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

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Lecture - 13
Aqueous Fluid Inclusions (Contd.)

Welcome to today's lecture. We will continue our discussion on the response thermal response of aqueous biphase inclusion and the response particularly to heating experiments. And these experiments we are calling as homogenization experiment, because our objective is to obtain or to attain the same homogeneous state from which the inclusion was trapped.

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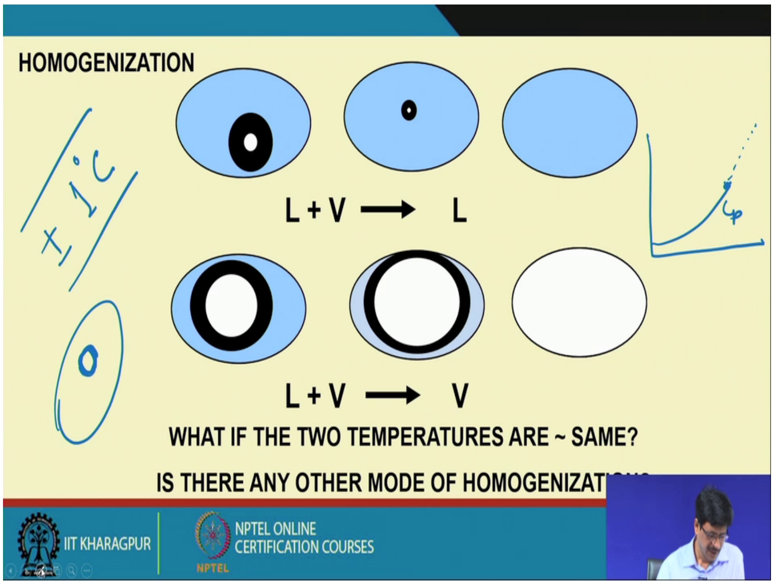

HOMOGENIZATION

L + V → L

L + V → V

WHAT IF THE TWO TEMPERATURES ARE ~ SAME?

IS THERE ANY OTHER MODE OF HOMOGENIZATI

To continue our discussion, we are discussing about the liquid vapor homogenization and there were two cases in which the inclusion would homogenize; either as L plus V to L for L plus V to V. And coming to little bit practical aspect we were discussing as to how we are assured that we have actually recorded the temperature of homogenization. There with forward increase in temperature, we will reach the temperature, which is a temperature homogenization, where the vapor bubble has disappeared and do we have recorded the temperature and those kind of a situation will give us.

So, when it comes to temperature of homogenization, means where we are working in a temperature of the order of more than 200 or 300, even sometimes more than that. So, there we, if we can reproduce the value to plus minus 1 degrees centigrade, then we say it is fairly acceptable, but sometimes there are problems like if we have.

So, that is what if we, if you want to actually assure that whether we have determined the temperature of homogenization I have been accurately recorded the disappearance of vapor. This may happen because the inclusions geometry maybe very irregular the, which will be demonstrating to some videos later that the inclusion geometry might be such that when the vapor bubble is getting reduced to very tiny size, it may just get hidden inside any of the margin and we may not be able to record the temperature homogenization by the exact point, it was in vapor bubble disappeared.

So, the best practice here is that, where we have recorded that temperature to cool the inclusion from that point to any lower temperature. If the vapor bubble actually did not homogenize, then the vapor bubble will start growing in size, which we will be able to observe from the very same temperature at which you have stopped heating and we are decreasing the temperature.

We will see that the vapor bubble is actually growing in size from some corner of the inclusion and so, then we know that the vapor bubble actually was, actually did it homogenize. We wrongly recorded the temperature homogenization, so then we have to again heat it and go at, go a little bit higher temperature then the temperature to which we these before and by these kind of a possessive cycling it would be possible to exactly recorded temperature of homogenization.

Now, talking about a situation where the there is no visibility problem, the inclusion is, the clarity of the inclusion is very good and we see that have recorded the temperature of homogenization accurately by disappearance of the vapor and from that point if we decrease the temperature, the vapor bubble will not instantaneously reappear, rather by a, by decreasing the temperature few tense of degrees from the temperature of homogenization, the vapor bubble will suddenly popup in a considerable size from any of the, any corner of the.

For example, if this has been the homogeneous, homogeneous inclusion then on decrease on decreasing the temperature, the vapor bubble will just reappear in a in just popup not exactly reappear, but just popup means suddenly make its appearance from any corner of this particular inclusion, then we are assured, we reached the temperature of homogenization, so that is why the replicate measurements and we controlled heating rate will be in a position to reproduce the temperature of homogenization by plus minus 1 degree celsius. If you have not taken enough care in our heating rate and also during the time of a homogenization experiment.

We also need to continuously focus on the bubble on the bubble, which is making very vigorous pseudo Brownian movement, so that we could record the temperature. If we go to temperature introduced the heating rate of even 0.5 degree centigrade per minute or so, there is absolutely, there is no it will be always easy to reproduce the temperature of homogenization by plus minus 1 degree celsius and this situation where is we discuss before this is a liquid plus vapor to vapor and here also the temperature at which the vapor completely fills the cavity also the similar principle can be applied.

If you have not reach the temperature of homogenization on decreasing the temperature, we can still see the reappearance of the liquid instantaneously just by decreasing the temperature, but if we have attend homogenization then the liquid again is going to suddenly reappear at a low much lower temperature compared to what was recorded is the temperature homogenization.

Now, other than these two, is there any other mode of homogenization that is of course, that is there. If I remember the phase diagram of unary water, this is the critical point and we discuss that actually fluid could have, if this is a critical isochore corresponding to if some 0.35 gram per cc.

So, the inclusion, the fluid when the mineral was going on the super critical region then let say inclusion was, inclusion was trap somewhere here or at this point and the fluid evolve after the entrapment, it evolved on the critical isochore then the vapor bubble would have formed at the point corresponding to the critical temperature. We know the its pure water is 374 degree Celsius, if it contains sodium chloride of variable weight percent and the critical temperature be higher.

So, what will happen here is, that we can think of and inclusion in which suppose its, a its being heated up, its heated and the temperature and the vapor bubble has just been reduced in it sized from an original larger size, it is just been reduce to size and this temperature is close to the critical temperature then suddenly during the homogenization would not be by for the reduction of the size of the bubble. The vapor bubble will not reduce in its size any further, but simply will, will disappear by fading of the meniscus means I can just say that it would you just fed the meniscus will fed there and it will become homogeneous.

So, that will be the homogenization, which will be a critical homogenization. So, that is it will be known as so, where the homogenization will be observable by fading of the meniscus.

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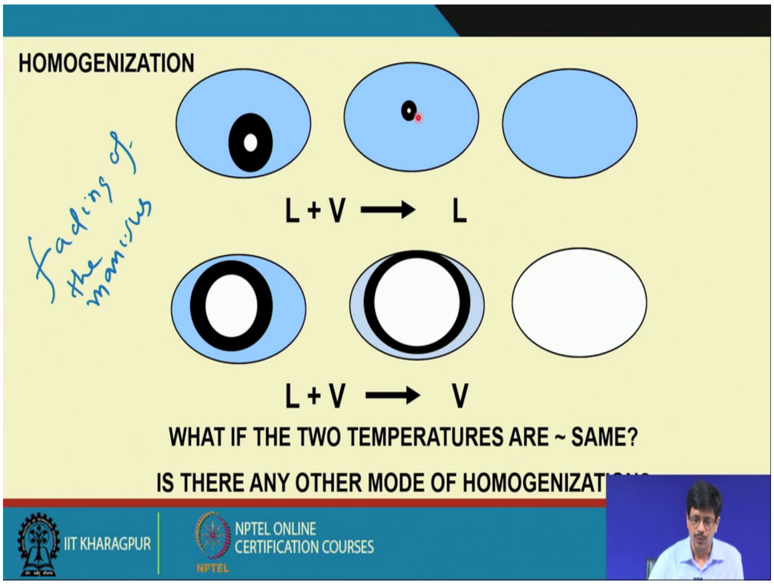

HOMOGENIZATION

Fading of the meniscus

$L + V \longrightarrow L$

$L + V \longrightarrow V$

WHAT IF THE TWO TEMPERATURES ARE ~ SAME?

IS THERE ANY OTHER MODE OF HOMOGENIZAT

So, if this is the liquid vapor interface the meniscus here as you see here in this case or is in this case. So, instead of so, when we reach the temperature instead of any further decrease of the size of the vapor bubble, it will just fade where will disappeared. So, that is actually is the critical homogenization.

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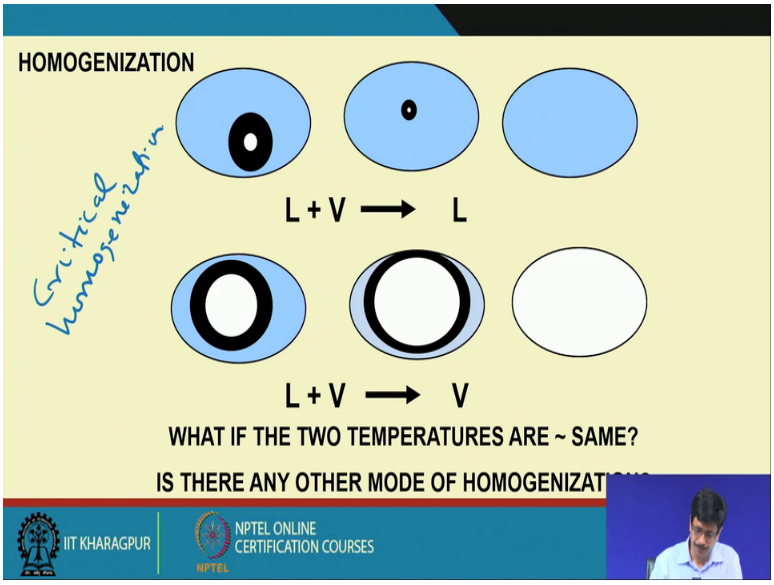

HOMOGENIZATION

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So, these are the three possible situations, in which aqueous biphase inclusion will respond to heating. We will consider heterogeneous the situation in which the entrapment is likely to be in homogeneous, later on we will not discuss them now.

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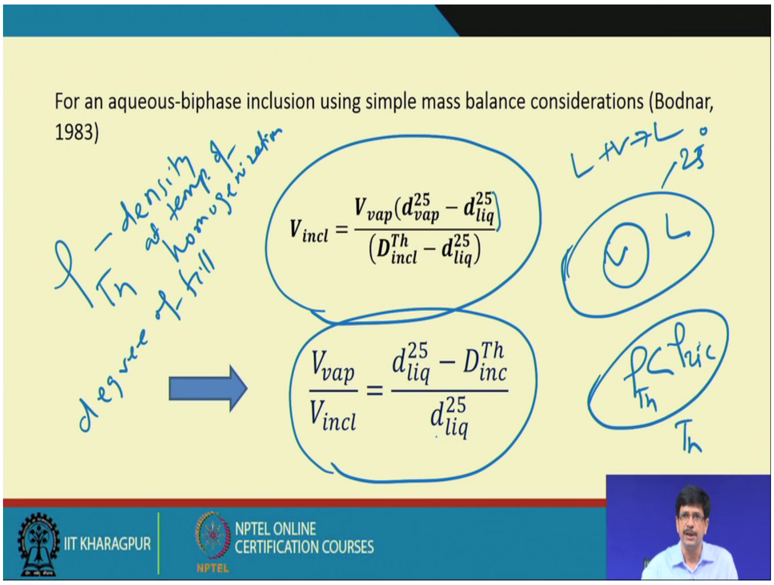

For an aqueous-biphase inclusion using simple mass balance considerations (Bodnar, 1983)

$$V_{incl} = \frac{V_{vap}(d^{25}_{vap} - d^{25}_{liq})}{(D^{Th}_{incl} - d^{25}_{liq})}$$

$$\frac{V_{vap}}{V_{incl}} = \frac{d^{25}_{liq} - D^{Th}_{inc}}{d^{25}_{liq}}$$

ρ – density

Th at temp. of homogenization

degree of fill

So, now the situation is that we sometimes need are the parameters, which was telling is the degree of fill the vapour, vapor plus liquid ratio, we can see this equation here, this actually came from a very simple mass balance consideration, because if we are having an inclusion here and this is a liquid, is the vapor if I consider the total mass of this particular inclusion the total mass is be mass of the liquid and plus the mass of the vapor. So, if we, we only know in terms of density.

So, when if we, if we consider the situation where the vapor bubble has homogenized L plus V L plus V to L, so, what we do exactly that we, we try to we calculate the density of the fluid at the temperature of homogenization. So, we designated as rho Th that is the density at temperature of homogenization and that is what exactly we calculate and we report and we characterize the volumetric property of the inclusion fluid in these particular parameter.

So, now this is a situation corresponding to 25 degree celsius or our room temperature and the inclusion becoming fully homogeneous is corresponding to the temperature homogenization. The density of the inclusion is actually when it is in 1 phase. So, now how, how we know that actually what has been the vapor by vapor plus liquid ratio at room temperature, what we call as the degree of fill, so by simple mass balance consideration.

So that, if I say that the mass of the vapor is volumetric density and here also the mass of liquid volumetric density here also the complete inclusion cavity also total mass. So, by doing this by calculating the masses or putting the expression of mass of the individual at the component liquid and the phase like liquid vapor and the total we this equation was proposed by one of the panniers worker of fluid inclusion Robert J Bodnar of homogeneous polytechnic United States.

So, this was the expression, which we can now what we can do here is that they the density or the vapor phase, if we neglect because we know that at room temperature, the density of this vapor will be very very negligible. So, if we neglect the density which, by which we will not be introducing in great error. So, if we neglect the density of the vapor phase like the expression, which you see here that the density of the vapor at 25 degree centigrade, so this can be so, here is a bracket missing.

So, this is the volume of the vapor into a factor which is density of the vapor at 25 degree centigrade minus the density of liquid at 25 degree divided by the density of the inclusion at homogenization temperature is the place of rho, it has been put as D and the density of the liquid at 25 degree centigrade temperature. As we, as we know the density of the liquid at 25 degree centigrade will higher than the density at temperature of homogenization where the temperature is higher because the density is by virtue of the temperature and the salinity.

So, salinity remaining fixed, the density will be lower as we increase the temperature. So, the rhoTh will always be less then the rho measured at 25 degree centigrade. So, by neglecting the density of the vapour, this equation could be reduced to a form like this that we vapor by the inclusion is simply the density of the liquid at 25 degree centigrade minus the density of the inclusion at temperature of homogenization divided by the density of the liquid at 25 degree centigrade. We can get the value of the vapor by vapor plus liquid.

So, that is why I initially suggested that there is absolutely no point in going for any visual estimation of the degree of fill or the v y v plus l liquid because we can always calculate this particular parameter depending on whatever we might, we might need to.

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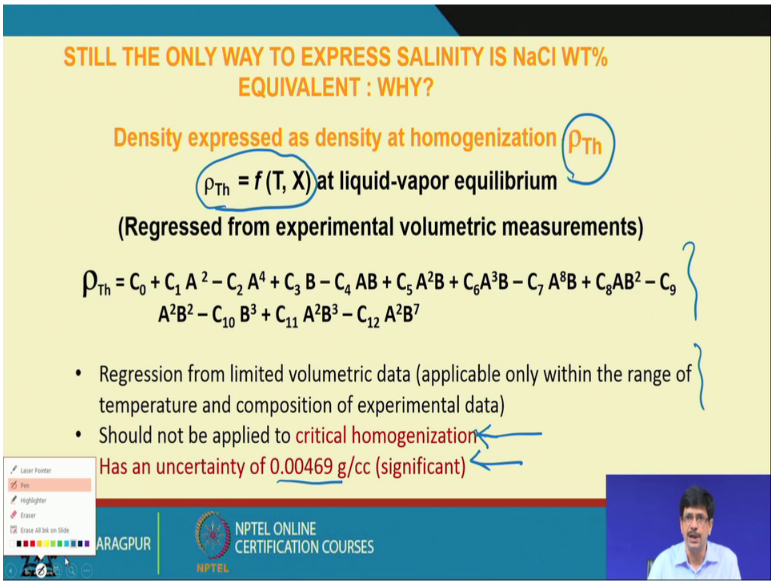

STILL THE ONLY WAY TO EXPRESS SALINITY IS NaCl WT% EQUIVALENT : WHY?

Density expressed as density at homogenization ρ_{Th}

$\rho_{Th} = f(T, X)$ at liquid-vapor equilibrium

(Regressed from experimental volumetric measurements)

$$\rho_{Th} = C_0 + C_1 A^2 - C_2 A^4 + C_3 B - C_4 AB + C_5 A^2B + C_6 A^3B - C_7 A^8B + C_8 AB^2 - C_9 A^2B^2 - C_{10} B^3 + C_{11} A^2B^3 - C_{12} A^2B^7$$

- Regression from limited volumetric data (applicable only within the range of temperature and composition of experimental data)
- Should not be applied to critical homogenization

Has an uncertainty of 0.00469 g/cc (significant)

So, as we know that from the freezing studies, we have approximated the composition of the liquid in terms of the weight percent means the depression in freezing point that would be caused if this inclusion content the entire result solid as NaCl and also with the assumption that the anion dominant anion which is responsible for depression of the freezing point is chloride and the density that is expressed as a density at homogenization is rho Th as I just mentioned here it is the density if you Th this is a, this is for any fluid inclusion work and they calculation of density of the homogeneous fluid is a, is essential this parameter has to be estimated.

Now, how this parameter can be as that we know that this parameter rho Th is a function of both temperature and composition X for composition is in terms of weight percent NaCl at corresponding to liquid vapor equilibrium whereas, been so, as I told that this particular system has been extensively studied volumetric measurement have been done experimentally and those have given enough scope for empirical treatment on empirical establishment of empirical relationship of density as a function of temperature and weight percent NaCl both.

So, the one which we widely used is again the one which is proposed by varner in 2019 183 quite some time back and if you see the situation that it content terms where the, where your the temperature is a, is temperature may be divided by 100 and B is the salinity in terms of weight percent NaCl an it one can always take is variable from doing the empirical fitting of the parameter. So, there experimentally determined volumetric measurements where the density is known and that is going to be regressed empirical fitted with salinity and temperature.

So, in that case conveniently one can possibly put this in temperature. I will of be always in form of 100. So, its better to normalise them by dividing to 100 and salinity will be only in the value of 10. So, by 10 and the a parameter is temperature by 100 and B is salinity by 10 and this equation where it goes to the power of in 7th, power of 7 in the salinity of power of 8 in temperature that we could see here.

So, anyway this regress from limited volumetric data is applicable only within the range of temperature and composition of experimental data these of course, depending on what is the range of temperature in composition in which the experiments are done and the applicability of the equation will be only be within that range, there has been many other forms I mean many other equations which also proposed.

So, this is and also the author cause and that this should not be, should not be used if there is a critical homogenization so; that means, we have to use different set of equation for under for calculating the density at temperature you did homogenization happens to be critical homogenization and we know the weight percent NaCl and we know what is a critical.

So, so such equations are also there to calculate the critical temperature for water containing variable concentration of sodium chloride and when the author propose this equation reported that its a did uncertainty in density calculation could be of the order of 0.4 0.00469 is 0.004 and we generally report density up to the third place of decimal.

So, this also to be kept in mind and this the density parameter we have to measure, but the report because when we measure this inclusion in large number, we have to see what kind of density variations we observing and accordingly we make our interpretation for the fluid in terms of its origin or the way it has evolved.

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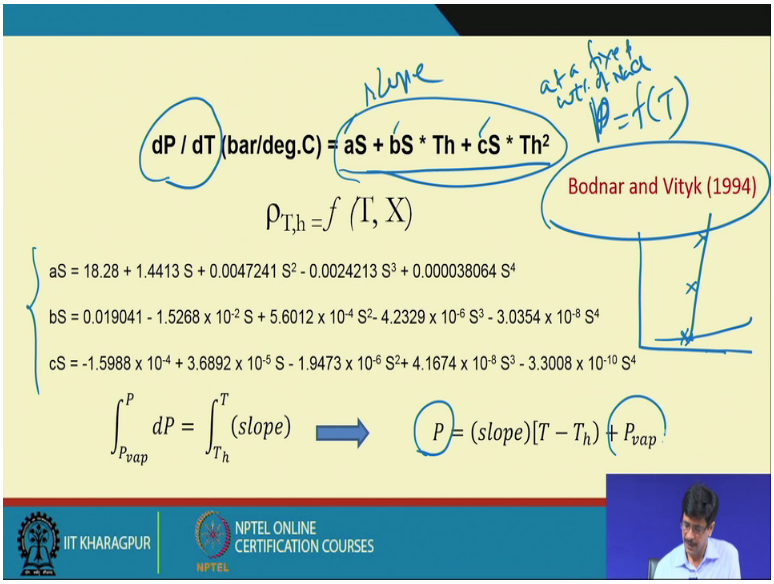

$$dP / dT \text{ (bar/deg.C)} = aS + bS * Th + cS * Th^2$$

slope

at a fixed wt% of NaCl

$P = f(T)$

Bodnar and Vityk (1994)

$$\rho_{T,h} = f\ (T, X)$$

$aS = 18.28 + 1.4413\ S + 0.0047241\ S^2 - 0.0024213\ S^3 + 0.000038064\ S^4$

$bS = 0.019041 - 1.5268 \times 10^{-2}\ S + 5.6012 \times 10^{-4}\ S^2 - 4.2329 \times 10^{-6}\ S^3 - 3.0354 \times 10^{-8}\ S^4$

$cS = -1.5988 \times 10^{-4} + 3.6892 \times 10^{-5}\ S - 1.9473 \times 10^{-6}\ S^2 + 4.1674 \times 10^{-8}\ S^3 - 3.3008 \times 10^{-10}\ S^4$

$$\int_{P_{vap}}^{P} dP = \int_{T_h}^{T} (slope) \Longrightarrow P = (slope)[T - T_h) + P_{vap}$$

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The other important parameter, other important exercise that a fluid inclusionist has to do from the microthermometric data is to construct an isochore and the isochore is essentially the isochore means we understand this the dP by dT slow like, like do you one this is our inclusion is the boiling curve and this line just straight line, straight line at least in case of the sodium chloride water system, where we say that the pressure we presume and its also quite clear that in such kind of binaries like sodium chloride and water the pressure of the fluid will be a linear function of temperature and there is a reason why and give at a fixed weight percent of NaCl, the pressure will be a direct is a direct linear function of temperature.

So, that is the reason why we say the dP by dT as to be constant. So, we need to calculate dP by dT and as has been shown here the source that is been taken the Bodnar and Vityk

1994, the dP by dT slope has been empirically fitted as a function of salinity and temperature of homogenization Th is temperature homogenization its a second degree equation in Th and linear in salinity with a, b and c parameters which have worked out the way it has been shown here. The aS, bS into Th and cS into Th square, so, here we could see that the parameters are again fitted as a function of salinity, which goes to the fourth order polynomial in salinity.

So, this coefficient, so, this only bS the very purpose of discussing this and the bringing these kind of procedure to your knowledge is that to making realise that the result of microthermometry need to be, there is a good amount of exercise at hand two after the microthermometric experiment are done and the temperature recorded different phase changes like the temperature melting of ice, temperature of melting of hydrohalite, temperature melting temperature of homogenization and so on.

So, this have to be used to make some rigorous and extensive calculations and sometimes it may not be and basic understanding of the very essential and it may not be possible to do my hand and that is the reason why fluid inclusion you have to take help of a computer, right computer codes are use available computer programs or software to calculate this parameters the isochore.

So, one need to have minimum 2 points, one point corresponding the temperature homogenization here, which is Th and at least another point are 1 or 2 point anywhere in space to construct the isochore. So, here so, if the dP by dT slope is given here which can be calculated. So, once it, once the slope is known then temperature the pressure at any particular temperature can be known by just integrating it and so this will be the slope, which is this parameter entire parameter which is worked out which is the slope with the help of the salinity and the temperature homogenization.

So, the pressure at any point will be the slope multiplied by the temperature at which we want to calculate it minus the temperature homogenization plus the vapor pressure, as you could see from here the integration would be a definite integrals. So, where they P will be equal to; that means, it will be P P minus P vapor. So, P vapor is a vapor pressure of that particular liquid of this known concentration of sodium chloride and which can be put in this kind of equations. So, if I calculate the pressure, pressure at the temperature of homogenization is the vapor pressure here.

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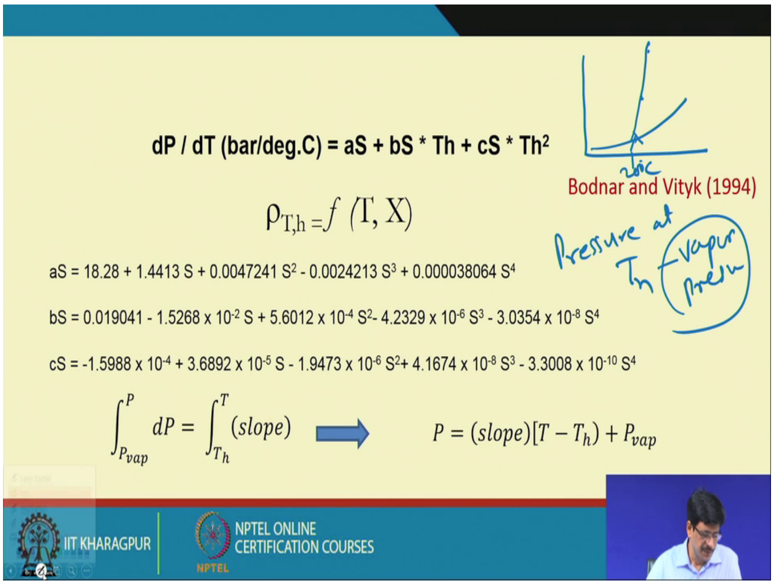

$$dP / dT \text{ (bar/deg.C)} = aS + bS * Th + cS * Th^2$$

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$$\rho_{T,h} = f\,(T, X)$$

Pressure at T_h - vapor presu

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$$\int_{P_{vap}}^{P} dP = \int_{T_h}^{T} (slope) \Rightarrow P = (slope)[T - T_h) + P_{vap}$$

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The temperature at sorry, the pressure, pressure at Th is the vapor pressure because that corresponds to the liquid vapor equilibrium coexistence. This vapor pressure can be calculated from standard formulation and so knowing the vapor pressure at any at the temperature homogenization and then the required temperature suppose for example, we want to, if the if the situation is that the temperature of homogenization has occurred at temperature of say 200 degrees centigrade and we need to conserve the isochore.

So, you will need to calculate the pressure, maybe I will calculated 300 degree centigrade and maybe at 400 degree centigrade and we will join the 3 2 points with the vapor pressure value to get the pressure at those corresponding points and construct the isochore.

So, that actually is an exercise, which can be done for a, or a single inclusion and if required it can be done for many such inclusions depending on what exactly one, one should do with a fluid inclusion data.

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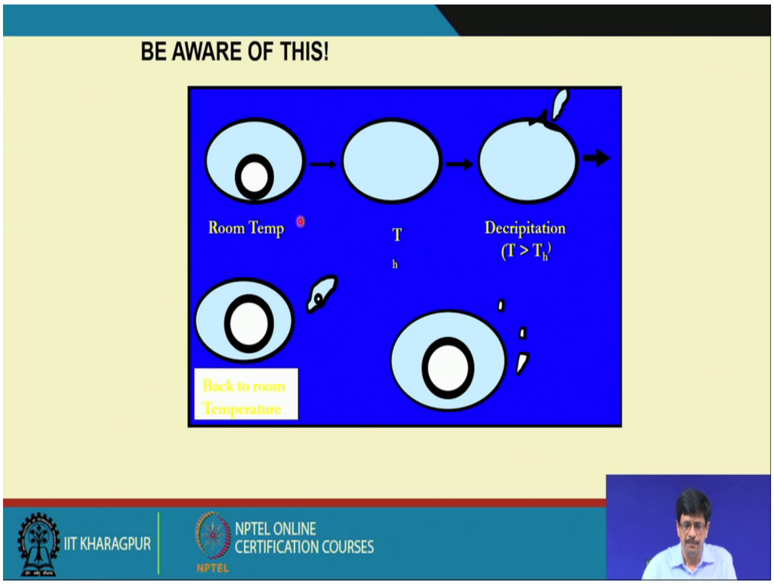

BE AWARE OF THIS!

Well so, we are here when we are discussing about the thermal response heating freezing, heating study heating to the aqueous biphase inclusions, we should be, we should remain ever about certain problems. So, that is what I have written here the be aware of this because as we know that when we have reached the temperature homogenization if you further heat the inclusion is going to follow the isochore.

So, if the isochore is a steep isochore; that means, heat actually the pressure, the pressure that is exerted by the fluid on the wall of the inclusion goes on increasing as we have discussed as you have mentions several are trying that quartz is a PV resource host quartz is a very suitable host to study fluid inclusion, because I have it, which stands on the internal pressure, because of absence of clave is one of the one such reason could be sited that.

Because there is no cleavage its a solid 3 dimensional network of the silicate SI of a tetrahedron the linkage and so, that is why it possibly would be able to it which stand higher pressure, but then there is always limit to what a host quartz will be able to which stand there could be some such situation to the host quartz already would be in a state of lower strength because of some reason or there could be fractures or there could be micro fractures around the inclusion and so on.

So, what will happen is that suppose this inclusion is the one which is not means we are trying to, we are doing a heating experiment for another inclusion, which is homogenizing at higher temperature, in this time this particular inclusion has already homogenized and the has been heated. So, any temperature on the isochore or beyond the temperature homogenization we can say it is overheated and the as the isochore there is followed by this particular inclusion is steep.

So, there is much increase in pressure with even increment with small increment in temperature. So, the pressure which is exerted by the wall will exceed the strength or the ill strength or the pressure that that the host crystal chore which stand and that is the reason why what happens some phenomena which takes place, which is we call as a inclusion decrepitates or decapitation is the total loss of the contact, it does not agree period, but it actually get leaked means the inclusion, because the thermal coefficient of thermal expansion is quite high and we are conducting the experiment at atmospheric pressure room normal pressure condition.

So, the pressure, then we always a differential pressure that is being exerted on the wall of the inclusion and that we exceed the yield strength. So, what happens here is exactly what happens if the content of the inclusion will be getting leaked. A small portion of the content of the inclusion will get leak and then again get sealed with in the very fairy of the very nearby to the host to the parent inclusion.

So, again when we decrease the when you are doing that recycling cycling of the temperature increase in lowering and increase of the temperature. We will find that the original inclusion as you could compared here the size of the vapor bubble has is become higher here because of the fact that the content has have been leaked and we will see a satellite inclusion, which is very much nearby and we might sometimes for have what it might happen that instead of just the leakage to form a very single satellite inclusion, it might also form a number of such small satellite inclusions and the parent inclusion which you can see.

So, these are the once its advised of course, will be getting to the this topic of how the inclusions are affected, when they are subjected to conditions which are different from their isochoric path of revolution details of it will look at it, but for the timing during routing thermometry its always expected that we should avoid taking measurements on such inclusions because of the fact that we may.

So, what will happen is that, why we will avoid the reason is very simple that if we take a temperature of homogenization for this inclusion, which is a, which as a result and which are earlier leaked then the temperature of homogeneous and that I will be achieving at the second stage will be higher than what was the actual original temperature of homogenization.

So, many a times when the some abnormally high values of temperature of homogenization are observed in sometime suspected that whether we are taking measurement of the homogenization experiment we are doing on an inclusion will possibly might have been early leaked. So, if we look at it carefully then presence of such kind of satellite inclusion will always give us a very clear cut indication that it was leaked earlier such kind of leakage of the inclusion also could have happened in nature itself when the rock was not exposed to the surface what was subjected to some perturbation after the inclusions were entrapped in the host mineral, which is very expected as we will be discussing such cases later.

So, in such kind situation keeps somehow we miss this clue still take the temperature of homogenization of this inclusion, which were earlier leaked the only problem that will be phasing is that will get higher temperature homogenization means the temperature homogenization, which would be in a way incorrect, there are many such.

So, now, here in this particular context the inclusion which are like pure carbonic inclusion where the dP by dT slope in much shallow and even if considering the fact that inclusion which is less than if that inclusion is overheated the chances of that particular inclusion leaking will be less compared to an inclusion where the density is high, because there they dP by that dT slope is high and then the other aspect is that it is also suggested from very elaborate study conducted by when you the exports that the chances of the leakage of these inclusions will always be higher for inclusion which are larger, means the inclusion which are of the order of 30, 40 microns in the maximum dimension.

If those inclusions are overheated, which all because the surface area is more and the pressure that is exerted on the inclusion wall it might be able to it, it might not be able to withstand whereas, these smaller inclusions will always escape or the transits of leakage of inclusions, which are smaller than a particular value will be always survival of those inclusions are, but higher.

So, but on the contrary there are situations that we always advise that because of certain regions, which will be discussing later that it is always the reliability of the microthermometry experiment is also better if the inclusion is larger than a certain value say for example, generally we are advised at do not subject inclusion to microthermometric experiments if it is less than 5 micron in and its maximum dimension, we will come back to the region 5.

So, for the timing to conclude there could be many aspects on which there will be lots of curiosity is lots of questions regarding the microthermometric experiments and the behaviour of the inclusion response of these inclusions to heating freezing cycles, but within this time frame these are some of the practical tips that would be offered and we will continue discussing on this in the next class.

Thank you.