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

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Lecture – 19

Microthermometry of Aqueous-Carbonic Inclusion (Contd.)

Welcome to today’s lecture. We will continue with our discussion on the methodology for estimation of a density and ISO in the construction of isochore for the aqueous carbonic inclusions from their total homogenization, the weight percent Na Cl content in the aqueous component, density of the carbonic component obtained from the partial homogenization temperature. We were discussing about the about using the modified or the Redlich Kwong equation which is essentially a correction to the ideal gas equation.

And, since we are handling with liquid, but these equations are formulated in such a way from experimental data and from theoretical consideration of interaction of this molecules that we can still use them in case of the liquids. And the only interesting thing about this particular mixture the particular fluid mixture is that the water which is a polar molecule carbon dioxide is non-polar.

So, it is it actually involves interaction of the polar and nonpolar molecule like carbon dioxide and water and that is basically the reason why we have a substantial non-ideality in the system and immiscibility, broad immiscibility field.

So, the formulation will any case be applicable within the limitations of immiscibility in the region and this also as we have a discussing this equation the formulation last class.

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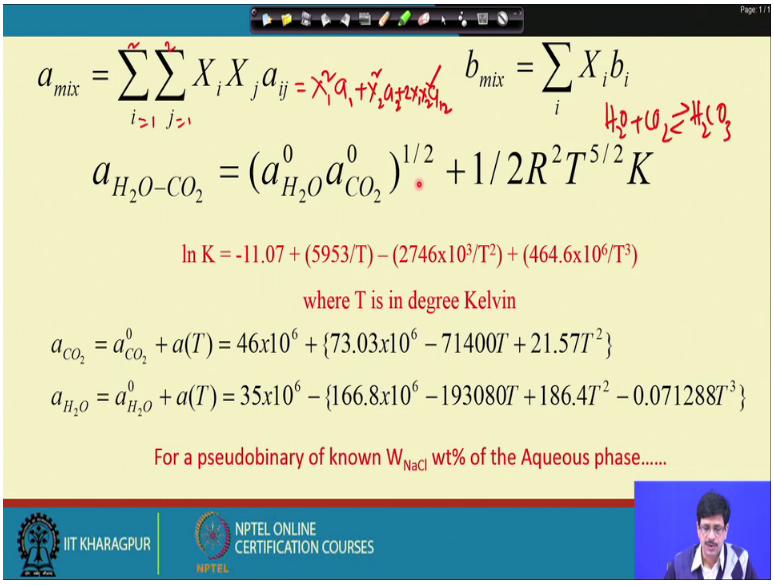

$$a_{mix} = \sum_{i=1}^{2}\sum_{j=1}^{2} X_i X_j a_{ij} = X_1^2 a_1 + X_2^2 a_2 + 2X_1X_2 a_{12} \qquad b_{mix} = \sum_i X_i b_i$$

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

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

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

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, here it is as we know that, this is I equals to 1 to 2 and j equals to 1 to 2 and this is actually expanded as X 1 square a 1 plus X 2 square a 2 plus 2 X 1 X 2 into a 1 2.

So, what we get here? We get the terms which are the pressure correction term the we can call it is a first non-ideal term. We can call b is a second non-ideal term. So, when a first non-ideal term we can get for the water as well as for carbon dioxide and for carbon dioxide considering it to be pure as methane free these values are like is shown here. They can be calculated.

So, when we, so now, here for the first 2 terms, we are using the pure first non-ideal term. But, in the expression, we get that there is a cross term which is a 1 2 which is coming here; that means, it is kind of a interaction term between these 2 components; water and carbon dioxide.

So, this particular component is very easily could I could possibly have been very easily worked out by taking the product of the pure the intercept value that the a 0 of one of the aqueous component and the a 0 of the carbonic component and take a square root. And there could possibly, we have come from that would have taken care of to give the cost for the first non-ideal parameter which is a, but, the fact that these 2 species water and carbon dioxide, they do react to give a product.

So, this if we put H 2 O plus CO 2 H 2 CO 3, because of that, their property, their P V T X relationship will be reflected by the by the degree to which this carbonic acid molecule will be formed.

So, this carbonic acid molecule in order to take care of that, we consider this reaction this H 2 O plus CO 2 H 2 CO 3 and the equilibrium constant. This particular reaction will have an equilibrium constant at and will be temperature dependent. So, this is kind of a equation which will which has been empirically fit as taking as the natural logarithm of the equilibrium constant as a function of temperature where the temperature is degree kelvin.

So, this formulations actually some of them will be like the situation here like the first non-ideal term that is a terms from carbon dioxide and water are tether is parameters into the functions of T, where the T is in degree Celsius and here we are what we are taking about the first component means, the aqueous component and the first non-ideal term of this a for H 2 O which is also a function of temperature.

Now, we are considering a pseudo binary. So, this water is actually not a pure water this is charge with sodium chloride. So, this a of the first non-ideal term for water needs to be refined for taking into by taking into consideration the W Na Cl which is also been done. So, taking a simple case here of a water and carbon dioxide. Let us take a situation where Na Cl is 0.

So, this will be the pure a term for water pure a term for a carbon dioxide and they are expanded in this way and this cross term which is the by the interaction of the molecules of H 2 O CO 2 which is put is a H 2 O CO 2 is the square root of the product of the a 0 H 2 O and a 0 CO 2 term plus a term containing the equilibrium constant R square T to the power of 5 by 2 K where a and K is a function of temperature.

So, the a purpose of giving you this a this little bit even outline of the method is that this temperature when we are considering or this temperature, this temperatures are all can be taken to be that temperature of total homogenization. Because, that is the temperature at which we are trying to calculate the molar volume which will be exactly on the phase boundary where the homogenization is taken place. The system has actually become homogeneous. So, there we want to calculate the molar volume or the density.

So, in all this formulations, this T in kelvin or this T in degree Celsius or all temperature of total homogenization. So, it can it just gives as an idea that the a amount of computation that we or the calculations that we do. Since these are many coefficient type of regression equation and they need to the demand that we use a computer and use a computer course. So, that we can possess data of many inclusions and their manual conclusion will be very cumbersome and time consuming.

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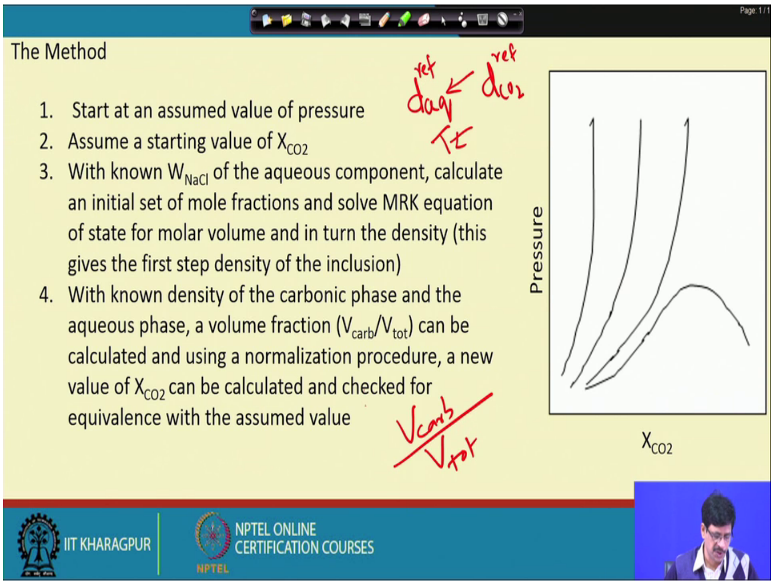

The Method

1. Start at an assumed value of pressure
2. Assume a starting value of X_{CO2}
3. With known W_{NaCl} of the aqueous component, calculate an initial set of mole fractions and solve MRK equation of state for molar volume and in turn the density (this gives the first step density of the inclusion)
4. With known density of the carbonic phase and the aqueous phase, a volume fraction (V_{carb}/V_{tot}) can be calculated and using a normalization procedure, a new value of X_{CO2} can be calculated and checked for equivalence with the assumed value

$d_{aq}^{ref} \leftarrow d_{CO_2}^{ref}$

T_t

$\frac{V_{carb}}{V_{tot}}$

Now, as discussed before the Redlich Kwong equation when we are expanding the non-ideal term of a and b is a regression equations of temperature and weight percent Na Cl when it is when we are considering a pseudo binary. So, there that equation can be expanded or can be re written in a in a polynomial of molar volume is a will be a third degree polynomial considering containing term of V cube V square V n are the constant the coefficient terms will be involving pressure temperature and the a and b parameter like here.

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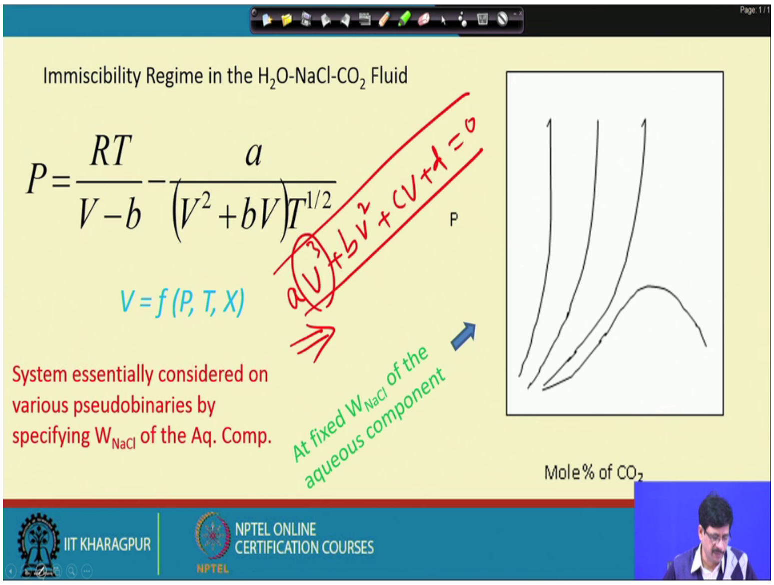

Immiscibility Regime in the H_2O-NaCl-CO_2 Fluid

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

$aV^3 + bV^2 + cV + d = 0$

$\Rightarrow$

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

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

At fixed W_{NaCl} of the aqueous component

So, since we have if we take the temperature and the R value is known and if we want to organize, re write this equation as a cubic equation in V. Then, it will be something like a into V cube plus b into V square plus C into V plus the equals to 0. We can put in this kind of a form and once if we put in this kind of a form, we will be in a position to solve this particular transcendental equation to solve for molar volume.

But here, there is a little bit of the trick involve because, this is a cubic equation in V. It will by conventional method of solution of this transcendental equation will result in 3 values of polar volume depending on what this situation is. So, here we use a judicious a numerical method. So, that we will be getting the route of this particular equation within a corresponding, within particular a constant, so that we get only one acceptable value because, as we know that 3 volumes for the 3 molar volumes for the particular fluid mixture is not acceptable.

If the happen to the come out to be always positive integers. Whereas, one it will only have a one value which will be acceptable. So, if device appropriate numerical method in which we can solve we find out the route of this particular equation which will be the molar volume of the fluid mixture. So, what essentially as far as again I am coming back to this particular diagram. So, what essentially we do?

So, when we start, we have the known parameter is temperature and only the W Na Cl of the aqueous component.

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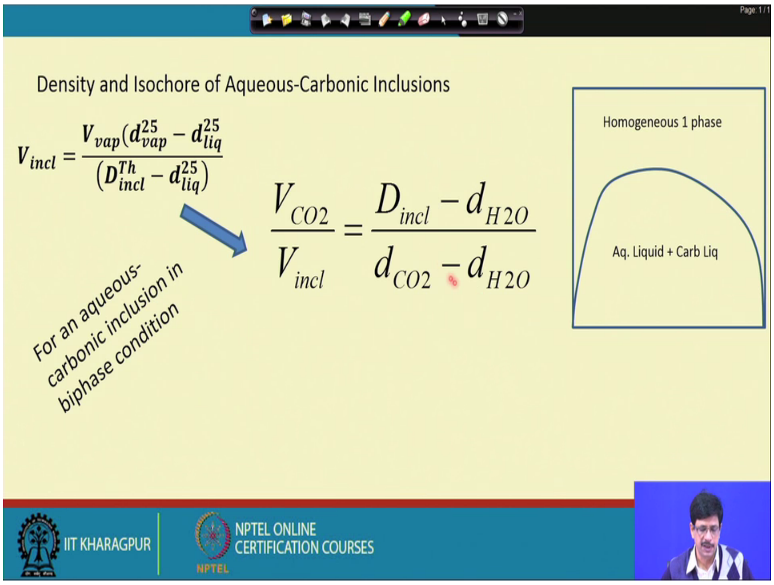

Density and Isochore of Aqueous-Carbonic Inclusions

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

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

For an aqueous-carbonic inclusion in biphase condition

And then, as we as said before we are also going to use this particular equation for calculation of the volume fraction of carbon dioxide. So, what we do? So, here; that means, when we say that the fluid mixture at the homogenization condition, we will be falling on this isotherms on the P X CO 2 pair.

So, that means, if we take certain assumptions of the carbon dioxide X CO 2 in the system and then calculate the mole fractions of the other parameters like X or if you have considering only a pure carbon dioxide water system X H 2 O and h CO 2 or if we are taking a pseudo binary with some fixed weight percent Na Cl, then we can also calculating the X Na Cl and X H 2 O based on a initial gas or initial assumption of the mole fraction of carbon dioxide

So, the method in brief which will be also be elaborated in and out that we start with an assumed value of a pressure. Let us say that, I have a inclusion has given as given a total homogenization temperature of 300 degree Celsius. So now, what we do? We start with an assumed value of pressure. In this, pressure could be a judicious assumption.

It could be anything between 500 to 2000. But, we start with an initial value the lowest value because, we can see here that it is if we kind of take some combinations of pressure and X CO 2, then we should be able to heat on one point on this salvos which will which will actually give us the correct value or the consistent pressure and X CO 2 value which will be falling on the correct isotherm.

But this exercise also does involve that once we have the temperature of homogenization, we could be in a position to construct such kind of an isotherm taking different combinations of the P X CO 2 which is possible. Now, we start with an assumed value of pressure and then, with that pressure, we also first start taking an assumed value of mole fraction of carbon dioxide. Let it this with a let it this from a very low value of 0.001 or 0.005 or even we can consider such kind of a diagram and can also choose a volume of X CO 2.

And now, with a known W Na Cl of the aqueous component, we are calculating a set of mole fractions and we are solving the modified Redlich Kwong equation from molar volume which is which looks quite straight forward. Now, once we get the molar volume, we can get the convert this molar volume value to density volume. Because, we have the molecular weight of this constituent components and the mole fractions and from that this molar volume in terms of cc could be cc per mole can be converted to a density volume of grams per cc.

So that, in that expression, becomes a density of the inclusions and already we have from standard formulation the density. So, what are the things which actually remain fixed in this condition? The parameters which remain fixed is do not change is the density of the aqueous liquid at the reference temperature that we have chosen. The reference temperature essentially will be corresponding to a homogeneous condition for the carbonic component. So, that particular reference temperature this aqueous liquid density is known.

And the temperature of homogenization is also one which we know. We always use that temperature because, that that we are not varying and then once we know the density. So, we know the density of the aqueous component, we know the density. Here also, the density of this CO 2 component the d aqueous is known d is known and D of CO 2 also at that reference temperature is also known.

So now, what we can do is, with our assume value of pressure and X CO 2, we calculate the first term of the equation which we propose there. It is the V of carbonic by the total V total which actually is given as the volume fraction. And as I said, this particular volume fraction can be converted into mole fraction by using a appropriate normalization procedure.

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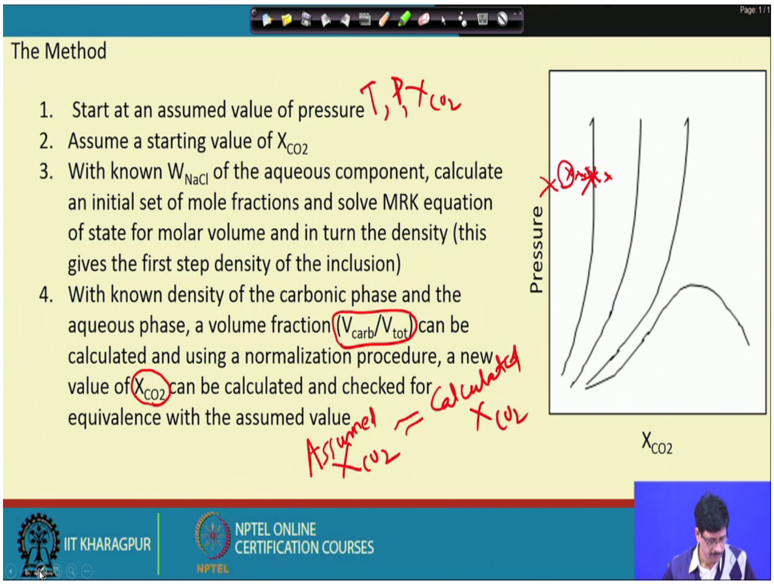

The Method

1. Start at an assumed value of pressure T, P, X_{CO_2}
2. Assume a starting value of X_{CO2}
3. With known W_{NaCl} of the aqueous component, calculate an initial set of mole fractions and solve MRK equation of state for molar volume and in turn the density (this gives the first step density of the inclusion)
4. With known density of the carbonic phase and the aqueous phase, a volume fraction (V_{carb}/V_{tot}) can be calculated and using a normalization procedure, a new value of X_{CO2} can be calculated and checked for equivalence with the assumed value

$$\text{Assumed } X_{CO_2} \approx \text{Calculated } X_{CO_2}$$

So now, with the known density of the carbonic phase and the aqueous phase and volume fraction V carb by V total which can be calculated and using the normalization procedure, a new value of X CO 2 can be calculated and checked for equivalence with assume value. For example, what exactly a mean by that that?

Suppose, we get, suppose you start with our X CO 2, we decided that we will take a particular value of pressure say, for example, a pressure corresponding to this point and it could be it could be here as well, could starting from the low pressure or any pressure that we can think of. Sometimes, when a computer when we are writing a routine calculation procedure, we might always put the pressure variation in a regular manner with the pressure range variation of a range of the pressure as well as with the carbon dioxide.

So, for example, if we start from a point something here and here and here and here and here, then for each for a each points, because that is not that is not actually corresponding to the correct isotherm, but then on this point we should be able to get an X CO 2 and that something calculation that we have done. But, that is X CO 2 will not be same is the X CO 2 that we have taken as an assumption. So, only on points corresponding to this talking it from the numerical point of view.

If we if we are matching the assumed value of X CO 2 and the calculated value of X CO 2 which comes from by using the equation of the mass balance with the densities of the different phases is related. So, here this is the point on the isotherm which is which only will be situation where our assumed value of X CO 2 or we can say that, you can call it assumed or can initial gas. So, this assumed value of X CO 2 would be equal to the calculated X CO 2.

The calculated X CO 2 will come from the fraction. The volume fraction that we get in each stage and then, here we know that we have this calculation procedure actually is converge and then the it has given as. So, with the temperature known, it is given as a consistent or a acceptable value of P and X CO 2 which will be falling on a correct isotherm. So, these are actually done by a by a by the procedure where we are comparing the X CO 2 value that we calculated and the X CO 2 value. That we have assumed in the subsequent stages.

So, as it looks like it might. So, happen that in a in a any particular chosen pressure, if we do this calculation, we might consume the entire range of initial gases of X CO 2 without getting any convergence and then, we have to choose another pressure. So, this is in a kind of a nested kind of a loop that we do the calculation. For any chosen particular value of pressure, we take the entire range of a X CO 2 initial gases and then check for equivalence of the assumed carbon dioxide mole fraction and the calculated carbon dioxide mole fraction.

And if we does not converge, then we move on to another pressure with a pressure increment. So, in a in a routine calculation procedure, what you could possibly do that X CO 2? We could chose ranges of various other pressure. Let us say, say from 500 or a say 200 bars to 2000 bars or 3000 bars and the X CO 2 from any of this the range, we can go from a 0.001 to 0.5 or 0.4 or 0.2 with an increment of 0.001. So, that only is making the calculation procedure only very intensive. But then, this is the only this is the way that it could be achieved ok.

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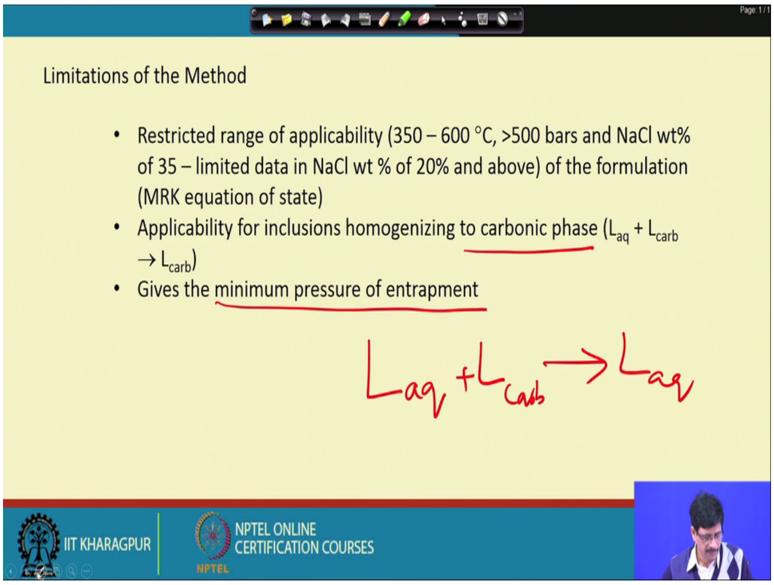

Limitations of the Method

- Restricted range of applicability (350 – 600 °C, >500 bars and NaCl wt% of 35 – limited data in NaCl wt % of 20% and above) of the formulation (MRK equation of state)
- Applicability for inclusions homogenizing to carbonic phase ($L_{aq} + L_{carb} \rightarrow L_{carb}$)
- Gives the minimum pressure of entrapment

$L_{aq} + L_{carb} \rightarrow L_{aq}$

So now, what the, so, this procedure is going to give us an acceptable value of the molar volume or in turn the density of the mixture fluid mixture which is a either a pure water plus carbon dioxide or it is a water charged with electrolyte and carbon dioxide. So, it is a representing the pseudo binary or the ternary and then we can.

So, once we know the molars volume, we can calculate the slope of the isochore by taking the dp by dt value or just calculate pressure at any other temperature any other temperature value and then get the isochore as shown from the series of diagram. So, the isochores could be plotted.

But then, we must also be aware of the limitations of this particular method. First of all, it is actually the semi empirical in nature. Some theoretical configurations and empirical fitting to observe a experimental data and in fact, this system, this Na Cl H 2 O and Na Cl CO 2 H 2 O system the experimental data is rather limited and the formulation that I am that was proposed on the literature which references which will be given. These are quite old. Now, there are many new method methods, new method, new formulations which are been proposed by many different workers which can also be consulted.

But, these are this approach of using a modified Redlich Kwong type equation has been quite popular. But, this here is that the original data set from which these equations where formulated where very limited on the ranges of compositions although it is although it is applicable. As you can see here, this equation sets that we have discussed is applicable from 350 to 600 degree Celsius and any pressures higher than 500 bars.

That means, if we get which is a of course, very unlikely, if we get a total pressure of homogenization of a carbon dioxide H 2 O inclusion, if it is comes out to be less than 500 bars, then it always rise a question that it possibly has gone beyond the range of applicability.

And the temperature similarly here is 350 to 600 degree Celsius and Na Cl weight percentage of 35. Although, it is said, but then the data points towards the higher concentration of Na Cl has been rather, sparse and there are many other refinement.

So, refinement to this particular the phase relations in this particular ternary has been a very challenging job and also there has been many attempts in till now. Being this particular system is being attempted to be formulated and better acceptable equations of state to be proposed. So, that better more accurate and more refine values of the density and the isochores could be calculated.

Now, here this also, there is another situation here that the applicability of this particular equation state is a only 2 situation where the carbon dioxide the homogenization is to a to a. Liquid phase means, we can we can very well apply when the homogenization process is L aqueous plus L carbonic to L aqueous. So, it is applicability is to homogenization to carbonic phase is a little bit of a there is some amount of some uncertainty which involves.

And then, as said before, this gives the minimum pressure of entrapment ; means, when we are we want to calculate the pressure of formation of this particular mineral or the temperature pressure condition of the fluid, then we cannot can only approximate it to the minimum pressure of entrapment because, we know that actually it is falling on. So, we have as we as we saw before.

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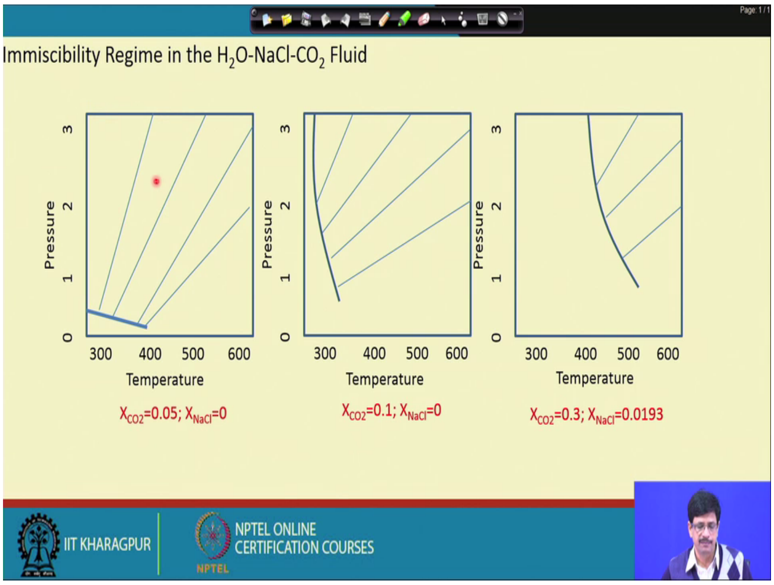

Immiscibility Regime in the H_2O-NaCl-CO_2 Fluid

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

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

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

So, it is actually falling on these where the inclusion could have been trapped anywhere in the one phase region. So, there is one of the limitations also that the it gives a minimum pressure of entrapment.

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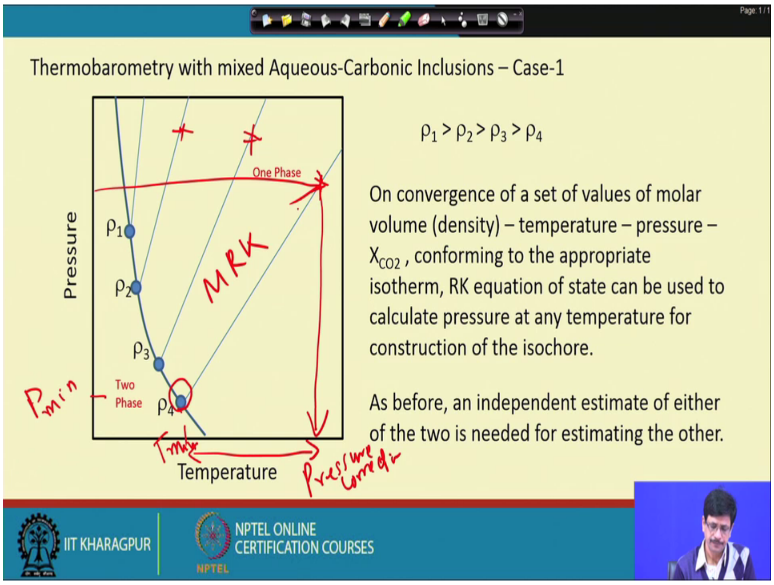

Thermobarometry with mixed Aqueous-Carbonic Inclusions – Case-1

$\rho_1 > \rho_2 > \rho_3 > \rho_4$

On convergence of a set of values of molar volume (density) – temperature – pressure – X_{CO2} , conforming to the appropriate isotherm, RK equation of state can be used to calculate pressure at any temperature for construction of the isochore.

As before, an independent estimate of either of the two is needed for estimating the other.

So now, let us discuss about the thermobarometry with this kind of mixed aqueous carbonic inclusion and in this as per our general understanding of the entrapment of homogeneous fluid and it is evolution and post entrapment phase changes that happens after the entrapment.

So, the case 1 here, so, whether we would be able to do the thermobarometry with mixed across carbonic inclusions, we will see the case 1 is simple, is general idea that the entrapment takes place anywhere on an isochore. Entrapment takes place anywhere on this isochore and which we are only able to constrain this temperature and pressure value corresponding to a total homogenization of this mixed aqueous carbonic inclusion.

So, that means, we would be able to get only a pressure which is the minimum pressure, pressure minimum and also this temperature at which the homogenization has taken place. This also, temperature minimum and normally is we see this mixed aqueous because, the carbon dioxide content in the in the in water at any different any particular temperature will always result in density decreasing.

So, here we see that the iso the density of the isochores are also dp by dt value is also goes to lower and lower values and just as we consider in case of our aqueous inclusions. It also can be thought of a exactly is a pressure correction.

If we are doing this exercise on a metamorphic rock and where in our mineralization which will be also be discussing in some degree of, we will elaborate the discussion on the when we discuss about applicability to metamorphic rocks.

So, if we are working on fluid inclusions in a mineral which is a part of an assemblies which gives us a good barometer, then in that condition, suppose we know what is the pressure and then we can always see that pressure the on the isochore. We drop a perpendicular and can get the temperature.

And this is also exactly the pressure correction that we discussed in case of the aqueous phase inclusion because similar case. So, once we; so, this particular isochore in case of the mixed aqueous carbonic inclusion is calculated on the bases of the same M R K equation. Because, the same values of a and b parameters we can use for a temperature of homogenization and the molar volume that we have converged with the pressure and molar volume.

So, we can calculate the pressure at any other temperature for because, we know that in on this particular isochore a molar volume is constant. So, once we concentrate the isochore, we can also get the similar situation. Then, get the 2 temperature of trapping of this homogeneous aqueous carbonic fluid and can do the and can do thermobarometry.

So, we will continue discussing on the thermobarometry of this mixed aqueous carbonic inclusion in the next class.

Thank you.