INDIAN INSTITUTE OF TECHNOLOGY MADRAS

NPTEL

National Programme on Technology Enahnced Learning
Chemical Engineering Thermodynamics
By

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Lecture 25
Reaction Equilibria

We have first representation of actions, the species.

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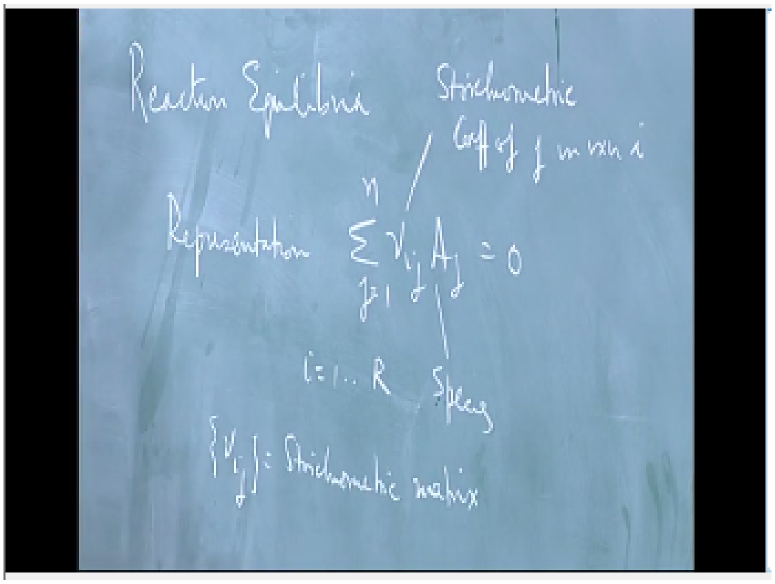

Reaction Equilibria

Strichiometric Coeff of j in rxn i

Representation $\sum_{j=1}^{n} \nu_{ij} A_j = 0$

$i = 1 .. R$

Species

$\{\nu_{ij}\}$: Strichiometric matrix

So j = 1 to n let us see and = 1 to R this νij is called strichiometric matrix. He said the significance of new ij is that DNij which is change in moles of J due to progress of reaction i. As the reaction progresses the change is, or we will just keep this as D Δ j will be the progress variable or D Δ i if you like, for reaction i and we have that break in ij like in Δ i, for each reaction i you change the number of moles of j is proportional to its strichiometric number.

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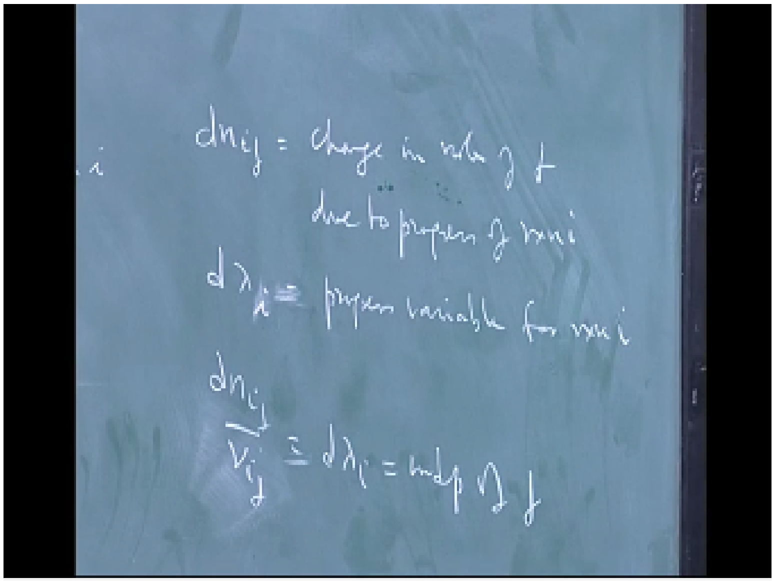

dn_{ij} = change in moles of j due to progress of rxn i

$d\lambda_i$ = progress variable for rxn i

$$\frac{dn_{ij}}{\nu_{ij}} = d\lambda_i = \text{indep of } j$$

By convention the strichometric coefficients are positive. These are remember, these are positive for products and negative for reactants. So if we look at equilibrium, simply I have a box in which many reactions take place. If there is facet homogeneous reaction and say equilibrium of homogeneous reactions. Actually it doesn't have to be homogeneous, it can be heterogeneous but thermodynamic equilibrium means phase equilibrium and reaction equilibrium.

So I can pretend that phase equilibrium first occurred and all the reactions occur in one phase. So forµlation would really be the same. Then I need Dg <= 0 at equilibrium at constant Tnp. At equilibrium you actually have Dg=0 is the criterion equilibrium but dg = -SdT + VdP + sum over 04.27 µi dni now this is 0, this is 0. So you get sum over i, µi dni = 0, make this j, actually it makes no difference. But Dnj is the total change in the number of moles of j. This = sum over I of dnij.

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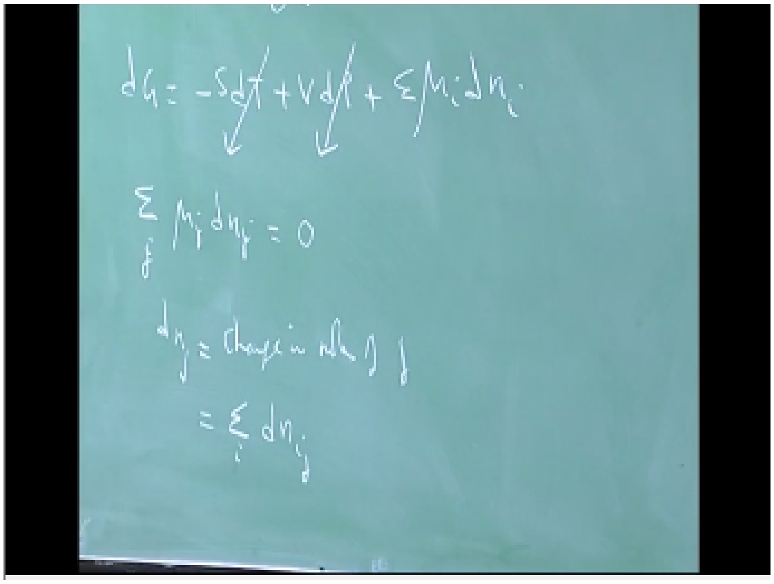

$$dG = -S\,d\cancel{T} + V\,d\cancel{P} + \sum \mu_i\, dn_i$$

$$\sum_j \mu_j\, dn_j = 0$$

dn_j = change in mole of j

$= \sum_i dn_j$

Remember define Dnij as change in moles of j due to progressive reaction i. If I sum over all the reactions I get the total change in moles of j. But Dnij = no j a times d Δi.

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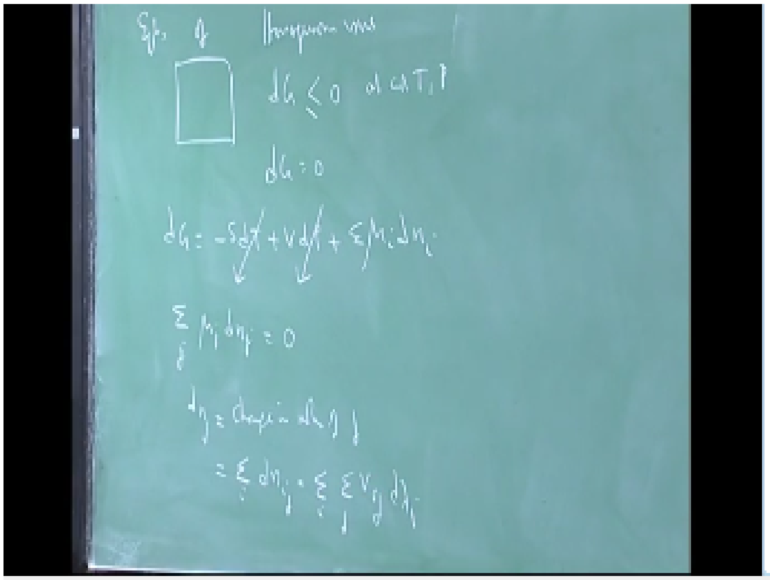

So if you call this equation 1, this is not a mathematical equation, this one is only a representation. This is 2, this is 3, and finally 4. Substitute this back, you get 06.16. I am getting two i's, where did I get 2 from, soμhere i, this is our species and not this j. This is correct. Dnij is simply, there is no sum over i, there is no sum over j, wondering what happened. Dnij is simply νij times t Δi so νij times D λi and there is is no sum over i.This is over all species, this is over all reactions. So like j equals 1, i equals 1 to r. This is sum over I d λi sum over j, this is Dg.

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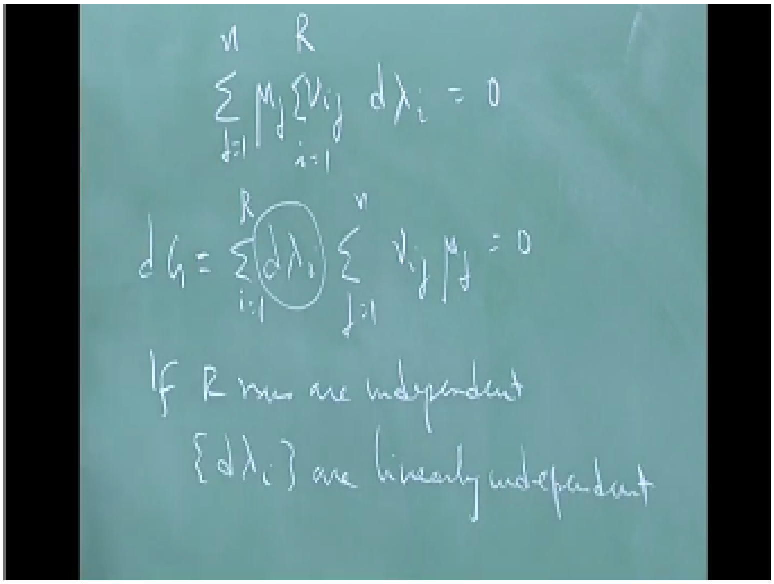

$$\sum_{j=1}^{n} \mu_j \sum_{i=1}^{R} \nu_{ij} \, d\lambda_i = 0$$

$$dG = \sum_{i=1}^{R} \boxed{d\lambda_i} \sum_{j=1}^{n} \nu_{ij} \mu_j = 0$$

If R rxns are independent

$\{d\lambda_i\}$ are linearly independent

This is the criterion equilibrium. Now if all reactions are independent and thermodynamics demands that Dg should be 0 regardless of the progress of any one reaction, then these quantities are linearly independent and you know from linear algebra that if a certain number of quantities, a set of quantities is linearly independent then the sum of the coefficient times this quantity will be equal to 0, only if each of the coefficients is 0. So this implies Σ over j = 1 to n of ν ij μ j should be = 0 for all i.

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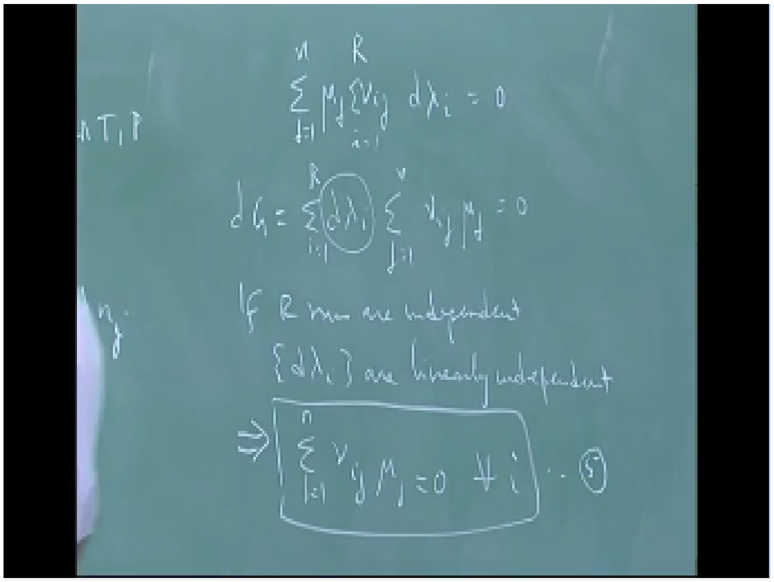

T, P

$$\sum_{j=1}^{n} \mu_j \sum_{i=1}^{R} \nu_{ij}\, d\lambda_i = 0$$

$$dG = \sum_{i=1}^{R} d\lambda_i \sum_{j=1}^{n} \nu_{ij}\mu_j = 0$$

n_j

If R rxn are independent

$\{d\lambda_i\}$ are linearly independent

$$\Rightarrow \boxed{\sum_{j=1}^{n} \nu_{ij}\mu_j = 0 \ \forall i} \cdots ⑤$$

So this is this the final criterion of equilibrium, equation 5. It is important that the reactions be independent as then the progress of each reaction is independent. This summation sum over j sum over i, I am just switching the sums. I am first summing over j and then summing over i. As long as the left hand side is finite, new ij will come there. First you have to do the summation then you have to do this, that is all. When I finish this summation I will have a function of i, that µltiplied by d Δ i. But the argument next step says that d Δ i are independent.

You µst have done vector algebra. You have CiVi=0, if Ci Vi =0 and the set Vi are independent, are linearly independent. This implies Ci=0 for all i.

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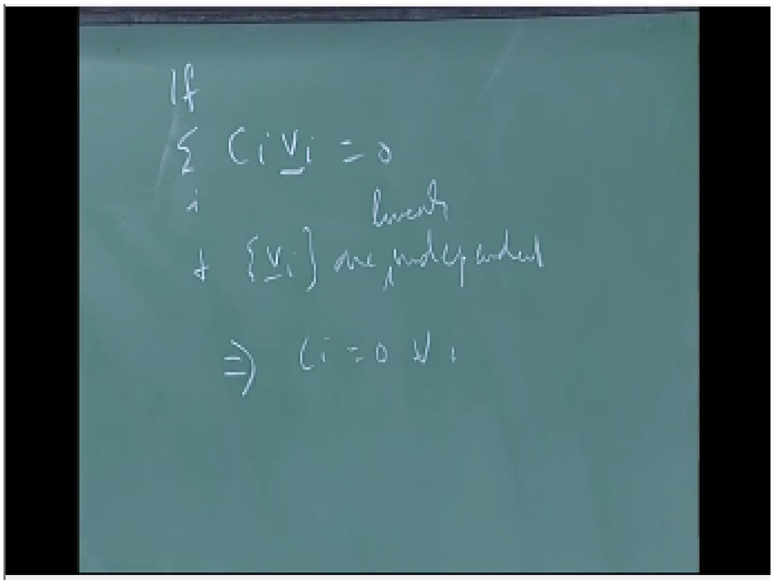

If

$\sum_i c_i \underline{v}_i = 0$

& $\{\underline{v}_i\}$ are linearly independent

$\Rightarrow c_i = 0 \ \forall i$

This is your usual vector decomposition also. When you decompose a vector and three dimensions into three components, the vector is 0 if only if each of the components is 0. It is the same way. So you get this result that if our reactions are independent, each has a progress variable that is independent at others. Thermodynamics demands that the coefficients should be 0 because if it was not 0, then I choose to progress that reaction for which it’s not 0 and change Dg. So if Dg changes, then the original situation could not have been at equilibrium. So if the system is at equilibrium.

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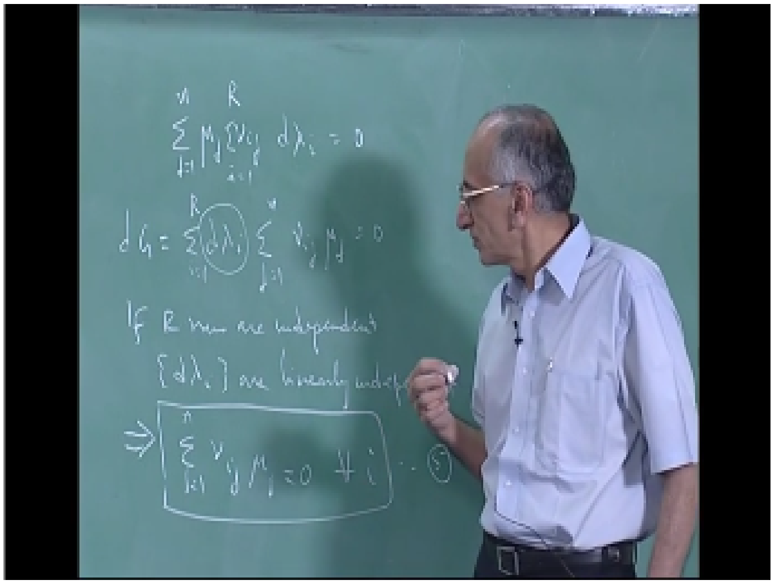

So if the system is at equilibrium then this is true but remember the representation of the reaction was ν ij Aj = 0, this is representation. This is not an algebraic equation. But if you have this representation, then the equilibrium criterion is simply obtained by replacing Aj by the chemical potential of j.

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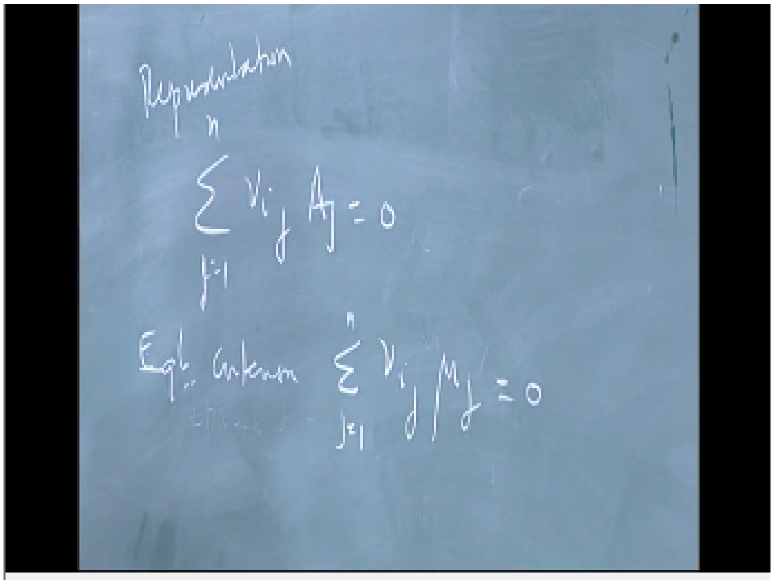

Representation

$$\sum_{j=1}^{n} \nu_{ij} A_j = 0$$

Eqb. Criterion $\sum_{j=1}^{n} \nu_{ij} \mu_j = 0$

Of course in this case as I said new ij=0 for all j not participating in reaction i.

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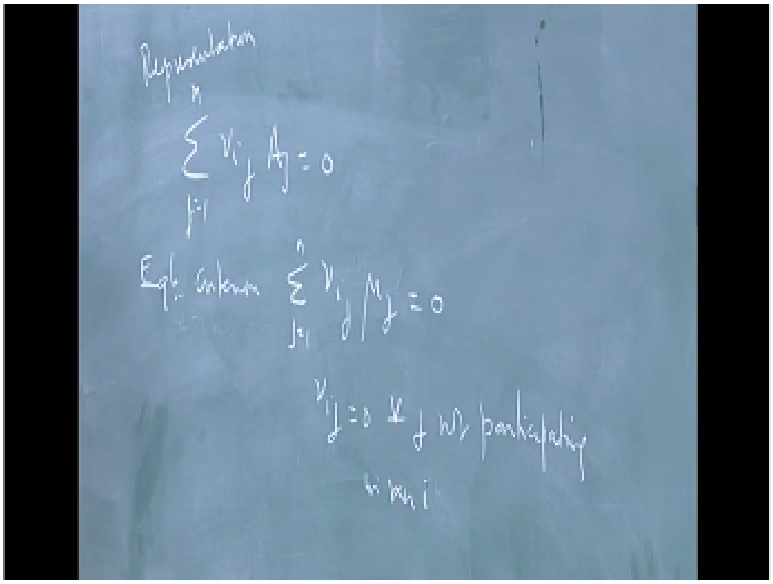

In large systems with many reactions, these matrices, this new ij matrix is often called as parse matrix because you may have 22 components, each of the reactions may involve only 2 or 3. So most of the new ijs will be 0. When large number of computational techniques, you deal with sparse matrices, you need special techniques. When computational is sparse matrices are difficult to deal with. So this is the criterion equilibrium but this is also equal to, remember that this is defined as Δ G, for any reaction i, is defined as Σ over j = 1 to n ν ij μ j.

This is for reaction i, the free energy change is exactly this. This is because if you write for example, let us say you are burning carbon, or let us say you get half O2, you got CO, I will write another reaction,Co + ½ o_2 giving you Co_2, so in this nomenclature we just rewrite this as 14.06. So this could be component 1, this could be component 2, this is 3 and this is 4. So the number of species at equilibrium is 4 and you write that coefficient matrix new ij is the same as for component 1 in the first reaction, its -1, for component 2 its -1/2, for component 3 its +1, for component 4 it is 0.

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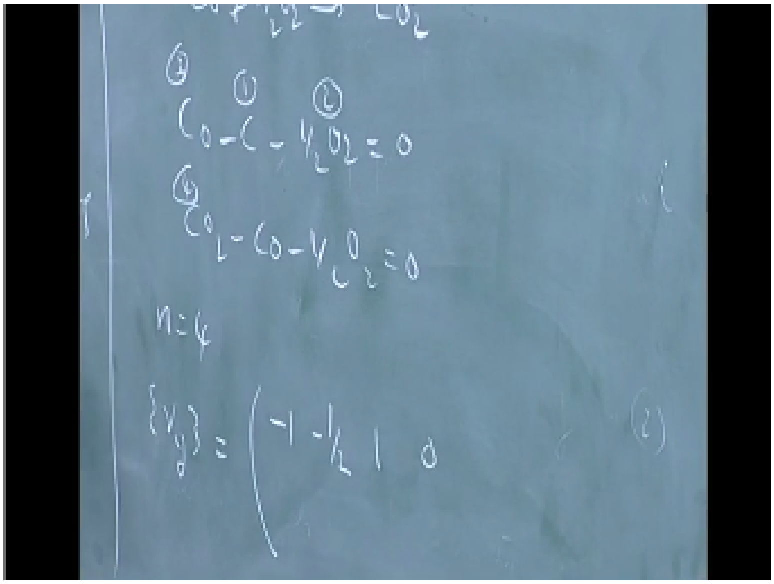

③ ① ②

$CO - C - \frac{1}{2}O_2 = 0$

④

$CO_2 - CO - \frac{1}{2}O_2 = 0$

$n = 4$

$\{\nu_{ij}\} = \begin{pmatrix} -1 & -\frac{1}{2} & 1 & 0 \end{pmatrix}$ (2)

For the second reaction component 1 is absent, component 2 is oxygen which is -1/2, for component 3 which is CO its -1, for component 4 CO2.

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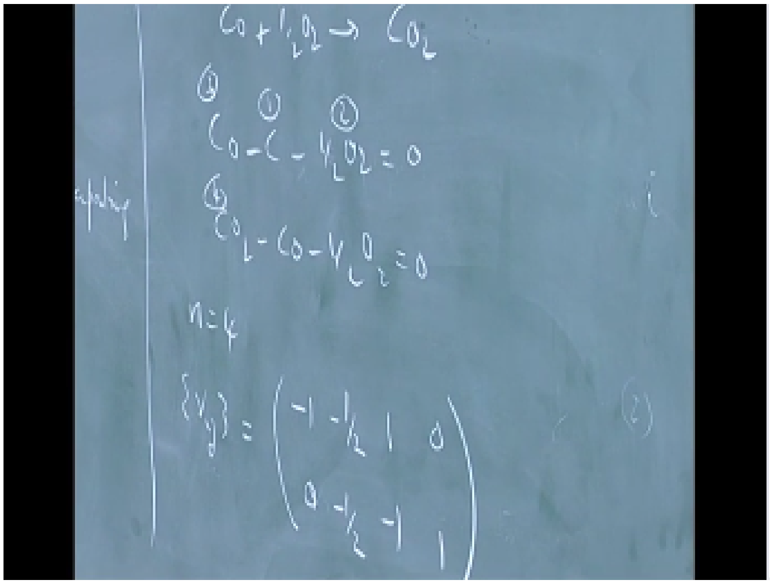

Because these are linear algebraic equations the number of independent equations is simply the rank of this matrix.

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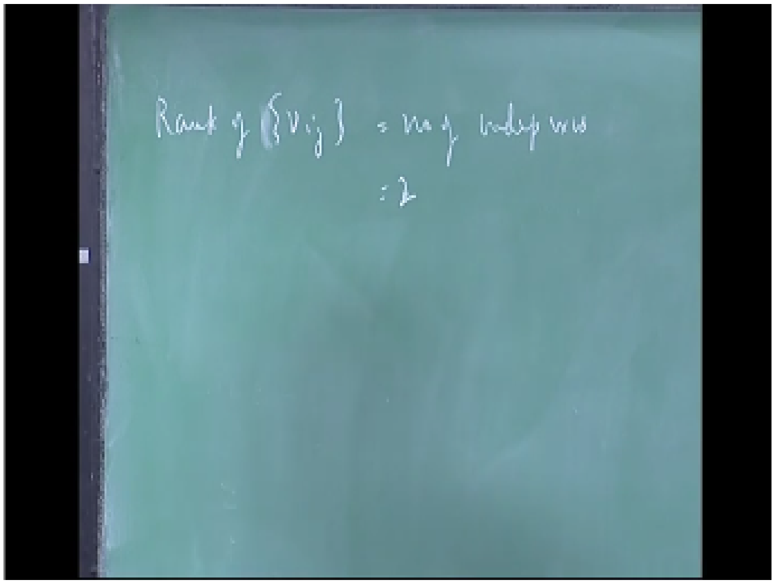

So in this case the rank of this matrix, rank of new ij is equal to number of independent reactions. In this case it is too clearly. Tank is of course the largest square matrix whose determinant is non zero. You could have written C+O2= CO2 but that would not have been an independent reaction because you can produce it by combination of the other two. So this Δ G for example, for this reaction ∂ G would be, let me write the change in, we may cite down the moles. Let us say at equilibrium, I will write these out = Co, Co + ½. Let us say I start with one mole of carbon and one mole of oxygen.

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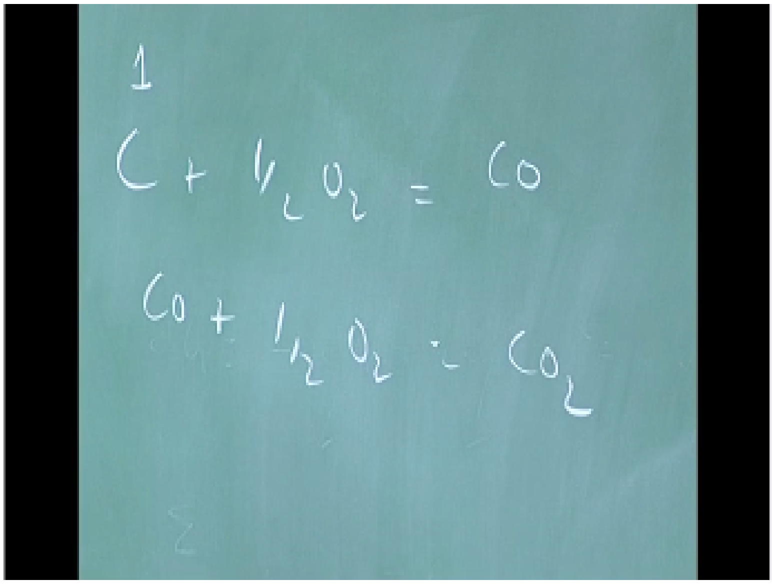

1

$$C + 1/2\, O_2 = CO$$

$$CO + 1/2\, O_2 = CO_2$$

Is initially this is, I will write here, initial carbon is carbon, first I should write it separately, species initial and moles at equilibrium. Now carbon oxygen, carbon monoxide and carbon dioxide. Initial moles 1, 1, 0, 0, this is arbitrary, you can start with any.

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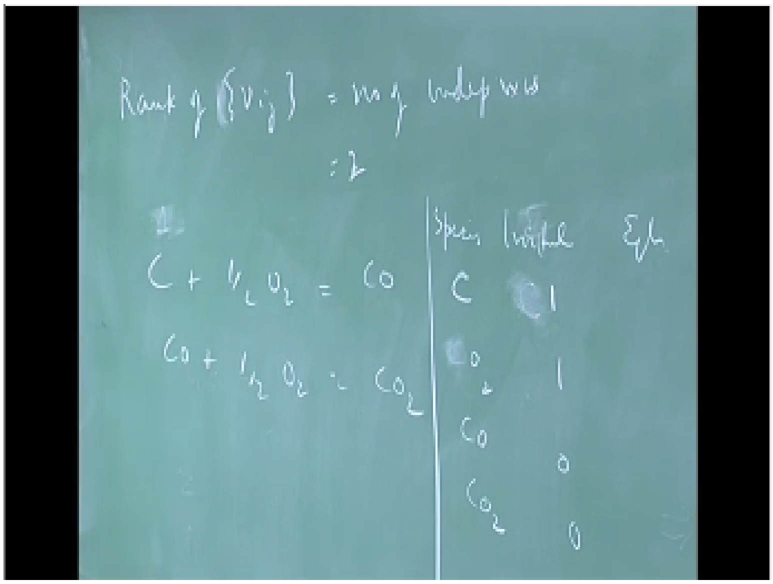

At equilibrium if this is 1-x1-x2, let us say at equilibrium, let x1 be equal to moles, CO produce in reaction 1, and x2 is equal to moles, CO2 produce in reaction 2. So oxygen is consumed in both its 1-x1/2-x2/2. Carbon monoxide, x1 is produced –x2, then carbon dioxide is x2. Actually I have chosen a bad example because I have chosen a heterogeneous system. Carbon started with, 1-x1 that is all, my mistake, sorry, thanks.

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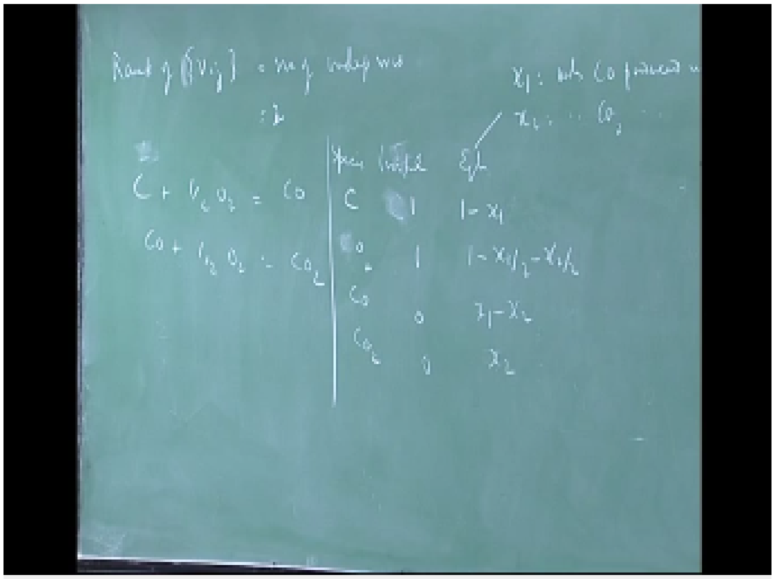

Only in the first reaction, 1-x1 is the value at equilibrium. So I have criteria of equilibrium, I have the first reaction which is, you call this component 1. This is 1, this is 2, this is 3 and this is 4. So for the first reaction I have carbon monoxide, for carbon monoxide the coefficient is 1 in the first reaction. So µ of carbonmonoxide – µ of carbon – ½ the chemical potential of oxygen = 0. The second reaction is µ4 -, oh these are numbers, correct, µ carbon is 1 and oxygen is 2. This is µ 4 - µ 3 – ½ µ 2 = 0.

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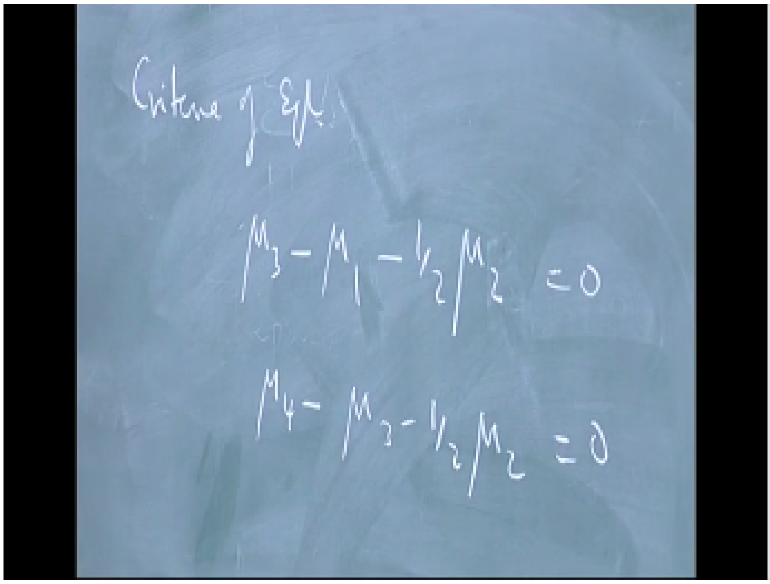

Criteria of Eqm:

$$\mu_3 - \mu_1 - \tfrac{1}{2}\mu_2 = 0$$

$$\mu_4 - \mu_3 - \tfrac{1}{2}\mu_2 = 0$$

Where did the Gibbs union equation go or is it still around? You cannot get rid of equations when you do not like them. Tell your guesses, is it still around or have you lost it? It is round right? What the Gibbs equation still demands is whether there is reaction or not sort of relentless, all μ1, μ 2, μ 3 etcetera have to satisfy the Gibbs equation.

So basically all of these will have to be functions of compositions such that the Gibbs equation is satisfied. Now suppose in this particular case I happened to have a solid end, a gas phase. So this is carbon, here I have CO2, CO and O2 and so I have two phases. So I have to write down the models, in this phase I have to write the Gibbs equation for components 2, 3 and 4. Component 1 is pure solid.

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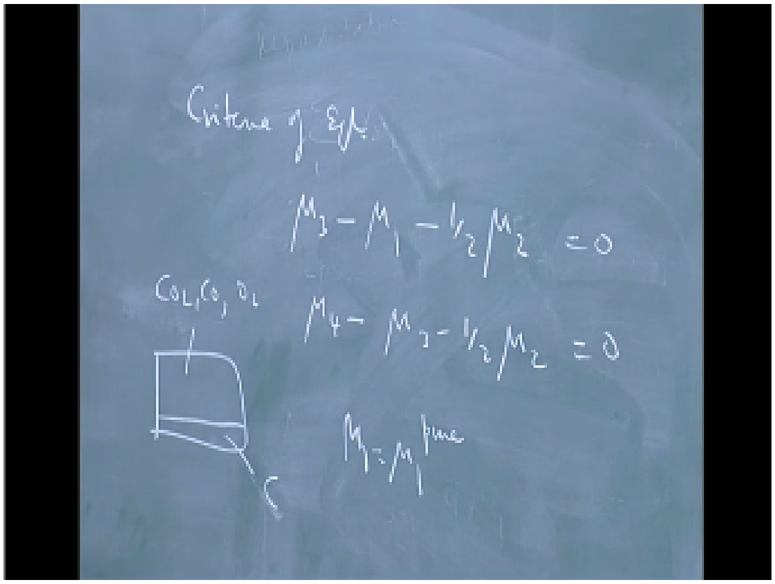

So I have first of all µ1=µ1pure, I could write an equation for it in terms of µ1 pure being in equilibrium with its vapour phase. µ 1 solid is equal to µ 1 vapour and I could include µ1 here. But I will write it as it is, I will tell you why. The others, µi= µi, all of the others are in the gas phase, so you will µi0 = RTln pyi times now i=2, 3, and 4. In the reaction equilibria context all you do is separate things, the things that depend on the completion and other things that depend on temperature and pressure.

Then if possible you separate out also the pressure dependence. Here µ i0 is the function only of temperature, µ1 pure is a function of temperature and pressure but you know the contents base the pressure depends the chemical potential is very weak so this is approximately equal to µ 1 pure at t and p equal to 1, means it is independent of pressure, that is the only important point.

That is effectively function of temperature alone. I want write this, I am interested in the composition at, I may be burning coal and all I want to make sure as for example there is no carbon monoxide because I want the fellow who is burning the coal to survive. That is all I want, carbon monoxide below as the level or as I said 0 reacts equilibrium.

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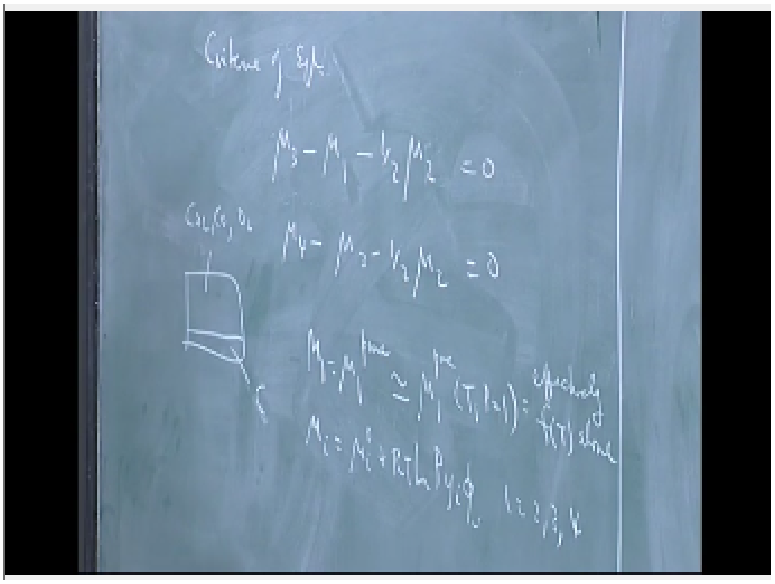

So I am asking that I want to solve this equilibrium equations for the composition at equilibrium and I can put constraints on it as a designer, so if I am writing these out, RTln pyi Øi contains the composition dependents, I will separate that out, I will get log of p3 y3 p3, µ1 is effectively independent of this thing, I will take the µ's to the other side, µ 0's the functions of temperature to the other side, µ 1 will automatically come to this side, ½ µ2 0 – or I will take the ratio p2 y2 p2 are half.

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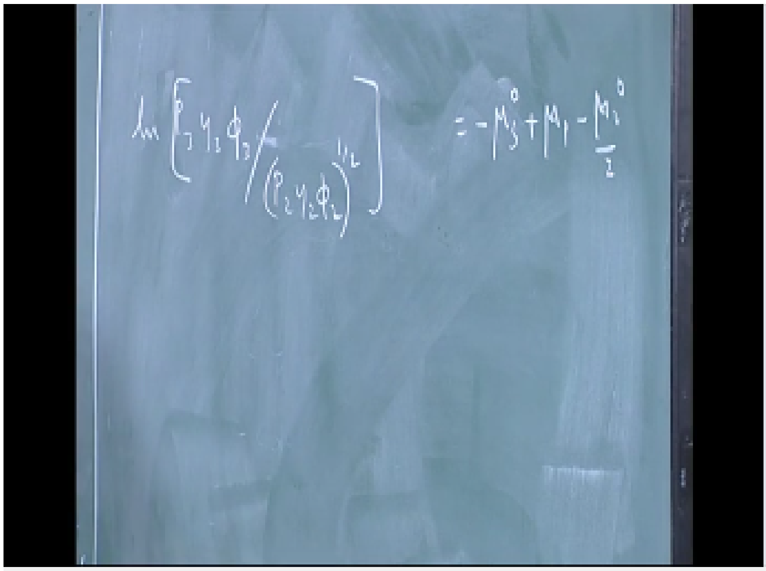

$$\ln\left[p_3 y_3 \phi_3 / (p_2 y_2 \phi_2)^{1/2}\right] = -\mu_3^0 + \mu_1 - \frac{\mu_2^0}{2}$$

This is your first equation, all these components are gas phases so I will get log of p4 y4 and p4 divided byp3 y3 Ø3 there is no pr sorry it just p3 equal to, these things are come to this side, it will become μ3 0 + ½ μ2 0 – μ4 0, because this quantity is called ∂ g we denote this ∂ g 0 for reaction 1. I put approximately because μ 1 is not μ 1 0, μ 1 is chemical potential of component 1 as a solid at the temperature and pressure of this system.

It is also the same as pressure equal to 1 but it is not in the gas phase so this super script 0 does not apply to that but ∂ g1 by 0 convention is simply the standard free energy change in the reaction with each of the components in its standard state. So carbon will be in a solid state, the others will be in a gaseous state and this quantity, the only thing that matters is that this quantity is not a function of pressure. It is a function of temperature alone, effectively a function of temperature alone.

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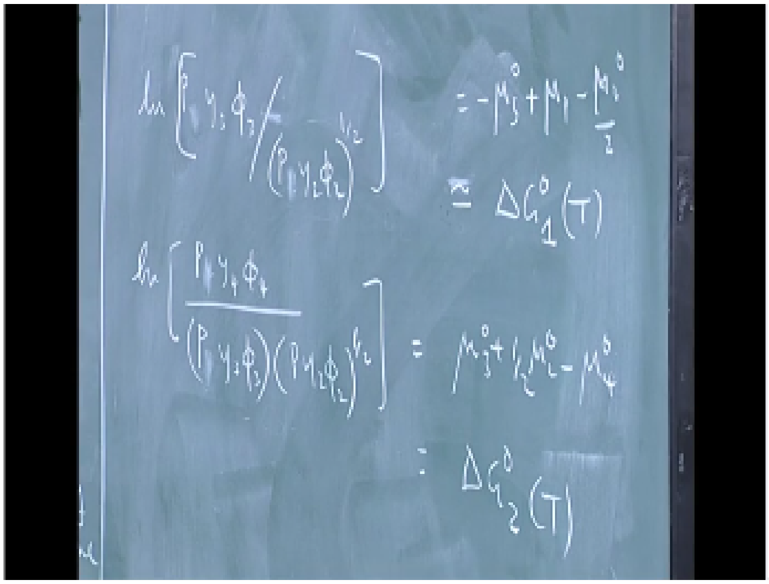

$$\ln\left[P y_3 \phi_3 / (P y_2 \phi_2)^{1/2}\right] = -\mu_3^0 + \mu_1 - \frac{\mu_2^0}{2}$$

$$\cong \Delta G_1^0(T)$$

$$\ln\left[\frac{P y_4 \phi_4}{(P y_3 \phi_3)(P y_2 \phi_2)^{1/2}}\right] = \mu_3^0 + \tfrac{1}{2}\mu_2^0 - \mu_4^0$$

$$= \Delta G_2^0(T)$$

Now for this particular system there is a coupling, mole fraction depends on both the reactions so let me write down the mole fractions. As far as gas phase is concerned this is not in the gas phase, this is solid, all these three are in the gas phase, so the mole fractions are determined only by these components.

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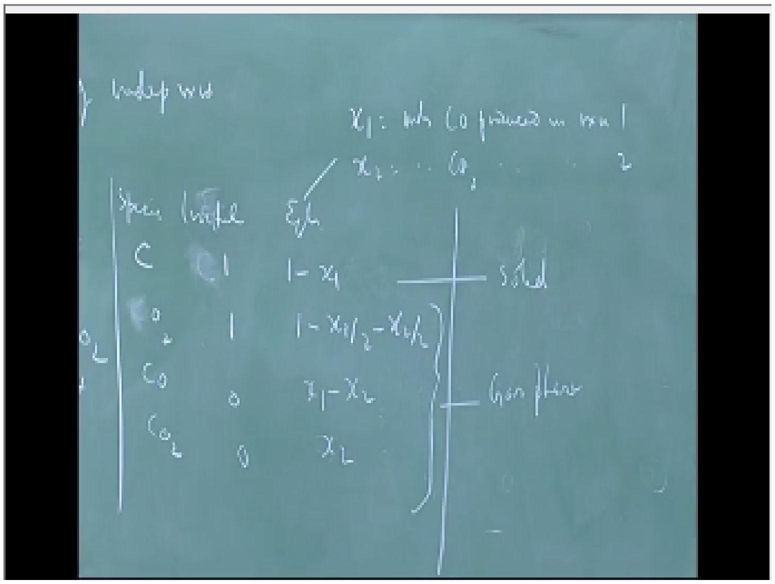

Species	Initial	Eqb
C	1	$1-x_1$
O_2	1	$1-x_1/2-x_2/2$
CO	0	x_1-x_2
CO_2	0	x_2

So total moles in the gas phase at equilibrium is 1 + x1/2, in counting only gas phase moles. Incidentally there is a convention is ∂ g 0, you have got a prime there to indicate that one of the components is not in the gas phase.

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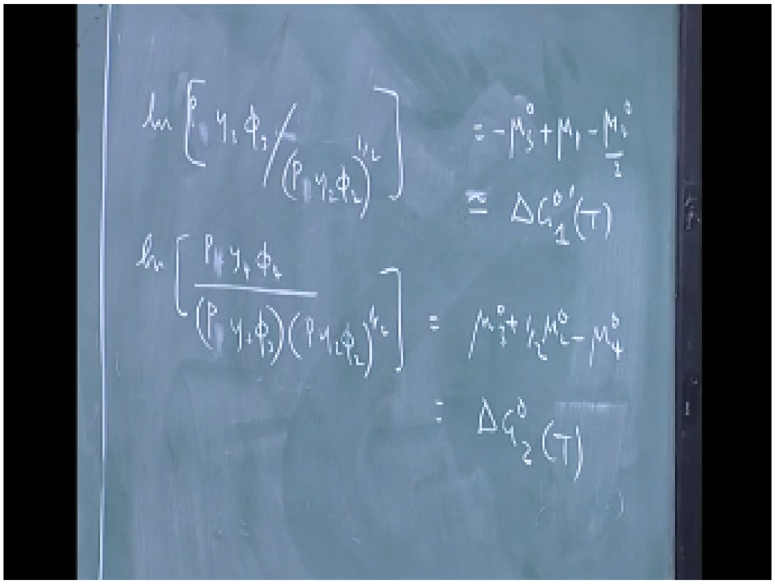

$$\ln\left[P y_1\phi_1 \Big/ \left(P y_2\phi_2\right)^{1/2}\right] = -\mu_3^0 + \mu_1 - \frac{\mu_2^0}{2}$$

$$\cong \Delta G_1^{0\prime}(T)$$

$$\ln\left[\frac{P y_4\phi_4}{\left(P y_3\phi_3\right)\left(P y_2\phi_2\right)^{1/2}}\right] = \mu_3^0 + \tfrac{1}{2}\mu_2^0 - \mu_4^0$$

$$= \Delta G_2^0(T)$$

The function temperature, the prime is often left out these days, because during convention was indicated you do put a prime on this ratio, I will tell you in a minute, so I can write down the mole fractions here, the mole fractions are simply 1 – x1/2 – x2/2 divided by 1 + x1/2, oh -, these are being added x2 – x2/2 are also there, okay, thanks.

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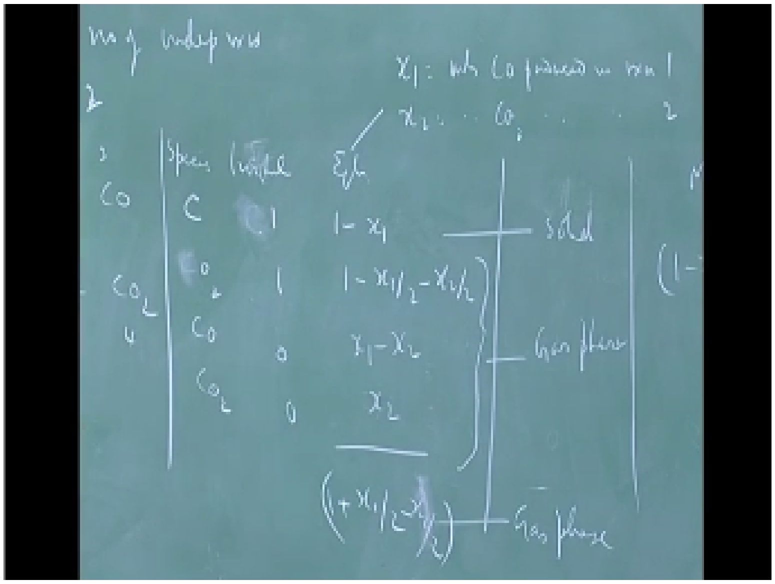

And so on, so you write this as number of moles by total number of moles, so I have this py3, y3 is actually 1 3 p3/ np and this np is this total moles at equilibrium and each of these is ni. So let me take this ratio, I have p per ½ and I combine these things, I write p per ½, I have y3 which is n3/ n total, this is n2/n total to the power ½, so I have n2 2 par times ɸ3 and pull out the nt per ½ here.

Incidentally that whole thing is actually fugacity of component 3 by fugacity of component 2 per ½, it is also equal to p per ½ by nt per ½ x all this, just write various forms of it, it is also = p per ½ x y3/y2 per ½ into ɸ3 per ɸ2 per ½ and this is equal to on the right hand side exponential of –∂ g 1 0/ rt.

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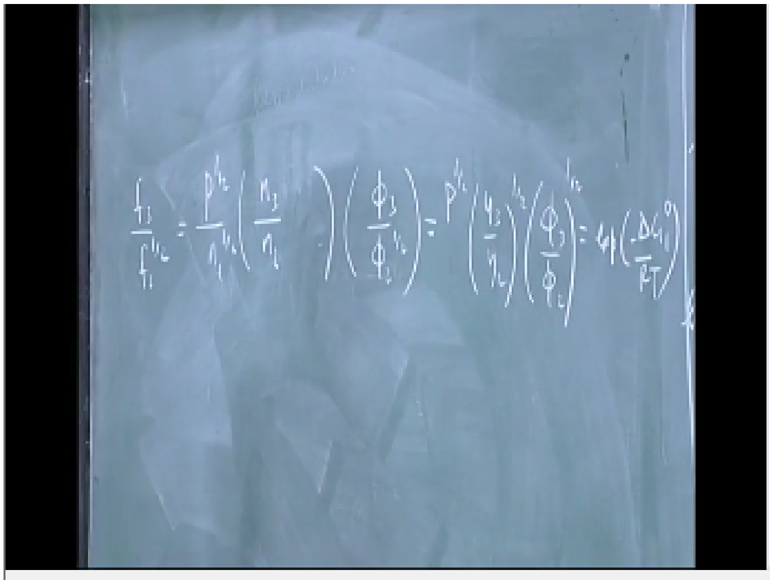

The secondary action is f4 by f3 f2 per ½, this is equal to 1 by p per ½, number of moles is np per ½, we got a numerator x if you like n4 by n3 n2 per ½ is also = nt by p per ½ x y4 y/3 by 2 per ½ is equal to exponential of, there is a lot of ways of writing the same equation because this ratio is a function of temperature alone so at a given temperature this is the constant, this is given a name kf is equilibrium constant in terms of a gas phase ratio of this. This is equal to equilibrium constant for reaction 2 again in terms of gases.

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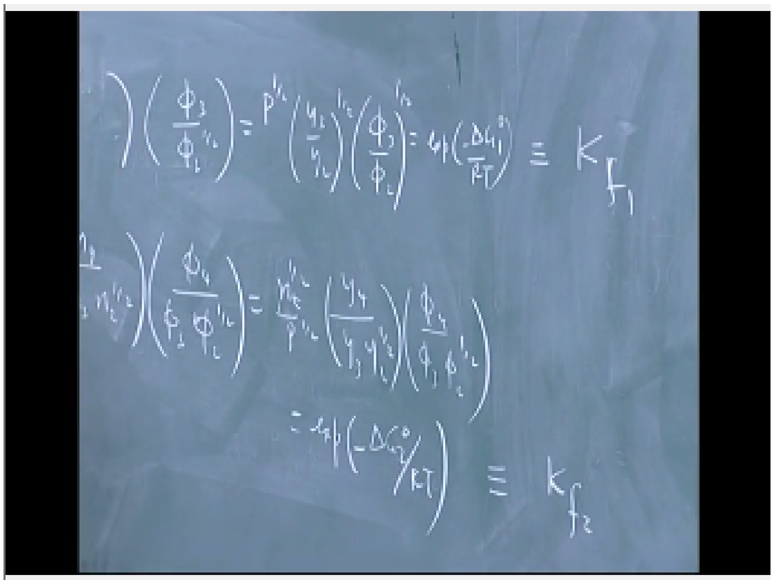

$$\left(\frac{\phi_3}{\phi_2^{1/2}}\right) = P^{1/2}\left(\frac{y_3}{y_2}\right)^{1/2}\left(\frac{\phi_3}{\phi_2}\right)^{1/2} = \exp\left(-\frac{\Delta G_1^0}{RT}\right) \equiv K_{f_1}$$

$$\left(\frac{\phi_4}{\phi_3\phi_2^{1/2}}\right) = \frac{n_T^{1/2}}{P^{1/2}}\left(\frac{y_4}{y_3 y_2^{1/2}}\right)\left(\frac{\phi_4}{\phi_3\phi_2^{1/2}}\right) = \exp\left(-\Delta G_2^0/RT\right) \equiv K_{f_2}$$

Now this is exactly product over I, each of these actually becomes product over j of f j to the power μij. In reaction 1, I must put a prime here to indicate that this only involves gaseous components. So if you take the first reactions cO and O2 are involved, f3 to the power 1 times f2 to the power -1/2 so that comes with a denominator, so this is a very compact notation, this is your k f prime so there should be a prime here to indicate that I do not include non ratio components in calculation.

This is valid even here so this is k of i, in the second case you do not have a solid component, you directly have, which forμlation you use, actually basically you need to solve for at equilibrium you are solving for x1 x2, the variables at equilibrium are x1 x2 pressure and temperature.

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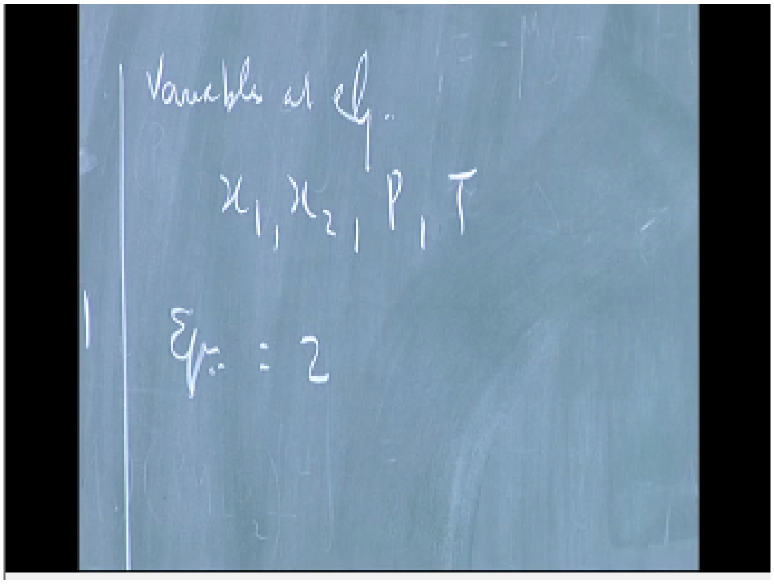

And you got 2 equations to solve for, I get a certain value for x1 - x2, I could change the temperature so that x1 - x2 is 0, and I demand, it is a very difficult and any reaction that x1- x2 will be exactly 0 but you can ask that it should to be less than 10 to the power of -10, some number, pre determine number.

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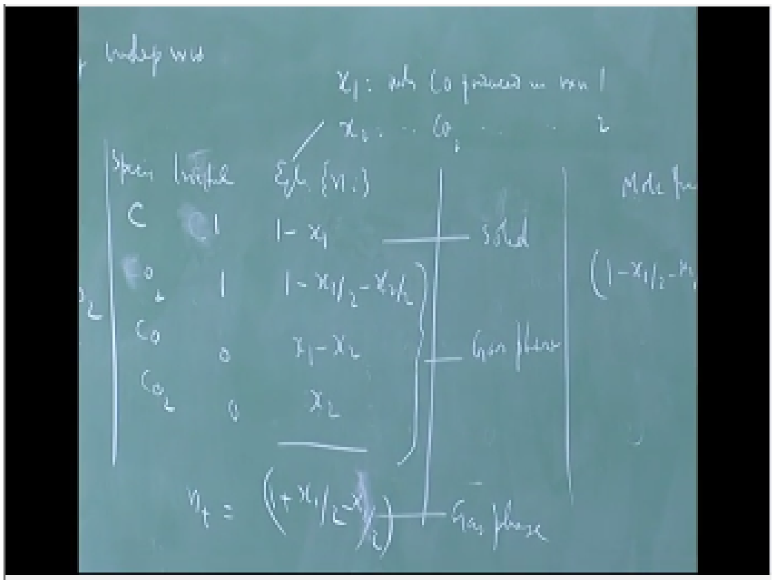

Then you can find the conditions under which this is true, for example if I fix the temperature then the right hand side is completely fixed. In practice what you do is carry out this reaction may be possible to carry out the reaction at one convenient pressure so you carry it out at some low pressure that the gas phase behaves ideally so all the ϕ are 0. For example because this ratio, it is a form of the ratio, this is f3 by f2 per half, there should be a per half here, right, n3 by n2 per half, so this is called k n for example and this is called kp and this is called ky and to add to the fun you can take the pn side and call it kp.

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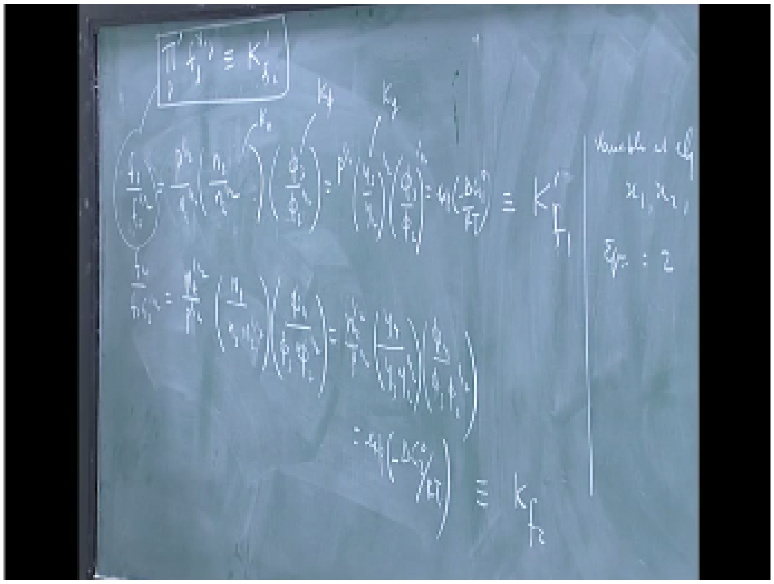

You can define, k is simply the symbol, k is by, in casae of y any donkey would simply be donkey to the power of ij for that, that is all, it is simply a symbol. The thing is depending on the kind of data you have available you can solve for different quantities. In fact reaction equilibrium is very easy, you could have in fact had, instead of k prime you could have used k itself except that you then add to this reaction set, carbon solid, this is solid, you will write to carbon gas and here you have saturation pressure this µ1 is solid pure will be – µ1 gas pure =.

Actually µ and gas will not be pure because once you have the gaseous phase carbon is going to be in combination with all of those, so this will be µ 1 0 + RTln pY1 Ø 1. Because y1 will be so small that effectively if the other components do not affect it you would have had µ 1 gas would be µ 1 gas pure which would have been µ1 0 + rtln p1 saturation times Ø 1 saturation so this will be almost effectively p1 saturation times Ø 1 saturation.

But the point is the whole treatment of reaction equilibria depends on the fact that µ 1 0 is a function only of temperature, but µ 1 0 + rtln p1saturation is also a function only of temperature.

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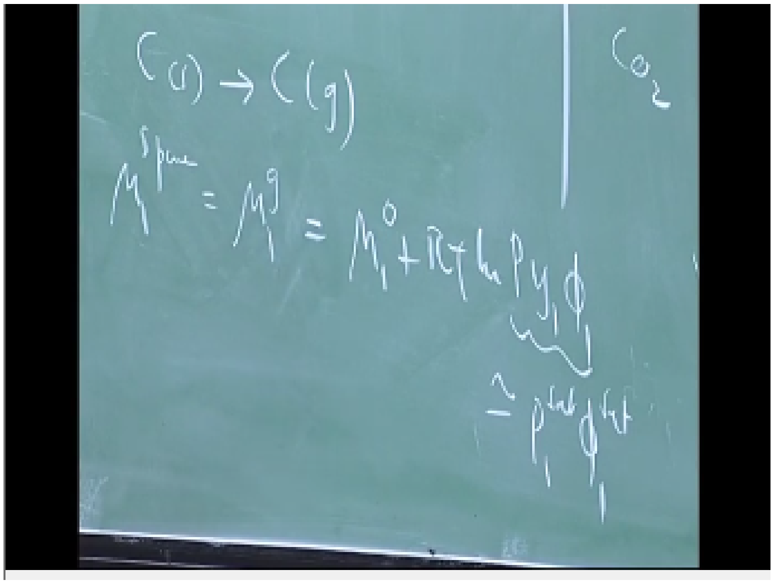

The number does not matter because what you do here, you have get an experimental value of ∂ g10 somehow, you can get that from others experiments or the combining others experiments, that is you can add and subtract reactions so that you get your desired reaction but this µst come from measurements of these quantity, for example if it comes from this reaction you have to measure y2 y3 and p at a sufficiently low pressure where ф3 ф2 are1.

If you do that then you get the quantity at one pressure, it is not a function of pressure so you can use it any other pressure. The entire treatment of equilibria again, permanent pressure, always duck the issue of calculating µ 1 0, you do not know that number but you know what it is, you know it is the chemical potential of pure one in the gas phase at temperature pm.

We do not want, so if you can extract the number for that or number for, a combination of µ zeros, you do not need the individual zero you get the value, if you do that then you get it from the tables and use these, in fact this is a function of temperature alone. The whole idea is to separate everything in definition. In fact I would always start with this forµlation, the µ ij, you can never go wrong in a fraction equilibria if you start with this forµlation. Then throwing the models for chemical potential depending on the phase in which they exist.

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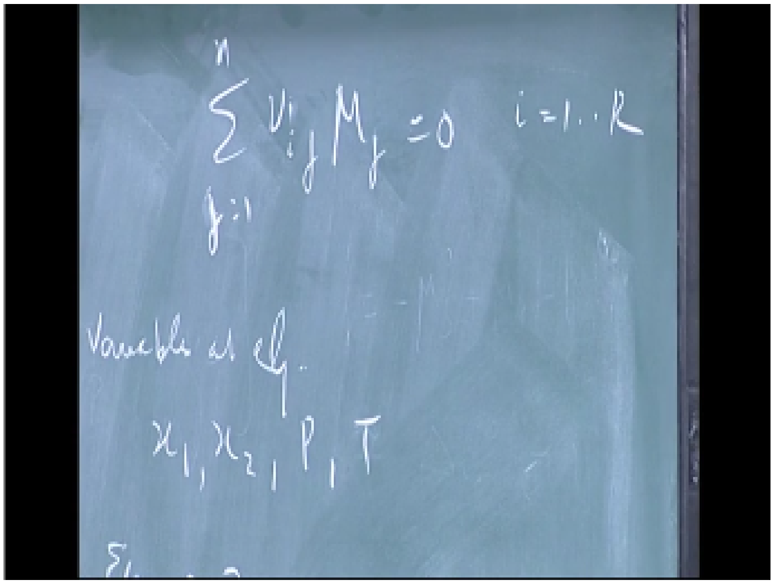

$$\sum_{j=1}^{n} \nu_{ij} M_j = 0 \qquad i = 1..R$$

Variable at eq..

x_1, x_2, P, T

If you think got used to doing this and this is already got the algebra being done for you so you can go ahead, actually I have carried out, I have done this for a µlti component system, I could start off with one but you have already seen the reaction equilibria. Very often you could have for example, you could have a catalytic reaction, in this case it is a different issue but if you had a more complicated reaction there, you have a catylist involved and very often the caylist gets poisoned because its surface is occupied by the carbon particles and therefore it becomes ineffective.

Then you can demand that the carbon deposition should be below a certain limit so you can have a set of reactions in which one of the constraints you throw in additionally is simply a design constraint, so the constraints are the equilibrium equation, thermodynamics poses an equilibrium criteria for every independent reaction that you write.

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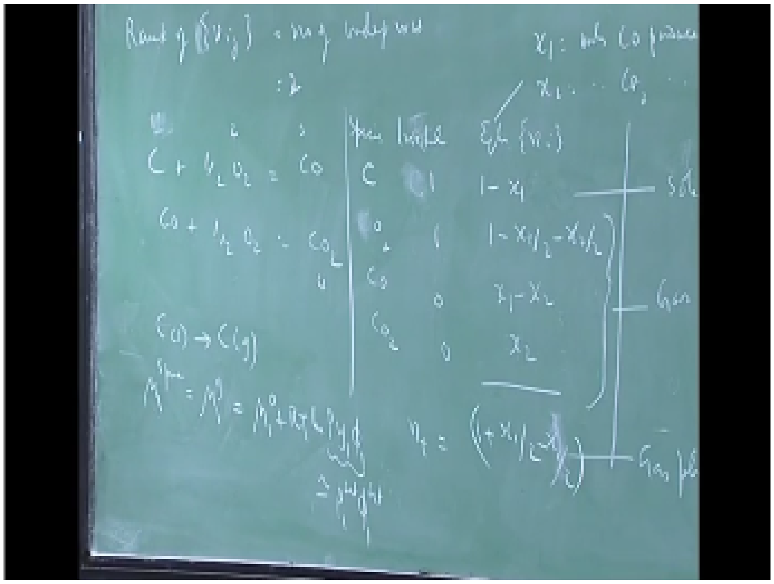

Then you may have a temperature constraint simply because the container may be carrying out reaction here and the refineries, for example one of the problems in the refineries is catalytic conversion, it is one of the largest economic drivers, depending on the market you may want to sell more diesel or you may want to sell more lubricating oil, so you may in the distillation column itself you may have a whole separation, so what you do is if you want more diesel you take this lubricating oil component, you need the heavy components.

You need a catalytic cracker. That is you heat it and decompose the higher molecular weight components into lower molecular weight components. Ultimately the diesel will be a lower molecular weight component and you feed this back to the disclation column it comes out in the diesel steam. In fact one of the big problems that they have is how do you get more diesel out of the system? That is how do you get more naphtha, how do you get more gasoline?

The other problem that present refineries has is the removal of sulphur. How do you desuplurize because the oil we get is crude oil which contains high sulphur component. Now if you do these cracking operations the catalyst is very effective initially but the carbon deposition makes the catalyst ineffective. So you can ask under these conditions, you can ask how can I make the carbon 0 at equilibrium? So I can ask that x1 should be equal to 1. This is a trivial problem, it does not make sense here but if I write down a more complex system, I can simply ask when does, when should the carbon deposition on the catalyst be very small?

So the whole set of reaction equilibrium problem, many of them are from Denby that I have given you, we will go through some of these. We will just ask various questions, for example, why does the, you know the basically the oars in inorganic chemistry. All the oars occur as a sulphide xeroxides. First question you can ask is why do they occur as sulphide xeroxides? You will find if you do a ∂ G calculation that is the lowest energy form. Then you have to look at the other questions are when you roast zinc sulphide why do you get zinc oxide, at what time, what temperature do you get zinc oxide?

Or if you use calcium or limestone you get calcium oxide but is calcium oxide stable? Can you store it? You will find after a while it becomes calcium carbonate because even at the low 10^{-2} carbon-di-oxide in the atmosphere the equilibrium contains a significant amount of calcium carbonate. You can calculate the equilibrium quantities of calcium carbonate and calcium oxide. So I think that is all, the real interest, the theory part of it is trivial. But doing the calculations has to do with the kind of data that you have.

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