic. Now here it gives us a very first indication that the inclusion fluid that we are looking at is not a pure water NaCl in fluid.

But it also does contain other cations and if it happens to be around minus 52; then we know that the dominant cation is sodium is calcium chloride. One important point also to mention here that many of the situations, we actually may not have the eutectic very well observable; if the concentration of the other cations are much less, which is usually the case.

So, that is why we are not considering the other sulphates or carbonates or bicarbonates system, but the fact is that they can be or they should be, but when we are attempting to approximate kind of a gross chemistry of the inclusion fluid such kind of diagram suffice.

So, here with increasing the; so, from the ternary eutectic which is minus 52 we slowly warm up the inclusion. And it follows this particular coetectic of hydro halite and liquid sorry hydro halite and ice because this is hydro halite and liquid and this is ice and liquid. So, this particular cotectic is the cotectic of coexistence of ice and hydro halite, where as this one will be hydro halite and halite.

So, as it moves on this particular coetectic or hydro halite and ice; as and when it reaches the temperature corresponding to this green circle; so, this particular temperature the hydro halite will melt out. Because our bulk original composition is water rich, this hydro halite will melt out and then it will enter into the ice plus liquid filed.

And once slowly warming inclusions as we did before it will go up the this isotherm minus 20 minus 15 minus 10 and so, for example, say its the last ice solid ice melts about corresponding to minus 6 degree Celsius.

Now, the situation is that what can we can do here that, we will again be calculating the weight percent NaCl equivalent, as whatever we have been able to determine from the last ice melting temperature and will be expressing in terms of weight percent NaCl. And we expect that is going to give us a gross value which could have been the cube, which is essentially a cumulative effect of the depression of freezing point caused by which chloride species.

Similarly if the inclusion fluid and in the this both in this case also it is a pure aqueous species, there was no solid phase. In this case also the bulk composition is slightly more sodium chloride compared to the first case and here the freezing behaviour will be such; so, it this and also the point the in the previous case; it will also give us a bit of an idea.

If we extrapolate the point parallel to the to the axis of this is H 2 O CaCl 2 widely we will intersect the NaCl CaCl 2 binary at a particular point and that is going to give us the CaCl 2 is to NaCl ratio; in case of the inclusion this particular first inclusion that we are discussing.

Or if the inclusion liquid the is the more sodium chloride rich compared to the first case; so, there the situation would also more or less similar to the case, it will have ternary eutectic a corresponding to the first melting will be observed corresponding to temperature of the ternary eutectic. And it will move on the hydro halite plus ice cotectic and at this particular point the ice will melt and it will enter into the hydro halite plus liquid filed as has been shown in a magnified in a blown up the diagram has been enlarged here.

This loop from the from this point which is indicated here with blue with warning; it will way cross the isotherms. And we know that from the binary the temperature of melting of hydro halite corresponding to the room temperatures solubility of a up to up to 26.3 weight percent.

It will be it can go to from anywhere from minus 21.2 to plus 0.1; as we saw before in the in the previous case when we are considering the water NaCl binary there the NaCl rich side, which will be from the eutectic composition to the room temperature saturation, the short curve, which was joining the binary eutectic to the room temperature saturation value of sodium chloride there the temperature can vary from the eutectic temperature of minus 21.2 to plus 0.1 degree Celsius.

So, this is what will is suppose is likely to happen here once it enters into the hydro halite plus liquid field and finally, the hydro halite with melt at this particular temperature. And we can calculate the weight percent NaCl equivalent by using the equation, which we have discussed before. So, this is how; so the practicality is that exactly remain in the same.

So, whenever there are phase changes expected because we generally do the replicate measurements; we get some idea exactly what point what temperature we are observing the phase changes And as we are will be approaching those values of temperature, there we need to have a very very control rate of warming the inclusion so, that this temperature could be recorded.

And as I have said before they have to be reproduced to limits of plus minus 0.1 degree Celsius in case of the freezing experiments. And which is usually is achievable with the devices that we were using and the practice good practice of micro thermometry that we can follow.

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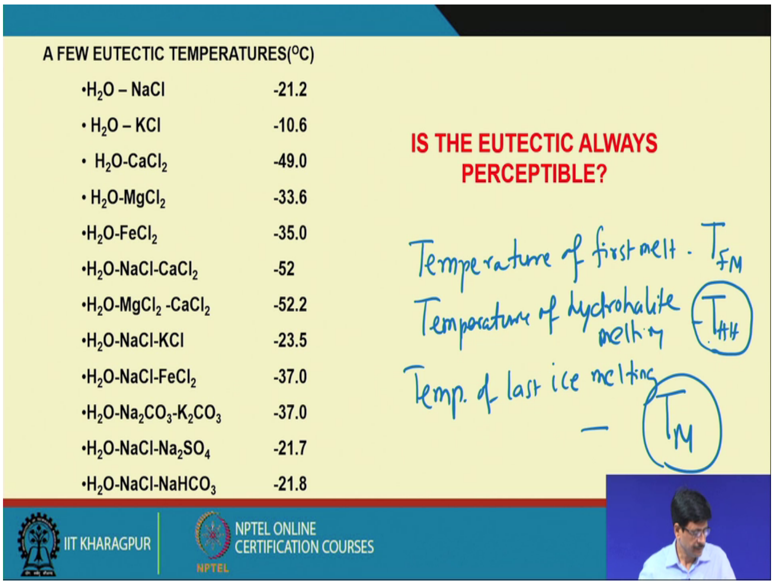

A FEW EUTECTIC TEMPERATURES(ºC)

•H_2O – NaCl	-21.2
•H_2O – KCl	-10.6
•H_2O-$CaCl_2$	-49.0
•H_2O-$MgCl_2$	-33.6
•H_2O-$FeCl_2$	-35.0
•H_2O-NaCl-$CaCl_2$	-52
•H_2O-$MgCl_2$ -$CaCl_2$	-52.2
•H_2O-NaCl-KCl	-23.5
•H_2O-NaCl-$FeCl_2$	-37.0
•H_2O-Na_2CO_3-K_2CO_3	-37.0
•H_2O-NaCl-Na_2SO_4	-21.7
•H_2O-NaCl-$NaHCO_3$	-21.8

IS THE EUTECTIC ALWAYS PERCEPTIBLE?

Temperature of first melt - T_{FM}

Temperature of hydrohalite melting - $\boxed{T_{HH}}$

Temp. of last ice melting - $\boxed{T_M}$

So, as I said that is in many of the cases say for example, we do see some of the cases the binary eutectic or the first melting temperature. Sometimes they may not correspond to exactly the sharp value of minus 52 or minus; so, it sometimes we find the if you are; if you have been able to confidently notice the over the temperature at which interracial liquid is forming, sometimes we find they do not exactly correspond to the known eutectic values.

So, that possibly ascribed that ascribed to one of the reasons is that the third component or whenever we are considering even a more complex brines because of the concentration is so, low that we generally miss out the actual eutectic value.

And I think that is should that is that could be what whatever we can say about the freezing behaviour the melting of the solids or the eutectic temperature and the (Refer Time: 12:17) of the liquid. And we measure we record them as temperature of first melting corresponding eutectic.

And we if we are able to measure the temperature of say for example, we can always denote the temperature of first melt as T F M; Temperature of First Melting. And sometimes if we can be clearly notice in case of such kind of ternary; if you can very clearly notice the temperature of hydro halite melting, we can denote it as T HH. And temperature of last ice melting which usually is represented as T M and this, but value is actually is the most important to us, to calculate the weight the salinity in terms of weight percent equivalent.

If so, if one can determine in case of ternary sodium chloride calcium chloride and water if one can determine the temperature at which the hydro halite melting; the extra information, which can be obtained from the ternary is could be NaCl CaCl 2 to ratio right.

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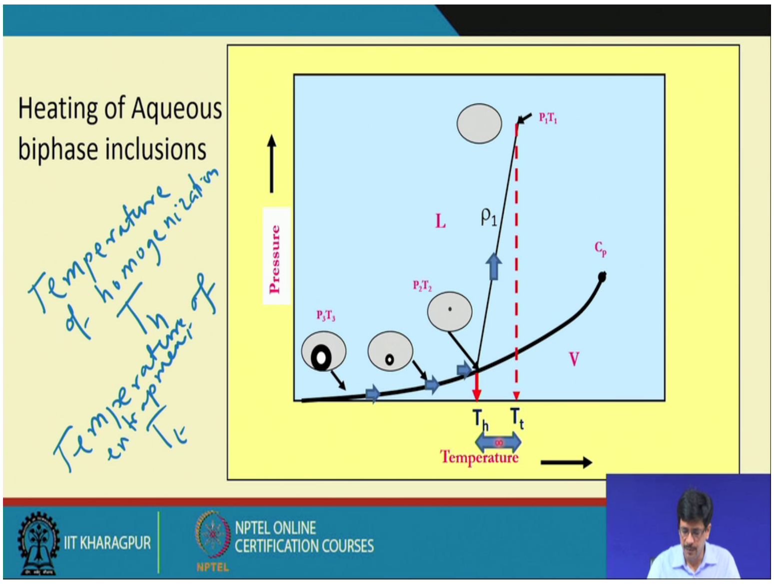

Heating of Aqueous biphase inclusions

Temperature of homogenization T_h

Temperature of entrapment T_t

So, now we could possibly; so that is in a very simple way we could illustrate to depict the response of aqueous inclusions which are essentially water plus electrolyte and their response to freezing.

And with the basic objective that we want to approximate the gross chemistry of the inclusion fluid and the best way that we could represented in terms of weight percent NaCl equivalent. Because there are many other system which are studied, but with when it comes to the practical and as we go to the advanced topics of knowing the chemistry of the inclusions; we can do by many other micro analytical technique.

But as far as the micro thermometry is concerned to constrain their bulk chemistry, gross chemistry and the thermal regime; we need to generate this sort of basic data. Now let us try to look at that what exactly the response of this kind of aqueous by freezing inclusions to heating.

This diagram we have already discussed in the context of entrapment; so, the fluid was entrapped in the host crystal at a temperature and pressure corresponding P 1 and T 1. And it has followed in isochoric path and after intersection of the after intersecting the boiling curve; the vapour bubble nucleated which also could be explained based on the differential coefficient of thermal expansion of the host solid and the liquid. And on further decreasing the temperature of further the lowering of temperature and pressure, corresponding to a situation, where we can we are seeing them at room temperature is P 3 and T 3 we see the aqueous biphase inclusion in its typical liquid plus vapour state.

Now, so it will be easier for us to understand that if we heat what exactly is going to happen? So, exactly the reverse is expected that was its going to mimic the process of a entrapment. So, if we increase the temperature; it is expected to move on the boiling curve which corresponds to liquid vapour coexistence. And it will go on this particular curve till it reaches the point where the vapour bubble disappears.

Means it actually becomes homogenous and it is may be represented by the last dot that we are seeing here and this will vanish and this will become a homogenous cavity filled with liquid at this point. So, we note down or we designate this particular point at which we observed this as the temperature of homogenization.

And we designate it is T h sometimes people quality T h L V of liquid vapour homogenization and which has been which is on the diagram we could see which is it is shown by the red arrow here it is T h temperature of homogenization. So, now the thing is that if you further heat this particular inclusion; then it is supposed to be or it is it should it will follow the isochore; the exactly the way it followed after its entrapment till the intersection with the boiling curve.

So, only problem here is that we have no way to actually come to this point of P 1 and T 1 because on this isochore as long as if even if we are going to heat there will not be any further phase change observable phase change; it will remain in its one phase state.

So, how we are going to determine that will be a issue which we will be discuss later. But then what one can say here is that if T 1 corresponds to temperature of entrapment means the formation condition of the host crystal and representing the geological environment in which our material of interest whether it is a rock or it is a o body that is form; so, it form at temperature of T 1.

And we also know that the processes never occur at any particular sharp temperature in does take place in any interval. And this particular temperature corresponds to the entrapment of this particular single fluid inclusion. And it should it would have followed the isochore and the condition of entrapment corresponds to T 1.

So, what we have been what we have been able to achieve here is that; we have approximated the temperature of the fluid, which was actually the temperature which is mentioned this T t as temperature of trapping, you can say temperature of trapping or temperature of entrapment which is designated as T t ok.

So, we know that by what value we have missed this particular because we have not been able to constrain from our homogenization experiment the value of temperature or entrapment. So, we are falling short by what is shown by this particular arrow; if we subtract T t minus T h the temperature difference that we getting is essentially is called as a pressure correction.

Why? It is known as pressure correction because had we known the pressure of entrapment of this particular inclusion, then we would simply drop the perpendicular on to the temperature axis and we will be able to know the temperature of trapping. Again I will repeat that if there is some independent consideration independent means of determination of pressure for the formation of this particular mineral in which this inclusion has been entrapped.

Say for example, suppose it happens to be as sphalerite in which I do a sphalerite geo biometry and I know that the sphalerite form that that particular pressure and I am analyzing the primary inclusion within that sphalerite or for that matter any other host. Or even if is even if I somehow constrain the environment and which this particular process from the happened at a pressure of P 1, then on the side if I construct the isochore and on this is isochore if I know the value of P 1, then I can drop the droplet on the T temperature axis and can get the temperature of trapping.

So, what essentially we are missing in this homogenization experiment is the value or we can say at the; we are approximating the temperature of trapping of the or the temperature of trapping or the temperature of fluid by our temperature of homogenization. And we know that we are following shot by a few degrees exactly at by what we do not know that is the understanding for the time being.

So, we have the pressure (Refer Time: 21:47) that is the parameter, which we call as pressure correction.

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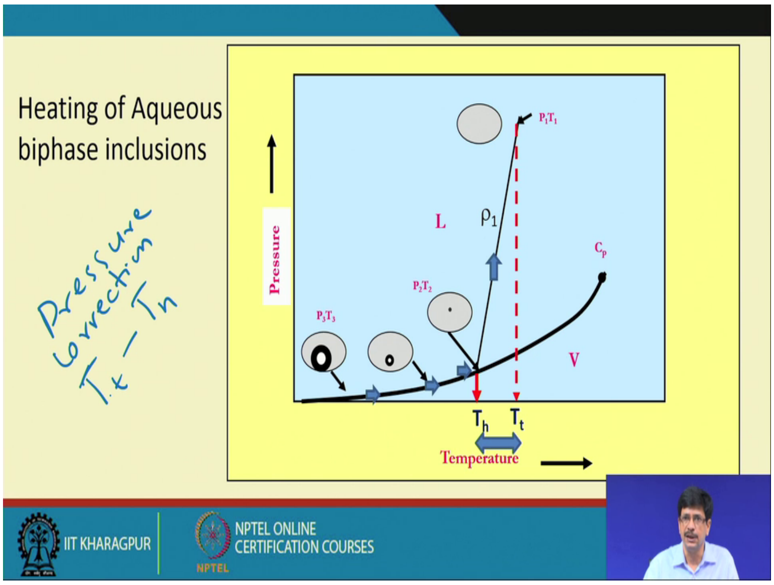

Heating of Aqueous biphase inclusions

Pressure correction $T_t - T_h$

Please remember it is a; the term is pressure correction, but what actually we get is the difference the temperature means; so, this gives us by what degree we fall short of actually estimating the true temperature of the fluid. But eventually will be able to do that because we know that our data that will be generating is will be the quantum of data will be more will be measuring inclusions hundreds a number.

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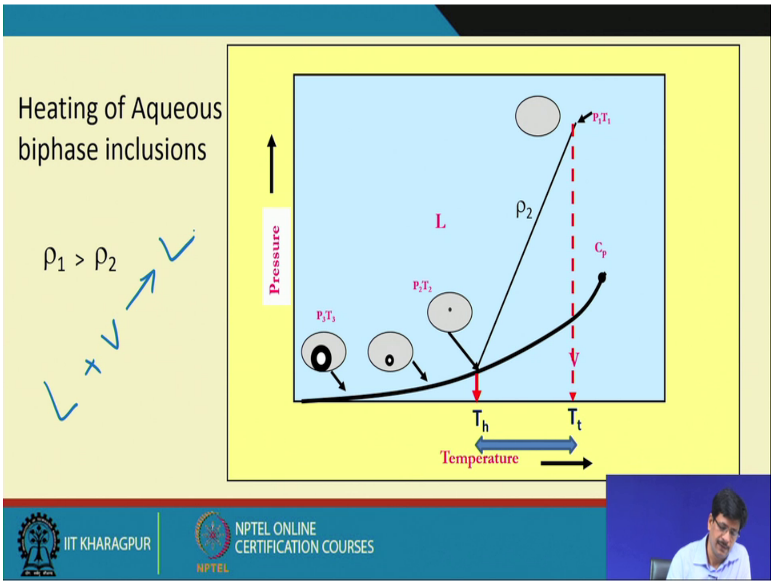

Heating of Aqueous biphase inclusions

$\rho_1 > \rho_2$

L + V → V

Well this is a situation in which suppose the inclusion which was inclusion fluid which was trapped as shown here corresponding to P 1 and T 1 and had a density much less than the one which we just discussed.

So, it is because of the density is less it has followed an isochore whose d p by d t slope is much less compared to replication fluid, let us say by virtue of the salinity the previous inclusion which we considered as a salinity higher than the inclusion which we are considering here. And because the salinity will be low the even if there entrapped is same temperature the density is less.

And it will follow a an isochore which will be d p d t slope will be much less compared to the previous one. So, here as you could see we also do the same experiment of homogenization by heating the inclusion at one atmosphere condition in our system. And we will have the vapour bubble gradually sinking in size till the point that vapour bubble will disappear. And we will achieve homogenization that will be essentially we can represent as L plus V giving rise to L.

So, it is a homogenization which is to the liquid phase means the cavity will become entirely liquid from the original assemblies of liquid plus vapour. So, here then as you could see that if the situation is such that were talking you are actually we are actually studying an inclusion which is much less dense, then the pressure correction is the magnitude of pressure correction is even more. So, denser is the inclusion, less will be the pressure correction and the vice versa.

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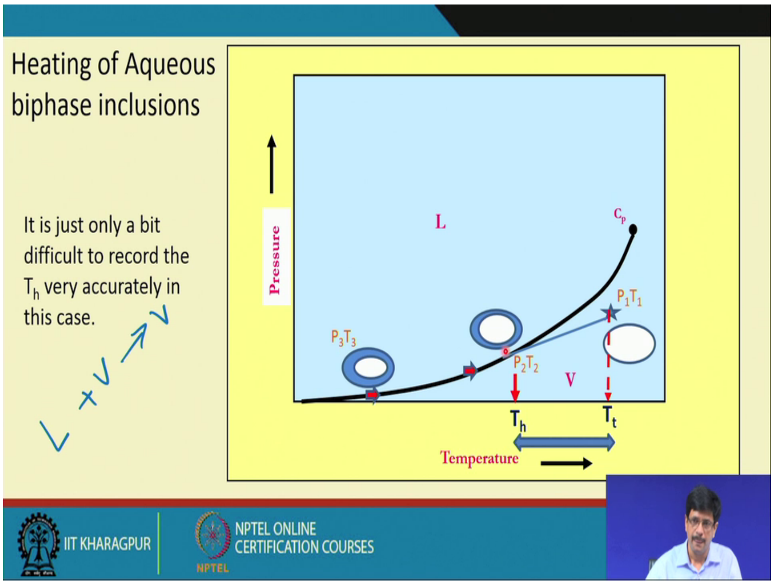

Heating of Aqueous biphase inclusions

It is just only a bit difficult to record the T_h very accurately in this case.

So situation as we said that well we always talk about homogenization entrapment and we also discuss that entrapment; so, this is the vapours table field in a pure water system or it can also be extra polluted water plus NaCl system, where the topology remains the same only with the change in the critical point and the position exact position of the boiling point with respect to pure water; this is vapour.

And let us say this P 1 and T 1 corresponding to this a star is the condition in which vapour is entrapped in the cavity a pure vapour a homogenous vapour.

So, its density is a vapour density is very negligible and we would expect it to follow a very shallow very less steep isochore which d p by d t slope will be very very low. But still it will follow an isochore and it will reach a point on the boiling curve where what will happen exactly to the reverse to the situation which we discussed for liquid each inclusion that from this vapour a rime of liquid will form because here is that situation corresponding to coexistence to liquid and vapour.

Similarly, when we go down in temperature and pressure the amount of liquid will increase. But still it will be observable as an inclusion where it will be liquid plus vapour inclusion we here it will be a vapour inclusion. Similarly following the same procedure if we heat this inclusion; we are we what we expect here that it will the vapour bubble will start increasing in its size will expand go and expanding till the point is reached where the vapour will fully fill the cavity.

So, here the homogenization will be in the mode of L plus V to V. So, with the previous case when we had L plus V to L; if we call it as liquid plus homogenization in this case we call it is a vapour phase homogenisation. The only trick here is that; it is very easy to record the disappearance vapour in a liquidrich inclusion, then it is to record a disappearance of liquid in a vapour rich inclusion.

Because the situation will be that; so, we are here so; that means, exactly at the temperature of homogenization the figure is a little exaggerated to show a prominent rim of liquid over here. But finally, what exactly is going to happen the vapour is going to completely filled cavity.

So, whether there is a very very negligible thin very thin rime of liquid still remaining will be at situation which will be little difficult to determine. So, that is why we say that the uncertainty in the measurement of liquid plus vapour to vapour is little more. So, liquid this particular homogenization of liquid plus vapour to liquid is likely to involve a bit of an uncertainty compared to a situation where the homogenization is by disappears of vapour.

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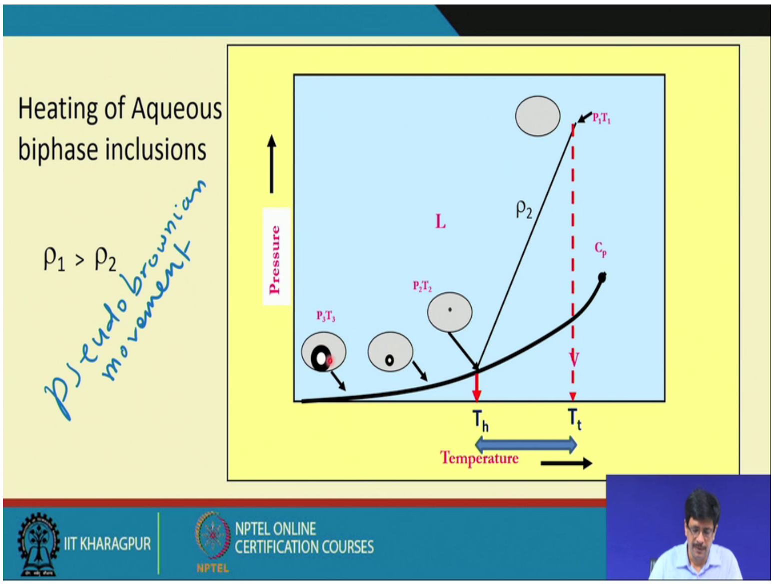

Heating of Aqueous biphase inclusions

$\rho_1 > \rho_2$

pseudo brownian movement

Because the vapour I will just; in this case I could just possibly discuss a little bit of practical situation is it happens in the aqueous biphase inclusions.

Now, what happens is you could possibly remember we were discussing something about something called as a pseudo brownian movement we all know Brownian movement it happens in gas molecules; we (Refer Time: 29:12) kinetic a theory. And we know that the molecules in a gas they undergo random movement which is basically we know that is called the brownian movement.

Now what happens in a aqueous inclusion aqueous biphase inclusion most of the cases. This particular a bubble in most in most cases is it is observed it undergoes some little; movement random movement, but not that very fast within the liquid region.

So, this is actually represented as a pseudo brownian movement; now what happens is that as and when the in temperature is increased and the vapour bubble becomes smaller and smaller in its size and just is. So, by in during that time the amplitude the pseudo brownian movement become very vigorous and the vapour bubble agreecutes very random movement inside the liquid area in inclusion cavity.

So, that actually helps us in determining the liquid plus vapour to liquid means liquid phase homogenization becomes for more easier to record. Because just about when the time when the inclusion is tending towards homogenisation attaining of the homogenous condition the vapour bubble inside which is reduced to just as a dark dot as we have been shown here exhibits very very rigours pseudo brownian movement.

So, then if we decrease the heating rate here exactly the way also we will follow the same kind of principal that in a first experiment we will crudely find that exactly at around what temperature the vapour bubble is actually disappearing. So, in the next time when we try to reproduce the value we will decrease the heating rate to a very workable value say 1 degrees per minute or even some kind of value.

So, that we would be able to see the focus on the vapour bubble and can monitor its presence or absence by virtue of the vigorous pseudo brownian movement that it exhibits. So, many times many fluid inclusion worker report about this movement of pseudo brownian movement in aqueous biphase inclusion. And they also take it into account for classifying them, but it is not a advisable thing to do by to classify inclusions where the bubble executing pseudo brownian movement or not.

Because sometimes we observe that this is this pseudo brownian movement is just because of a little bit of being thermally agitated which can even be of achieved by the light; the substance condenser like that is coming and the light energy falling on the inclusion can also make it make the bubble move in a little a random way, but the rate will be pretty slow.

So, there are aqueous biphase inclusions, which will exhibit variable degree of pseudo brownian movement and almost startic to verifiable. But as and when the homogenisation is reached the pseudo brownian movement becomes very vigorous. And that also you recall when I was saying that to which inclusion type to start with for our micro thermometric experiments.

And the carbonic the pure carbonic inclusion whose temperature homogenisation can go up to maximum 31.1 degree Celsius and we all and as we know we are working in a room temperature where the temperature could be 24, 25 or 22 to 25 degree Celsius that means, the inclusion will be very much close to its temperature of homogenization. So, the pseudo brownian movement is sometimes is the rather more prominent or more vigorous in case of pure carbonic biphase inclusions.

So, those are the ones which very easy to identify and also to record the homogenization temperature in them where the temperature only has to you need to be increase to values of 30, 31, 32 or even sometimes much lower than that.

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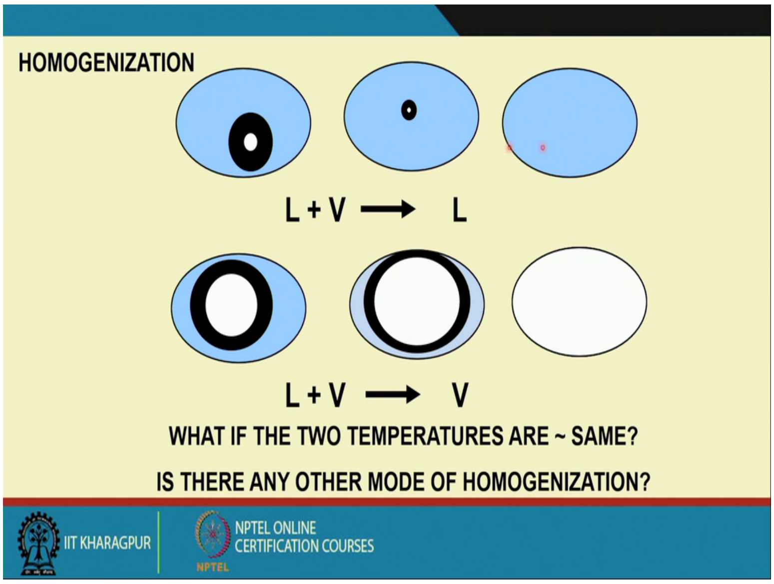

HOMOGENIZATION

L + V ⟶ L

L + V ⟶ V

WHAT IF THE TWO TEMPERATURES ARE ~ SAME?

IS THERE ANY OTHER MODE OF HOMOGENIZATION?

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Well, so this is the penetration that I have I have discussed here. So, it is the L plus V to L and this is L plus V to V and as I told that in this case the vapour bubble increases in its volume goes and expanding till it fields the whole cavity like shown on as shown here.

It will be not impossible to measure, but it will involve little bit of uncertainty which can always be better by this process. So, one of the very important practical aspect of doing homogenization experiment is that how actually we more precisely record the temperature of homogenization in case of a liquid vapour inclusion.

What we see on the forward direction when we increase the temperature from room temperature to the homogenization temperature; the vapour bubble will disappear and we have recorded that. Now if we decrease the temperature from that point onwards we should, we expect the vigour the vapour bubble will nucleate there.

But what exactly happens the vapour bubble does not exactly nucleate at the temperature homogenization. Means if you start to decrease the temperature from the home temperature homogenization, it will not reappear instantly, but it you require cooling to a to some greater degree by 10, 20 or 30 times will be much much more interval of lowering of the temperature at which the vapour bubble it just pops up from any other corner of this inclusion.

So, that gives us the assurance that actually we reached the temperature of homogenization. So, we will continue on continue discussing on the thermal response of the aqueous phase inclusion in the next class.

Thank you.