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Chemical Engineering Thermodynamics

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Lecture 29

Simultaneous Relations

This is co2 h2, this is called reformer.

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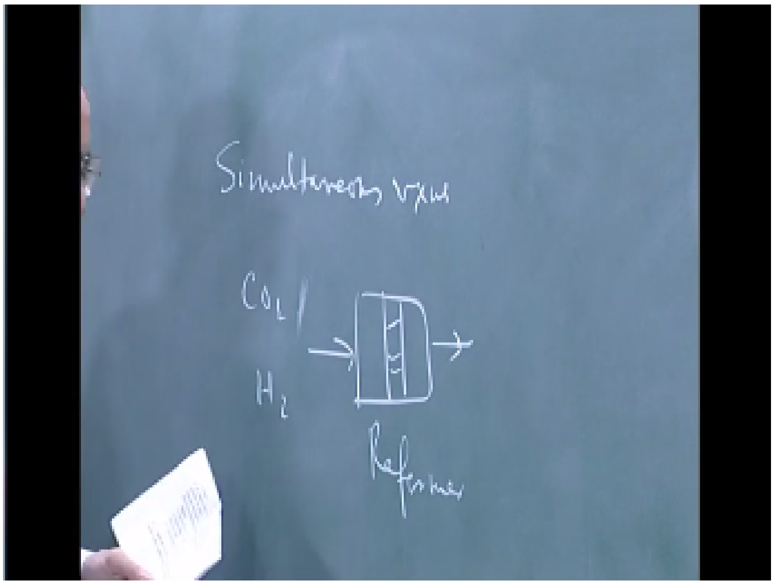

The petroleum industry is full of such reactors actually, they have to keep rearranging the molecules, if they want carbon monoxide you cannot say for to store carbon dioxide except that you get some carbon monoxide here, what you have here is carbon monoxide (c02) hydrogen (H_2o) and carbon.

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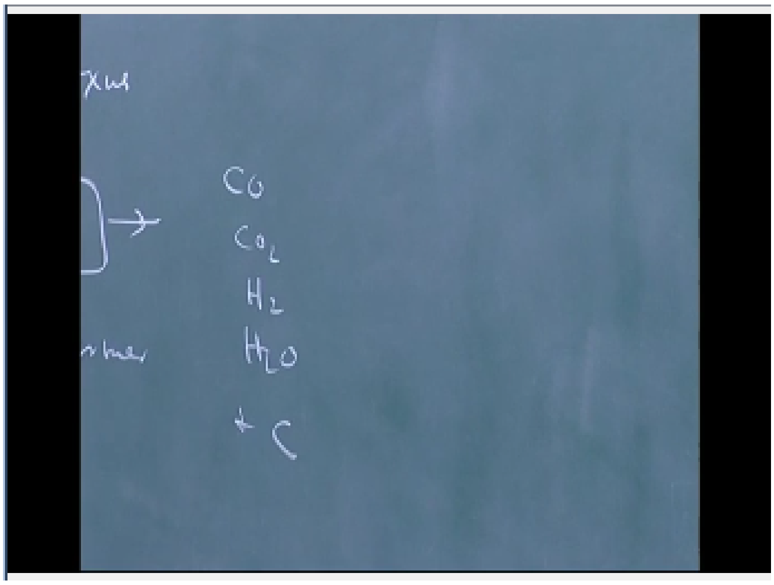

The reactions given Co2 +H2 ----> co+$H_2$0, then Co + H2 ---> C + $H_2$0. In these cases the KP values are given at 1000 degrees so not much work for you, in fact log kp values, log to the base kp 10 is given.

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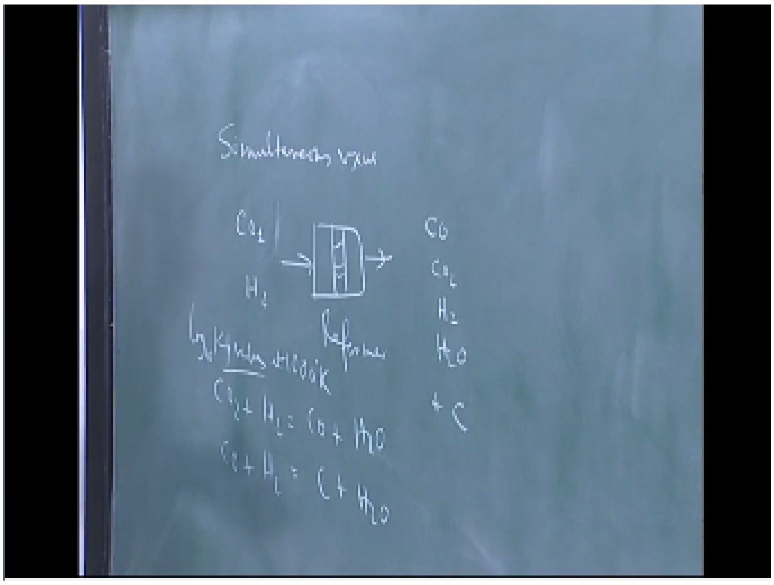

For the first reaction, this is -02, the second one is -05, then two more reactions are given, this is given as 07, this ratio is given 1:1.

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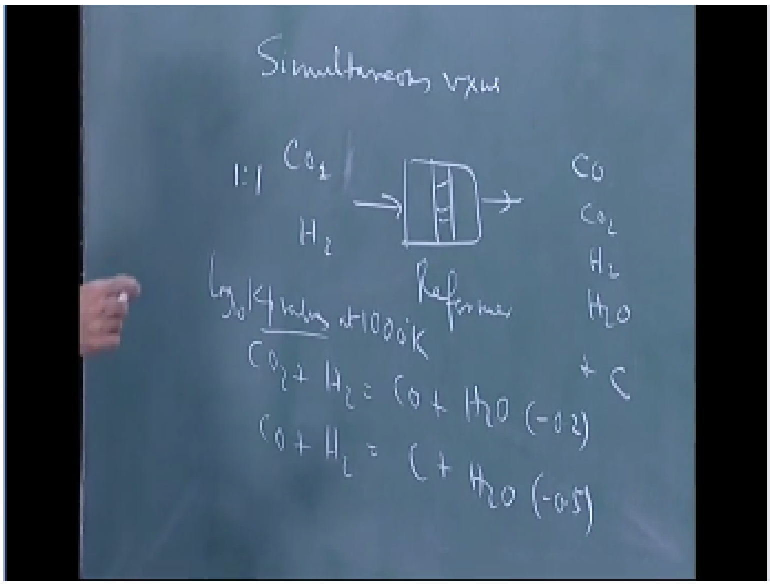

$\log_{10} K$ values at 1000K

$CO_2 + H_2 = CO + H_2O$ (-0.2)

$CO + H_2 = C + H_2O$ (-0.5)

The problem in such reactions is it is typical of reactions where a solid carbon is formed, need not be carbon, there are many complicated reactions in organic chemistry where you have something that has formed in the solid phase usually that ends up poisoning the catalyst, so it is generally called coke, when they say coke it does not mean carbon necessarily, it means any organic solid substance that is formed during the reaction that ruins the catalyst and it ruins the catalytic activity.

So the idea is to prescribe how much of this can be formed and sometimes there is a tolerance so they will say you are permitted exactly, in this problem it says if exactly 25% of the carbon coming in is carbon dioxide made deposit on the catalyst at what pressure should the reactor operate, that is the question. Temperature is usually fixed, this is more like its considerations, process considerations, probably the particular process has carbon dioxide and hydrogen available at 1000 degrees so it is no point cooling it and then heating it.

For fast kinetics and so on so they operate at 1000 degrees but they want to know essentially if this should be .25, that is 25% of carbon entry as co_2, that is specified. The question is what is the pressure, range of pressures, it says actually it should be less than.

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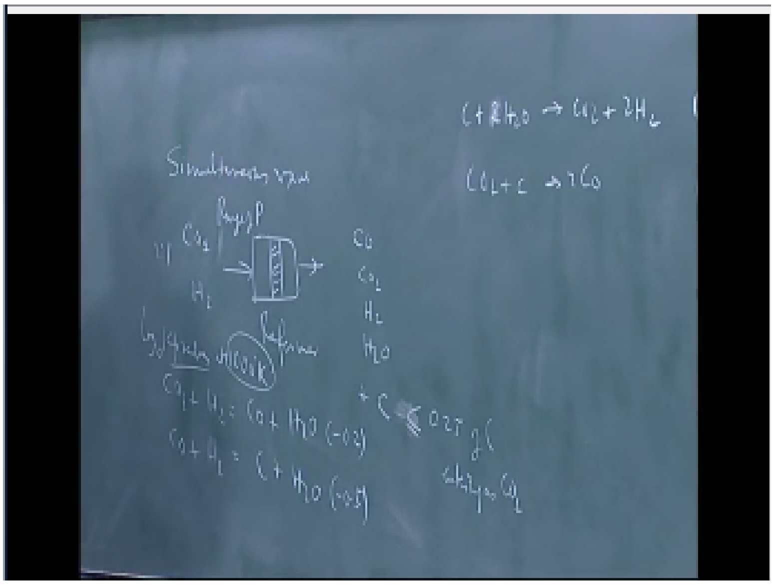

So four possible reactions are given, in all these cases the reactions are listed without reference to how many independent reactions you have, so the first step is to find out the number of independent reactions.

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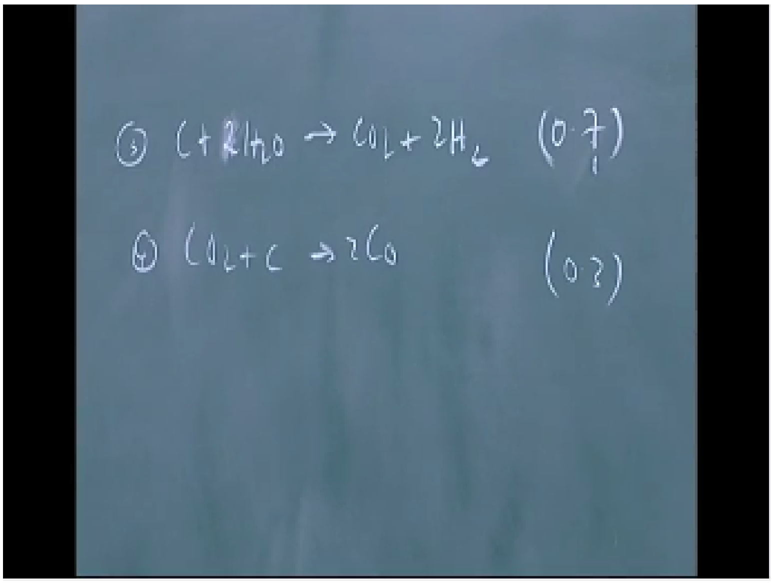

③ $C + 2H_2O \rightarrow CO_2 + 2H_2$ (0.7)

④ $CO_2 + C \rightarrow 2CO$ (0.3)

And for number of independent reactions you have to write down the psychometric metrics, you can do that or you can do this by a simple rule for which in fact I think I told you the rule, the number of independent reactions, it will be interesting to see if you can come up with an exception. This rule is only a holistic rule, it is right 99.9% of the time, if you can come up with a set of reactions for which it is wrong I would be very interested.

The rigorous rule is simply this, you take this tachometric metrics in this case and take its rank, that is the number of independent reactions.

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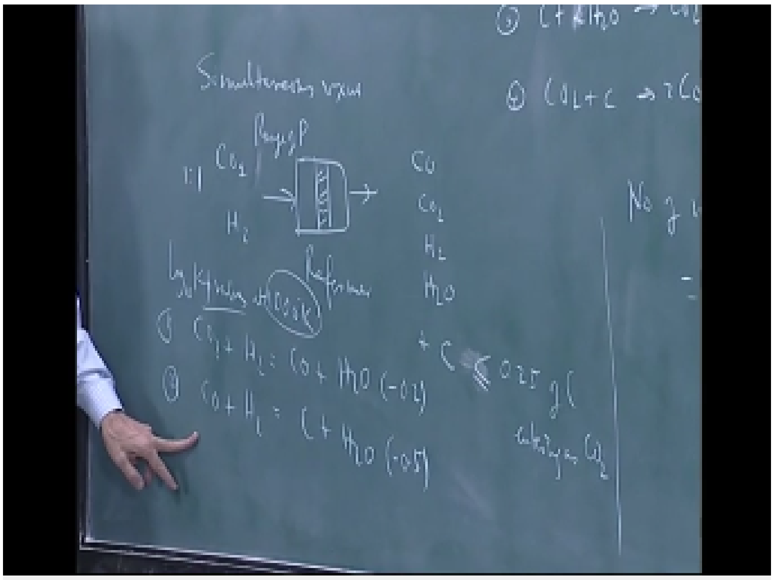

That is simply the theory leads from linear algebra so you can work that out but the simpler thing is to take the number of species at equilibrium, in this case 5, minus number of elements required to produce them.

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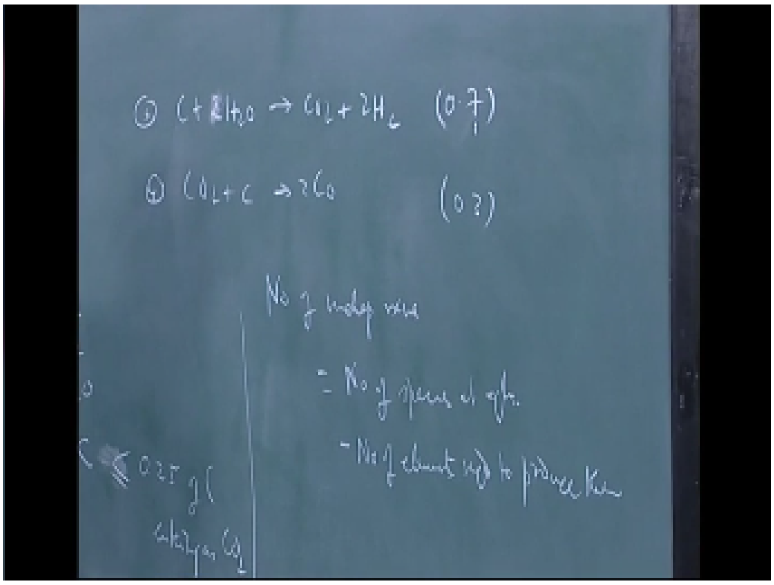

In this case it is 5 species at equilibrium – 3 elements, these three elements is carbon, hydrogen and oxygen, so with those three you can produce all of them therefore the number of independent reactions is 2. We should more rigorously, it is the rank of this tachometric metrics.

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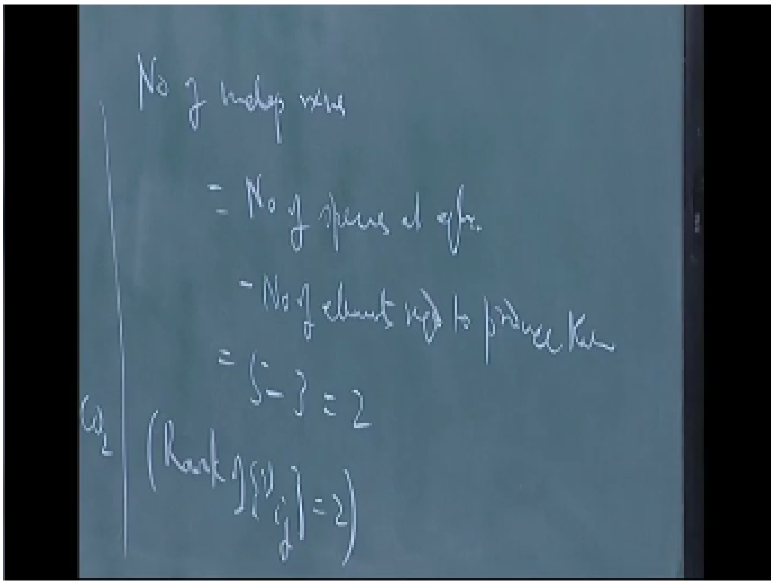

The trouble about finding the rank of a metrics is that you have to take all 3/3 and show that all the determinants are 0, by the time the quiz time will be over, so it takes you all of 50 minutes to find out if, to ensure that the rank is not free but in many cases you have 2 reactions so you can choose any two reactions. Normally the way to choose this is like this, you have to ask for pressure, choose one reaction that is unaffected by the pressure and one reaction in which the carbon, you know there is specification on carbon so make sure you choose one reaction in which carbon is produced.

That is a convenient way and in this case it may be reactions one and two because but here the number of modes does not change therefore it is unaffected by the total pressure in the total number of moles and this one produces carbon, so you can choose any two actually, it does not matter which one you choose, the final result will be the same but for your computational purpose it is much easier to do it this way otherwise you will solve simultaneous equations for the pressure.

Let us look at equations 1 and 2, the first reaction is that k_p we will use k_p and then go to k_f if necessary, we will assume $k_f = k_p$ we can verify if the pressure is high you can go and correct it next time, correct for k_p if p is large that will be the second iteration so we will take kp1 and it is = so total pressure by number of moles 2 the power of ∂ by 1.
You will get all these species, call this component 1 and this will be 2, this can be 3, this can be 4 and this is 5.

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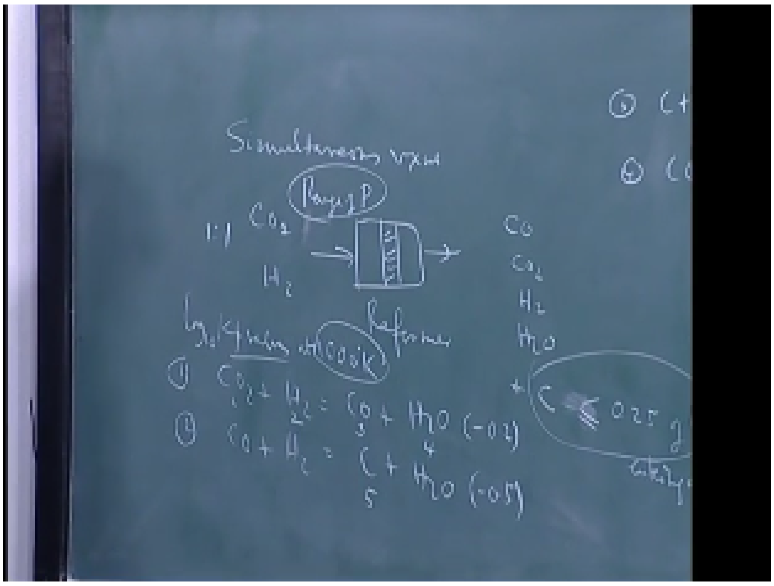

So let me write out the, this is simply 3n4 by i1 and 2. This is equal to exponential of whatever is given, -02. If you look at reaction 2, again the same rule, you should write kp prime reaction 2 involves a solid so you leave out the solid when specifying the, so it will be n4/n2n3. This is = exponential of -05. Actually it is not even exponentials, 10^{-2} given as log to the base 10.

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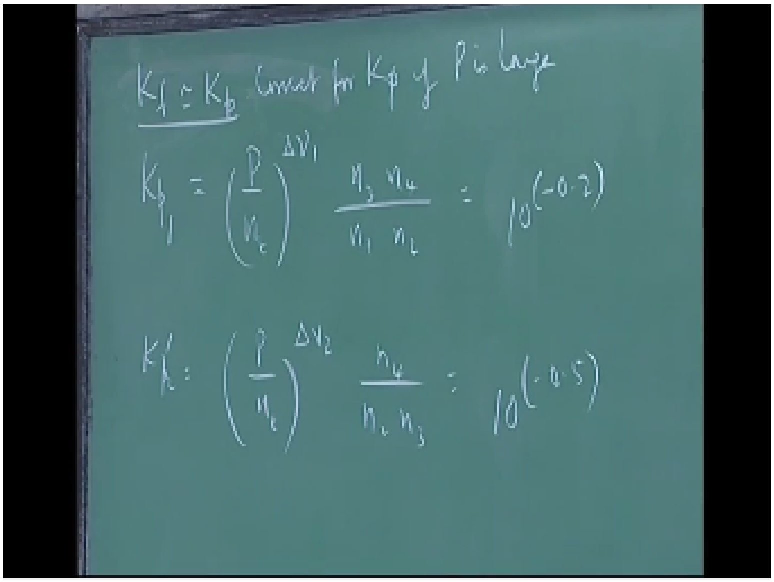

$K_f \simeq K_p$ Correct for K_p if P is large

$$K_{p_1} = \left(\frac{P}{n_t}\right)^{\Delta\nu_1} \frac{n_3 n_4}{n_1 n_2} = 10^{(-0.2)}$$

$$K_{p_2} = \left(\frac{P}{n_t}\right)^{\Delta\nu_2} \frac{n_4}{n_2 n_3} = 10^{(-0.5)}$$

We will workout the moles at equilibrium, so it is good to do a degree of freedom calculation to begin with. Number of degrees of freedom is simply the number of components minus the number of phases +2 minus the number of independent reactions. So you get 3 degrees of freedom.

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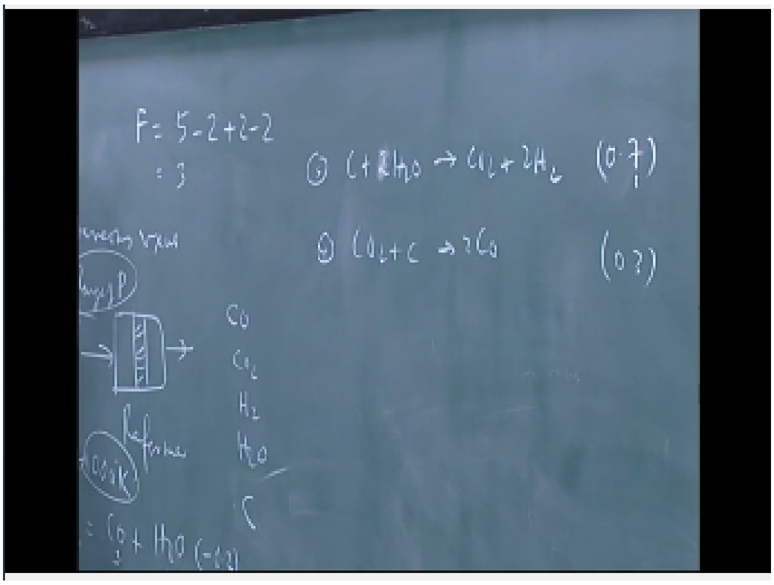

Right, this is components, this is phases. So one solid phase, carbon is present. This +2, this is by Gibbs and this is number of independent reactions.

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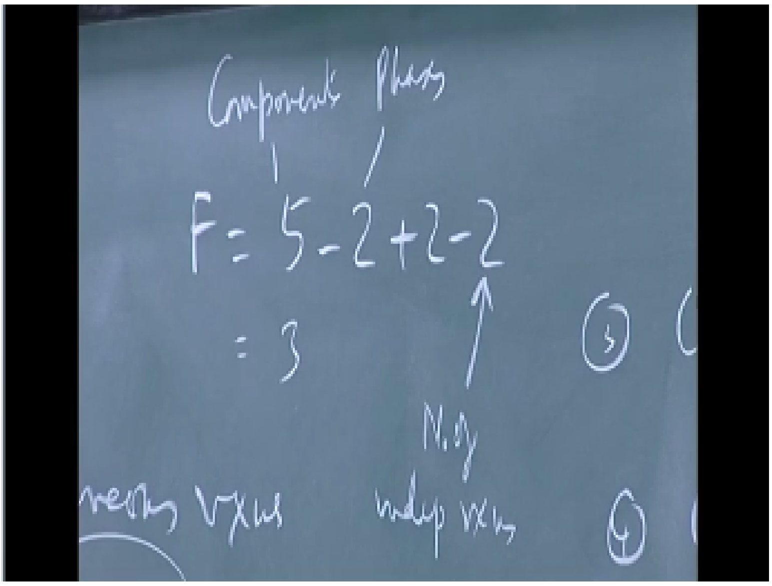

3 degrees of freedom, here the temperature has been fixed, if 2 degrees of freedom left what are the 2 degrees of freedom? And I want you to find the pressure, so you must tell me the independent ones that I am fixing. That is a special constraint, I have to put it in. Correct, that is a constraint. So it will determine. So let us say you lost 1 degree of freedom by that specification. If you say carbon deposition should be 0.25 for 1 mole, what else? There is 1more degree of freedom. Let us do the problem and come back to it because there is, it is a bit tricky but it is nice to know the degrees of freedom before you do a problem. But let us discuss it here.

First of all I have carbon monoxide in the output. Let us assume that x1 moles of let us say carbon dioxide or hydrogen, let us take hydrogen, x1 moles of hydrogen are converted in reaction 1, and x2 moles of hydrogen are converted in reaction 2.

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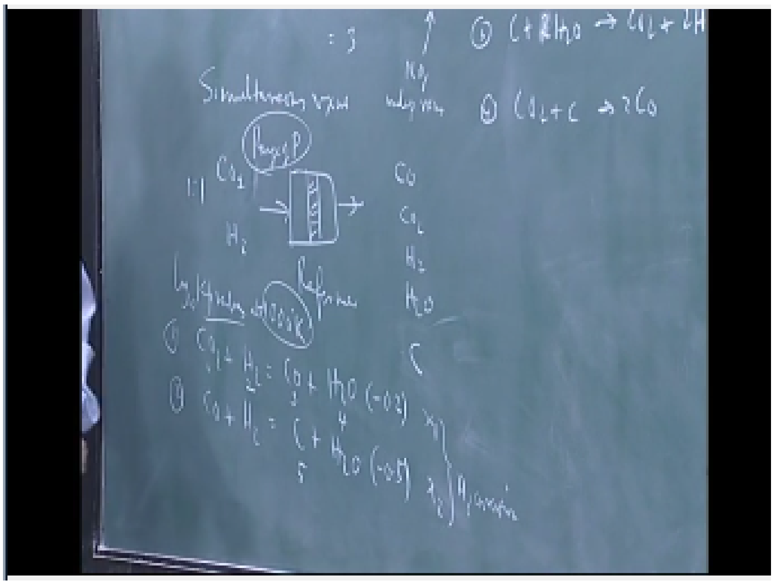

And each reaction has one independent progress variable. The progress variable is the same as the change in the number of moles of one of the species. Normally it is taken for a product species, maybe I will say H2O; so we will say H2O conversion, H2O formation. The same as this but the minus sign.

So if x1 moles of, water is not an input so this is x1+x2 at the outlet and if you look at carbon monoxide this is produced in reaction 1, x1 will be produced, x2 will be consumed. If you look at carbon dioxide it is consumed here, it is not produced at all. So it is 1-x1, 1 enters and x1 is consumed. We look at hydrogen it is consumed in both reactions so it is 1-x1-x2. Carbon is produced only in reaction 2.

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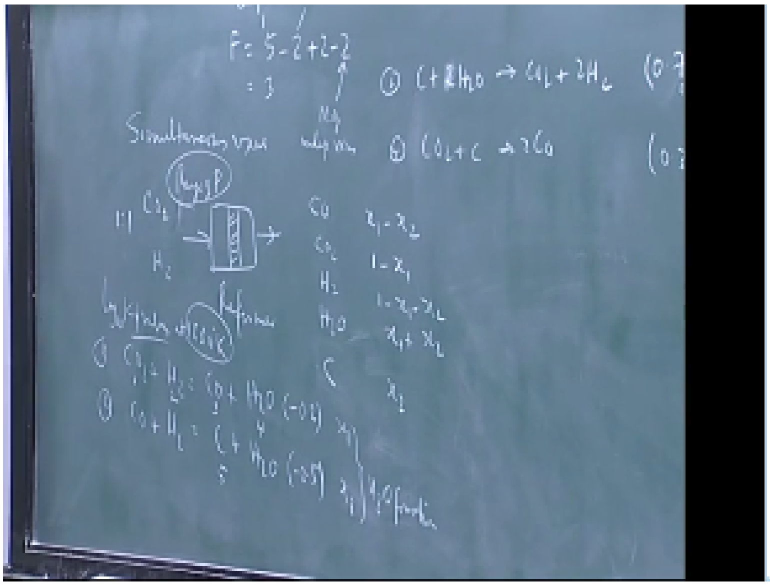

Then for reaction 1 ∂ μ 1 is 0, ∂ μ 2 prime, the prime comes in because the solid psychometric coefficient of the solid does not count. So it is 1 -1 -1 so it is -1.

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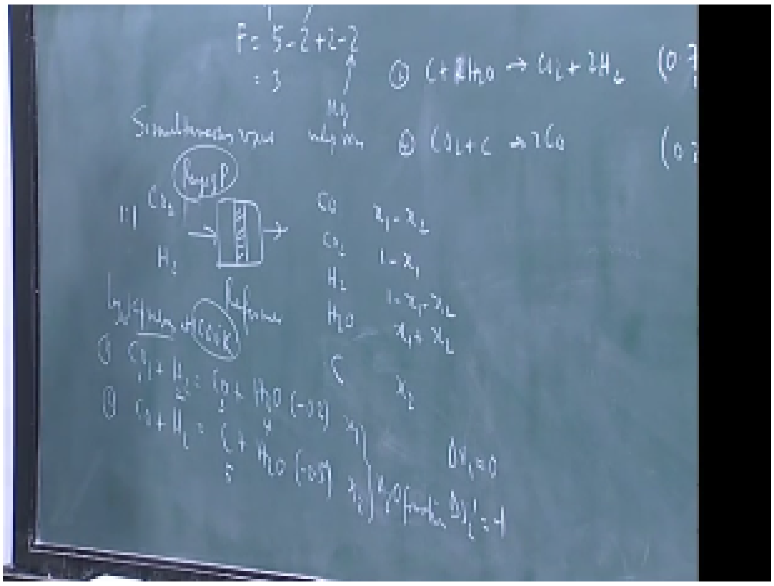

So I should have written, when I say prime here, I mean prime here also. So the first equation, this is zero so I do not have to worry about this, I have to count the total moles. Total moles in gas phase so you should make sure that you do not count the carbon. This is solid.

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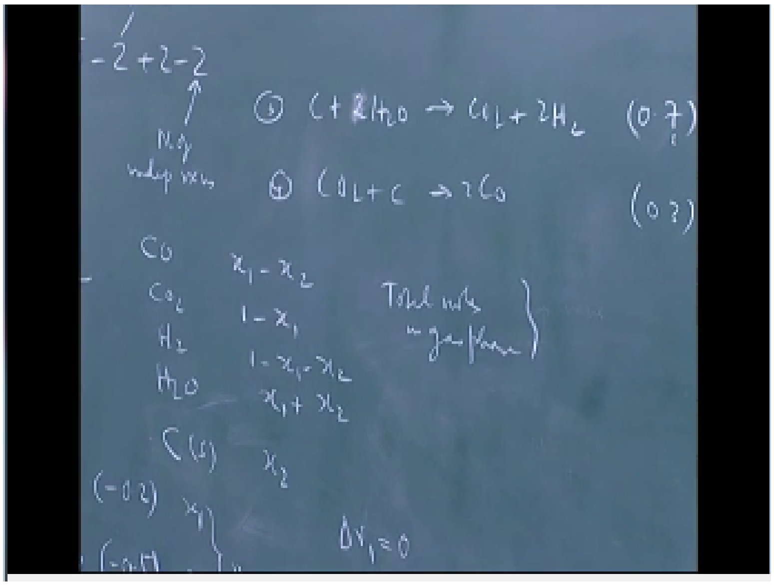

So total moles is 2 and x1-x1-x1+x1 so x1 does not appear, -x2-x2+x2-x2. Only this part counts.

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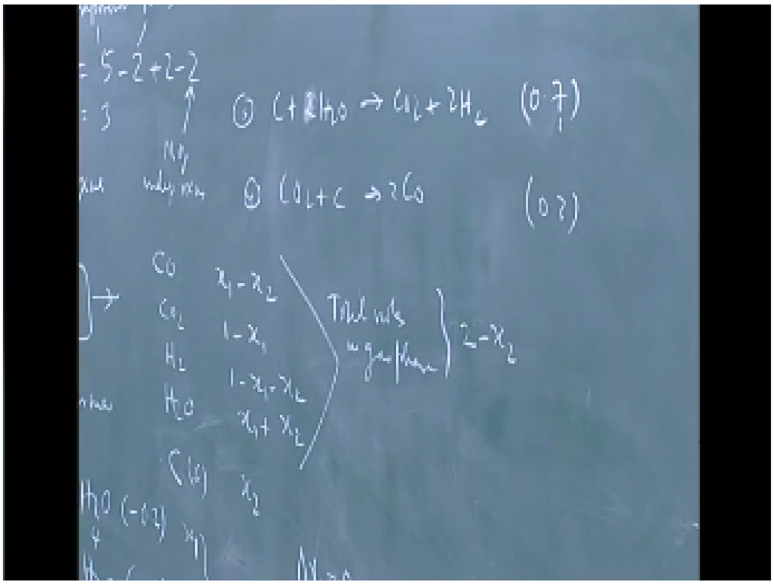

So I have N3, is this in the correct order? Now carbon monoxide is 3, and CO2 is 1, H2 is 2, H2O is 4. So I have N3 which is x1-x2 into n4 which is x1+x2. May n1 is 1-x1, n2 is 1-x1-x2, this is 10 to the power -02. This one will be 1/P, 2-x2 the total number of moles because ∂ node 2 is -1 into nt/p into n4 which is x1 + x2 divided by n2n3, 1 –x1–x2, n3 is x1-.

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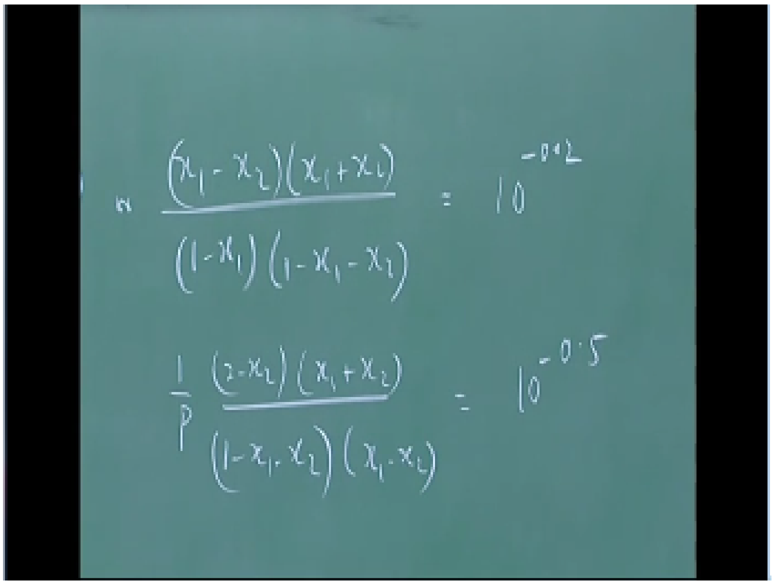

$$\frac{(x_1 - x_2)(x_1 + x_2)}{(1 - x_1)(1 - x_1 - x_2)} = 10^{-0.2}$$

$$\frac{1}{p}\frac{(2 - x_2)(x_1 + x_2)}{(1 - x_1 - x_2)(x_1 - x_2)} = 10^{-0.5}$$

So I have x1, x2 and p at two equations but three unknowns. So you need one constraint at least, that constraint has been given to you. First question is if the carbon deposited is 0.25, what is permitted you assume and then ask when will it be less? Right, so if x2 is given as 0.25, so given.

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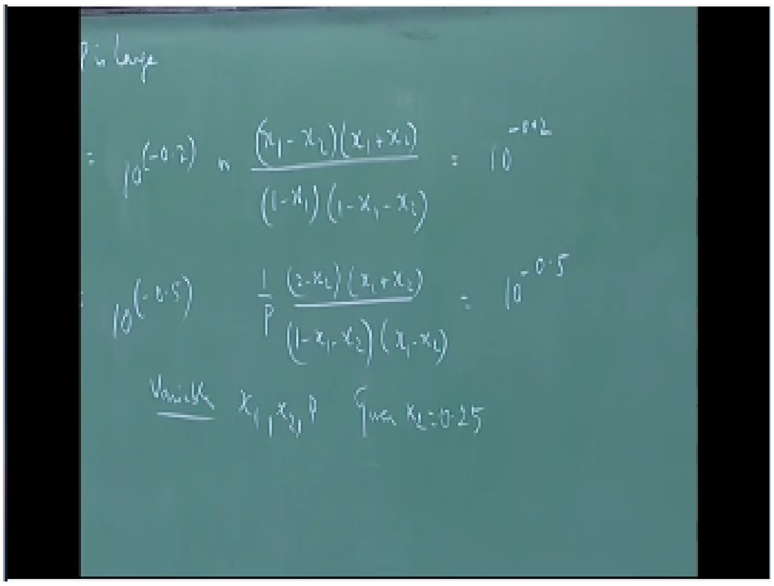

P is large

$= 10^{(-0.2)} \quad \frac{(x_1 - x_2)(x_1 + x_2)}{(1-x_1)(1-x_1-x_2)} = 10^{-0.2}$

$10^{(-0.5)} \quad \frac{1}{p}\frac{(1-x_2)(x_1+x_2)}{(1-x_1-x_2)(x_1-x_2)} = 10^{-0.5}$

Variables x_1, x_2, p given $x_2 = 0.25$

And straight forward, so you can solve the first equation for x1 and then solve the second equation for p, can you do this? So we get some numbers for discussion. X2 is 0.25, so you are talking about x1--.25 into x1+,25, so that is $x1^2$-0.0625 divided by 1-x1 will remain, it is only a quadratic. This is 0.75-x1=to the power of -02.

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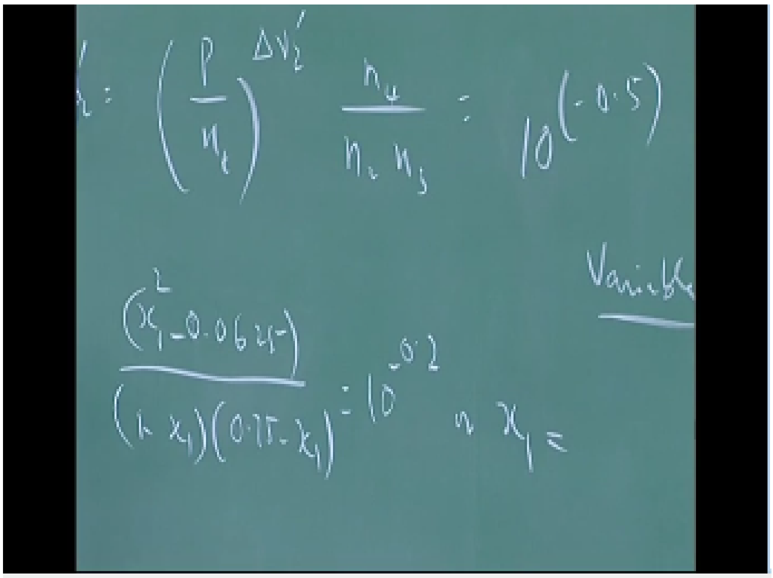

This is just a quadratic so you will get two roots, tell me both roots in case one is negative we will of course drop it. Talking about x1 squared into 1-10 to the power of -02, then x1 comes from here. This is -1-.75-1.75 into 10 to the power of -02 into x1, then the constant is 0.75 into the power -2, I will come to that, so it is -0.0625+.75 x10^{-2} -0.2.

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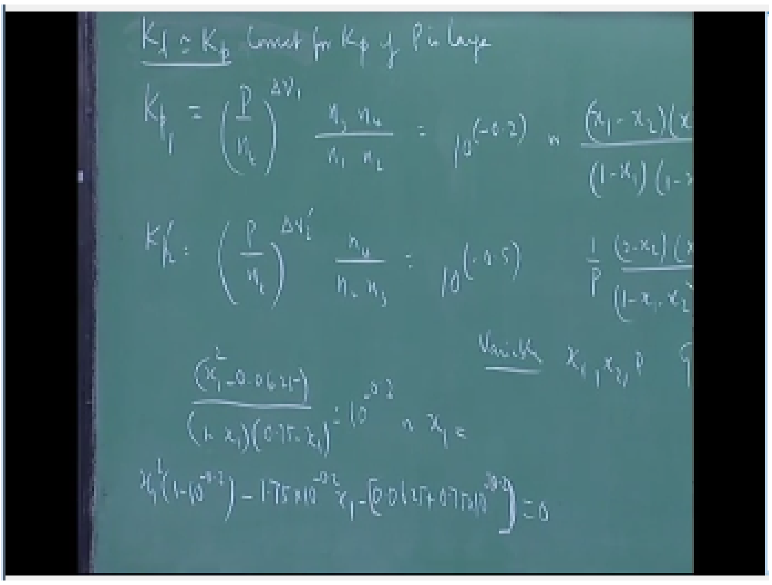

What do you get for x1? Either two roots 0.425, there is only one calculator so you are the final voice. Hoping somebody else would have won it. We will come back to degrees of freedom. So what do you get for P? For X2 = 0.25 you have X1 = 0.425, that P you can do. P is simply $10^{0.5}$ X 2-X2 which is 1.75. X1 + X2 is 675/0.325 x X1-X2 is 0.155, 175 sorry.

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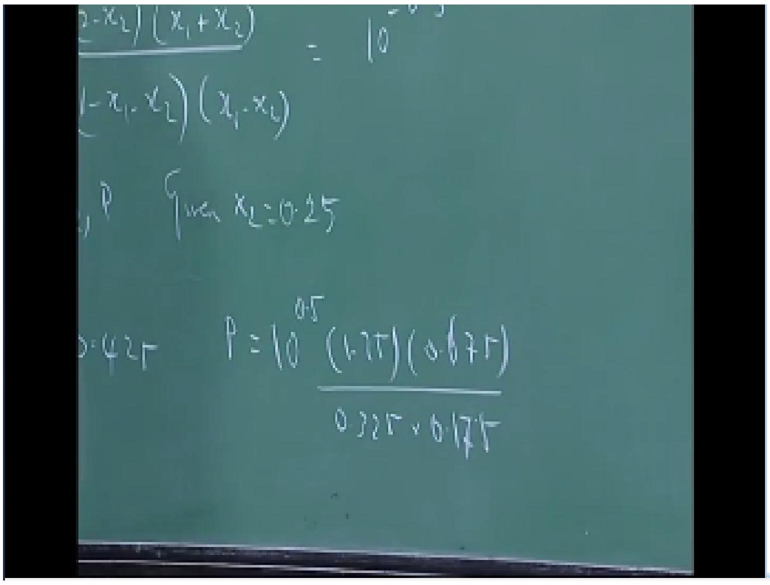

What do you think? About 60 actually, it is very high, there is a competitive here, I did not notice, got some more, what 60, about 65. Notice P will come out in atmospheres because of the convention. The μ 0 was by definition a chemical potential at the temperature T and one atmosphere. Now how will you decide what range of pressures to operate at? What I want is 0.25 or less of carbon.

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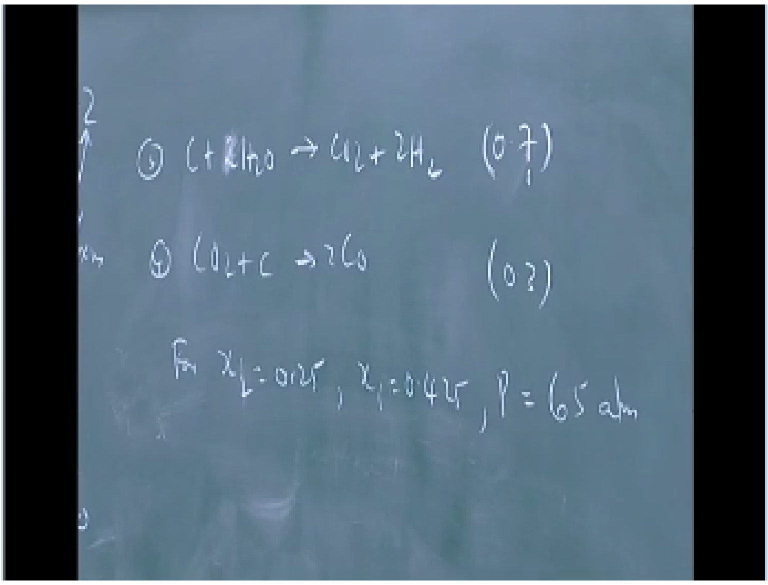

This is the calculation for exactly 25% of the carbon being deposited, if I wanted less this reaction should proceed less, what happens to this reaction is increase the pressure. This reaction is unaffected by pressure. So you are looking at one reaction effected by pressure. If the pressure increases what happens? You think you are comfortable with Le Chatelier's principle that simply says things will happen in such a way as to prevent what is already happening which is applicable to Governments, which is applicable to IIT, everything, something is happening well things will happen so as to prevent it.

So here what happens if you increase the pressure, that what happens when the, see number of moles decreases right therefore the pressure will decrease. So a decrease in pressure will oppose it and increase in pressure will favour this reaction, correct?

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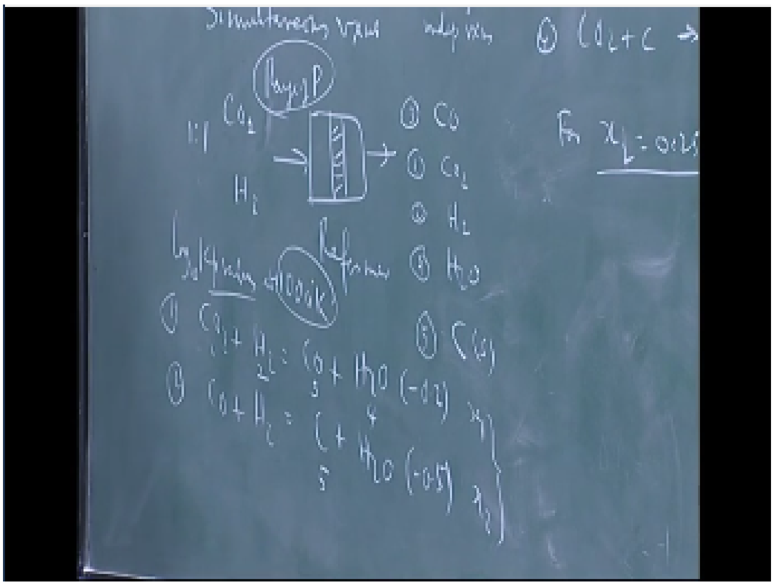

So if P is greater than 65, so first of all number of moles of carbon is X2, notice X2 increases as P increases.

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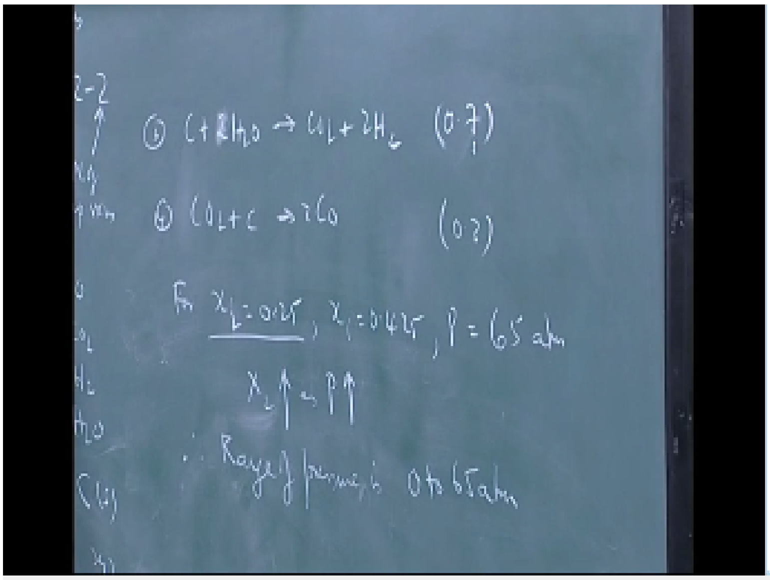

Therefore range of pressure is simply 0 to 65, say that again because eventually we need 0, we should also calculate what X1 between X2. So that will be the prevent moles for the pressure. We will try that out, you are saying this is one, the other possibilities you are saying I want X1 greater than zero, right? Carbon is actually assumed, okay X1 should be greater than X2. So you put X1 = X2 and calculate the pressure here. So when X1 = X2, this side is zero.

What is the conclusion? You started the…. this has to be $10^{-0.2}$ so X1 – X2 cannot be zero. Only a fraction of the carbon monoxide that is produced here can anyway be consumed here, maybe 99.999%. So this problem does not arise in this cases. As long is the pressure is less you will get, now what happened to the degrees of freedom, number of degrees of freedom as we calculated it was 3. I fix the temperature. I should have the freedom to fix. I fixed the carbon deposition, so two variables are fixed. What happened to the third degree of freedom? Pardon? No by degrees of freedom I mean three variables that I can fix independently, when the system becomes invariant. I did not fix it. Is this a constraint?

No tell me, is this a constraint on the degrees of freedom, is this also an input constraint? Actually it is, but it is not always this, the point is this, hydrogen and oxygen are in the ratio 1:1 and they remain in the gas phase, there is the constraint that in the gas phase hydrogen to oxygen ratio should be one, where as the minute I produce carbon, for carbon there is no such constraint because part of it can be in the solid phase and part of it can be in the gas phase.
So all elements that remain in a single phase are constrained by input ratios, the ratios of elements that remain in a single phase are constrained by the input ratio. Not elements like

carbon in this case, as soon as you have carbon deposition thermodynamics will not tell you the extent, it will only tell you both phases exist.

It will tell you what fraction, it will not tell you what fraction should be in the solid phase, what fraction should be in the gas phase. You are right, but you are right only to the extent that you are talking about the ratio of oxygen to hydrogen. So in reaction systems as in other degree of freedom that is lost, so we will leave this here and discuss degrees of freedom here. I think I am right it out. Degrees of the number of components -2. Minus actually number of independent reactions, -1 this is for special constraints they are always there.

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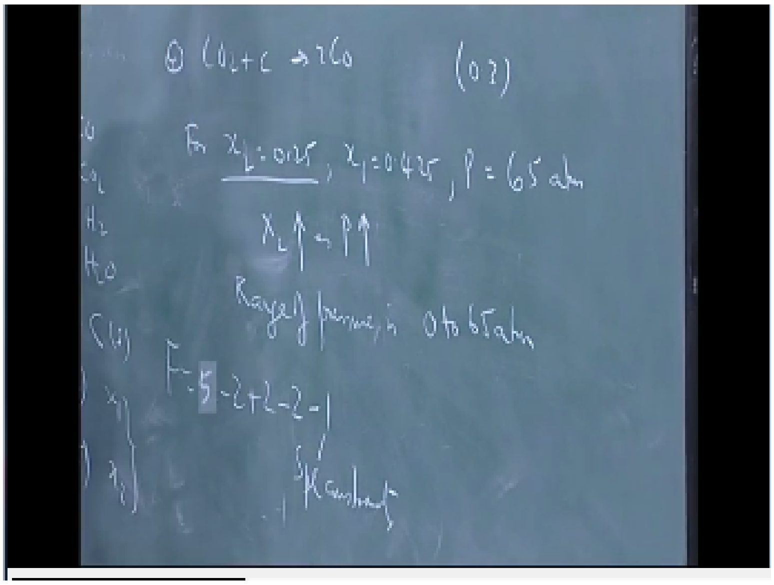

In this case, X2 = 0.25. Minus again in other special constraint, I suppose I should write -2 for special constraints, one of them is this, the other is ratio of hydrogen to oxygen in gas phase. The carbon and the gas phase is not so constrained although I sent only one atom of carbon for every mole of oxygen part of it can deposit in this solid phase. So I have no constraint in the gas phase. See it does not matter how the components rearrange themselves, they are all in the gas phase. And in the gas phase oxygen and hydrogen ratio is restricted to one.

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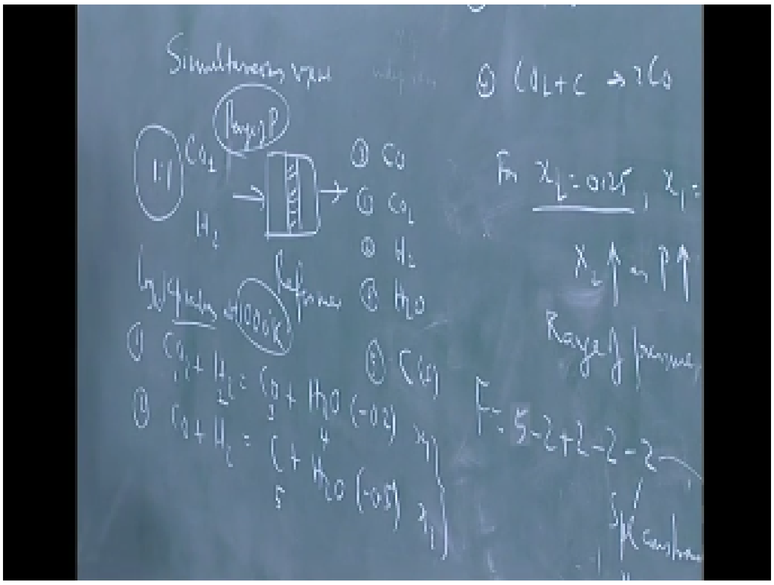

Oxygen may be in CO, CO2 or H2O it can be in three different places, but the same oxygen is redistributed, same hydrogen is redistributed. The ratio is constrained to be one. So I could use 1:A and ask if there is an optimal value of A if I want readjust this. In this particular problem 0 to 65 the very convenient thing, I mean thermodynamic permits you a whole range of pressures and including low pressures. So I probably operated one atmosphere, zero I will have to worry about what leaks in, more than one I had worry about what leaks out, so I just operated one atmosphere and be done with it.

But if I was using this incidentally as a process for producing carbon, this carbon may be activated carbon depending on its structure depending on the way I get it, depending on the surface area I get may be very useful. So I may actually use it, then I may see rather than constrain it as X2=0.25 or less, say atleast 25% must be carbon, really depends on your local interest.

If I do that then I will have to go to 65 atmospheres, do you think by changing this I can change that pressure? Suppose I use 1:A, can keep one of them as always one, because its only the ratio that matters. It is possible if I send in more carbon I am likely to get more carbon in the input and then I am likely to get more in the output. So you can keep this as 1:A and what should A be. A may turnout to be .2 or something, maybe an optimal value, obviously you will have one degree of freedom. So you can choose A and do this calculation. It is a lot of routine things, but you have to do the analysis clearly and then submit it for calculations. In fact the biggest problem as I told you once in the present chemical industries, that they have online control for many of these things.

So online control the operator sitting there will have to control the input in such a way that he gets the desired output and the whole calculation in a chemical industry is online control problem is mainly troubled by delay, that is you measure the product if it is not of the desirable quantity send the difference as input for controlling and that measurement comes too late. So if it comes after one day your batch is spoiled, that day's production is spoiled. So what they have do is act quickly. So they have a model of the process. So they run all the disturbances in the input through the model and the model predicts what is going to happen and on the bases of that prediction that is used in the feedback, in that model prediction the hard disk part of it is thermodynamic package.

Because you have to go and calculate thermodynamic properties and come back and that takes a long time. The thermodynamic package itself, see typically here two equations, this is two, if you have 14 simultaneous equations you can run into all kinds of troubles solving them because they are non linear equations. You often have to give guess values and start them off, if it was a quadratic you would solved it directly.

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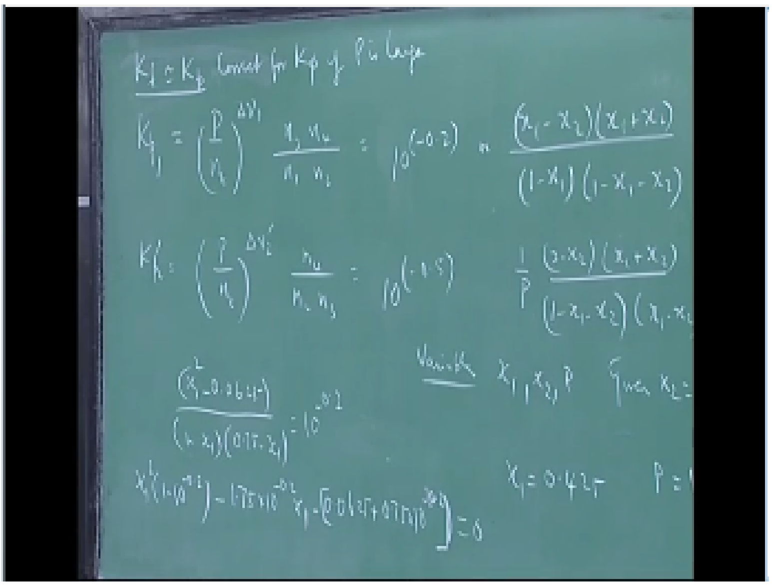

Up to cubic under certain conditions you can solve directly otherwise you are going to guess it right, you will do a u turn option on it and this can go haywire depending on your guess and in thermodynamics it is very, very sensitive because if your x goes negative then all those equations are meaningless. Therefore you will get, it will complain, it will say you are trying to take the square root of a negative number and all kinds of complaints and so what you need is a whole package that will do this.

Incidentally there is a thumb role that you should do in all numerical calculations, generally true in engineering but I may as well tell you its particularly true in thermodynamic packages. If you are solving for some variable X as a root of an equation, if you are doing a neutral option search what is, what is option, is it, I have forgotten, roph is it?

I have forgotten, it is not famous some how it got tagged, so you start off with a guess value, what will it does neutron option does this, then it converges hopefully. So after this is iterations on the X axis. So you guess this, this is the beginning value X10 then this is X11. This is X12 and so on. The thumb rule about neutron diffraction is that is predict the correct direction of the change, but it often over predict the change, so what you do is its take X1 0, you will find a ∂ X and add it you will get X1 1.

So this value is often negative. If this is zero you often go oscillating on either side, but thermodynamics will not permit you to get negative mole fractions. First of all there will be a log X1 somewhere. So you will say log of a negative number and it will throw you out. So the thumb rule in these things is to say X1N is X1N-1 the previous value + ∂ X predicted from neutron diffraction ∂ X1 neutron diffraction or any other technique that you have.

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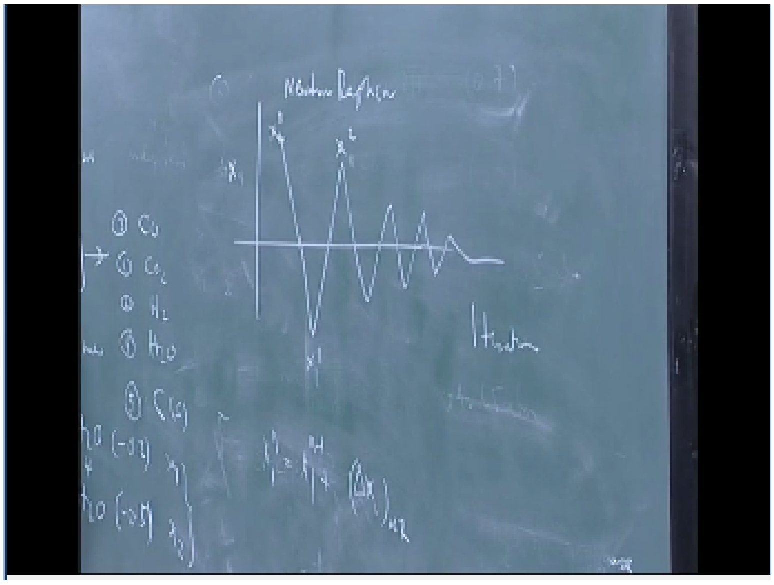

If you are using Picard's iteration you will still get a ∂ X, so the thumb rule here is multiply it by a moderating factor beta. Beta is a factor, usually beta is chosen if you do not want to do a detail analysis beta is chosen as 0.1 in chemical engineering. This is just experience on a large number, what it says is the μ X1 prime will not go here, it will take the direction of change proposed by neutron diffraction, but take only one 10th of value. So the second value will be here. So it will hopefully go like this. You will not oscillate violently. This is very important for practical computations.

This is an other problem that I want to discuss, I do not know if I discussed this problem of lime stone decomposition. I do not know if you see it these days, it is a long time since I travelled by train and when you will travel by train do you see this skills that have you seen this or have you, maybe you will not recognize them. Have you seen devices like this from the train with some smoke coming out? These are actually what you have is a great thing here and there is opening here and what they do is add CACO3, calcium carbonate from the top, they add some coal, you should write it this way, there is a place for cleaning things up but what they do is add CACO3 and coal carbon and then what comes out here, either they add carbon here or sometimes they just burn it fuel, usually it could be charcoal or it could be, actually they wont do this carbon is too expensive.

So this could be even firewood. Firewood is bit tricky because you cannot get the temperatures required very often. So what you have here is co2 coming out, reaction is some

CACO3 giving you CAO+CO2. This is solid, this is gas. So very conveniently for K_P1 is equal to simply partial pressure of CO2.

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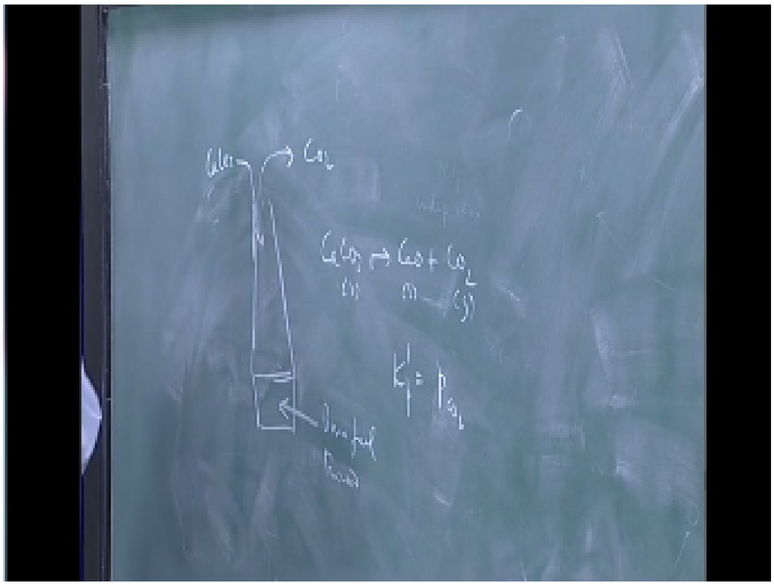

This is total pressure into YCO2. In the atmosphere partial mole fraction of carbon dioxide respectively 10^{-2} 10^{-3} so if this is equal to of course exponential of $-\partial$ G 0/RT. This part is thermo. This is a function of temperature low. So what you do is calculate the temperature at which this total partial pressure of carbon dioxide is one atmosphere being absolutely safe, there is no way if the whole atmosphere was CO2 you will be dead anyway so you cannot have any interest in the proceedings.

You start up calculate this to be one atmosphere and ask when is what is the temperature at this typically ∂ G0 is given you can calculate this is known to be final degrees infact most of the people in the atleast the older people in the villages will tell you, they wont tell you 500 degrees. They will show you a stove which burning with firewood and say that colour of the flame they can tell you what the temperature is. So they will tell you this colour comes there then the temperature is 500 degrees.

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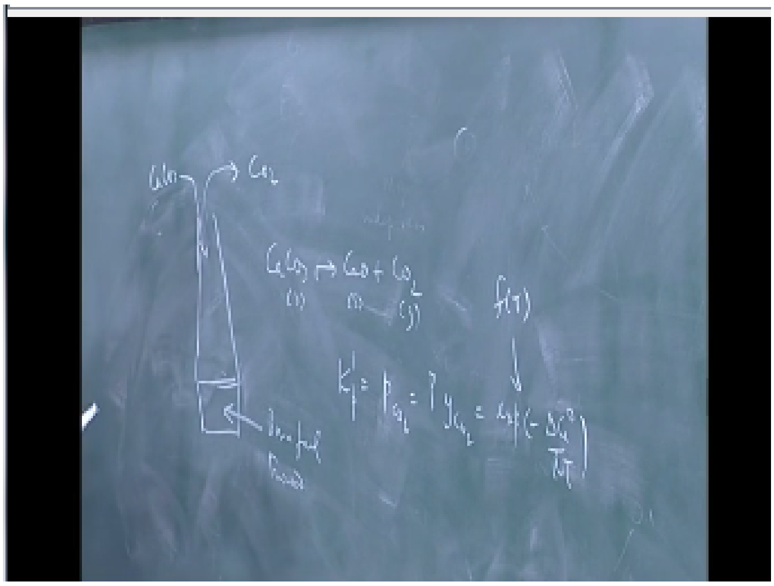

And the temperature 500 degrees they know that they are getting calcium oxide here. They will not even bother to test, it will just pull it out and use it give you the times stone CACO3 give you, this is standard formation data colour is ∂ G 0 and ∂ H0. Here ∂ is 0 to 298, it is also 298. This is -269.780, this is -288450. That is correct. For CAO its -144400 and -151900 then for CO2 is -94260 and -94052, but let us ignore ∂ CP for now.

So you have to go through this of course. D ∂ 0 /DT is ∂ CP0, if I have taken this is zero then ∂ zero is constant. The you have D of ∂ G0/T, by DT is –∂ head 0 / $T^{2.}$ Your ∂ D0 /RT = ∂ G0 298/298 + ∂ H0 /RN simply if you integrative you get just 1/T, so its 1/T -1/298. So if you want one atmosphere for this partial pressure of carbon dioxide simply said this is equal to zero for TCO2 = one atmosphere. Actually these are not ∂ G0 values I apologise this GF and HF for the pure compound you have to calculate ∂ G0 for this reaction. So you do this calculation you can show it's about 500 degrees centigrade. So needs of these reactions you don't have to play its so safe, anyone have partial.

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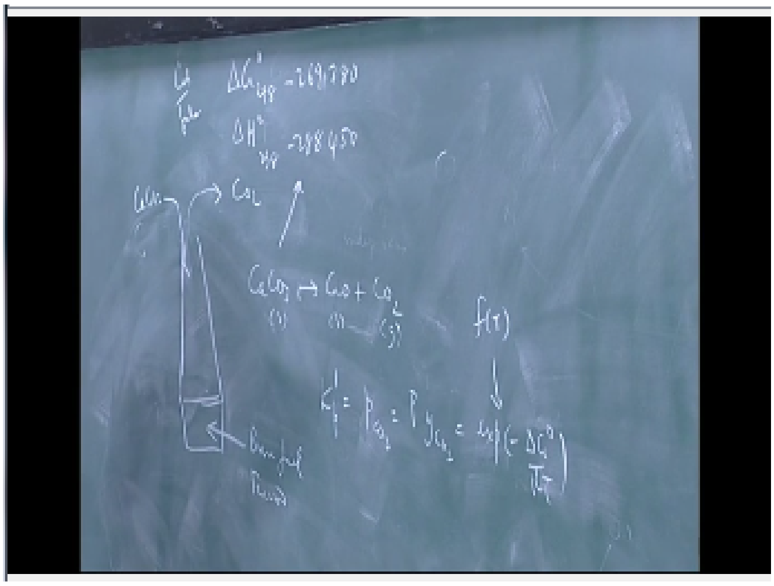

Pressure equal to 0.5 calculation of 0.1 you are not really worried about carbon oxide. Except that you don't want carbon dioxide they sit here and ruin you again. If all the carbon dioxide sits here you will have partial pressure one atmosphere locally so it will spoil your reaction. You must have flow as long as there is flow there is no problem. This is hot, so this will rise, you must have enough vents here for the air to go through and overcome the pressure drop. This what happens, this becomes a pact bed, so solids packed up to here, lots of pellets, and so you have to overcome this pressure drop and the gas will have to go out.

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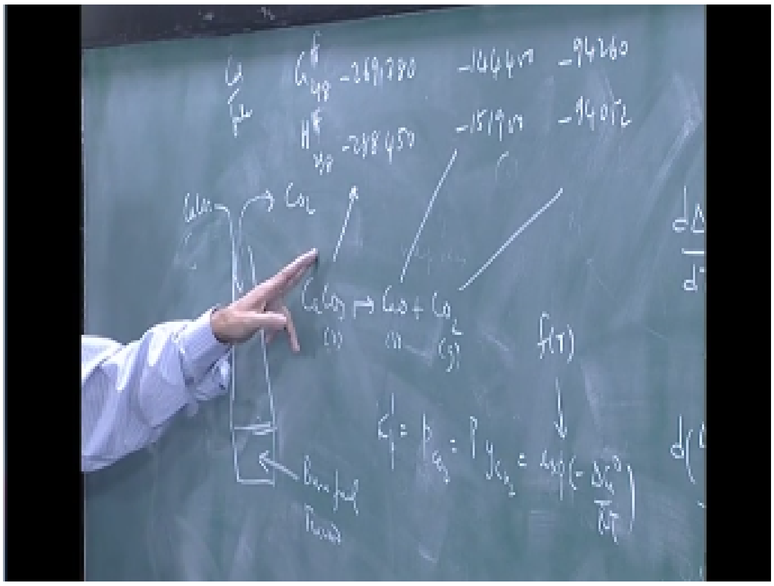

So the buoyancy will have to be sufficient to take care of the pressure drop for that and very often they will do something very clever. They will throw in a few stones and you wonder why the fellow is doing that. It is actually to produce as the limestone decomposes it forms CAO and if you have some stones the CAO is smaller, so it will pack very tight up to prevent that you put this simply stones, sensible thing is to put these stones that are available right there and just throw them in.

Actually the guy is doing a very clever job of keeping the porosity of the bed at proper value, that if you have all same size particles your porosity will decrease. If you all same size particles you will have a reasonable porosity. If you have particles of different size they will pack in tighter over a period of time. So the idea is to have a base of stones that are of a reasonable size that provide the porosity and then the others will.

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