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

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## Lecture - 18
## Microthermometry of Aqueous-Carbonic Inclusion

Welcome to today's lecture. We shall continue our discussion on the response of aqueous-carbonic inclusions to heating frizzing cycles. These inclusions are present in a typical triphase; that is a liquid aqueous liquid, carbonic liquid and carbonic vapour or in biphase like a like the 2 liquid carbonic liquid and aqueous liquid with a vapour phase nucleating at a temperature lower than the room temperature.

And we have (Refer Time: 00:52) through the response of these type of inclusions to frizzing and subsequent warming up these inclusions to record a phase changes and as we discussed in the last class. The melting of the solid carbon dioxide and the partial homogenization of the carbonic component to either to vapour phase or to liquid phase are very easy to record and these changes are very well observable under the microscope while doing experiments in a heating frizzing stage.

And total homogenization of such inclusions to either to the carbonic liquid or to aqueous liquid is also observable as and when it actually is achieved without effective without the crepitating the inclusion. Because we know that with gradual increasing mutual solubility between carbon dioxide and the aqueous component, the as we are heating the inclusion more and more internal pressure is exited on the inclusion walls.

And depending on the size of the inclusion, the inclusion if they are of more that the larger size inclusions and they are very likely to decrepitated or burst with the loss of the content. And those inclusions just lost and we cannot make any further observations on them. So, the only tricky affair about these inclusions and their thermometric response is the formation of these clathrate phase.

And the melting of the clathrate phase which has to be precisely recorded and there it most of the times it becomes a little problematic, because the practical tips that we the try to give in the last class that when we see that the meniscus between the 2 liquid that the carbonic liquid and the aqueous liquid become distinct.

And when the boundary is actually defuse because formation of this carbon dioxide clathrate and many a times it so happens that the bit of a metsibility and the clathrate melting is also observed. So, only on those cases where the clathrate melting is well recorded with different visibility, such data can only be accepted.

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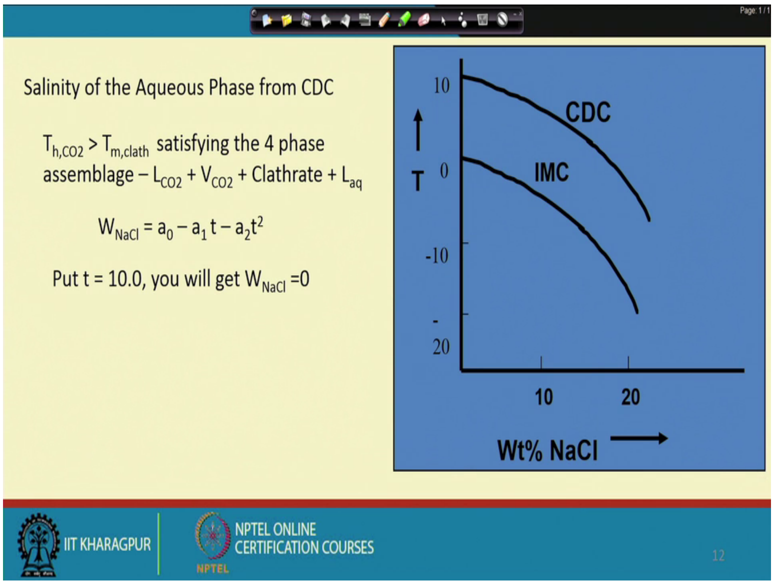

Salinity of the Aqueous Phase from CDC

$T_{h,CO2} > T_{m,clath}$ satisfying the 4 phase assemblage – $L_{CO2} + V_{CO2}$ + Clathrate + $L_{aq}$

$W_{NaCl} = a_0 - a_1 t - a_2 t^2$

Put t = 10.0, you will get $W_{NaCl} = 0$

And if we look at the diagram again which what we discussed. That this is the these 2 curves they represent the depression in the dissolution temperature of the carbon dioxide clathrate compare to the ice melting curve both of which get depressed when the aqueous liquid is charged with electrolytes a variable concentration. Here we are showing the aqueous liquid is from 0 weight percent NaCl to any higher. And such kind of curves can be can be approximated with equations.

Like the one which is a second order equation in the temperature dissolution of clathrate. And if we recall such melting temperature, such kind of equations will be valid for situations where the temperature of partial homogenization of the carbonic phase is greater than that of the temperature of dissolution of clathrate.

Means, the temperature of partial homogenization has to be at temperature above 10 degree Celsius. Corresponding to the pure aqueous liquid which will make the clathrate melt at exactly 10 degree Celsius and then we have to adopt separate set of equations if the temperature of homo partial homogenization of the carbonic component takes place before the temperature of dissolution of clathrate.

So, temperature so, in that case it will not corresponding to that 4 phase the condition. And there is separate sets of equations have been devised in both liquid phase as well as vapour phase homogenization they are available in the literature. We will see the equations later on. But there in any case function of the temperature of dissolution of the clathrate and again similar kind of with the fit parameters.

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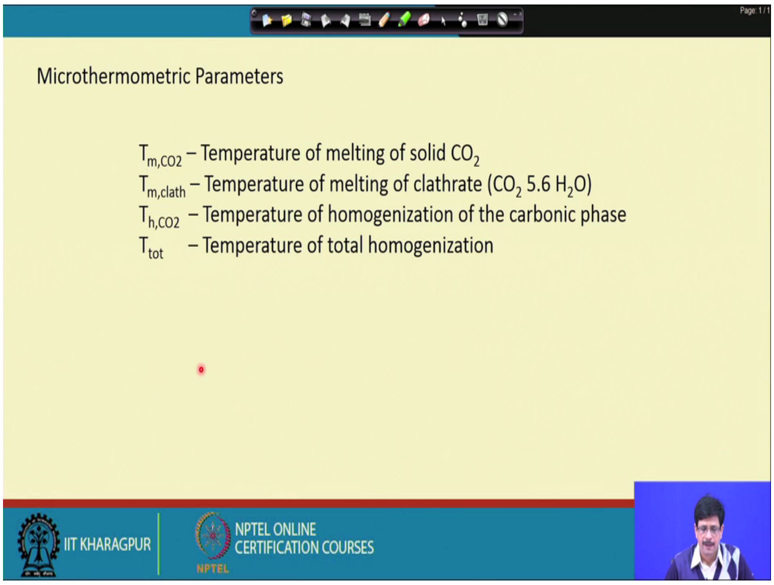

Microthermometric Parameters

$T_{m,CO2}$ – Temperature of melting of solid $CO_2$
$T_{m,clath}$ – Temperature of melting of clathrate ($CO_2$ 5.6 $H_2O$)
$T_{h,CO2}$ – Temperature of homogenization of the carbonic phase
$T_{tot}$ – Temperature of total homogenization

So, we have to summarise the microthermomtric parameters that we are actually from the aqueouslic carbonic inclusions is that temperature of melting of carbon dioxide; which happens at minus 56.6 if the carbon dioxide is pure. In such in kind of situations also the carbonic liquid could be having the variable concentrations of methane. In those inclusions also we can expect the carbon dioxide melting to be taking place at temperatures below minus 56.6.

The temperature of melting of clathrate it can happen any anywhere between 10 degrees Celsius to minus 20. Temperature of partial homogenization of carbon dioxide it can also happen at temperature less than or equal to 31.1. And it can be at any lower temperature depending. So, that will only indicate the density of the carbonic component, in the aqueous mixed carbonic inclusions and a temperature of total homogenization.

So, as before as it is done to the other the inclusion types like the aqueous biphase or aqueous poly phase or the pure carbonic inclusion. So, these inclusions also we need to determine the density and the isochore construction of the isochore. In the previous cases in the pure carbonic and the aqueous inclusions we have such kind of readily available regression equations.

Where we can put the value of the temperature or the celerity, and then get the density or in case of the pure carbonic inclusion we get the temperature of visualization of the carbon dioxide liquid. Or giving input and the methane variable methane concentration, and we can calculate the density; however, these situations we do not have such kind of very straight forward equations in which we could put the values and you can get the density.

Because here the density is the molar volume is a complex function of temperature reassure and composition. The composition here in this case is actually defined by the composition of the carbonic component even if it happens to be pure then the total concentration of the carbon dioxide in terms of X CO 2 of the fluid. And also the weight percent NaCl equivalent of the aqueous component so, that is why the situation is a little bit a indirect in the in case of the aqueous carbonic inclusions.

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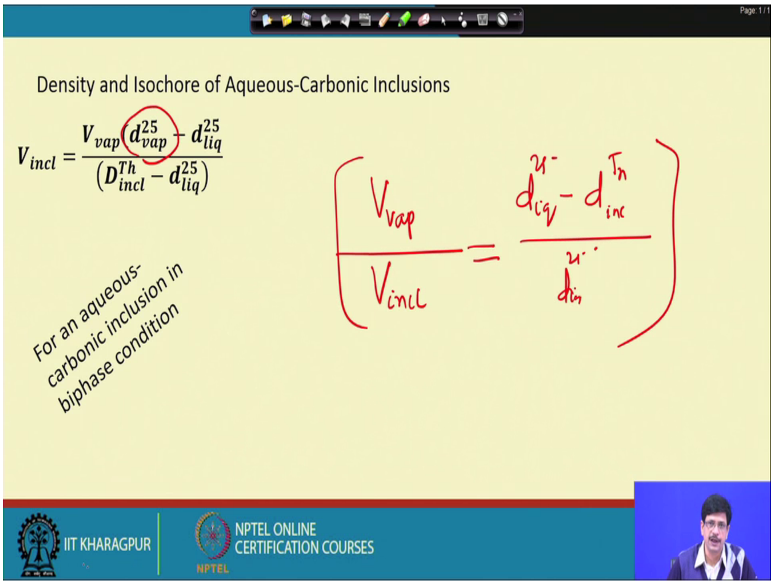

Density and Isochore of Aqueous-Carbonic Inclusions

$$V_{incl} = \frac{V_{vap}(d_{vap}^{25} - d_{liq}^{25})}{(D_{incl}^{Th} - d_{liq}^{25})}$$

For an aqueous-carbonic inclusion in biphase condition

$$\left(\frac{V_{vap}}{V_{incl}} = \frac{d_{liq}^{25} - d_{inc}^{Th}}{d_{in}^{25}}\right)$$

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So, we will in this class we will try to discuss a little bit about the methodology which is adopted from workers in the field of fluid inclusions and also some additional input in house. If I recall in the situation of an aqueous biphase inclusion so, last variance considerations and density of the inclusion at temperature of homogenization and a density of a liquid aqueous liquid at a reference to temperature let us say 25 degree Celsius.

Using that we use to calculate something which is the vapour by vapour plus liquid; we use to calculate the volume of the vapour divided by the total volume. So, volume of the inclusion which is the volume of the vapour plus the liquid, and we neglect by neglecting the density of the vapour phase at 25 degree Celsius. We rearrange this equation and we got this value as a function of the density of the inclusion at the density of the liquid at 25 degree centigrade, minus the density of the inclusion at temperature of homogenization divided by the density of liquid at 25 degree Celsius.

So, by this the ratio that we get that we can see at the V by V plus l of the volume fraction of the vapour, which sometimes is an important parameter even not getting the different modes of homogenization. But we can see how the degree of fill of the vapour plus liquid ratio what changing.

Now we can use the same equation to a situation where there is if we consider the aqueous carbonic inclusion and its biphase condition let say this is the aqueous liquid, and this is the carbonic liquid, considering the situation where the vapour phases already homogenized.

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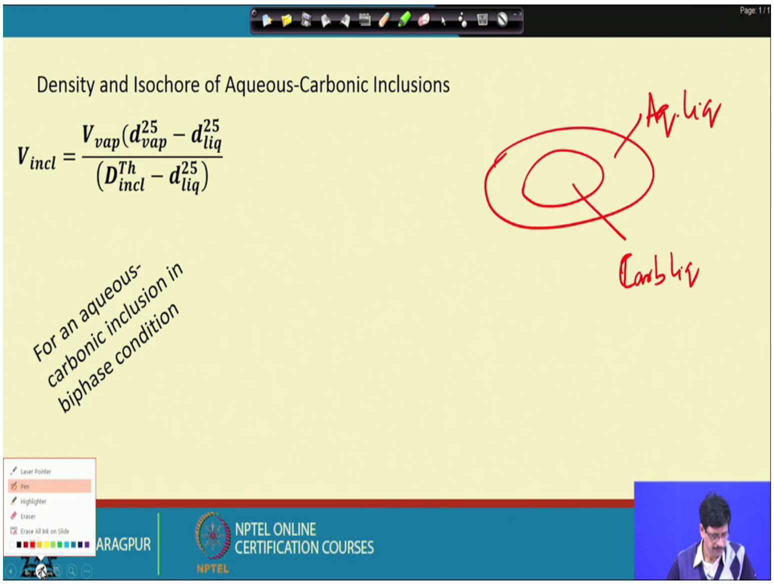

Density and Isochore of Aqueous-Carbonic Inclusions

$$V_{incl} = \frac{V_{vap}\left(d_{vap}^{25} - d_{liq}^{25}\right)}{\left(D_{incl}^{Th} - d_{liq}^{25}\right)}$$

For an aqueous-carbonic inclusion in biphase condition

So, this could happen at any temperature and near about a reference temperature close to room temperature. So, this situation we can also apply such kind of a massmelons consideration. And can have the situation pertaining to a to an aqueous carbonic inclusion in it is 2 phase condition.

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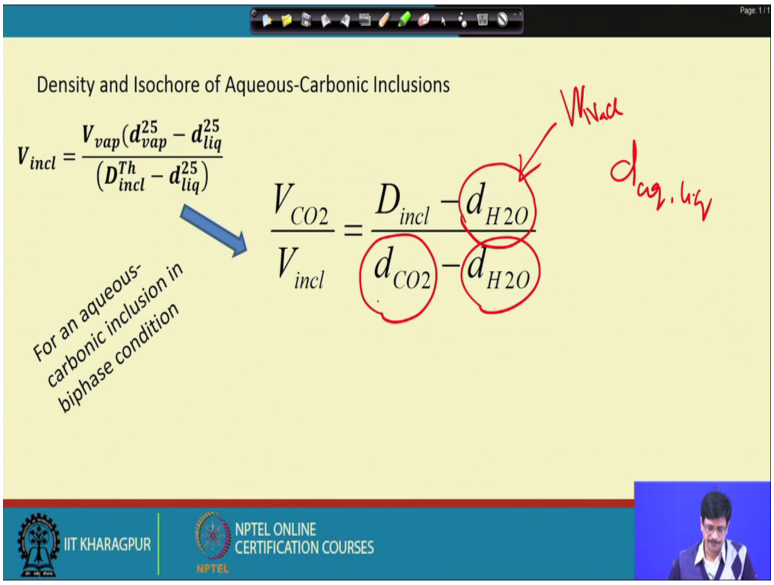

Density and Isochore of Aqueous-Carbonic Inclusions

$$V_{incl} = \frac{V_{vap}(d_{vap}^{25} - d_{liq}^{25})}{(D_{incl}^{Th} - d_{liq}^{25})}$$

For an aqueous-carbonic inclusion in biphase condition

$$\frac{V_{CO2}}{V_{incl}} = \frac{D_{incl} - d_{H2O}}{d_{CO2} - d_{H2O}}$$

Unlike the aqueous inclusion scenario, here we can say that the carbonic phase is representing what was the rapper phase in case of an aqueous biphase inclusion. And the liquid of this liquid phase was actually the liquid aqueous liquid also here in this case the dh what will aqueous liquid. And the density of the inclusion is same as the density of the inclusion at total homogenization. So here since we cannot neglect the density of the carbonic component at room temperature so, we have to take into consideration and the equation could be rearranged in this manner.

So, here what are the parameters here that this is the density of the inclusion which we do not know right now. And this is the one which we the exercise before us is actually to calculate the density of the inclusion at the temperature of total homogenization; the density of the aqueous phase at the d H 2 O whatever written here this density is the density of the aqueous liquid.

We can always consider that at the temperature at which we obtain a 2 phase condition. Anything between 31.2 in a lower temperature and so that we can apply this particular equation and this kind of these kind of formalism the methodology essentially does not involved any visual estimation of any of this phases like the carbonic phase or the aqueous phase.

So, this value this density of the aqueous liquid can be calculated from standard formulations when we know the W NaCl in terms of weight percent from the dissolution of the clathrate. So, the same term here in the denominator. And the density of the carbonic component is also obtained from the temperature of partial homogenization by usual equations which we discussed before. So now, the job at hand is to calculate the density of the inclusion at the temperature of homogenization. And this is the ratio which is given which is giving which will give us the volume fraction at the carbonic component.

So, this volume fraction of the carbonic component can be converted into a mass faction and intern the mole fraction if we do some kind of a normalization. Like, we can consider that let the inclusion be 100 ccn from that from the volume fraction.

So knowing the aqueous liquid density and then the mole fraction of the NaCl and H 2 O in the aqueous component and then do a normalization procedure so that this volume fraction can be converted into a mole fraction; which will be given in details in the calculations which will be provided to you and then handout.

So now, with this we do not know this parameter, and they one so to calculate to ultimately have a faction of the volume of the volume fraction of carbonic component, we will have to calculate the density of inclusion with the other 2 parameters known. This particular equation when it is putting this way, it actually corresponds to a 1 in situation in the fluid inclusion.

So, it can always this particular equation can always we checked for a consistency; that means, if we have the density of the this particular right hand side of the expression with this density of the total inclusion, and the density of the aqueous phase and the carbonic phase, then we can always go on refining this as we take different values of the different approximations on the mole fraction of carbon dioxide. But then use this particular equation as a cross check as to where there the both the sides are matching. So, which we will be discussing detail about the passes.

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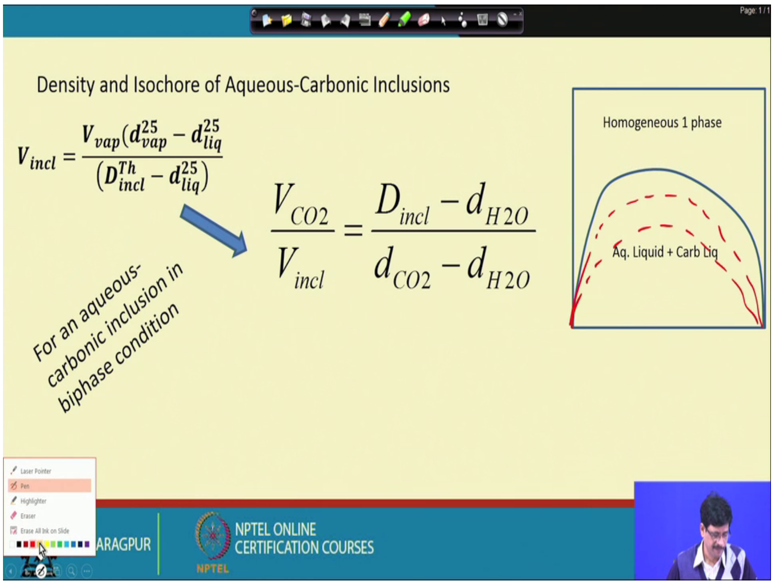

Density and Isochore of Aqueous-Carbonic Inclusions

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

For an aqueous-carbonic inclusion in biphase condition

$$\frac{V_{CO2}}{V_{incl}} = \frac{D_{incl} - d_{H2O}}{d_{CO2} - d_{H2O}}$$

So, here this is the phase diagram of the aqueous carbonic system. Here it is the H 2 O CO 2 this can be considered, then presenting CO 2 binary where the aqueous component has a fixed weight percent NaCl. So, we can have such kind of solvers, separating the 2 liquid region from a homogeneous 1 phase or 2 liquid phase region. Separating a homogenous 1 phase region also a similar way in which we use to see the pure H 2 O or CO 2 frame phase diagram. So, the situation that we are talking about is that our inclusion is would have been trapped at any temperature in this 1 phase region.

And with the decreasing temperature the inclusion as a post entrapment phase change got splitted up to 2 component that is aqueous component and carbonic component, and the aqueous component has some vapours and NaCl or other ellipsoid dissolved in it. As we discussed before such kind of (Refer Time: 16:51) are very much pressure and dependent.

We can have the homogenous 1 phase gradually expanding with higher and higher pressure this dot boundary actually goes down with expansion of the homogeneous 1 phase region, and the contraction of the 2 phase situation and the vice versa with decreasing pressure the immiscible regime which is defined by the presence of the 2 liquid expands at lower pressure.

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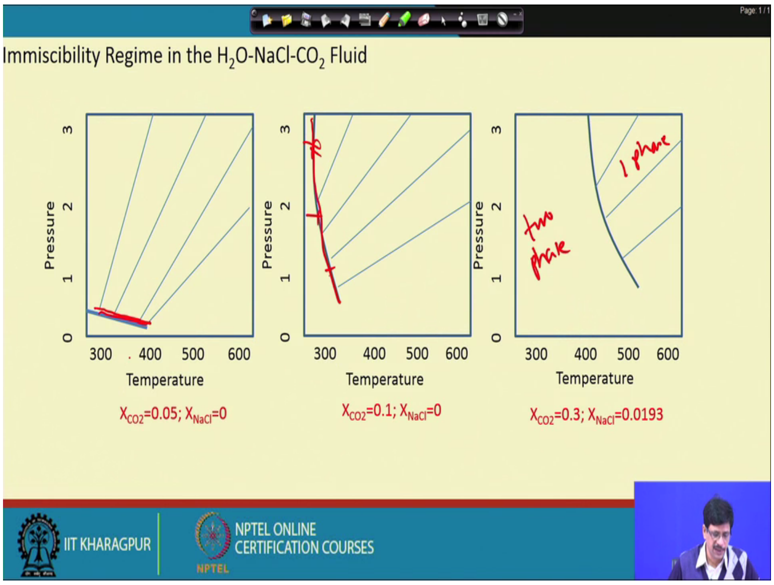

Immiscibility Regime in the $H_2O$-NaCl-$CO_2$ Fluid

$X_{CO2}$=0.05; $X_{NaCl}$=0

$X_{CO2}$=0.1; $X_{NaCl}$=0

$X_{CO2}$=0.3; $X_{NaCl}$=0.0193

And so, at different pressure so, these phase diagrams which are also taken from literature they representing the same phase like what we did for the pure water or the water NaCl system. In this case, we can also have them for the pseudo binaries in the X 2 NaCl CO 2 system considering the compositions to be at fixed carbon dioxide mole fractions and fixed NaCl mole fraction.

And have the phase diagram drawn showing the 1 phase and the 2 phase conditions. Here below this particular curve is the 2 phase 2 liquid stable condition of the immiscible regime. And in this region it is the miscible regime. And as you could see here and these are these are essentially not critical curves, but these are curves; which will be drawn at or the different taking the consideration that the 2 phase boundary at different pressures and different compositions in terms of NaCl weight percent and X CO 2.

So, here we could just the what is evident from here is there compare if we compare these 2 diagrams here the it is NaCl free the X NaCl is equal to 0 in both the cases whereas the carbon dioxide concentration is increased from 0.05 to 0.1. And we see that the 2 phase region is kind of expanded and it has an kind of an inverse relationship; that means, with increasing temperature we are getting decreased with the decreasing temperature we get higher and higher pressure at this curve becoming almost parallel the y axis.

And if we consider these 2 diagrams here the X CO 2 is higher from 0.1 to 0.3 and X NaCl is also from 0 to 0.193 may be corresponding to some 6 weight percent NaCl in the aqueous component. So, this divide the region into the 2 phase this is a 2 phase region. This is the 2 phase region and this is the 1 phase region.

And this thin lines are the isochors, this thin lines are the isochors and these isochors going from 1, 2, 3, 4 they represent these isochors of lower and lower density. And their dp by dt slope is also decreasing. And as per our understanding, the inclusion under consideration which is present as a mixed aqueous carbonic inclusion in it is biphase or triphase condition as we see them in room temperature. And by the assumption of homogeneous entrapment, which was entrapped at any pressure temperature condition in the 1 phase stability region. So, these are these are the trajectory of points of equal density and these isochors. So, the inclusions are going to follow. So, once we get the homogenization so, these boundaries either this or this or this, we will actually be corresponding to the conditions of homogenization. For example, when we say that inclusion is homogenizing a total homogenization; that means, it could be anywhere on this in this curve or anywhere on this curve, any point.

And that is that is the condition to the total homogenization condition. So, the total homogenization once we obtain the total homogenization condition. The inclusion is assumed follow and isochors depending on the density. And the same logic also holds here, that we need to have some independent consideration or pressure or temperature to ascertain the other or to do thermodiometry, which we see later.

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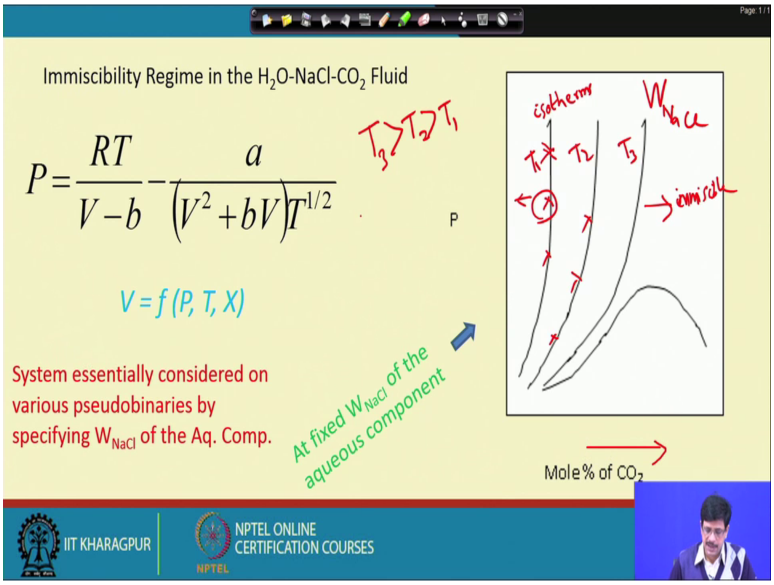

Immiscibility Regime in the $H_2O$-NaCl-$CO_2$ Fluid

$$P = \frac{RT}{V-b} - \frac{a}{\left(V^2+bV\right)T^{1/2}}$$

$T_3 > T_2 > T_1$

$V = f(P, T, X)$

System essentially considered on various pseudobinaries by specifying $W_{NaCl}$ of the Aq. Comp.

At fixed $W_{NaCl}$ of the aqueous component

Now, such diagrams what we have seen here is the since our molar volume is a function of pressure temperature and composition. So, we can only think off having such kind of the phase diagram with like the like the one shown here 2 of the composition variables are kept fixed or the composition is kept fixed so that we can prompt them on the PT diagram.

Such kind of diagrams also we can translate onto a pressure X CO 2 diagram. So, these in this pressure X CO 2 diagram these are the isotherms, these are the isotherms, and here the difference is that the on this pressure and X CO 2 where X CO 2 is increasing in this direction. Here the 1 phase region is one which is to the left of this diagram, and the 2 phase region is towards the right of the diagram. So, here this is the immiscible region and this is the region of 1 phase. And as such we see so this temperature if this is temperature T 1, this is T 2, this is T 3. Then T 3 is greater than T 2 is greater than T 1.

Say for example, this could be 250 degree Celsius, this could be 300 degree Celsius or this is 350 degree Celsius. So, these represent also the phase boundary separating the 1 phase from the 2 phase on a pressure X CO 2 diagram and similarly, when you are obtaining the total homogenization, the homogenization taking place corresponding to points anywhere on this 2 phase boundary.

Depending on and these kind of diagrams also have to be constructed at fixed W NaCl of the aqueous component as we know that we have a taken this phase diagram and a pressure and X CO 2 diagram; that means, we have to have a fixed temperature and fixed W NaCl. So, this individual curves represent the 2 phase the boundary between the immiscible and the miscible regime and; that means, the when we are obtaining the homogenization, total homogenization it corresponds to the value of unique combination of pressure and temperature pressure and X CO 2.

For example, if suppose if our NaCl is 6 weight percent, and the temperature of total homogenization is 250 degree Celsius, then the total the inclusion the homogenization condition could be could be anywhere on this P X CO 2 curve. So, we need to concern exactly where it is? Whether it is here or suppose for example, we get a point reach a point here, then we know that it is actually falling on this particular isotherm.

So either the case the phase diagram that we discussed on the pressure temperature phase diagram or on this particular phase diagram. When we try to calculate the density so, density means which is related with the molar volume. So, is definitely the situation is that the molar volume is a function of pressure temperature and composition.

Here what we do not know X CO 2. We know the X NaCl in the aqueous component. And we do not know the X CO 2. So, if we want to so, for example, if we want to take help of this kind of a equation as we all know that these equations are essentially they all go to real gas. And the inclusions that that we are considering and not gases, but we there in their liquid state. Still these equations can be used if we have a combination of theoretical considerations and empirical fitting of the experimental data, we can combine and kind of a fit semi empirical equations which would be applicable to the liquid state also, depending on the temperature and pressure ranges of the experimental data that is available.

So, this is all the same redlines curved equation which we will be using here, to calculate the density. We see how we do that. So, this system is essentially considered on various pseudo binaries by specifying with W NaCl of the aqueous component. And you see how we proceed for our calculation of the density of the total inclusion.

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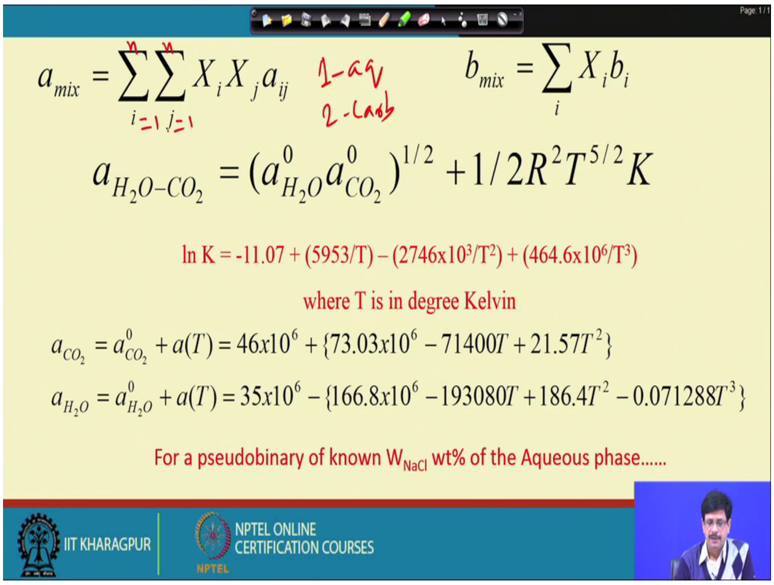

$$a_{mix} = \sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j a_{ij} \qquad b_{mix} = \sum_{i} X_i b_i$$

1-aq
2-Carb

$$a_{H_2O-CO_2} = (a^0_{H_2O} a^0_{CO_2})^{1/2} + 1/2R^2T^{5/2}K$$

$\ln K = -11.07 + (5953/T) - (2746 x 10^3/T^2) + (464.6 x 10^6/T^3)$

where T is in degree Kelvin

$$a_{CO_2} = a^0_{CO_2} + a(T) = 46x10^6 + \{73.03x10^6 - 71400T + 21.57T^2\}$$

$$a_{H_2O} = a^0_{H_2O} + a(T) = 35x10^6 - \{166.8x10^6 - 193080T + 186.4T^2 - 0.071288T^3\}$$

For a pseudobinary of known $W_{NaCl}$ wt% of the Aqueous phase......

That is, the total molar volume the total density of the aqueous inclusion of the mixed aqueous inclusion at the temperature of total homogenization. So, if you are using the modified redlines curved equation to start with a redlines curved equation. So, we have to so, here is essential is a mixture it is a pseudo binary, it is a mixture, and in this our mixture terms the a and b the pressure correction term and the volume correction terms the can be expanded in a form that this mixture is summation over i and summation over j.

So, here actually i should be varying from 1 to n and similarly also j varying from 1 to n. And this can be expanded as; so, here if we are considering depending on the system that you are choosing here. So, if since we are considering a pseudo binary. So, it means we will have 2 or components. So, we will take i n is equal to 2. So, here I will be varying from 1 to 2. And so, this kind of a equations could be expanded with terms which will be coming like.

So, here if we take 1 for the aqueous component and the 2 for let us say carbonic component. So, in this equation we will have the when both i and j are equal to 1, you will have the X 1 square. I can write it here.

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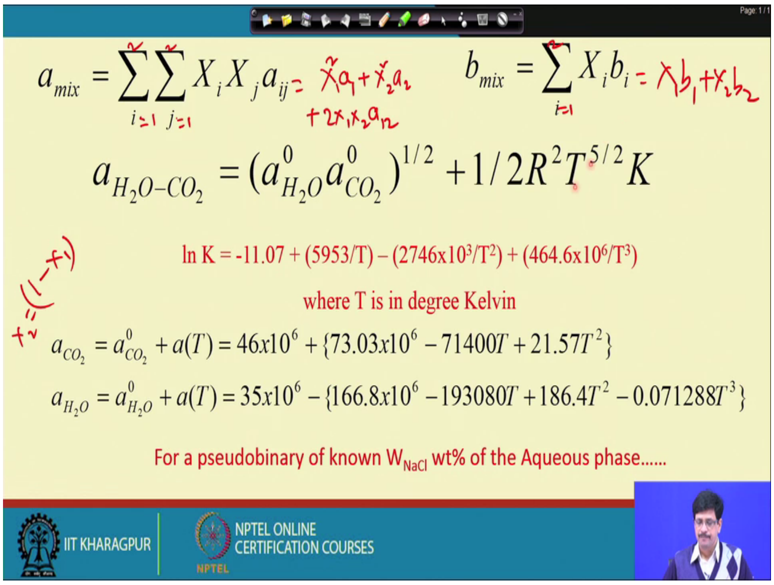

$$a_{mix} = \sum_{i=1}^{2}\sum_{j=1}^{2} X_i X_j a_{ij} = x_1^2 a_1 + x_2^2 a_2 + 2x_1x_2a_{12} \qquad b_{mix} = \sum_{i=1}^{2} X_i b_i = x_1 b_1 + x_2 b_2$$

$$a_{H_2O-CO_2} = (a^0_{H_2O} a^0_{CO_2})^{1/2} + 1/2R^2T^{5/2}K$$

$$x_2 = (1 - x_1)$$

$\ln K = -11.07 + (5953/T) - (2746x10^3/T^2) + (464.6x10^6/T^3)$

where T is in degree Kelvin

$$a_{CO_2} = a^0_{CO_2} + a(T) = 46x10^6 + \{73.03x10^6 - 71400T + 21.57T^2\}$$

$$a_{H_2O} = a^0_{H_2O} + a(T) = 35x10^6 - \{166.8x10^6 - 193080T + 186.4T^2 - 0.071288T^3\}$$

For a pseudobinary of known $W_{NaCl}$ wt% of the Aqueous phase......

So, this is i equals to 1 to 2, j equals to 1 to 2. So, this becomes X 1 square a 1 plus X 2 square a 2, plus 2 X 1 X 2 into a 1 2. So, that means, we are getting the term so, since it is a binary, in any case any of the compositional terms like the mole faction could be replaced by 1 minus the other.

That means, X 2 could be always be putting as 1 minus X 1 and here as we know. So, this is the; suppose the mole fraction of the aqueous component, this is the mole fraction of the carbonic component. And this will be the a of H 2 O and this will be a for the aqueous component, and this will be a for the carbonic component. For the time being we will consider the system to be methane free.

So, a 2 will be considered corresponding to the pure term, these are correction term for pure carbon pure carbon dioxide. And here the pressure correction term for the aqueous component as we know it is not pure it is charge with pseudo employed, but that can be handled. And then the similarly the b term also it is i equals to 1 to 2. So, here it will be simply as X 1 b 1 plus X 2 b 2.

Means here the b of carbon dioxide which is known, as we know that they the values are available in literature as pressure term and temperature independent and the b for aqueous can be also we calculated. So, we will continue discussing on this particular method of determination of density and the isochore for the mixed aqueous carbonic inclusion from available information on the partial homogenization of the carbonic phase.

The W NaCl of the aqueous component and having a total homogenization which has been they produced and without the inclusion actually leaking. And doing the homogenization experiment so that we homogenize the carbonic in the aqueous carbonic inclusion and also when we cool them. They come back to their original position, original configuration. So, we will continue discussing in the next class.

Thank you.