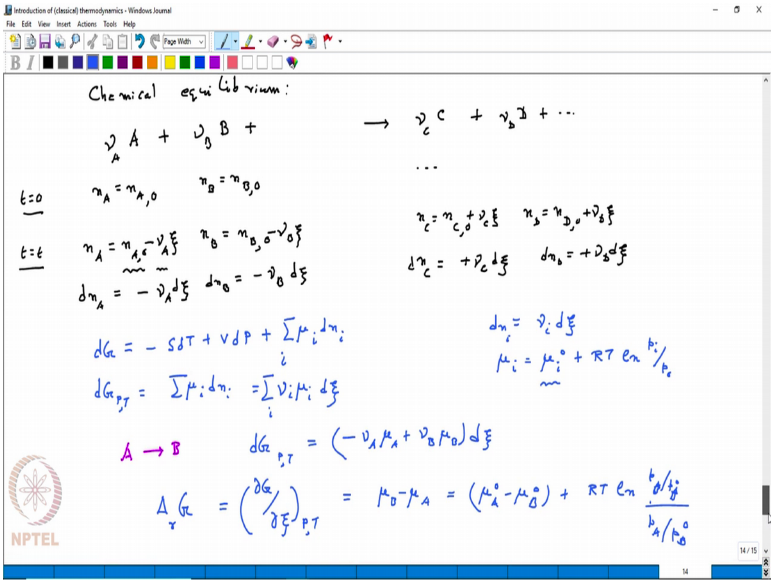
Advanced Chemical Thermodynamics & Kinetics
Prof. Arijit Kumar De
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 05
Review of Classical Thermodynamics 05

(Refer Slide Time: 00:14)



Chemical equilibrium:

$$\nu_A A + \nu_B B + \cdots \longrightarrow \nu_C C + \nu_D D + \cdots$$

$t=0$ $\quad n_A = n_{A,0} \quad n_B = n_{B,0}$

$t=t$ $\quad n_A = n_{A,0} - \nu_A \xi \quad n_B = n_{B,0} - \nu_B \xi$

$dn_A = -\nu_A d\xi \quad dn_B = -\nu_B d\xi$

$n_C = n_{C,0} + \nu_C \xi \quad n_D = n_{D,0} + \nu_D \xi$

$dn_C = +\nu_C d\xi \quad dn_D = +\nu_D d\xi$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

$$dG_{P,T} = \sum \mu_i dn_i = \sum_i \nu_i \mu_i d\xi$$

$dn_i = \nu_i d\xi$

$\mu_i = \mu_i^\circ + RT \ln p_i/p_0$

$A \rightarrow B \qquad dG_{P,T} = (-\nu_A \mu_A + \nu_B \mu_B) d\xi$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \mu_B - \mu_A = (\mu_A^\circ - \mu_B^\circ) + RT \ln \frac{p_B/p_0}{p_A/p_0}$$

So, in this section we will be concluding our initial discussion on the Review of Thermodynamics or Classical Thermodynamics. So, in this part we will discuss chemical equilibrium. So, we will be particularly considering a reaction a general reaction of the type let us say a A plus b B or maybe we can actually write the stoichiometry of the reaction in terms of notation as nu A.

So, A and B are reactants and let us say C and D are products and then we ask this question like at time 0 let us say what is the amount of the any product let us say n A is something like n A 0, where n A 0 corresponds to the amount of n A at time 0. Similarly n B corresponds to n B 0 at time 0 and so on and in this way if you ask that at any arbitrary time let us say when time is t what is the amount of n A.

So, this will be the initial amount n A 0 minus it will have nu A into xi, where xi is the advancement of the reaction and similarly n B will be n B 0 minus nu B into xi and similarly n C will be n C 0 plus nu C into xi the plus sign is here because the n C, C and

D are products. So, with respect to time they actually accumulate and we will have n D 0 plus nu D into xi.

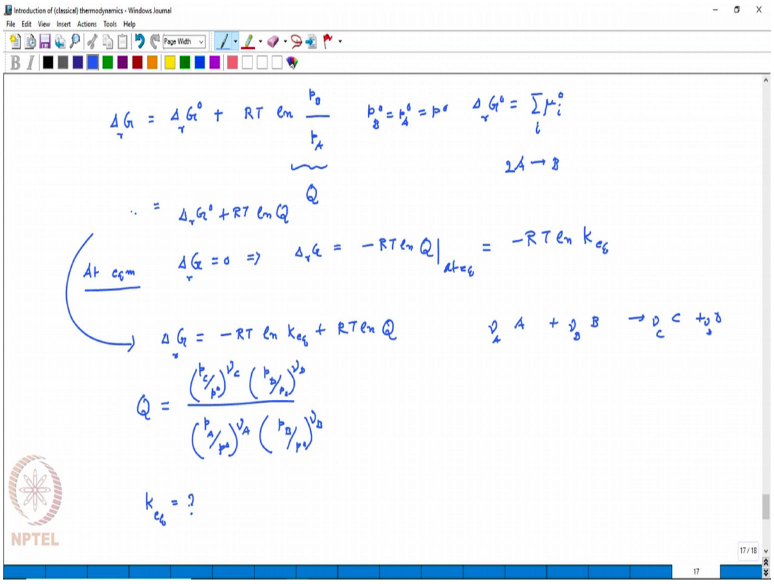
Now, if you ask if you take the derivative now or the differential d n A. So, that will be look at it here carefully. So, n A 0 is a constant nu is also constant. So, it will be simply minus nu a into d xi similarly d n B that will be minus nu B into d xi and similarly d n C which is the differential change in amount of C will be plus nu C into D xi and similarly for d n D it will be plus nu D into D xi. And then we can actually combine everything and ask this question what is the change in Gibbs free energy we know that for an open system the Gibbs free energy will be minus S d T plus V d P plus the change of the most of the constituent. Here at the constituent I am writing as i. So, i is basically A, B, C and D and we have nu i d n i.

Now, the way I have written it here when I write it for A and B I should write nu i for A I have to write minus nu i because I have to include a negative sign in the stoichiometry. So, at constant pressure and temperature it is just the nu i d n i and we can actually now express it in terms of the d xi. So, instead of n in a nu notation here we can actually write it as a mu the chemical potential, because that was what usually the textbook right it is for chemical formation and the nu we are preserving for the stoichiometry. So, the mu i as we can see here is nothing but mu i is nu i times D xi we including the sign and then we can actually write it as the d n i part not the mu i. So, this should be the d n i part and then we can just write it as nu i mu i into d xi with the sum.

For example we can simplify it let us say for A reaction which is going from A to B and then it is only the constituents are A and B then we can show that the d G at constant pressure temperature is nothing, but will have A to B. So, for A if I take the summation it will be minus nu A mu A plus nu B mu B into d xi. So, we can ask this question now what is this quantity del G del xi. So, it is basically the differential change in Gibbs free energy per unit advancement of the reaction at constant pressure and temperature that is simply as we can see is the difference in the chemical potential of A and B and which actually we define as the reaction Gibbs free energy. So, it is a change in Gibbs free energy for a reaction that is why we write suffix r here and that is just difference of the chemical potential of the constituents.

So, again any mu we can actually write it as mu i 0 plus R T ln p i by p 0 and then we can actually replace it and what we see here we will have some terms like mu A 0 minus mu B 0 if we collect the standard state chemical potentials and then we will have RT ln p A by p A 0 divided it will be B because A has a negative sign and then I will have p A by p B 0. So, this is basically the reaction free energy and then we can further say.

(Refer Slide Time: 06:58)



$$\Delta_r G = \Delta_r G^0 + RT\ln \underbrace{\frac{p_B}{p_A}}_{Q} \qquad p_B^0 = p_A^0 = p^0 \qquad \Delta_r G^0 = \sum_i \mu_i^0$$

$$2A \rightarrow B$$

$$\therefore = \Delta_r G^0 + RT\ln Q$$

At eqm

$$\Delta_r G = 0 \Rightarrow \Delta_r G = -RT\ln Q\Big|_{at\ eq} = -RT\ln K_{eq}$$

$$\Delta_r G = -RT\ln K_{eq} + RT\ln Q \qquad \nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$$

$$Q = \frac{\left(\frac{p_C}{p^0}\right)^{\nu_C}\left(\frac{p_D}{p^0}\right)^{\nu_D}}{\left(\frac{p_A}{p^0}\right)^{\nu_A}\left(\frac{p_B}{p^0}\right)^{\nu_B}}$$

$$K_{eq} = ?$$

So, now, you can actually define let me first rewrite it the reaction Gibbs free energy the way we got it is something like a combination of mu 0's if we write it as the standard set chemical potential a standard set of the reaction Gibbs free energy which is nothing, but the differences of the mu i's mu i 0's.

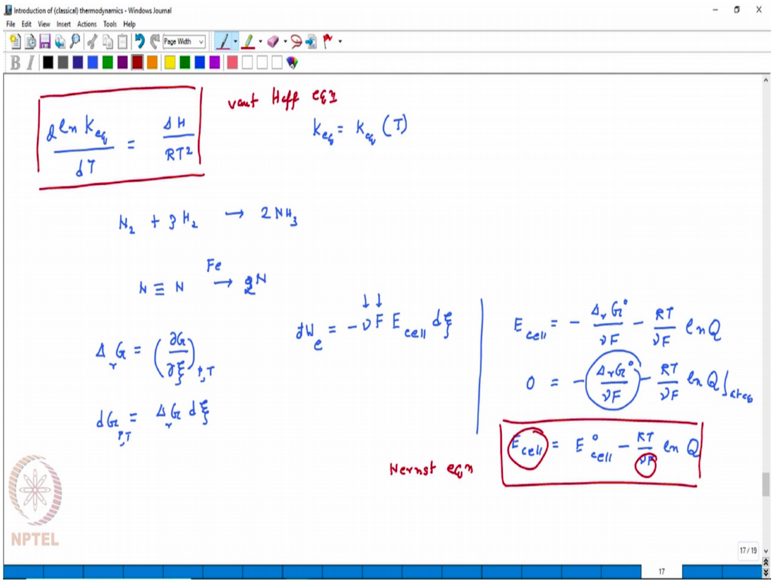
So, basically for reactants it will be negative and for products it will be positive because it is coming directly from the stoichiometry and then the other part which will have is basically RT ln p B by p A because the standard state for p B and p A are basically same in this case in every case of course, but if we have a stoichiometry something like of the reaction something like say a 2A is going to B then we should have actually raised the there will be a nu i also associated with it.

So, overall what we can write for this reaction is if we have this quantity which we define as the reaction quotient. So, we write it as delta r G naught plus RT ln Q and we also define that when at equilibrium. So, there is no forward reaction or backward reaction. So, the reaction Gibbs free energy is 0, which gives basically delta r G is minus RT ln Q at equilibrium and at equilibrium we replace the Q as equilibrium constant which is K equilibrium.

So, we can just rewrite this equation again that the reaction Gibbs free energy is nothing, but minus RT ln K equilibrium plus RT ln Q, where Q is the quotient. So, the quotient will be the equilibrium quotient if the system has reached equilibrium and then we can also do it for a general reaction in the sense that if we preserve the stochiometry number the nu i's also. So, then eventually one can show that this quotient will be nothing, but the pressure of the let us say the way we started it A plus B is going to C plus D with the stochiometry questions as nu A nu B nu C and nu D.

Then in the numerator we will always have the products we will have p C by p 0 to the power nu C p D by p 0 to the power nu D and then we will p A by p 0 to the power nu A and p B by p 0 to the power nu B and then we actually say that a reaction what will be the effect of external conditions like say pressure temperature or say inert gas on the equilibrium constant; that we try to understand.

(Refer Slide Time: 10:52)



$$\boxed{\frac{d \ln K_{eq}}{dT} = \frac{\Delta H}{RT^2}}$$

vant Hoff eqn

$$K_{eq} = K_{eq}(T)$$

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$N \equiv N \xrightarrow{Fe} 2N$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

$$dG_{p,T} = \Delta_r G \, d\xi$$

$$dW_e = -\overset{\downarrow}{\nu} \overset{\downarrow}{F} E_{cell} \, d\xi$$

$$E_{cell} = -\frac{\Delta_r G^\circ}{\nu F} - \frac{RT}{\nu F} \ln Q$$

$$0 = -\frac{\Delta_r G^\circ}{\nu F} - \frac{RT}{\nu F} \ln Q \Big|_{at\, eq}$$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{RT}{\nu F} \ln Q}$$

Nernst eqn

And, then if we carry out the maths we will see that these equilibrium constant it can be like you can have many effect on the effect of say inert gas or say temperature for that actually we use a principle which is known as the (Refer Time: 11:07) principle already you know these things, so, I am just giving you overview and then we talk about the effect of inert gas and talk about suppressed association or enhanced association depending on the stochiometry of a reaction and also we talk about the temperature dependence which is related to the van't Hoff equation and there we showed I mean you can actually look at the video for my earlier course where we showed that this quantity instead of ln K equilibrium we can actually write it as a d ln K equilibrium after some manipulation and then you can easily show for any reaction it is basically connected to the change in enthalpy divided by RT square.

Now, if the reaction is exothermic, so, then delta H will be negative. So, with respect to increase in temperature actually you have the reaction rate the equilibrium constant will be less and for an endothermic reaction if I came from increasing that temperature I will have basically a equilibrium constant that value of the equilibrium constant will be increasing.

So, the equilibrium constant is a function of temperature normally. So, if we do not change the temperature that constant will not change, then what we can say from this is that for endothermic reaction increasing the temperature we will give you more and more I mean ratio of the product, but for endothermic exothermic reaction it is the other way because heat is released and something is absorbing. So, you have a lower temperature you have a quenching of the heat, but for exothermic reaction you usually need optimal temperature the reason is actually enough to break bond to activate the molecules.

So, one of the very good example is the catalytic reduction of nitrogen to form ammonia which is extremely important for our survival. It is an industrial important reaction and which actually is the key reaction to produce many fertilizers and here this reaction is exothermic which means heat is produced in this reaction and then if you reduce the temperature too much the reaction does not occur. Because initially you have to break this nitrogen-nitrogen triple bond to get basically radical form of the nitrogen which are adsorbed of course, on a surface of metal usually it is a iron catalyst is used, but this triple bond breaking actually needs a lot of energy for activation. So, to overcome that energy barrier you need an some initial temperature otherwise the reaction will not occur and that is why we talk about the optimal temperature.

And, moving on then we actually discussed in the earlier course that what about electro chemistry or the thermodynamics of electrochemical cells and there is the same concept that you start with the concept of the reaction Gibbs free energy which we just developed and that by definition it is basically the change differential change in Gibbs free energy per unit advancement of a reaction, but this reaction is now an electrochemical reaction and it should be of course, at constant pressure and temperature because we have dropped with the two terms p d p and s d t and then we kind of equate that the work done or the differential work done I am writing d cross again because the work done is not an state function or this d cross W is not an exact differential.

The electrical work done if you think that I am moving a positive charge across a potential then it will be minus nu F the E cell which is the electro motive force of the cell and times the d xi. So, we can now think that this d G will be nothing, but equal to delta r G and times d psi of course, this is that constant pressure and temperature and then we can compare these two equations and then we can actually get an expression for the electrochemical electro motive force of the cell and then we will get the differences in the reaction Gibbs free energy which at the standard state which for the reactant minus product divided by nu F.

So, here F is the Faraday constant and nu is again the number of electrons which are being changed in an redox reaction which are involved in the redox reaction divided and then we have one factor RT by nu F and we are keeping the same notation nu usually many textbook actually write it as n RT ln Q and then one can actually write that at equilibrium again this will be 0. So, then I will have minus delta r G nu F minus RT divided by nu F ln Q at equilibrium.

So, this constant is nothing, but something like an equilibrium constant, but we just write it for cell reaction because it is equilibrium constant divided by the nu F. So, we use usually that notation which you write it as E 0 cell which is the standard this chemical or the electro motive force of the cell electrochemical cell in the if everything is in the standard condition and then minus RT by nu F ln Q where Q is the reaction quotient and this equation we call as Nernst equation. And from the Nernst equation one can actually get the electro motive force of a cell, but when you do a problem you have to always remember that what drives the cell reaction is the free energy. So, you have to always take the nu F times E cell to understand the driving force of a of any electrochemical cell and this equation is known as the Van't Hoff equation.

So, in the next few lectures we will be first starting with the advanced topics. So, where we will not give you a overview of phase diagram or the multi component phase diagram here because that has been already covered in earlier courses and it is mostly covered in engineering thermodynamic courses. And second point here is that so, from in the next set of lectures we will be covering a few aspects of the intermolecular interactions, where we will first talk about what is the driving force behind formation of the liquid state and then we will be talking about the self assembly of macromolecules and where we will show that how basically what is the fundamental physics behind say coagulation or a flocculation of colloids and what is the stability of colloids those kind of issues.

So, we will be talking about the overall electrochemical aspects of this thing of this macroscopic system, but of course, will also give you some aspect of understanding to some level of understanding of the microscopic picture also.

Thank you.