Thermodynamics And Kinetics Of Materials

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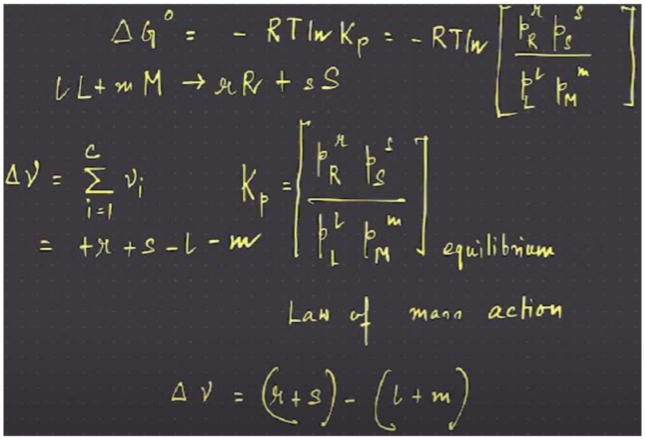
Lecture 38

Elements of thermodynamics of interfaces and thermodynamics of irreversible processes

As we are talking about reaction thermodynamics right, thermodynamics of reactions in multi-component systems and we are looking at multiple reactions. So when we looked at multiple reactions again we did the conservation of elements, we had also this equilibrium constants and as a result we had several equations and we can solve them numerically. Now this equation basically is called the law of mass action right and delta nu basically is R plus S minus L plus M for this reaction where L moles of L react with M moles of M right. So basically L moles of M react with M moles of M to produce R moles of R which is one product and another these are the products right R and S are the products. So this is a product, this is another product and these are the reactants L and M react right and if you see this is R plus R plus S and this is minus L minus M and that is the delta nu or sum over the all nu. So basically if you do the sum so this is the sum over nu or this is the change in there.



$$\Delta G^{\circ} = -RT\ln K_p = -RT\ln\left[\frac{p_R^{r}\,p_S^{s}}{p_L^{l}\,p_M^{m}}\right]$$

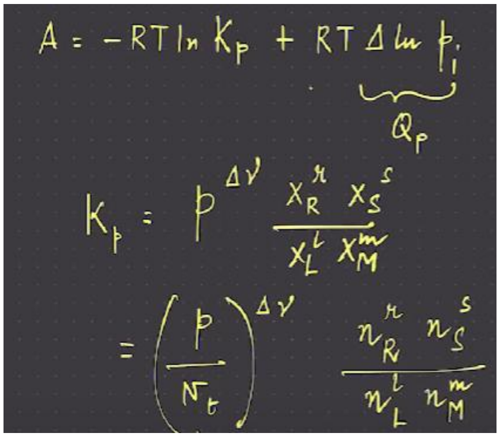
$$lL + mM \rightarrow rR + sS$$

$$\Delta\nu = \sum_{i=1}^{c}\nu_i \qquad K_p = \left[\frac{p_R^{r}\,p_S^{s}}{p_L^{l}\,p_M^{m}}\right] \text{ equilibrium}$$

$$= +r + s - l - m$$

Law of mass action

$$\Delta\nu = (r+s) - (l+m)$$

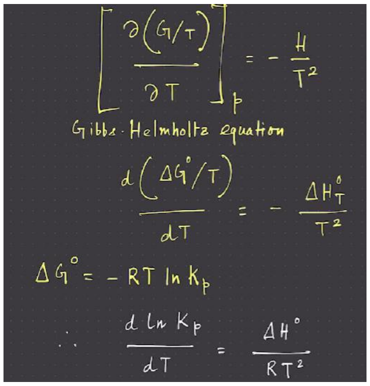


$$A = -RT\ln K_p + \underbrace{RT\,\Delta\ln p_i}_{Q_p}$$

$$K_p = p^{\Delta\nu}\,\frac{X_R^{r}\,X_S^{s}}{X_L^{l}\,X_M^{m}}$$

$$= \left(\frac{p}{N_t}\right)^{\Delta\nu}\frac{n_R^{r}\,n_S^{s}}{n_L^{l}\,n_M^{m}}$$

So delta nu or the way we have initially introduced it, it is basically the sum nu i right, sum nu i is the same as delta nu is nothing but sum nu i. So basically if I look at delta nu, delta nu is nothing but sum of i equal to 1 to whatever be the number of species 1 to say c and this is basically nu i right. So basically and as I told for products it is plus and for reactants minus so basically this basically becomes if you look at this reaction it is R plus R plus S minus L minus right the same thing that we have drawn right. So basically and also we know this right that A equals to minus RTLN kp plus RTLN RT del n theta LN pi and that is nothing but RTLN qp and you have this relation.



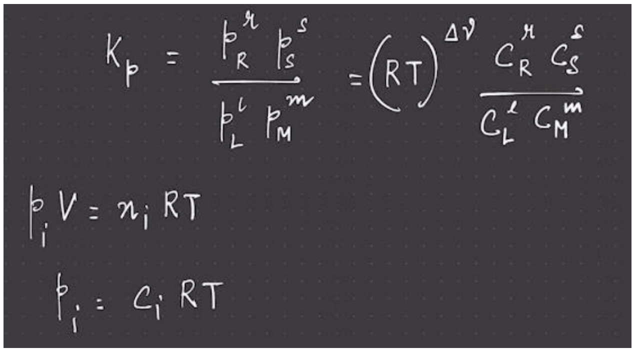
$$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{H}{T^2}$$

Gibbs-Helmholtz equation

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta H^\circ_T}{T^2}$$

$$\Delta G^\circ = -RT\ln K_p$$

$$\therefore \quad \frac{d\ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

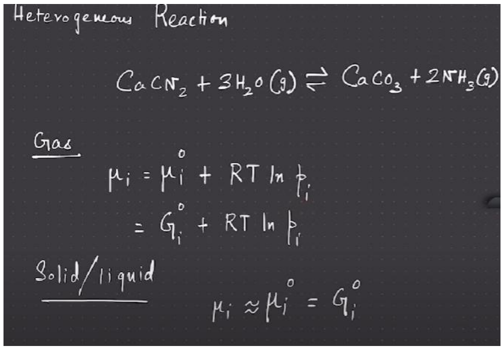


$$K_p = \frac{p_R^r\, p_S^s}{p_L^l\, p_M^m} = (RT)^{\Delta\nu}\,\frac{C_R^r\, C_S^s}{C_L^l\, C_M^m}$$

$$p_i V = n_i RT$$

$$p_i = C_i RT$$

So and you have also the almost gives almost equation from which you can write this like the del LN means how the equilibrium constant changes the as a function of temperature and it is related basically to the delta H0, the delta H0 or delta HT0 whichever you call it and that is the delta H0 of the reaction right and delta H0 can be in endothermic or exothermic right reactions can be in stomach or stomach that is something that we have explained. Now if you have all gases so many a times what we do is we basically can also use ideal gas law like piV equals to Ni RT or pi equals to Ni by V RT so this becomes RT so Ni by V is nothing but the concentration right so Cr to the power R, Cs to the power S this is basically Cr is basically concentration of R in most per unit volume right you can also have so this is where I was basically pointing to you can also have heterogeneous reaction and one of the heterogeneous reactions is like oxidation where you have a metal which is solid which combines with oxygen which is gaseous and forms a metal oxide which is again a solid. So here also calcium senite right Cn2 so this is calcium carbonitride you can tell carbonitride because this is calcium Cn2 right so carbonitride so if you look at that so this is basically a solid this is basically a solid now it reacts with water vapor which is gaseous forming calcium carbonate and ammonium



Heterogeneous Reaction

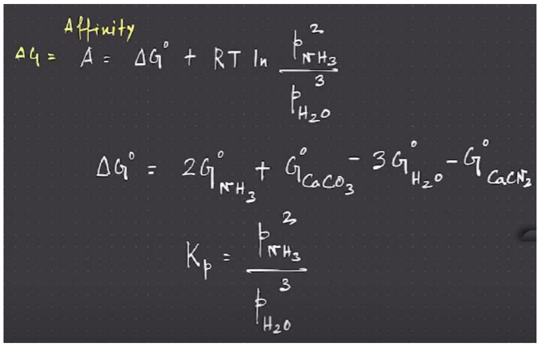
$$CaCN_2 + 3H_2O(g) \rightleftharpoons CaCO_3 + 2NH_3(g)$$

Gas

$$\mu_i = \mu_i^0 + RT\ln p_i$$
$$= G_i^0 + RT\ln p_i$$

Solid/liquid

$$\mu_i \approx \mu_i^0 = G_i^0$$



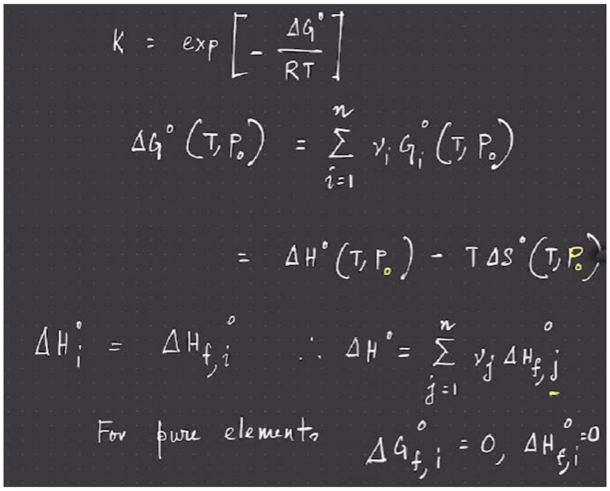
Affinity

$$\Delta G = A = \Delta G^0 + RT\ln \frac{p_{NH_3}^2}{p_{H_2O}^3}$$

$$\Delta G^0 = 2G^0_{NH_3} + G^0_{CaCO_3} - 3G^0_{H_2O} - G^0_{CaCN_2}$$

$$K_p = \frac{p_{NH_3}^2}{p_{H_2O}^3}$$

right it produces ammonia so basically it's giving you again so it is giving you on solid again here reacts with gas to form a solid and the gas. Now for gas you will write mu i equals to mu i0 plus RTn and pi where pi is the partial pressure of component i in the gaseous step right gi0 plus mu i0 is nothing but gi0 and RTn and pi is basically pi is the partial pressure of i in the gaseous step right but for solid or liquid you have mu i which is nothing but mu i0 or gi0 right there is this term is no longer present right. Now if you have that then A that is affinity so again this is affinity, affinity is nothing but some sort of a is basically delta g we can write this as delta g sorry so is equal to delta g0 plus RTn now if you see RTn pi is only for 3 h2o as well as for 2 NH3 right so basically RTn pi or RTn ph2 right RTn ph2 and then RTn p NH3 is also there right and you are looking at that now you have the product right product has this coefficient of 2 so basically if you look at this this becomes mu 0 plus RTln p NH3 however you remember that and this is basically on the on the product side and on the reactant side is mu 0 plus RTln ph2o however if you remember A is nothing but some mu i mu i right so mu i means basically you have now in this case you have minus 3 so this becomes now this becomes minus 3 mu 0 minus 3 RTln ph2o right partial pressure of water vapor and you have plus right because it is a product side 2 mu 0 for NH3 so this is mu 0 water and this is mu 0 NH3 minus plus 2 RTln ph3 so that's why you get in the numerator p NH3 squared and the denominator you get ph2 cubed and you have delta G0 now delta G0 is basically 2 delta G0 of NH3 plus G0 Cs Cs3 minus 3 G0 H2o minus Cs Cn2 right so this is what it is because you can you not only have this term or you not only have these two terms you also have so for mu 0 the standard potentials of the standard free energies you have these states right every product comes now only thing the solid products you have only mu 0i which is nothing but G0 H0 right so basically you have G0 of NH3 you have G0 of Cs Cn3 so these are the products right so basically if you look at the stoichiometry this is plus 2 this is plus 1 right this is plus 1 this is plus 2 and this is minus 3 and this is minus 1 right that's the idea so but Kp that is the equilibrium constant is related to the partial pressure of the gaseous reactants and products right this is the gaseous product and this is the gaseous reactant right so that's that's the idea right so basically you have this right delta G0 again is basically summation mu i Gi0 T and as a function of P and P0 right now if you have that basically G i0 or delta G0 can be written as delta H0 minus T delta S0 right this is the definition G goes to H minus TS or delta



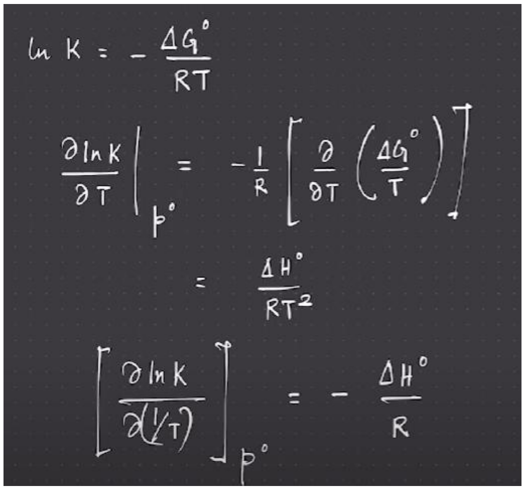
$$K = \exp\left[-\frac{\Delta G^\circ}{RT}\right]$$

$$\Delta G^\circ(T, P_0) = \sum_{i=1}^{n} \nu_i G_i^\circ(T, P_0)$$

$$= \Delta H^\circ(T, P_0) - T\Delta S^\circ(T, P_0)$$

$$\Delta H_i^\circ = \Delta H_{f,i}^\circ \quad \therefore \Delta H^\circ = \sum_{j=1}^{n} \nu_j \Delta H_{f,j}^\circ$$

For pure elements $\Delta G_{f,i}^\circ = 0, \ \Delta H_{f,i}^\circ = 0$



$$\ln K = -\frac{\Delta G^\circ}{RT}$$

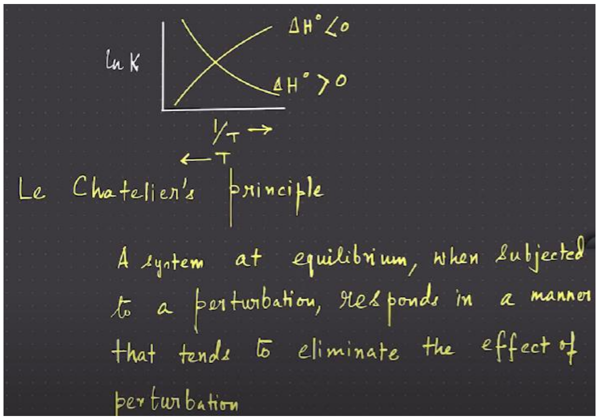
$$\left.\frac{\partial \ln K}{\partial T}\right|_{P^\circ} = -\frac{1}{R}\left[\frac{\partial}{\partial T}\left(\frac{\Delta G^\circ}{T}\right)\right]$$

$$= \frac{\Delta H^\circ}{RT^2}$$

$$\left[\frac{\partial \ln K}{\partial (1/T)}\right]_{P^\circ} = -\frac{\Delta H^\circ}{R}$$

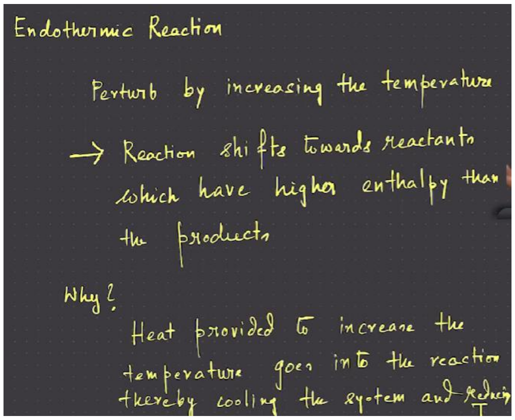
G goes to delta H minus T delta S now you are keeping say for example P0 fixed okay so P0 you are keeping S fixed now you are telling that delta H is 0 delta H is 0 is nothing but delta H formation right because delta H is 0 is for each species now you are thinking of the formation enthalpy of each product okay formation enthalpy of each product so basically you have the formation enthalpy of each product and you are basically delta H0 basically is then the sum from J equal to 1 to N and is the number of species of constituents and you have again nu J nu J is the stoichiometric coefficient and that is positive for products and negative for reactants multiplied by delta HFI0 for each component right for each component so as a result however remember the delta G formation for the component or delta H formation of component when the component is a pure element of or the species of pure element is 0 right and also you know that you can basically you know the Helmholtz Giselle-Moltz equation but you also know the other relation right TH equals to Cp dT so for each component I can write DH equals Cp dT so basically I can do the reaction at different temperatures and we can calculate say for example nu so for example if I am calculating nu I right this one this guy so if I am calculating this at different temperatures if I want to do it at different temperatures so at how do I add this temperature effect because each component has a heat capacity and heat capacity itself can be a function of temperature so you have Cp dT right remember Cp can itself be a function of okay so basically as you can see here that this is this is that so now if I basically want to see how the equilibrium can constant change with temperature at a fixed pressure P0 okay by the way I have used up P0 there are various ways but just to be consistent for a given pressure or something I am using the super state P0 so here also I am using super state does not really matter just to be uniform in component P0 is a total pressure P0 is the total pressure now P0 is fixed P0 is fixed and you are looking at del N k del T again you are basically looking at the Helmholtz Giselle-Moltz equation so which gives you delta H0 by RT square but why delta H0 where is the minus sign gone the minus sign is gone is because ln k itself is ln k is minus delta G0 by minus right it is minus delta G0 by RT so if you have this you have so since ln k is minus so basically you get say minus delta H by T square right so basically minus minus becomes plus so this right if you look at the Giselle-Moltz equation yeah see there is a minus H by T square right it is a minus sign so basically now you are looking at the correction and once you have done the correction you basically get this delta H0 by RT square right so del ln k del 1 by T because you have del ln k del T and this becomes R1 by RT square now if I take T square here so if I take T square on this side so basically del 1 by T is minus nothing but minus 1 by T square and there is a minus sign right so minus sign I am putting it again here I am putting it here but there is a 1 by T square so 1 by T square is there and as you can see it has this 1 by T square and as a result this entire thing is nothing but minus delta H0 by RT.

Now if you look at that if it is okay del ln k del 1 by T at constant pressure P0 is equal to minus delta H0 by RT. Now if you see that if I plot ln k versus 1 by T so 1 by T is increasing this way that means T is increasing the other way because if T increases 1 by T decreases right so if you now look at this if you look at this so T is decreasing towards the origin T is decreasing towards the origin and 1 by T is increasing away from the origin right if 1 by T increases 1 by T increasing means so if you look at this so it is basically now this is where again the velocity should not come so if you look at the principle if T increases this way if actually 1 by T has to be plotted here so as temperature increases 1 by T decreases correct so as temperature increases 1 by T decreases so as a result T itself is increasing towards the left and 1 by T is increasing towards the right as temperature increases as temperature increases 1 by T decreases so if 1 by T is increasing this way then the temperature is decreasing this way temperature is decreasing towards the right temperature is increasing towards the left. Now if that is so if you plot this you get if you see there is a minus sign why I am doing all this because there is a minus sign if I plot del ln k del 1 by T at constant pressure which is equal to minus delta H naught by T. Now if you look at that you have ln k versus 1 by T now if you look at that you have the slope here in one case the slope is positive when delta H naught is negative when the delta H naught is negative then you have that means you have exothermic right this is basically exothermic reaction and this is endothermic right where there is absorption so endothermic follows the other way if you look at ln k versus 1 by T then basically endothermic goes this way while exothermic goes the other way. Now there is a very important principle which I think many of you know which is called large atelier principle which tells that a systematic equilibrium when substitute for perturbation responds in a manner that nullifies or eliminates the effect of perturbation nullifies or eliminates the effect of perturbation.



Le Chatelier's principle

A system at equilibrium, when subjected to a perturbation, responds in a manner that tends to eliminate the effect of perturbation



Endothermic Reaction

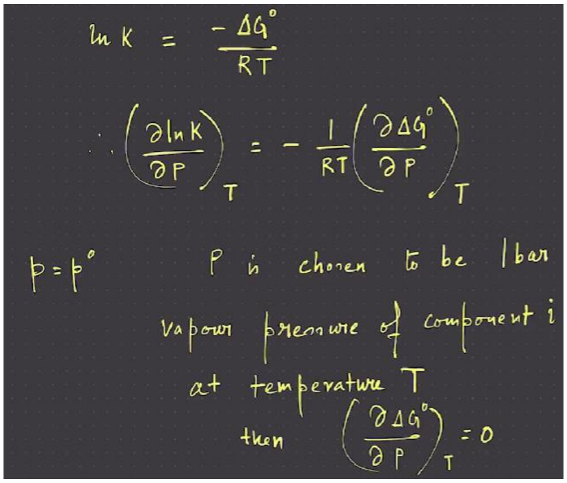
Perturb by increasing the temperature

→ Reaction shifts towards reactants which have higher enthalpy than the products

Why?

Heat provided to increase the temperature goes into the reaction thereby cooling the system and Reducing T

So basically if you look at endothermic reaction think of an endothermic reaction taking place ln k increases as a function of 1 by T right as 1 by T increases ln k also increases and del ln k del 1 by T is basically positive right for an endothermic reaction. Now if you see that part so if I perturb the system by increasing the temperature then what happens reaction now if I have increased the temperature I have basically endothermic reaction means it absorbs C2 for the reaction to occur right the for the reactants to react and form products you require to supply heat to the reaction. Now if you see that if I just increase the temperature of the system then what happens the reaction shifts towards the reactants because it has higher enthalpy than the products right so if I have endothermic reaction then the reactants will have higher enthalpy right because the reactants you supply you are supplying heat right and then products form. So you are supplying heat the products the reactants are absorbing the heat and then only products are forming. So if the reactants have had enthalpy the products now if I increase the temperature the effect is such that reaction will shift towards the reactants why because heat provided to increase the temperature goes into the reaction thereby cooling the system and reduction of heat right if I am increasing the temperature of the system though then you are basically going back to the you are basically reaction is shifting towards the reactants because the the if it which shifts towards the reactants that heat provided to increase the temperature will go into the reaction right because that it requires to absorb it to complete the reaction right.



$$\ln K = \frac{-\Delta G^\circ}{RT}$$

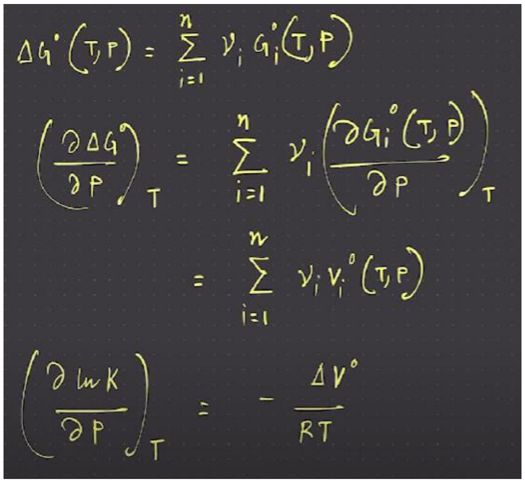
$$\therefore \left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{1}{RT}\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T$$

$p = p^\circ$ P is chosen to be 1 bar

vapour pressure of component i

at temperature T

then $\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T = 0$



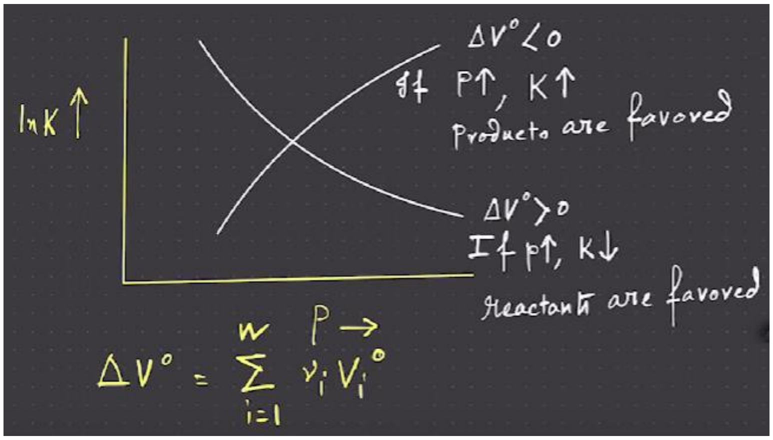
$$\Delta G^\circ(T,P) = \sum_{i=1}^{n} \nu_i G_i^\circ(T,P)$$

$$\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T = \sum_{i=1}^{n} \nu_i \left(\frac{\partial G_i^\circ(T,P)}{\partial P}\right)_T$$

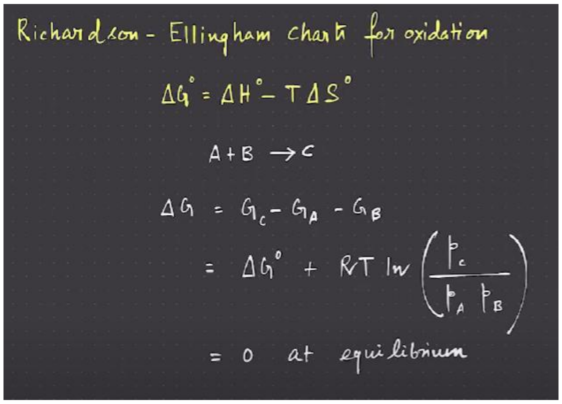
$$= \sum_{i=1}^{n} \nu_i V_i^\circ(T,P)$$

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^\circ}{RT}$$

So as a result the the reactants since the reactants have higher enthalpy then we have to so basically heat provided to increase the temperature goes into the reaction. Now if it goes into the reaction that means like the the reaction is absorbing more heat or reaction is absorbing heat thereby cooling the system. So if I increase the temperature I am supplying it to the system the the way the system will behave as to nullify this effect that is as to reduce the temperature of the system how does it do that by basically shifting towards the reactants because reactants will require to absorb it to form products so if the reaction reactants have absorbed this excess heat basically the system means cool and the temperature decreases right. This is something that you have to understand so basically the way the system will behave nullify that so if you have imposed some effect on it so basically this is very important that when circular perturbation responds to manner that tends to eliminate the effect of perturbation basically you have increased the temperature as a result you want to see for an atomic reaction what is basically delta H is negative. It is negative means products for this reactants is negative the products has less enthalpy so basically if products have less enthalpy it is the diameter reactants that temperature in the system if I have to increase the temperature I am supplying more heat now this heat basically can go to the reactants and this heat can be utilized to the reactant because the reactants will absorb this heat and then they will form products and as a result as a result the system will cool down and it will nullify the effect of increasing temperature right that is the idea so this is what I endothermic reaction.



For exothermic it is very similar say for example if it is an exothermic reaction then it is a the products have higher enthalpy than the reactants and as a result if I increase the temperature if I increase the temperature since the products are higher enthalpy it wants to release that heat so basically you move towards the product so basically you will have a movement towards the reaction will move towards the product right so it will shift towards the product so more product will be barbed because product has more enthalpy so that ultimately if the product has more enthalpy so it is basically rejecting the heat right up to the surrounding as a result decreasing the temperature so if I increase the temperature the reaction will proceed in such a way as to decrease the temperature of the system or cool the system that is the idea. Now if you think of p now you are telling that this is the basically the dependence of k on temperature that dependence on the of the equilibrium constant temperature now what about the dependence of equilibrium constant of pressure now if you do that you have if p is p naught say for example p is chosen to be the one bar or the pressure of component i so it can be chosen to be one bar which is basically the atmospheric pressure or the pressure of component i you can also choose the operation of component i as that standard pressure then basically delta then the delta g naught does not vary however if we take the system pressure to the pressure then there is a variation right because see you have delta g naught basically is basically again given by nu i g i naught t right this is for the system now del del so basically this is a relation right delta g naught t p is i equal to 1 to n that is for all components this is g i 0 t now if you look at that del delta g del p at fixed temperature is basically nu i and then delta g i 0 del p right at a fixed temperature now basically del g del p is nothing but v right del g del p is nothing but v so i have to write the v properly right v i 0 is the basically the volume of the species i volume of species i in the standard state right in the standard state that is the pure state that is the only that species exists okay and nu i is the stoichiometric coefficient right now if you look at that if you look at that so you see del g this is del g naught del p now del and g naught has a nu i right g naught has a nu i right so del g naught del p is basically summation of nu i v i naught p now if i have that del g del p is that so you have del g del p right and you are looking at del n k del right k del n k del p which is basically if you look at that that del n k del p is nothing but minus 1 by r t del delta g 0 by del right del delta g 0 del now del delta 0 0 del p basically is the 1 now if you have that if you if you do this combination then basically you eliminate the nu i right you eliminate the nu i and you get the overall that the equilibrium constant the change in pressure within pressure is equal to minus delta v naught by r t now if you see if delta v naught is less when their products are formed then as pressure increases the k also increases right because as products are forming the volume is basically the delta v naught is basically negative that means volume of products is that of react than that of reactant so as a result um as k as pressure increases k will also increase in the case where delta v naught is less than 0 however when delta v naught is greater than 0 then if if delta v naught is greater than 0 delta v naught is basically v products minus uh v naught products minus v naught reactant so basically right with v naught because nu i v i so delta v naught as i showed you is equals to summation i equal to 1 to n right summation i equal to 1 to n and this is nu i v i right nu i v i so basically nu i v i naught is positive for products so this difference between products and reactants right if delta v naught is greater than 0 that means the products are product product is having more volume now if product is having more volume if pressure is increasing then you want to reduce the reactant the the the equilibrium constant so that you know that effect of increasing pressure is nullified right if delta v naught is positive if delta v naught is positive you basically if you increase the pressure the equilibrium constant actually comes down right because reactants are filled right because it has more volume right the products have more volume when delta v naught is less than 0 when delta v naught is less than 0 products are filled okay so if you if you look at the temperature dependence and pressure dependence you understand very carefully the law of chatelier principle now there is also another law of chatelier principle which becomes very useful when you look at this charts and charts for oxidation of metals right again i will look at the reaction of pure oxygen but you can also look at the co co2 ratio or h2 h2o ratio right and i am looking at a reaction like a plus b a combines with b to form c



Richardson - Ellingham charts for oxidation

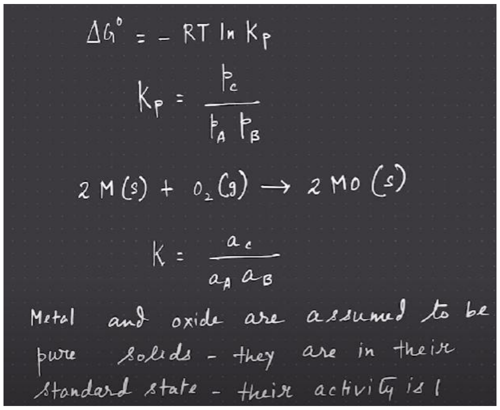
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$A + B \to C$$

$$\Delta G = G_C - G_A - G_B$$

$$= \Delta G^\circ + RT \ln\left(\frac{p_C}{p_A\, p_B}\right)$$

$= 0$ at equilibrium



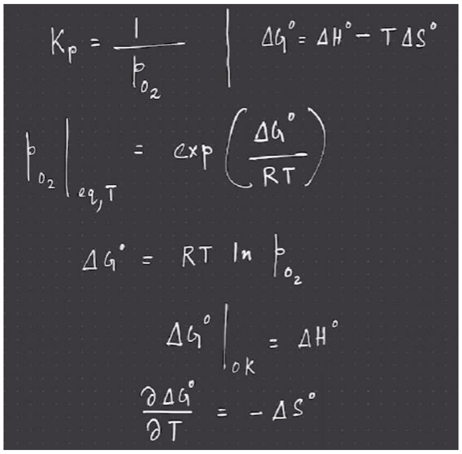
$$\Delta G^\circ = -RT \ln K_p$$

$$K_p = \frac{p_c}{p_A\, p_B}$$

$$2\,M(s) + O_2(g) \to 2\,MO(s)$$

$$K = \frac{a_c}{a_A\, a_B}$$

Metal and oxide are assumed to be pure solids - they are in their standard state - their activity is 1 right and you have basically delta g is g c minus g a minus g so again it is equal to say it is equal to 0 and now delta g naught is basically minus RTN and k p that's what we have seen and kp is pc by pa times pb where pc is the partial pressure of c and pa and pb are partial pressures of a and b now if you have a heterogeneous reaction where metal is a solid right in this case the metal is a solid it reacts with the gas and forms a solid now if it reacts with the gas and forms a solid first thing that you notice is that if it is reacting with the gas it is consuming the gas gas has much higher entropy right much higher entropy than the solid right as a result the gas is the sole contributor to entropy and as a result when as the oxygen gets consumed or the gas phase gets consumed but it is oxidizing so what happens this reaction basically inherently is a reaction which you have negative enthalpy right within the system there is a negative enthalpy in the system now right if as long as the metal is solid right so metals and also as simply pure solid that is there in the standard state and their activity is one right so basically if that is so if i look at the equilibrium constant kp equals to



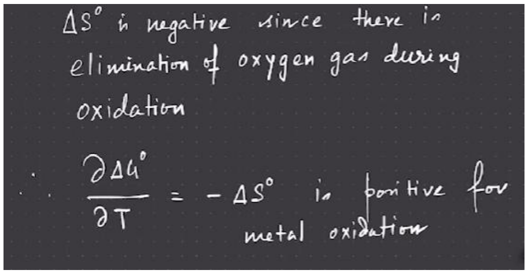
$$K_p = \frac{1}{p_{O_2}} \qquad \Big| \qquad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$p_{O_2}\Big|_{eq,T} = \exp\left(\frac{\Delta G^\circ}{RT}\right)$$

$$\Delta G^\circ = RT \ln p_{O_2}$$

$$\Delta G^\circ\Big|_{0K} = \Delta H^\circ$$

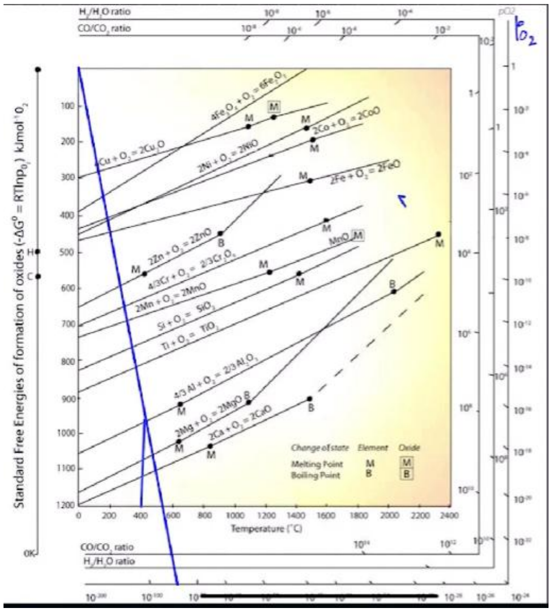
$$\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ$$

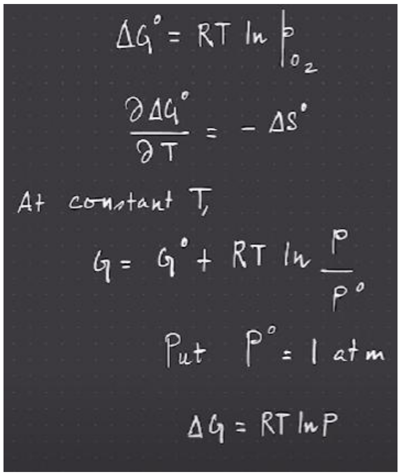


ΔS° is negative since there is elimination of oxygen gas during oxidation

$\therefore \quad \frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ$ is positive for metal oxidation

it is just nothing but because you have only oxygen partial pressure so it is nothing but 1 by p right 1 by po2 which is equal to kp now if you look at that what is the po2 at equilibrium okay at a given difference what is the po2 at equilibrium you have delta g naught which is RTL and po2 and delta g naught at 0 k there is no entropy change so delta g naught at 0 k basically comes delta h naught and del delta g naught del t is minus delta s now delta s naught is negative right since there is an elimination of oxygen gas during oxidation now if delta s naught is negative and del delta g naught del t is minus delta s naught it is always positive right the slope delta g naught del t is always positive for any chemical reaction so this is from which comes um uh cambridge i have so which has to see means a pretty common license i have taken this chart in this chart you have different oxides different metals and oxide formation if you look at that slope is positive as we saw del delta g naught del t is minus del delta g naught del t is minus delta s naught now if it is minus delta s naught you will wonder why the slope is positive because delta s naught itself is negative why it is negative because you are consuming all the oxygen right so delta s naught itself is negative so minus of delta s naught will basically give you a positive slope minus of delta s naught will give you a positive slope now you have this positive slope but in order of you know reactivity these oxides are being arranged for example iron oxide okay it goes to quite high right about thousand degrees iron oxide typically is very stable right and then you have a nickel oxide so is it very stable so if you have increasing so basically if you see this is a standard free energy of formation of oxides now the standard free energy formation of oxides basically if you if you look at that so what do you you have to suggest say for example which will be more stable alumina or nickel oxide okay so basically if you look at alumina it has a much lower standard





$$\Delta G^\circ = RT \ln p_{O_2}$$

$$\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ$$

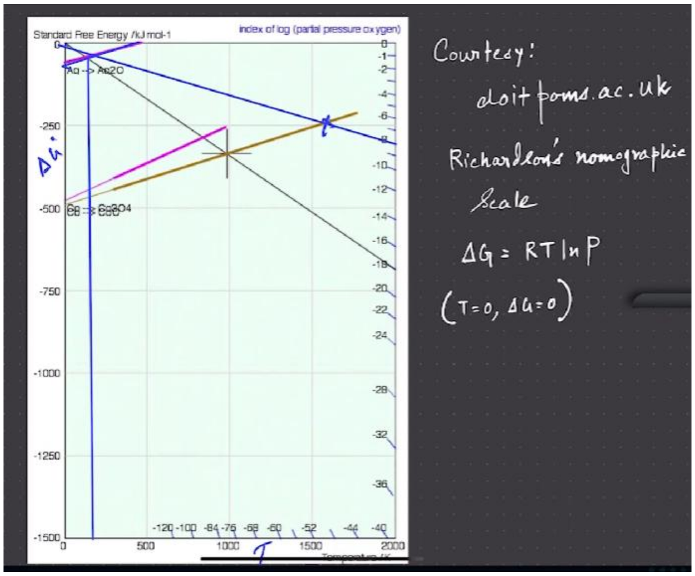
At constant T,

$$G = G^\circ + RT \ln \frac{P}{P^\circ}$$

Put $P^\circ = 1$ atm

$$\Delta G = RT \ln P$$

free energy value right or much sorry much higher standard free energy value but this is remember this is negative value because delta g naught is minus RTLm p naught right minus RTLm right because you have 1 by p o 2 right 1 by p o 2 if you look at that k p is 1 by p o 2 so it is basically minus RTLm so delta g naught is minus RTLm if you can look at that that is exactly what is now if that is that is inherently if it is negative then basically delta g naught is basically becoming minus RTLm k p minus RTLm k p is k p is 1 by p o 2 so delta g naught equals RTLm p o 2 right so this RTLm p o 2 and if you can see here the more negative the energy the more negative the standard free energy the the the more stable the oxide the more stable the oxide now there is one interesting point that i want to tell that at constant temperature for example g equals g naught plus RTLm p by p naught this is correct right this we we have no argument about this right but put p naught equal to 1 at this time then basically you get delta g plus RTLm p right then so basically if you put uh so delta g is RTLm p now if you look at that so put p naught equal to 1 atmosphere right so you are putting p naught equal to 1 atmosphere and if you are putting p naught equal to 1 atmosphere then basically RTLm p minus RTLm p naught and RTLm p naught is basically 0 and you have RTLm p here and you have delta g right so that's right now if you look at this that the delta g that is g minus g naught right delta g is RTLm p right delta g naught is RTLm p right now how do i know what is oxygen pressure for a given reaction say for example if you look at that you



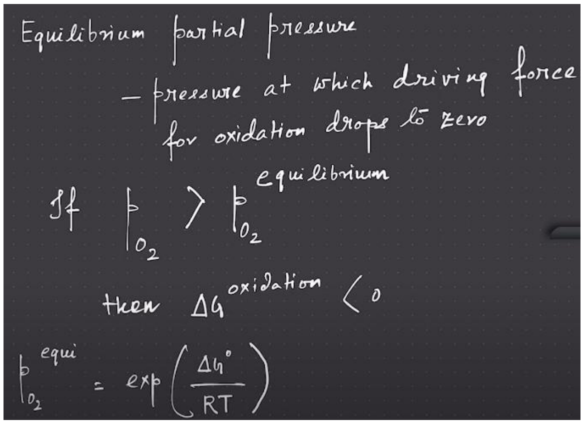
Courtesy:
doitpoms.ac.uk

Richardson's nomographic scale

$\Delta G = RT \ln P$

$(T=0, \Delta G=0)$

have this scale nomographic scale of oxygen pressure pressure now if you look at this conversion say for example you are looking at the conversion of nickel to nickel oxide or cobalt oxide or so on or silver to silver oxide and so basically what you are doing is from the origin you are starting to draw a line for the desired you know for the desired temperature you are starting to draw a line here and this point cuts here and then what you basically do is that if you extend this point if you extend this point you beat the low-level scale and you are getting something like 10 to the power minus 18 right 10 to the power minus 18 is what you get right this is log partial pressure so since it's log partial pressure what i am telling is the partial pressure is like 10 to the power minus 18 and this is basically at certain temperature it is lower temperature right it is certainly at a much lower temperature this is at a lower temperature. Now if you look at the curve Ag2Ag2 silver oxide again it has a positive slope why because delta S naught is negative minus delta S naught is del G basically del so if it is you are looking at del G del T right it's a function of so exact so x-axis is temperature right and y-axis is minus of so you have temperature and here you have delta G. Now if that is so now you look at a high temperature reaction say for example a reaction that is occurring here now if you look at this you will have an oxygen partial pressure value which is much much higher now this is actually not that big because the higher the temperature the oxygen partial pressure value is much larger right higher than at higher temperatures right this is at some temperature of 1500 or 1400. The point that i am trying to say here is that at higher temperature why is it that at higher temperature you have more oxygen pressure at higher temperature as you are oxidizing you are consuming oxygen now if you are consuming oxygen if your partial pressure becomes less any at any temperature so as you are consuming oxygen your oxygen partial pressure is reducing now if your oxygen pressure for example at higher temperature falls below say in this case like 10 to the power minus 9 if it falls below that basically the reverse reaction becomes possible that is silver oxide decomposes or dissociates into silver and oxygen right so basically as you go to higher temperatures the partial pressure requirement increases right it is like 10 to the power minus 9 if you can see here so it is like 10 to the power minus 9 so that the blue line if you see that what i have drawn here right it becomes 10 to the power minus 9 right but see at much lower temperatures like here you basically had 10 to the power minus 19.



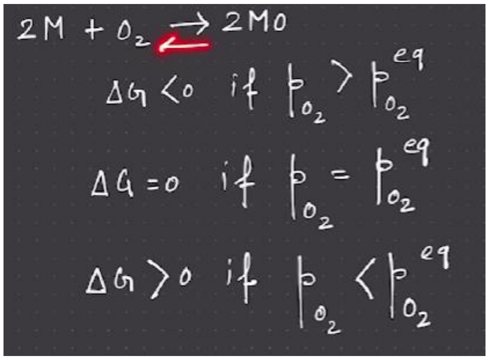
Equilibrium partial pressure

– pressure at which driving force for oxidation drops to zero

If $p_{O_2} > p_{O_2}^{equilibrium}$

then $\Delta G^{oxidation} < 0$

$$p_{O_2}^{equi} = \exp\left(\frac{\Delta G^\circ}{RT}\right)$$



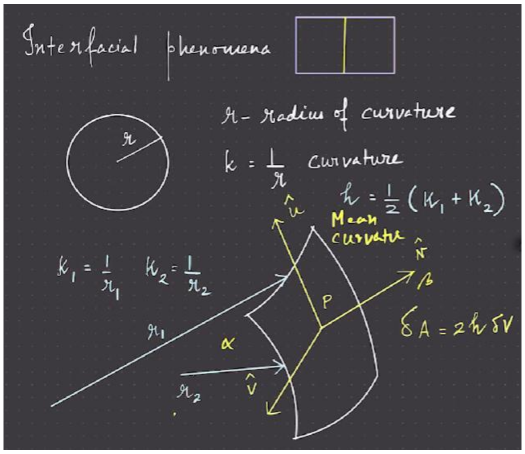
$$2M + O_2 \rightleftarrows 2MO$$

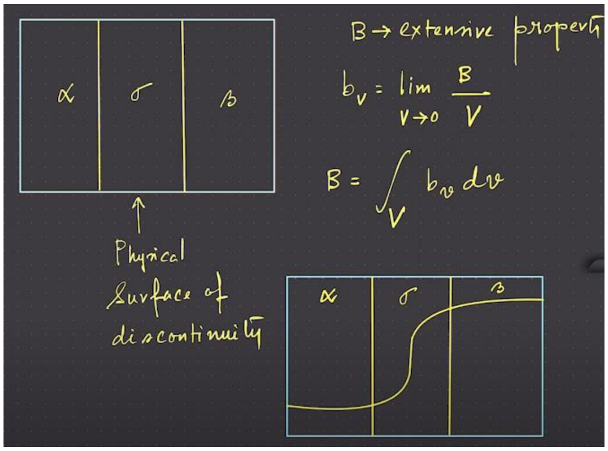
$\Delta G < 0$ if $p_{O_2} > p_{O_2}^{eq}$

$\Delta G = 0$ if $p_{O_2} = p_{O_2}^{eq}$

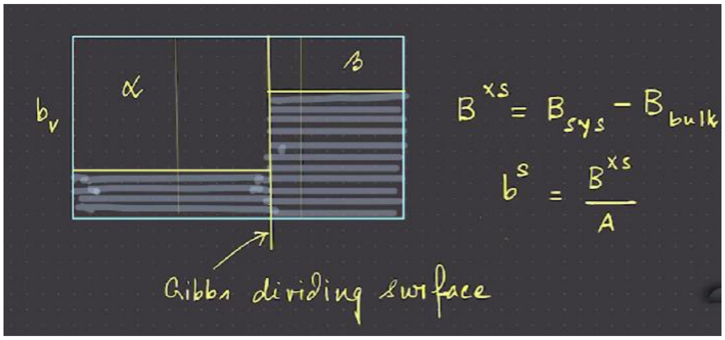
$\Delta G > 0$ if $p_{O_2} < p_{O_2}^{eq}$

Now problem is 10 to the power minus 9 atmospheres is that if you are above it then there is no problem right oxide is stable however if you fall below it and that is what exactly will happen as your reaction proceeds as your reaction proceeds that is exactly what will happen right so basically equilibrium partial pressure is a pressure at which the driving force for oxidation drops to zero there is no driving force for oxidation anymore right you basically are getting now if po2 is greater than po2 equilibrium then delta g oxidation is less than zero so the reaction will proceed far correct but if po2 becomes less than po2 it becomes less right if it is less if it is greater then there is no problem right you have 10 to the power minus 9 as the threshold value if you are always greater than once nine if your oxygen partial pressure is greater than 10 to the power minus 9 then there is no problem there is no problem of destabilization however if the oxygen partial pressure falls below that po2 equilibrium that is read from the nomenclature scale then what happens is the reverse reaction becomes possible that is instead of going from silver so if instead of going from silver to silver oxide i can go from silver oxide to silver or alumina to aluminum right so basically we have to be very very careful here that and very very careful here that the partial pressure of oxygen at equilibrium then there is no problem the oscillation proceeds but on the other hand if it is less than if it is less than po2 that means falls below and this is a particular problem at a higher temperature at higher temperature for example po2 may be less than in such a case that instead of going from m plus o to so if i want to balance it so close to now if you see right this is the reaction now if you see as this reaction is happening at high temperature as it is happening the driving force has to go to 0 so basically as driving force goes to 0 basically you have basically the partial pressure at which the driving force goes to 0 and then what happens your partial pressure starts falling down and it starts falling below that threshold pressure the threshold partial pressure at that given temperature right at a given temperature particularly at high temperatures then what starts happening the reverse reaction starts happening the forward reaction stops right so this is the idea of so basically M2 M plus O2 is 2 MO so this is the reaction now if you see delta G is less than 0 if pO2 is basically greater than pO2 however it is equal to 0 if pO2 equals to pO2 and it is greater than 0 if pO2 is less than pO2 now if partial pressure of oxygen is less than pO2 equilibrium then the delta G of the reaction of the forward reaction becomes false as a result the forward reaction does not ceases and you get a reverse reaction you get a reverse reaction yes that is the MO basically is now dissisting with the metal and oxygen



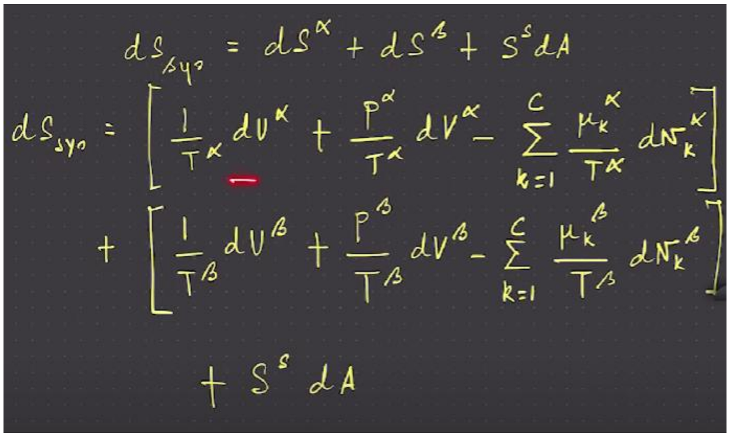


now I'll very quickly describe interfacial phenomena interfacial phenomena I have not described so far so all our phase diagrams assume that you have alpha phase beta phase or all these phase but these phases share a boundary and that boundary is the phases are infinite in extent and they share a boundary which is completely flat however in real systems you have particles and the particles of curvature right particles like if you have a spherical particle then there is a curvature with it right because there is a radius of curvature and inverse of radius of curvature is what is called curvature right but if you look at if you look at a straight line say for example you have a huge alpha phase say for example you have this alpha phase and then you have say beta phase so basically if I draw this correctly you have think of sub volumes right in the composite system if you think of sub volumes in the composite system and say for example in the sub volume then this is a flat interface flat interface means if I have a completely flat interface then basically the radius of curvature is infinity or curvature is one by infinity which is zero right and you remember there are two terms here h which mean curvature mean curvature so if you look at this plane if you look at this plane right this is like a dividing surface between alpha and beta think of this this is a record you have alpha here you have beta here and then in this plane basically you have a plane normal that's the surface as a surface normal and as you can see that there are two radii right in this surface there are two radii one is r2 to define the surface you require two radii what is r2 another is r in such a place you have you have two curvatures right one is one by r1 another is one by r2 for spherical particles or if you have completely spherical surface then basically one by r1 equals to one by r2 so it becomes like half into two by r and that is basically nothing but one by r when you are basically looking at a sphere however it is not always sphere right so as a result we need to understand okay this definition so one of these definitions is called mean curvature so this is the mean curvature right and this mean curvature is going to basically this mean curvature particularly for non non flat surfaces that is spherical surfaces or cylindrical surfaces or something like that it has a big effect right on



$$B^{xs} = B_{sys} - B_{bulk}$$

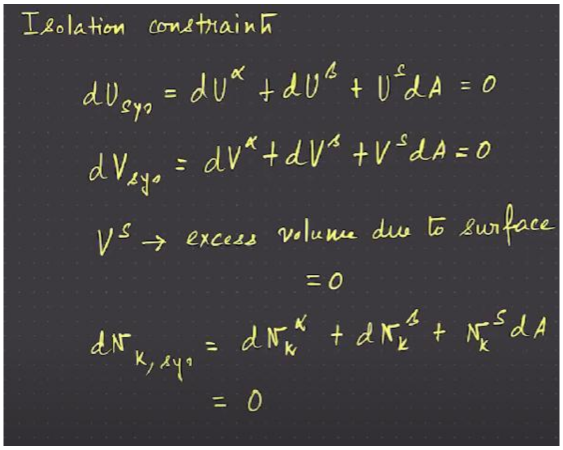
$$b^s = \frac{B^{xs}}{A}$$



$$dS_{sys} = dS^{\alpha} + dS^{\beta} + S^s dA$$

$$dS_{sys} = \left[\frac{1}{T^{\alpha}} dU^{\alpha} + \frac{P^{\alpha}}{T^{\alpha}} dV^{\alpha} - \sum_{k=1}^{C} \frac{\mu_k^{\alpha}}{T^{\alpha}} dN_k^{\alpha} \right] + \left[\frac{1}{T^{\beta}} dU^{\beta} + \frac{P^{\beta}}{T^{\beta}} dV^{\beta} - \sum_{k=1}^{C} \frac{\mu_k^{\beta}}{T^{\beta}} dN_k^{\beta} \right] + S^s dA$$

different phase transformations that take place right it also has a big effect on the solubility right so this is something that i have to tell and remember Gibbs is the one who basically looked at the surface excess and wanted to have understand the surface excess later kahn and hilliard and all these guys have improved it a lot but initially it was Gibbs and Gibbs thought of a physical surface of discontinuity between alpha phase and beta phase and he named it as sigma phase now in that physical surface of discontinuity if you have some property so if you have an extensive property and if you have a par volume intensive property limit v tends to zero b by v so b is an extensive property but vv is an intensive property then basically if you look at the profile of vv as a function of distance what do you see you have this intermediate region which is basically which is basically your dividing surface right this is basically it's not really a dividing surface it's like a transition zone between one one bulb to the other one like alpha to beta is a part and then there is a physical surface of discontinuity now this physical surface of discontinuity i have exaggerated it when i drew but if you look at that the variation of the small bv so this is small bv the way it varies so most likely it varies like this most likely it varies this way right if that is so right this this this s-shaped curve right so basically you have this s-shaped curve and if you see that s-shaped curve the middle region basically is indicating the physical surface of discontinuity now if you look at that Gibbs came up with a sharp interface model and he told that there is a sharp so in this transition region physical surface of discontinuity you basically he constructed a dividing surface you construct the dividing surface called it gives dividing surface and on these surface he is basically looking at the excess properties right excess excess properties basically system with interface minus part so i have alpha phase beta phase and i have this alpha beta they are basically the total system so you have alpha phase you have beta phase and you have alpha beta and on the other hand in in in bulk you have alpha phase separately beta phase separately a piece so b system minus b bar basically gives you this this b basis which gives you b access right the excess associated with the extensive property b so excess as you can say or you can think of like interfacial energy excess or free energy excess or whatever it is now the point is if you have the free energy excess and if you know the cross sectional area basically so for a for a for a for a material for a for a bulk you have a material property an extensive property and if you tell entropy is like the excess property and if i want to express entropy for the volume then basically i have to divide by volume however if it's a surface property i have to only divide by a right the excess property has to be divided by area and gives you a surface is nothing but a two-dimensional area that separates two three dimension volumes once the alpha bulk alpha number is bulk beta right now if i continue this so basically if i continue this what i have essentially is an extra term ssd now if i go on doing this i have this extra term so if you see this is d s this again i am looking at the same equilibrium approach i am looking at expanding it and you have this additional term ssd now again if you look at the isolation constants you have du is equal to 0 dv c is equal to 0 and vs is basically the x-voluntary surface which is again 0 right x-voluntary



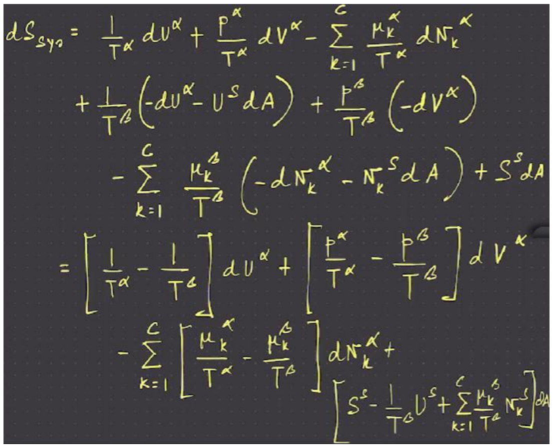
Isolation constraint

$$dU_{sys} = dU^{\alpha} + dU^{\beta} + U^{s} dA = 0$$

$$dV_{sys} = dV^{\alpha} + dV^{\beta} + V^{s} dA = 0$$

$V^{s} \rightarrow$ excess volume due to surface $= 0$

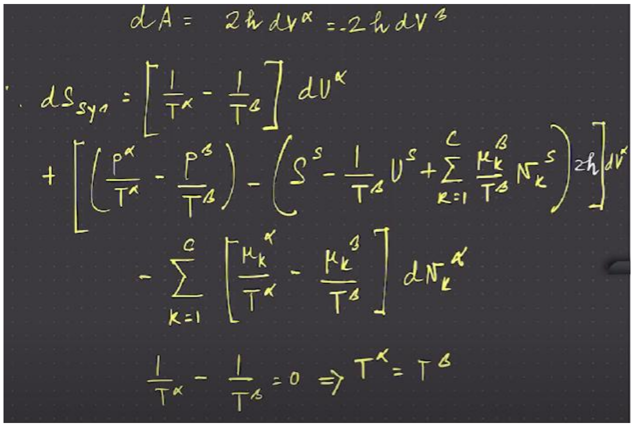
$$dN_{k,sys} = dN_k^{\alpha} + dN_k^{\beta} + N_k^{s} dA = 0$$



$$dS_{sys} = \frac{1}{T^{\alpha}} dU^{\alpha} + \frac{P^{\alpha}}{T^{\alpha}} dV^{\alpha} - \sum_{k=1}^{c} \frac{\mu_k^{\alpha}}{T^{\alpha}} dN_k^{\alpha} + \frac{1}{T^{\beta}}\left(-dU^{\alpha} - U^{s} dA\right) + \frac{P^{\beta}}{T^{\beta}}\left(-dV^{\alpha}\right) - \sum_{k=1}^{c} \frac{\mu_k^{\beta}}{T^{\beta}}\left(-dN_k^{\alpha} - N_k^{s} dA\right) + S^{s} dA$$

$$= \left[\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right] dU^{\alpha} + \left[\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\beta}}{T^{\beta}}\right] dV^{\alpha} - \sum_{k=1}^{c}\left[\frac{\mu_k^{\alpha}}{T^{\alpha}} - \frac{\mu_k^{\beta}}{T^{\beta}}\right] dN_k^{\alpha} + \left[S^{s} - \frac{1}{T^{\beta}} U^{s} + \sum_{k=1}^{c} \frac{\mu_k^{\beta}}{T^{\beta}} N_k^{s}\right] dA$$

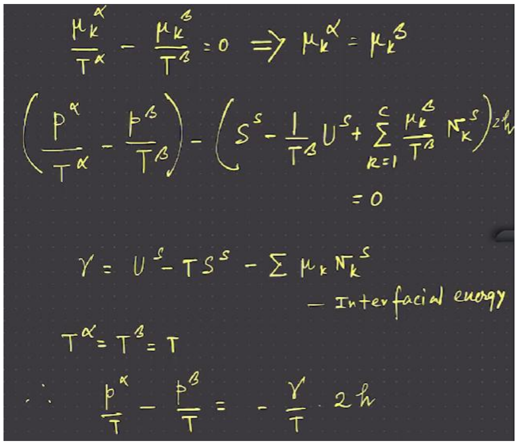
surface is 0 and dnk then it's of each element of the system dnk is equal to 0 now if you have that and you continue doing this so basically from the isolation constraint you can do what you can write dv alpha in terms of dv v tan ps you can write du alpha in terms of dv tan ps so or and ux so exactly that's what i am going to do here so if you do a little bit of manipulation so basically you have one by t beta and here it was du beta d instead of u beta i have written du alpha and you have also us that is the u surface times t right again you have here say for example nks times t now all these terms which are basically surface dependent have come up and also you have the excess entropy of the surface right this term you should not call now if you have that you can rearrange to get the different equilibrium functions for example the s c now gives you this so this is the equilibrium condition that you get p alpha plus t beta and then one by t alpha minus one by t beta into du alpha plus p alpha by t alpha minus t beta by t dv alpha because i am substituting and here also mu alpha minus mu k beta so basically if you look at that and you have this t n k alpha so this is the chemical equilibrium this is the pressure mechanical temperature thermal right now we have that think of da so da how does the relation between da and dv that is surface and volume so da is related to dv by so i am



$$dA = 2h\, dV^{\alpha} = -2h\, dV^{\beta}$$

$$\therefore dS_{sys} = \left[\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right] dU^{\alpha} + \left[\left(\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\beta}}{T^{\beta}}\right) - \left(S^{s} - \frac{1}{T^{\beta}} U^{s} + \sum_{k=1}^{c} \frac{\mu_k^{\beta}}{T^{\beta}} N_k^{s}\right) 2h\right] dV^{\alpha} - \sum_{k=1}^{c}\left[\frac{\mu_k^{\alpha}}{T^{\alpha}} - \frac{\mu_k^{\beta}}{T^{\beta}}\right] dN_k^{\alpha}$$

$$\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}} = 0 \Rightarrow T^{\alpha} = T^{\beta}$$



$$\frac{\mu_k^{\alpha}}{T^{\alpha}} - \frac{\mu_k^{\beta}}{T^{\beta}} = 0 \Rightarrow \mu_k^{\alpha} = \mu_k^{\beta}$$

$$\left(\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\beta}}{T^{\beta}}\right) - \left(S^{s} - \frac{1}{T^{\beta}} U^{s} + \sum_{k=1}^{c} \frac{\mu_k^{\beta}}{T^{\beta}} N_k^{s}\right) 2h = 0$$

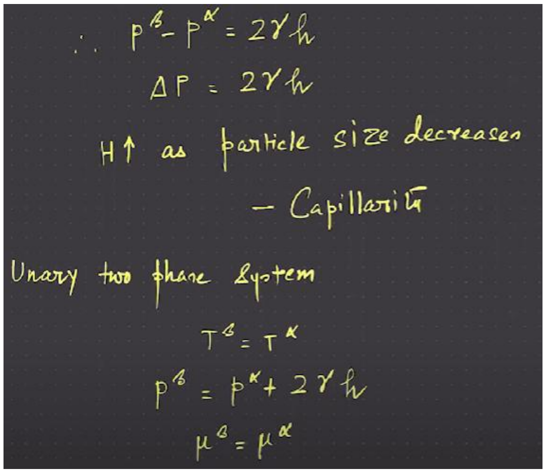
$$\gamma = U^{s} - TS^{s} - \sum \mu_k N_k^{s}$$

— Interfacial energy

$$T^{\alpha} = T^{\beta} = T$$

$$\therefore \frac{P^{\alpha}}{T} - \frac{P^{\beta}}{T} = -\frac{\gamma}{T} \cdot 2h$$

not giving the full derivation d is related to dv by this mean curvature which is h so da equals to th times dv alpha okay or right you you are looking at alpha phase then 2h dv alpha and you have also so what is dv alpha basically it is same as minus 2h dv b correct now you have all this terms so you have the thermal equilibrium you have thermal equilibrium you have mechanical equilibrium you have also chemical equilibrium however there is this term s s minus one by so you basically have this term s s minus one by t beta u s plus k equal to one to c u k beta by t beta right i should not read the equation but you can see here it is s minus u by t plus mu by t okay and mu by t is summed over all components right all components now so if you have that and also you have this chemical equilibrium right this now if you have that you you basically see the pressures are equal temperatures equal but you have this term extra term which is s s minus one by t beta right we are using t beta here for for normalizing so t beta also we have found right we found t beta yeah so t beta is basically one of one temperature in the beta phase so basically p beta by t beta and you can have a look at this and if you arrange rearrange all of these so basically you have a term you have a term so basically one by t alpha so we have a term here right this is one by t beta and this is us right this is the excess term now if you look at that mu k alpha equals to mu k beta equal to zero or mu alpha plus mu beta then p alpha equals to t beta however you have the term in the brackets which is this term in the brackets this term in the brackets now if you look at this term in the brackets if you look at this term in the brackets and do a little bit of rearrangement right if you do a little bit of rearrangement that means us minus ts minus sigma uk and k so basically you see cos t alpha equals to t beta right p alpha equals to t beta equal to t now gamma if i can write this so t alpha equals t beta equal to t so p alpha equals to p beta and so you have now minus of gamma by t right gamma by t so gamma i am defining as us minus ts minus us minus ts u minus ts us minus ts s minus mu n k s right n k s is basically the interfacial interfacial concentration now if you see this all these terms this energy entropy and mole number contributed right so basically you have p alpha minus p beta equals to 2 gamma h and this is like a capillary relation right p delta p equals to 2 gamma so if you if you go on doing all these derivations you go on doing all these derivations you at one point you will find that say for example in a unity two phase system t beta is t alpha but p beta is p alpha plus 2 gamma and mu beta again equals to mu n now if you plug in all of these you can show that the you can show that for curved interface the capillary effect will be



$\therefore\ p^\beta - p^\alpha = 2\gamma h$

$\Delta P = 2\gamma h$

H↑ as particle size decreases

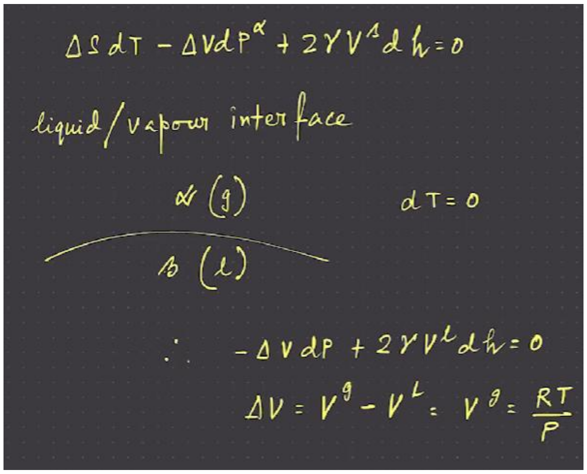
— Capillarity

Unary two phase system

$T^\beta = T^\alpha$

$p^\beta = p^\alpha + 2\gamma h$

$\mu^\beta = \mu^\alpha$



$\Delta S\, dT - \Delta V\, dP^\alpha + 2\gamma V^\beta\, dh = 0$

liquid/vapour interface

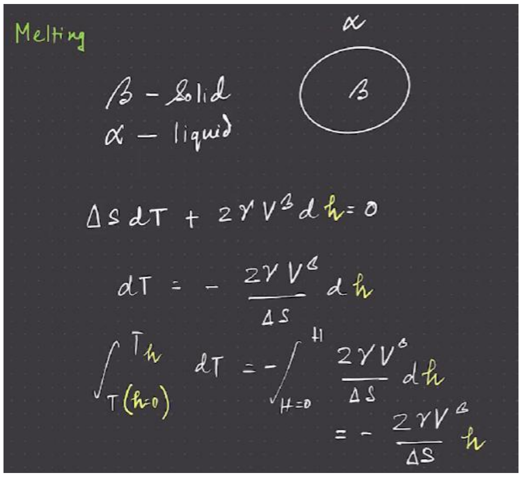
$\alpha\ (g)$ $dT = 0$

$\beta\ (l)$

$\therefore\ -\Delta V\, dP + 2\gamma V^l\, dh = 0$

$\Delta V = V^g - V^L = V^g = \frac{RT}{P}$

different the capillary length will be different okay and basically you can write in delta v in terms of r to the p then you have the other process of melting right where so here what is happening your your pressure has increased right because of the curvature p beta equals to p alpha again this is positive curvature if your curvature would have been negative they would have decreased so basically for the two-phase system uh unary two-phase system on the other hand if you look at melting you basically see that i'll directly go to the i'll directly go to the main result the main result is t curvature so basically this is th okay let's call h h means basically the mean curvature so th plus t naught minus 2 gamma vs by delta s into x so basically so you have this entropy change and 2 gamma vs by 2 times yes this is correct right t naught minus 2 gamma vs by 10 x into x because this is coming from here right if you if you look at that this is the equation that you get right how does it how do you get this equation you have delta s dt like s dt and you have 2 gamma v beta which is equal to 0 right so s dt minus v dp is what i'm trying to look at so basically you have um yeah so if you look at that here you have minus delta v dp so you can basically prove right because this is delta s dt minus v delta v dp plus 2 gamma v beta dt now if you look at that you have delta v dp and you have 2 gamma this thing right and you are basically taking delta v equal to 0 so you get basically you get basically delta v again you can take as r t by p so basically you get a different type of an equilibrium right at cause of the pressure right because of the the the the curvature because the curvature right right there is a the the there is a change right again in melting their melting point say for example the melting point of the curved solid okay which has a positive curvature is going to decrease right is going to decrease than the melting point that was there when originally the liquid solid surface was flat right it is going to decrease and here you can do a little bit of manipulation now if you look at that you have 2 gamma and v s v s is what v s is the excess quantity associated with the volume correct associated the volume so beta is the solid alpha is the liquid and you have delta s dt and 2 a 2 gamma v beta right v beta is the the the the the volume of the beta phase so if you look at this minus 2 gamma v beta by delta s so basically T x is a gearing you should not use s basically this is basically the beta minus 2 gamma v beta beta that is the change in the time now that is basically T h basically reduces this is what I am trying to say you again go through it you again go through it I am not going through it very I am going through it pretty fast okay if you go through it slowly then you will understand what I am trying to say say for example if you have understood this particular that is capillary right you have understood capillary you see that there is an extra pressure right so basically p beta is now not equal to p alpha but it is equal to p alpha plus 2 gamma h where h is the main currents right and gamma is the inter measurement measure now if you look at melting again have a look at melting so before that what I have established we have established some very simple ground rules that is for a linear tube phase system how does the equilibrium change T beta has to be equal to T alpha p beta is p alpha plus 2 gamma h where h is the main current measure mu beta equals to mu 1 right and you have this term this this this equations right these equations are already there you know these equations this one and this one now you are basically looking at d mu beta and you have s beta dt because dt d beta equals t alpha equals t and then you have v beta and then you have dp alpha plus 2 gamma d h why this basically is because dp beta is dp beta so it is because of this relation dp beta equals dp gamma plus 2 gamma you can also have 2 hd gamma but the point is that we do not currently we are not using it because if you have an excess in an excess quantity like a gamma you have is the area area and this is interfacial energy per unit area so if I do d of a gamma you have actually two terms one is called ad gamma right and you have gamma d in general we look at the gamma da part we do not look at the ad gamma part that in general but however if you have the ad gamma basically what does it mean it basically means that that there is a differential with respect to the uh the with respect to the interfacial energy okay and this is basically some sort of a intervention if you think of this intervention energy is uh it's like a force right it's joules per meter square or it is like newton's from a newton per meter cube so if you think of this this is of it's it's it's it's has this it's like a top term right so I do not want to go deep into the top term right now I do not want to go to the ad gamma contribution but what I am telling is da gamma for us now is nothing but gamma times d but there is a change in it right so that's that now if I am looking at if I am looking at that so basically I



Melting

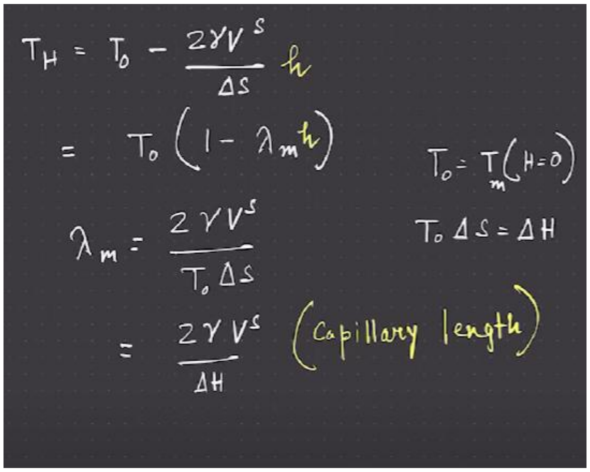
β - Solid
α - liquid

$$\Delta S\, dT + 2\gamma V^{\beta}\, dh = 0$$

$$dT = -\frac{2\gamma V^{\beta}}{\Delta S}\, dh$$

$$\int_{T(h=0)}^{T_h} dT = -\int_{H=0}^{H} \frac{2\gamma V^{\beta}}{\Delta S}\, dh$$

$$= -\frac{2\gamma V^{\beta}}{\Delta S}\, h$$



$$T_H = T_0 - \frac{2\gamma V^{s}}{\Delta S}\, h$$

$$= T_0 \left(1 - \lambda_m h\right)$$

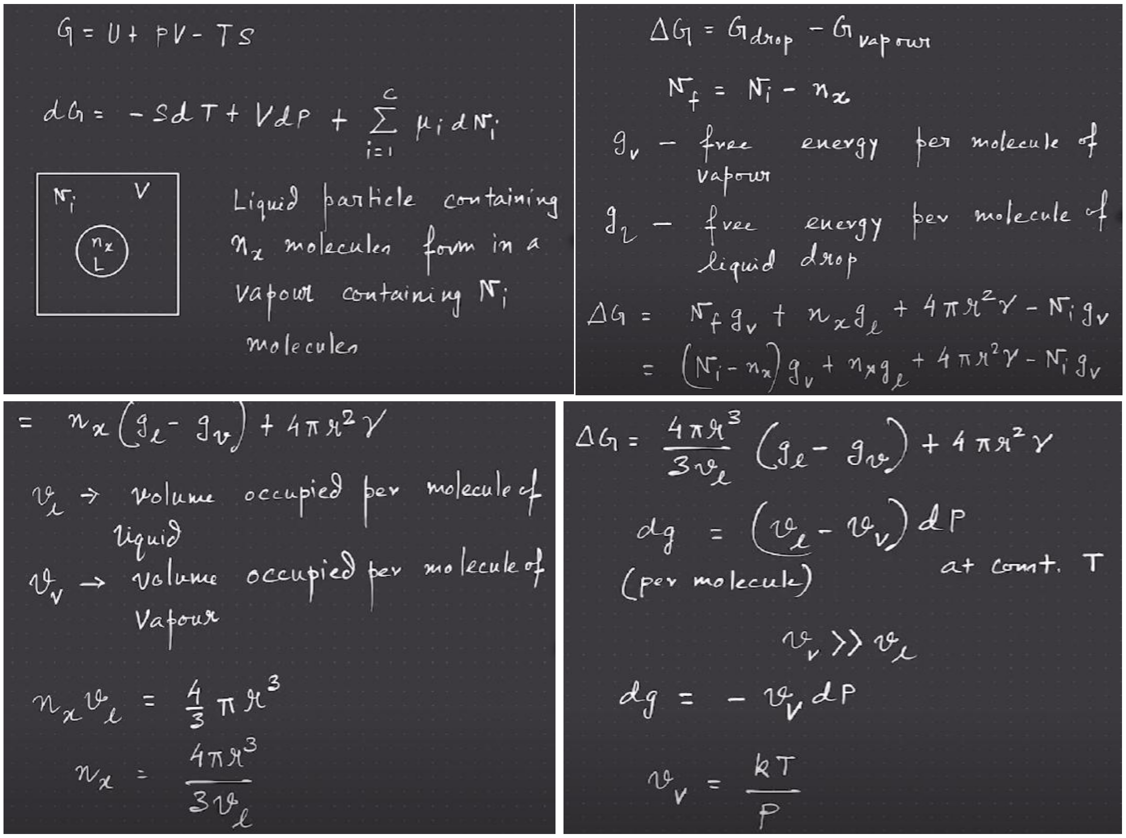
$$T_0 = T_m(H=0)$$

$$\lambda_m = \frac{2\gamma V^{s}}{T_0 \Delta S}$$

$$T_0 \Delta S = \Delta H$$

$$= \frac{2\gamma V^{s}}{\Delta H}$$ (Capillary length)

get this delta v which is v gas minus v liquid but v gas minus v liquid is very v liquid is very small compared to v gas so basically delta v is nothing but v gas so v gas is nothing but RT by v right v gas is nothing but RT by v now you are looking at melting temperature now if you use the same argument you basically see delta s dt plus 2 gamma v beta dh which is equal to 0 right 2 gamma v beta gh is the extra term that you have and you have dt equals to minus 2 gamma v beta by delta s and you are doing an integration



$$G = U + PV - TS$$

$$dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dN_i$$

Liquid particle containing n_x molecules form in a vapour containing N_i molecules

$$\Delta G = G_{drop} - G_{vapour}$$

$$N_f = N_i - n_x$$

g_v – free energy per molecule of vapour

g_l – free energy per molecule of liquid drop

$$\Delta G = N_f g_v + n_x g_l + 4\pi r^2 \gamma - N_i g_v$$

$$= (N_i - n_x) g_v + n_x g_l + 4\pi r^2 \gamma - N_i g_v$$

$$= n_x (g_l - g_v) + 4\pi r^2 \gamma$$

$v_l \rightarrow$ volume occupied per molecule of liquid

$v_v \rightarrow$ volume occupied per molecule of Vapour

$$n_x v_l = \frac{4}{3}\pi r^3$$

$$n_x = \frac{4\pi r^3}{3 v_l}$$

$$\Delta G = \frac{4\pi r^3}{3 v_l}(g_l - g_v) + 4\pi r^2 \gamma$$

$$dg = (v_l - v_v)\, dP$$

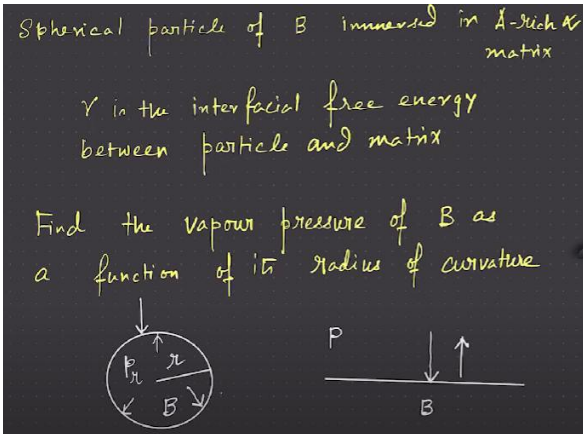
(per molecule) at const. T

$$v_v \gg v_l$$

$$dg = -v_v\, dP$$

$$v_v = \frac{kT}{P}$$

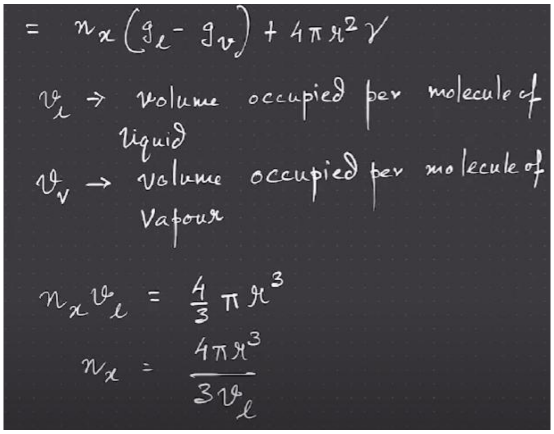
so basically what you see as the particle becomes spherical or smaller having the radius of curvature the which is non-zero curvature with non-zero curvature you basically see a reduction in the material now if you have a spherical particle that is immersed in an air age matrix this is also known as interesting phenomenon what you basically can see is that the liquid particle containing so basically this this equation the equation that we derived is called this equation is basically called Kelvin's equation and the Kelvin's equation the crux of the equation is this so delta g is 4 pi 4 pi 4 third pi r cubed by v l and g l minus g v that is the free energy of the liquid phase minus the free energy phase and you have 4 pi square gamma 4 pi r square gamma is basically for a spherical particle right you are taking a spherical particle and you have basically some nx molecules in the liquid phase so the liquid phases just come out right so you have this v which is immersed in an air age matrix and gamma is the energy find the break position of v as a function of its radius of curvature and that is exactly what here so you you go through this okay so you go through this and you basically you get there is something so this equation is a very famous equation called Oswald Freund equation again this will not be a part of the exam so the interfacial phenomena i don't want to go deep into it but what i want to tell are very the crux of it is this you have this liquid that is condensed in a paper phase you have a large paper phase and there is a liquid there is a small droplet of liquid that has condensed now the liquid particle contains nx molecules from and they form in a vapor so basically they contain nx molecules and formula vapor means which contains initially ni molecules now you have an f nf is basically ni minus nx now delta g is for g drop minus g vapor okay and you can now write g v the small g v as the free energy per molecule of vapor small g l as a free energy per molecule of the liquid drop and then you have delta g



Spherical particle of B immersed in A-rich matrix

γ is the interfacial free energy between particle and matrix

Find the vapour pressure of B as a function of its radius of curvature



$$= n_x\left(g_l - g_v\right) + 4\pi r^2 \gamma$$

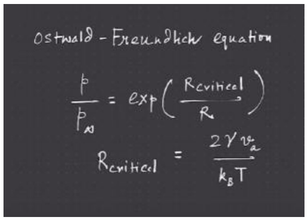
$v_l \rightarrow$ volume occupied per molecule of liquid

$v_v \rightarrow$ volume occupied per molecule of Vapour

$$n_x v_l = \frac{4}{3}\pi r^3$$

$$n_x = \frac{4\pi r^3}{3 v_l}$$

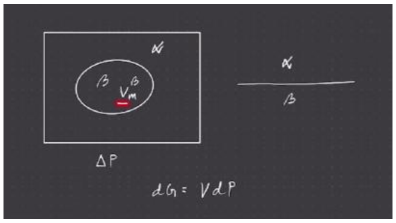
which is basically if you look at that you have nf times g v g v is per molecule nx times g l and then you have 4 pi r square comma because you r is the radius of the drop right r is the radius of droplet 4 pi r square comma because and gamma is the the interfacial energy so basically you have this and then what has gone ni g v so minus nx now if i go on expanding so what i get is nx which is nf minus ni gl minus g v plus 4 pi r square comma now vl is the volume of weight per molecule of the liquid and vv is the volume of weight per molecule of the vapor now you see nx is the number of molecules times vl which is the volume of weight per molecule of the vapor of the liquid now nx times vl is nothing but 4 pi r2 so basically nx equals 4 pi r2 pi 3v now that's the liquid droplet right and now delta g is nothing but 4 pi r3 by 3 vl gl minus gv plus 4 pi r square comma right that is the surface area that is the surface energy contribution now you have dg which is vl minus vv times dp right v liquid minus v vapor right this is this is volume per so this is volume per molecule pl minus vb times t this is all per molecule at a constant temperature right so vdp minus sdt minus t is not so basically it is plus minus vv dt why because vl vb is much much greater so and vb i can think of this as per molecule right so we can use the the the ideal gas law so v vapor equals to nothing but kbt by p where kb is the postman constant right so kb here now what i got is delta g right the small delta g this small delta g basically is telling you minus kbt and p by p by p infinity now you see there is a change in the display energy okay p is now the pressure right p is not the vapor pressure between the liquid and the salt liquid in the vapor however originally it was p infinity right it has changed from p infinity so if you look at that you have delta g is 4 3 r cube by vl ln p by p infinity plus 4 pi r square now if you now if you want to find out r if you want to find out r the easiest way is to solve for it how do i solve i demand that del delta g del r equal to 0 so that gives me the critical radius that gives me the critical radius the droplet okay that gives the critical radius the droplet so then what we basically encounter is the oswell-praunlisch equation and where you get this r critical which is 2 gamma v by u right so there



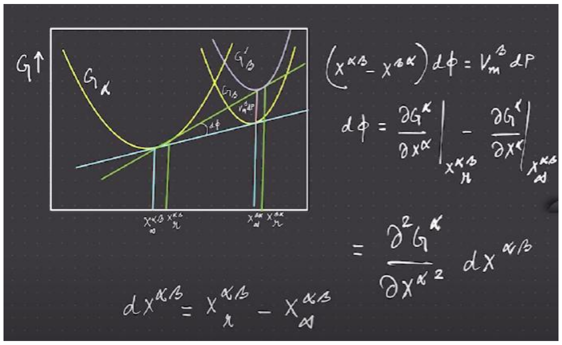
Ostwald - Freundlich equation

$$\frac{p}{p_\infty} = \exp\left(\frac{R_{critical}}{R}\right)$$

$$R_{critical} = \frac{2\gamma v_\alpha}{k_B T}$$



is another very important effect called skips transfer effect say for example you have this alpha beta equilibrium and this is the molar volume of the beta phase and this is in equilibrium the alpha phase now have a look at this when initially the yellow curve is g alpha and another yellow curve is g beta and you alpha and beta share a flat interface with curvature 0 or radius of convection infinity however if the particle the beta prime not the the beta particle is a sphere or a circle then what happens the energy basically if you look at the common tangent so you have the blue tangent when you had the original yellow curves now your g beta has shifted up right it has shifted up why why is shifted up because there is an excess pressure there is an excess pressure delta p which is basically the expression is nothing but delta p which is basically 2 gamma by r now with this excess pressure basically you have this dm delta p basically so vdp so dg equals to vdp right dg equals to vdp or delta



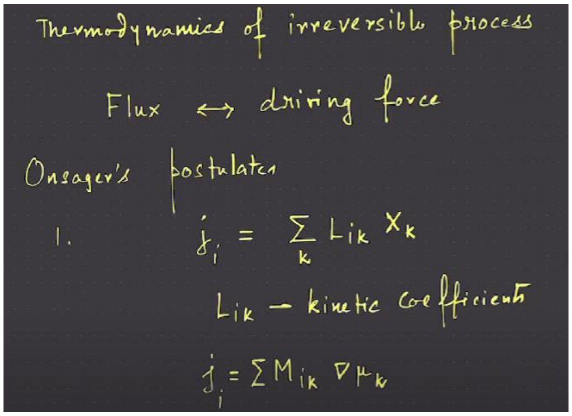
$$\left(x^{\alpha\beta} - x^{\beta\alpha}\right) d\phi = V_m^\beta dP$$

$$d\phi = \left.\frac{\partial G^\alpha}{\partial x^\alpha}\right|_{x^{\alpha\beta}_r} - \left.\frac{\partial G^\alpha}{\partial x^\alpha}\right|_{x^{\alpha\beta}_\infty}$$

$$= \frac{\partial^2 G^\alpha}{\partial x^{\alpha 2}} dx^{\alpha\beta}$$

$$dx^{\alpha\beta} = x^{\alpha\beta}_r - x^{\alpha\beta}_\infty$$

g equals to v delta p so this v delta p this increase that is given by this orange line here will lead to another this if you look at this now the green line this is your new tangent now if you look at the common tangent you have seen so initial equilibrium was here right this blue lines right this this was the one like as soon as i go to this one i have this guy this guy and you can basically come in so basically what happens this comes because of if you look at this this is nothing but it's chemical potential right so this is basically mu a mu b alpha equals to mu b beta or mu b alpha equals to mu beta that you see that condition for your new curvature basically gives rise to a shift in composition right there is a right shift there is a right shift in composition by the way right of both combinations the particle is the matrix and this is called gill's conservation okay so i have derived it here but you can also derive it by your on your own and so you can do this you can basically see that finally you will see that the delta p equal to 2 gamma i by r and you are basically looking at the phase boundaries now if you look at



Thermodynamics of irreversible process

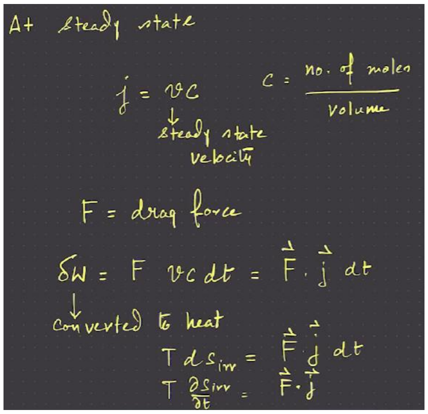
Flux ↔ driving force

Onsager's postulates

1. $\dot{j}_i = \sum_k L_{ik} X_k$

L_{ik} – kinetic coefficients

$\dot{j}_i = \sum M_{ik} \nabla \mu_k$



At steady state

$\dot{j} = vc$ $\quad c = \frac{\text{no. of moles}}{\text{volume}}$

v ↓ steady state velocity

F = drag force

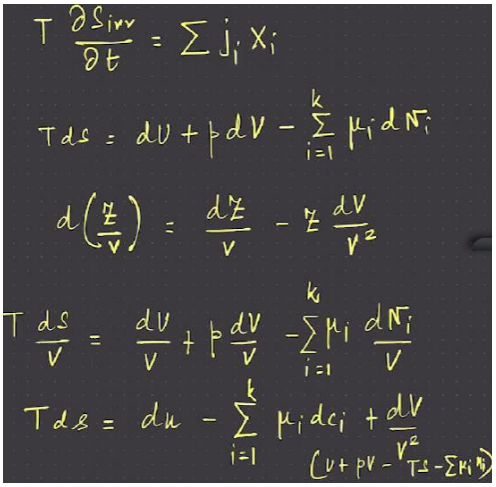
$\delta W = F\, vc\, dt = \vec{F} \cdot \vec{j}\, dt$

δW ↓ converted to heat

$T\, dS_{irr} = \vec{F} \cdot \vec{\dot{j}}\, dt$

$T \frac{\partial S_{irr}}{\partial t} = \vec{F} \cdot \vec{j}$

the phase boundaries there is definitely the equilibrium has shifted the phase boundaries are also shifted that's all i wanted to tell and you can actually apply these ideas in multi component system i am not talking about gills adsorption and langmuir adsorption isotherms uh here however if you want to have some separate lecture on it you please ask me we can do it um means i can i can give you some help there again i can basically but again the interfacial thermodynamics although it is covered i briefly covered it now and i touched it now what i am telling is that this is not going to be a part of the final exam you don't have to look at it right now but this is a very very important topic and interfacial thermodynamics on its own is like a subject now comes the kinetics part see the kinetics part here again the way i thought is that i introduced the onsager's post-traumatic see there is this dragging force like there is a so we have already done this basically we looked at like if there is a driving force if there is a chemical potential difference that chemical potential difference the driving force and as a result there will be mass transfer now if i have mass transfer at what rate the mass transfer happens is what gives you kinetics similarly if i have uh uh uh uh uh temperature gradient like t alpha and t beta are not equal then there is a heat transfer heat transfer happens from hot hot body to cold body in such a way so as to equalize so this heat transfer again basically again there is a rate of heat transfer right if there is heat transfer there's a rate of heat transfer now how do i come to this base so basically if you look at onsager so onsager uh um uh a famous scientist okay everyone Nobel prize for statistical contributions statistical mechanics basically onsager uh physics so basically onsager postulated that the flux is proportional to force so this capital x here is a force in fact let us call this yeah it's capital x the north so i'll tell you so you have x as force driving force and we are telling some of all forces so basically there is a flux which is proportional to the force flux there is a relation between flux and driving force and flux is what flux of species is basically or flux of any quantity say flux of quantity means basically you can like heat transfer per unit area per time okay the amount of energy transfer per unit area per unit time is basically heat flux amount of species transfer per unit area per unit time is that for that particular uh concentration of species transferred per unit area per unit time is the flux is a mass it's it's a compositional flux right molar flux you can also have mass flux so the flux is basically some quantity that is basically passing per unit area per unit time as a response to the driving force and as a response for driving force this flux will happen and this flux is part is finally going to drive the system towards equilibrium right so flux is proportional to driving force driving force count because of some inequality right t alpha is not equal to t beta or mu alpha is not equal to mu beta so in response you have this right so basically flux is proportional to force and onsager postulated that it is linearly proportional so you have this onsager coefficients or this can be coefficients which are some like and some like a has some properties like it has positive definite SNR right so basically if i give you an example so you have for example the species concentration this is the flux this is compositional flux which is proportional to driving force driving force is basically mu is your for mu is your chemical potential and grad mu is your driving force why because u is your potential energy f equals to minus d u d x right so that is exactly what we are looking at so mu is your chemical potential energy and the derivative of energy the special derivative energy gives you the driving force the special driving force as a result of which there will be flux of this particular species and the flux is in terms of say compositional flux of say molar flux the species i of the species i will have a flux in response to this time of course so that the equality the again the chemical potential equality is established at equilibrium right so basically another thing that onsager pointed out is that flux is nothing but velocity which is a steady state velocity of the particles times the concentration say for example if i'm looking at molar flux molar flux that is number of moles of certain species is basically transferring per unit area upon time now if i look at means basically a concentration of species i am looking at the mass transfer so if you have the polar flux then molar flux at steady state basically it is basically the molar flux is basically equal to the steady state velocity times composition or concentration the concentration is number of moles per unit volume as you see that number of moles per unit volume so moles by volume at velocity is length by time so this becomes moles and volume by length is basically so length by volume right volume by length is the area right so basically that's exactly what we are doing now if you have this flux then there is a drag force now if there is a drag force then basically if there is a drag force now if you look at this then there is a work done to overcome this drag force so if you have f times v c but times dt now if you see this is force this is force and you have velocity and you have concentration so this basically basically nothing but flux right so you have force then flux and you have this time interval so basically this basically gives you what f dot j f dot j dt and this is nothing but delta w right this basically because why to work on this drag force what is happening as the flux is happening there is a work done and this work done in response to the drag force and this work done is completely converted to heat now and this converted to heat is an irreversible conversion there is an entropy production and if you see this is the what i am probably talking about t ds irr which is basically so delta w is nothing but delta q delta q is nothing but t ds irr that is irr is basically for irreversible so which is basically you have a rate of change of so basically you have a entropic production rate rate of entropic production right ds ir the irr is the irreversible part of the entropy which is getting produced as a result of all these processes right now if you look at that full velocity v times dt is displacement you can think of this way v times dt is nothing but display velocity times dt is nothing but displacement and you have the force and force times displacement is nothing but okay so basically what we are telling is you have this relation which is basically got the rate of internal production which has to be positive for a process to go on right now again i don't want to go into the algebra but i want to tell say for example now if i add the continuity equation now again continuity equation which is a very important equation of kinetics is nothing but something or some quantity in so basically it comes from quantity in minus quantity out if you remember initially we looked at open system so that's what i am trying to do equals to rate of accumulation or diffusion and remember that you can also have quantity generated within the system like quantity generated within the system for any time and you can have like quantity destroyed so all this this is this gives you a generalized conservation law for the quantity that quantity can be hit the quantity can be mass it can be even momentum right and each of these basically give rise to this different type of rate equation say for example it gives you navier stokes equation give you mass transfer equation or diffusion equation and if you look at that continuously so basically if you look at that you see this is this is a so this is the energy this is the continuity law for energy this is the continuity equation for energy this is nothing but a conservation equation all continuity equations are conservation equations grad dot j is basically grad dot j is basically divergence of flux right the divergence of flux and and



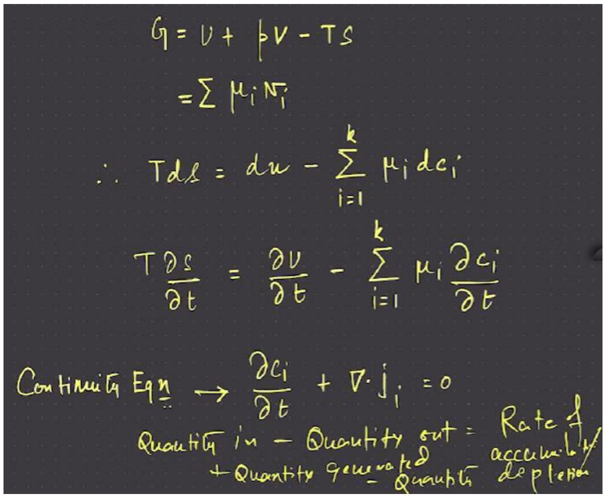
$$T\frac{\partial S_{irr}}{\partial t} = \sum j_i X_i$$

$$T\,ds = dU + p\,dV - \sum_{i=1}^{k} \mu_i\, dN_i$$

$$d\left(\frac{Z}{V}\right) = \frac{dZ}{V} - Z\frac{dV}{V^2}$$

$$T\frac{ds}{V} = \frac{dU}{V} + p\frac{dV}{V} - \sum_{i=1}^{k} \mu_i \frac{dN_i}{V}$$

$$T\,ds = du - \sum_{i=1}^{k} \mu_i\, dc_i + \frac{dV}{V^2}\left(U + pV - TS - \sum \mu_i N_i\right)$$



$$G = U + pV - TS$$

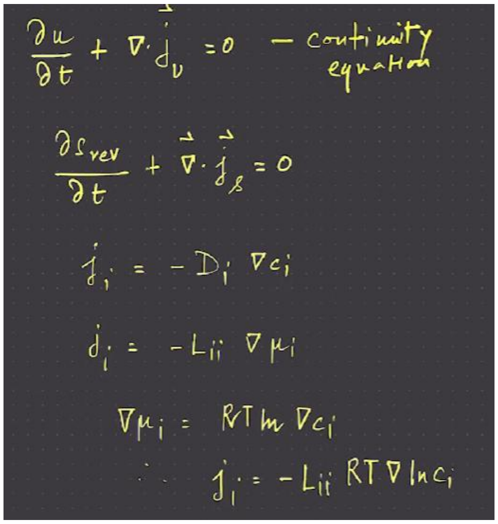
$$= \sum \mu_i N_i$$

$$\therefore\ T\,ds = du - \sum_{i=1}^{k} \mu_i\, dc_i$$

$$T\frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \sum_{i=1}^{k} \mu_i \frac{\partial c_i}{\partial t}$$

Continuity Eqn $\rightarrow \frac{\partial c_i}{\partial t} + \nabla \cdot j_i = 0$

Quantity in − Quantity out + Quantity generated − Quantity = Rate of accumulation/depletion you have this accumulation so basically the state this is this statement is nothing but del u del t plus this is energy coming in minus energy going out plus energy getting accumulated right this part is energy in minus out this part is energy in minus out and this this part and this part is the accumulation of energy and this basically there is a rate of accumulation and this gives rise to continuity equation if you use this continuity equation this is then also applied for entropic



$$\frac{\partial u}{\partial t} + \nabla\cdot\vec{j}_U = 0$$ — continuity equation

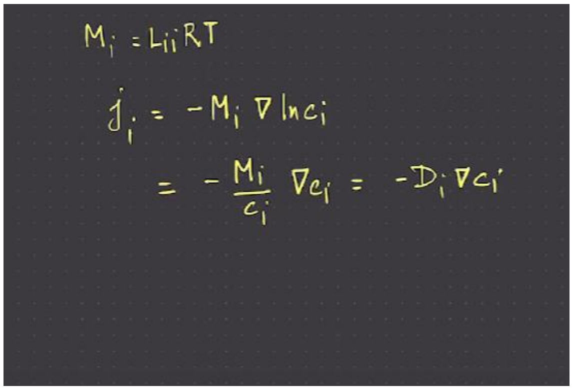
$$\frac{\partial s_{rev}}{\partial t} + \vec{\nabla}\cdot\vec{j}_s = 0$$

$$j_i = -D_i\nabla c_i$$

$$j_i = -L_{ii}\nabla\mu_i$$

$$\nabla\mu_i = RT\ln\nabla c_i$$

$$\therefore\ j_i = -L_{ii}RT\nabla\ln c_i$$



$$M_i = L_{ii}RT$$

$$j_i = -M_i\nabla\ln c_i$$

$$= -\frac{M_i}{c_i}\nabla c_i = -D_i\nabla c_i$$

production right and this is the entropic flux right now if you think of that the flux can also be written like Fick's law right this is called Fick's first law j is proportional to grad c right the composition of gradient but in general as you see from on sagar it is flux is proportional to force grad c is not driving force but that mu is driving force because mu is enhanced so according on sagar this is a more fundamental relationship so as you look at kinetics you will see that thermodynamics gives you the driving force and in response to driving force there is flux and the flux and forces are such that the rate of entropic production is always positive so this is how kinetic laws are in general developed okay so if you have any doubt again here here this itself this kinetics of materials can itself be a full three credit course and we will we will discuss this later so but if you have any problem if you have any problem to relate thermodynamics to kinetics and if you have any problem to relate flux to force then basically please write to me in my to my email id and i will be i'll be happy to answer your questions so thank you so much for listening to all the lectures and if there is any doubt please do write to me