Environmental Chemistry and Microbiology

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Lecture -06
Chemical Equilibrium-I

Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself Professor Anjali Pal. We are both from Civil Engineering Department of IIT Kharagpur. We have divided the course into two parts. The first part, Environmental Chemistry will be covered by me and the second part Environmental Microbiology will be taught by Professor Sudha Goel.

In the module 2 which we will start today, I will discuss about the chemical equilibrium. The chemical equilibrium is a very important topic for Environmental Chemistry and in my next 5 lectures I will throw some light on this topic.

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Chemical Equilibrium

Topics covered:

- Reversible reaction
- Concept on Equilibrium
- Kinetic approach to equilibrium
- Law of mass action
- Activity and activity coefficient

The first lecture of today will cover the following topics: Reversible reaction, concept on equilibrium, kinetic approach to equilibrium, laws of mass action, activity and activity coefficient.

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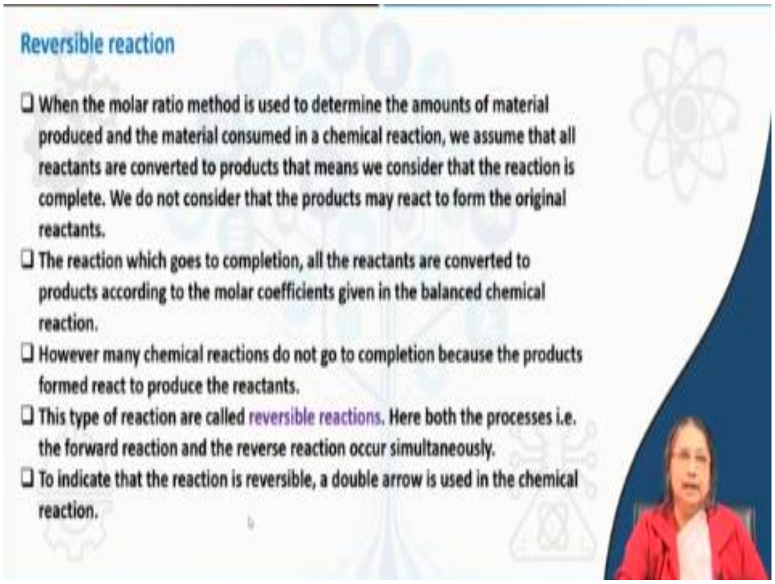

Reversible reaction

❑ When the molar ratio method is used to determine the amounts of material produced and the material consumed in a chemical reaction, we assume that all reactants are converted to products that means we consider that the reaction is complete. We do not consider that the products may react to form the original reactants.

❑ The reaction which goes to completion, all the reactants are converted to products according to the molar coefficients given in the balanced chemical reaction.

❑ However many chemical reactions do not go to completion because the products formed react to produce the reactants.

❑ This type of reaction are called reversible reactions. Here both the processes i.e. the forward reaction and the reverse reaction occur simultaneously.

❑ To indicate that the reaction is reversible, a double arrow is used in the chemical reaction.

We all know that when in a chemical reaction, we want to know how much product is formed or from how much reactants we always use the balanced equation for certain reaction. So, in molar ratio method when we want to determine the amounts of material produced and the material consumed in a chemical reaction, we assume that all reactants are converted to the products. That means 100% conversion. We never consider that the products may react to form the original reactants also. But in most cases the reaction does not go to completion.

All the reactants are converted to products according to the molar coefficients given in the balanced chemical reaction. In the complete reaction 100% conversion occurs. But almost all the chemical reactions do not go to completion. It is so because the products formed, react to produce the reactant. That means opposite reaction also occurs. The reactants also react and the products also react to form the reactants. That means reactants form the products and at the same time products also form the reactants. These types of reactions are called the reversible reaction. Here both the processes (that means the forward reaction and the reverse reaction (also sometimes called backward reaction)) occur simultaneously and to indicate that the reaction is reversible we always use a double arrow in the chemical reaction.

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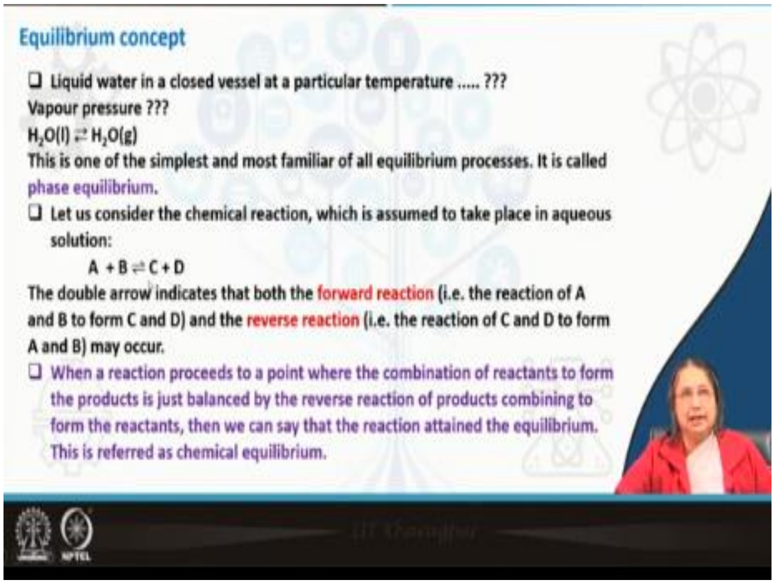

Equilibrium concept

- ❑ Liquid water in a closed vessel at a particular temperature ..... ???

Vapour pressure ???

$H_2O(l) \rightleftharpoons H_2O(g)$

This is one of the simplest and most familiar of all equilibrium processes. It is called phase equilibrium.

- ❑ Let us consider the chemical reaction, which is assumed to take place in aqueous solution:

$A + B \rightleftharpoons C + D$

The double arrow indicates that both the forward reaction (i.e. the reaction of A and B to form C and D) and the reverse reaction (i.e. the reaction of C and D to form A and B) may occur.

- ❑ When a reaction proceeds to a point where the combination of reactants to form the products is just balanced by the reverse reaction of products combining to form the reactants, then we can say that the reaction attained the equilibrium. This is referred as chemical equilibrium.

What is the equilibrium concept? The simplest equilibrium is the equilibrium of water as liquid and water as gas (shown below as follows:).

$H_2O(l)\leftrightharpoons H_2O(g)$..(1)

That means if you take some water that liquid water in a closed vessel and if you keep it for some time at a certain temperature the phase transfer will occur. Then after some time, the equilibrium will be reached. At that equilibrium point some amount of water in the liquid form will be converted to gaseous form. On the other hand, same amount of gas will be converted to liquid water. This is not the chemical equilibrium, but it is called phase equilibrium. For chemical equilibrium, we have to consider a chemical reaction:

$A+B\leftrightharpoons C+D$...(2)

In the reaction (represented by equation (2)) the molar ratio of A and B is taken as 1:1 and that of C and D is taken as 1:1. The double arrow represents both the forward reaction (i.e. the reaction of A and B to form C and D) and the reverse reaction (i.e. the reaction of C and D to form A and B).

Now what is equilibrium? In this case we will call it chemical equilibrium (not phase equilibrium).

What is chemical equilibrium? When a reaction proceeds to a point where the combination of reactants to form the products is just balanced by the reverse reaction of products combining to form the reactants, then we can say that the reaction has attained the equilibrium. That means at an equilibrium point what will happen? A and B will react to form C and D. At the same time same amount of A and B will be produced by C and D. That means we can say in a simple way no more conversion takes place. This is the chemical equilibrium.

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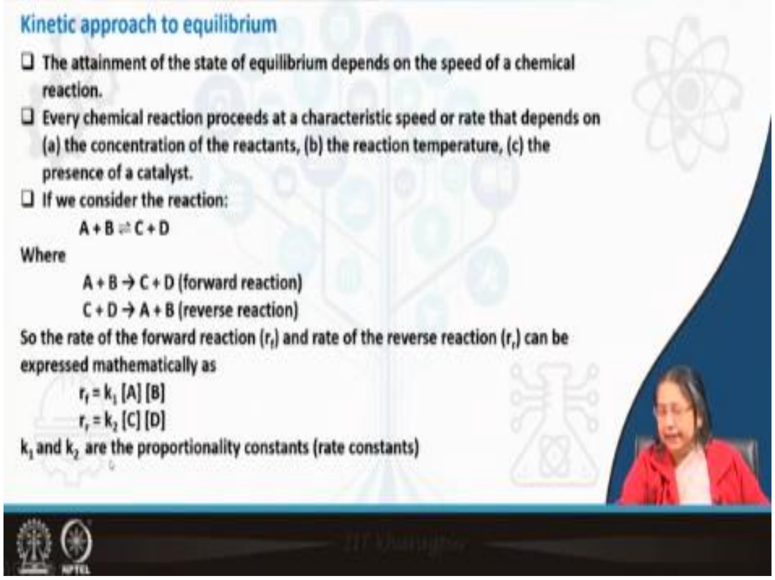

Kinetic approach to equilibrium

- The attainment of the state of equilibrium depends on the speed of a chemical reaction.
- Every chemical reaction proceeds at a characteristic speed or rate that depends on (a) the concentration of the reactants, (b) the reaction temperature, (c) the presence of a catalyst.
- If we consider the reaction:

$$A + B \rightleftharpoons C + D$$

Where

$A + B \rightarrow C + D$ (forward reaction)

$C + D \rightarrow A + B$ (reverse reaction)

So the rate of the forward reaction (r_f) and rate of the reverse reaction (r_r) can be expressed mathematically as

$$r_f = k_1 [A] [B]$$
$$r_r = k_2 [C] [D]$$

k_1 and k_2 are the proportionality constants (rate constants)

Now there we can have this type of equilibrium by considering the kinetic approach also. The attainment of state of equilibrium depends on the speed. Say, for example, when we start the reaction, A and B combines and reacts to form C and D. So, when the reaction just starts then the reaction process is fast but after some time when it is reaching towards the equilibrium, then we can say that the rate of the forward reaction and the rate of the backward reaction is the same. The forward and reverse reaction can be represented as follows:

$A+B \rightarrow C+D$ (forward reaction) ....(3)

$C+D \rightarrow A+B$ (reverse reaction) ....(4)

That means A + B is going to give C + D (i.e, the forward reaction) and C + D is giving A + B (i.e., reverse reaction). That means in the forward reaction we know that it depends on the concentration of A and B (i.e., reactant concentration) and there is a constant which is called the specific rate constant or rate constant.

The rate of the forward reaction (r_f) and reverse reaction (r_r) can be mathematically expressed as follows:

$r_f=k_1[A][B]$....................................(5)

$r_r=k_2[C][D]$....................................(6)

k_1 and k_2 are the proportionality constants (rate constants)

So, when these two rates are same then what happens?

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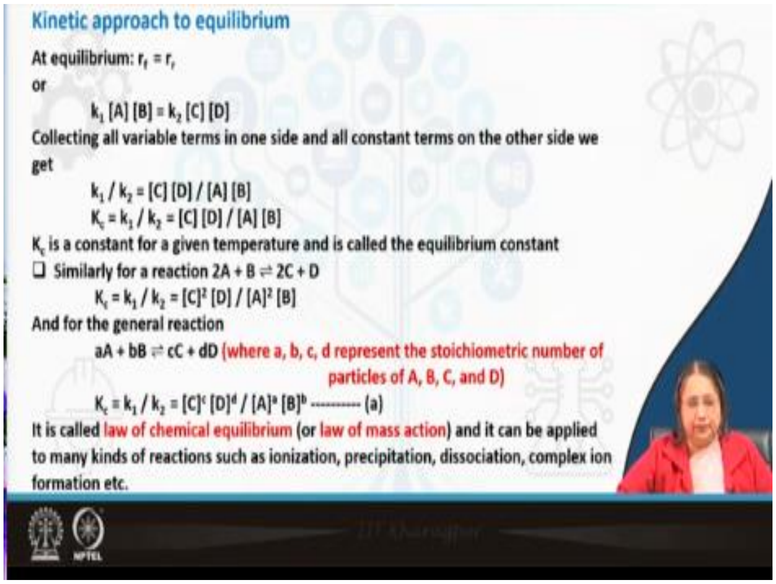

Kinetic approach to equilibrium

At equilibrium: $r_f = r_r$

or

$k_1 [A] [B] = k_2 [C] [D]$

Collecting all variable terms in one side and all constant terms on the other side we get

$k_1 / k_2 = [C] [D] / [A] [B]$

$K_c = k_1 / k_2 = [C] [D] / [A] [B]$

K_c is a constant for a given temperature and is called the equilibrium constant

☐ Similarly for a reaction $2A + B \rightleftharpoons 2C + D$

$K_c = k_1 / k_2 = [C]^2 [D] / [A]^2 [B]$

And for the general reaction

$aA + bB \rightleftharpoons cC + dD$ (where a, b, c, d represent the stoichiometric number of particles of A, B, C, and D)

$K_c = k_1 / k_2 = [C]^c [D]^d / [A]^a [B]^b$ --------- (a)

It is called law of chemical equilibrium (or law of mass action) and it can be applied to many kinds of reactions such as ionization, precipitation, dissociation, complex ion formation etc.

At equilibrium these two rates (r_f and r_r) are equal. So, equating (5) and (6),

$$k_1[A][B]=k_2[C][D]$$

$$\text{or,} \frac{k_1}{k_2}=\frac{[C][D]}{[A][B]}$$

$$\text{or,} K_c=\frac{k_1}{k_2}=\frac{[C][D]}{[A][B]}\text{.........................}(7)$$

K_c is a constant for a given temperature and is called equilibrium constant.

You always remember that the rate constant is always represented as k and equilibrium constant we always represent by K. In many books also I have seen they that they are confused and sometimes for the rate constant also they use al K, but this is not okay.

So, this is the simplest case I have expressed. I have told that all the stoichiometric molar ratios are 1:1. So, considering another type of reaction where stoichiometric molar ratios are not 1:1,

$2A+B\leftrightharpoons 2C+D$...................................(8)

So, in this case (equation (8)),

$$K_c=\frac{k_1}{k_2}=\frac{[C]^2[D]}{[A]^2[B]}\text{..............................}(9)$$

In general,

$aA+bB \leftrightharpoons cC+dD$ (where a, b, c, d represent the stoichiometric number of particles of A, B, C and D)................................(10)

So,

$$K_c = \frac{k_1}{k_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{...............................(11)}$$

It is also called the law of chemical equilibrium or law of mass action and it can be applied to many kinds of reactions as ionization reaction, precipitation reaction, dissociation type of reaction, complex ion formation. This is the basics of the chemical equilibrium. We will see different many different applications of this type of expression.

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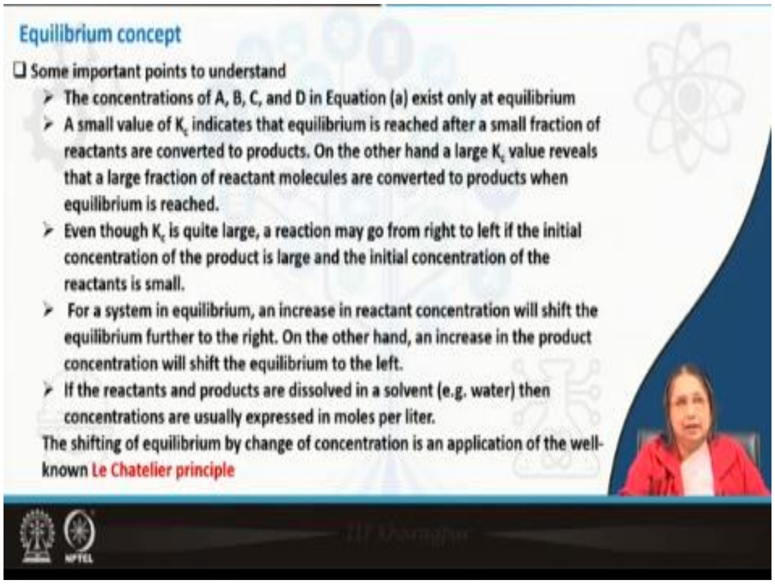

Equilibrium concept

❑ Some important points to understand
  - The concentrations of A, B, C, and D in Equation (a) exist only at equilibrium
  - A small value of K_c indicates that equilibrium is reached after a small fraction of reactants are converted to products. On the other hand a large K_c value reveals that a large fraction of reactant molecules are converted to products when equilibrium is reached.
  - Even though K_c is quite large, a reaction may go from right to left if the initial concentration of the product is large and the initial concentration of the reactants is small.
  - For a system in equilibrium, an increase in reactant concentration will shift the equilibrium further to the right. On the other hand, an increase in the product concentration will shift the equilibrium to the left.
  - If the reactants and products are dissolved in a solvent (e.g. water) then concentrations are usually expressed in moles per liter.

The shifting of equilibrium by change of concentration is an application of the well-known Le Chatelier principle

Now in the equilibrium concept, some important points we have to understand when we go for the equilibrium expression. Say, for example, the concentrations of A, B, C and D in equation (11) exist only at equilibrium.

When you obtain a very small value of K_c, what does it mean? That means that the equilibrium is reached after a small fraction of reactants are converted to products. That means the product obtained is less compared to the reactants that we are taking and on the other hand, for a large value of K_c it means that the large fraction of reactant molecules is converted to products when the equilibrium is reached.

On which side the equilibrium will shift, you can understand from the value of K_c. For a system in equilibrium when you increase the reactant concentration then what will happen? It will go towards the right. The forward reaction will go on. On the other hand, if you increase the product concentration then it will go to the reverse direction, this is the actually explained by the Le Chatelier principle. I will go to this later but for the time being you please remember this thing that K_c value is constant, but how much it is towards the right-hand side or it is towards the left-hand side that will be decided by the concentration of the reactants and the products.

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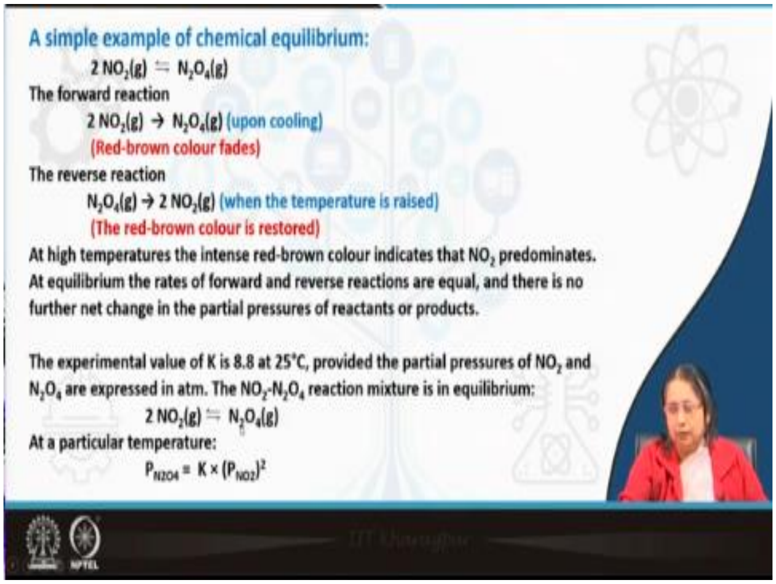

A simple example of chemical equilibrium:

$2\,NO_2(g) \leftrightharpoons N_2O_4(g)$

The forward reaction

$2\,NO_2(g) \rightarrow N_2O_4(g)$ (upon cooling)

(Red-brown colour fades)

The reverse reaction

$N_2O_4(g) \rightarrow 2\,NO_2(g)$ (when the temperature is raised)

(The red-brown colour is restored)

At high temperatures the intense red-brown colour indicates that NO_2 predominates. At equilibrium the rates of forward and reverse reactions are equal, and there is no further net change in the partial pressures of reactants or products.

The experimental value of K is 8.8 at 25°C, provided the partial pressures of NO_2 and N_2O_4 are expressed in atm. The NO_2-N_2O_4 reaction mixture is in equilibrium:

$2\,NO_2(g) \leftrightharpoons N_2O_4(g)$

At a particular temperature:

$P_{N2O4} = K \times (P_{NO2})^2$

Now, we shall see some examples of reaction where color change is observed.

$2NO_2(g) \leftrightharpoons N_2O_4(g)$.................(12)

The forward reaction is:

$2NO_2(g) \rightarrow N_2O_4(g)$...............(13) (upon cooling) (N_2O_4 is a dimer of NO_2)

(The red-brown color fades)

The backward reaction is:

$N_2O_4(g) \rightarrow 2NO_2(g)$..............(14) (when the temperature is raised)

(The red-brown color is restored)

Now think about these reactions ((12) to (14)). So, depending on the temperature you can see different colors. If you take a N_2O_4 in a closed vessel and if you cool it or if you heat it you will see the two different colors that is prevailing.

You can visualize it because it is two different things at two different colors. That is why you can see it when you do it in a closed vessel and if you properly maintain the temperature. At high temperatures the intense red brown color indicates that NO_2 predominates. At equilibrium the rates of forward and the reverse reactions are equal and there is no further net change in the partial pressures of reactants or products. This is the equilibrium condition and the experimental value of K_c is 8.8 at 25° C. You will always see that when the K_c value is mentioned we must tell about the temperature because it varies with temperature. We have also seen when I explain the acid bases. I have told that either K value or K_b value or K_w value vary with the temperature. So, temperature is very important.

Now if we express both in terms of partial pressure, then this value of K_c value will be different. Now partial pressure of N_2O_4, NO_2 are expressed in atmosphere. Then at the at the particular temperature (say at 25^0 C) the equilibrium expression will be like this:

$P_{N_2O_4}=K\times(P_{NO_2})^2$.................(15)

You have to consider this then K is nothing but the here it is partial pressure because it is gas. This is the expression you always do in case of either gaseous equilibrium or in the aqueous equilibrium.

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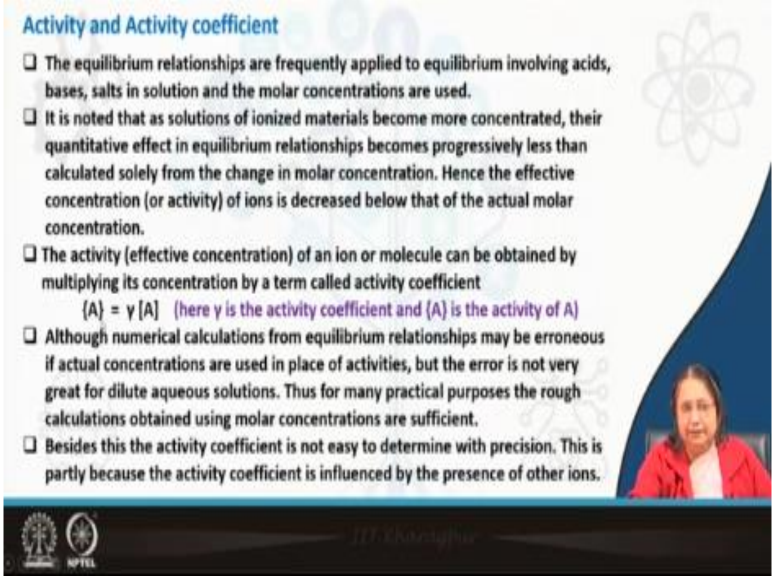

Activity and Activity coefficient

- ❑ The equilibrium relationships are frequently applied to equilibrium involving acids, bases, salts in solution and the molar concentrations are used.
- ❑ It is noted that as solutions of ionized materials become more concentrated, their quantitative effect in equilibrium relationships becomes progressively less than calculated solely from the change in molar concentration. Hence the effective concentration (or activity) of ions is decreased below that of the actual molar concentration.
- ❑ The activity (effective concentration) of an ion or molecule can be obtained by multiplying its concentration by a term called activity coefficient

  $\{A\} = \gamma [A]$ (here γ is the activity coefficient and {A} is the activity of A)
- ❑ Although numerical calculations from equilibrium relationships may be erroneous if actual concentrations are used in place of activities, but the error is not very great for dilute aqueous solutions. Thus for many practical purposes the rough calculations obtained using molar concentrations are sufficient.
- ❑ Besides this the activity coefficient is not easy to determine with precision. This is partly because the activity coefficient is influenced by the presence of other ions.

So, concept is the same but you have to use different types of concentrations. In terms of gas if it is gas then you have to use the partial pressure. If it is in ion form in the aqueous solution then moles per liter.

Now let us come to activity and activity coefficient. This is also very important for equilibrium relationship. It is expected that we always use the dilute solution. When it is dilute solution then concentration the express that we should express the concentration in moles per liter. But as the concentration is increased then that means not for very dilute solution but the concentration is higher. Then this activity term should come. why? Because when there are many ions then they have the influence on each other. In that case, it is noted that as solutions of ionized materials become more concentrated their quantitative effect in equilibrium relationships become progressively less than calculated solely from the change in molar concentration. That means in that case at higher concentration the molar concentration if we use then there may be some error. Hence the effective concentration we have to use which is also called activity and the expression the relationship between the activity and the concentration is like this:

$\{A\}=\gamma[A]$..........................(16)

γ is the activity coefficient. So, when we express the activity, we use the second bracket. When we use the concentration, it is in moles per liter, then this is the third bracket.

So, in case of dilute solution, we can tell that activity is same as the concentration. But in case of concentrated solution, we have to consider the activity term. Numerical calculations from equilibrium relationship may be erroneous in actual concentrations, if actual concentrations are used in place of activities. But the error is not very great for dilute aqueous solution. In that case, we can consider that activity is same as the concentration and we use mostly the dilute solution.

For practical purpose the rough calculations obtained using molar concentrations are sufficient. That means we do not have to bother that we have to use the activity term. Besides this the determination of the activity coefficient is not a very easy task. We cannot determine it with precision. This is partly because the activity coefficient is increased by the presence of other ions.

That means for practical purpose we use the concentration term and we ignore the activity coefficient. One reason is that it is very difficult to determine this thing. Another thing is it is for practical purpose it is sufficient to use the concentration. We do not have to use always the activity term.

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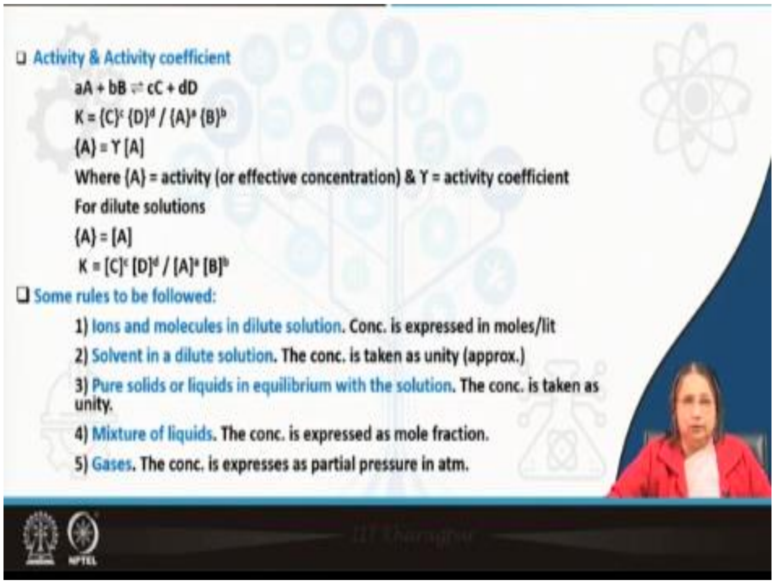

❑ Activity & Activity coefficient

$aA + bB \rightleftharpoons cC + dD$

$K = \{C\}^c \{D\}^d / \{A\}^a \{B\}^b$

$\{A\} = \gamma [A]$

Where {A} = activity (or effective concentration) & γ = activity coefficient

For dilute solutions

$\{A\} = [A]$

$K = [C]^c [D]^d / [A]^a [B]^b$

❑ Some rules to be followed:

1) Ions and molecules in dilute solution. Conc. is expressed in moles/lit
2) Solvent in a dilute solution. The conc. is taken as unity (approx.)
3) Pure solids or liquids in equilibrium with the solution. The conc. is taken as unity.
4) Mixture of liquids. The conc. is expressed as mole fraction.
5) Gases. The conc. is expresses as partial pressure in atm.

Now if we use the activity term for more accuracy in the reaction where a moles of A reacts with b moles of B and then produces c moles of C and d moles of D. Then in that case K should be should follow this expression:

$$K=\frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}....................(17)$$

That means {C} is the activity. So, in all cases we have to use the activity terms.

And then we all know that activity is nothing but $\gamma \times$ concentration and then for dilute solution we can think that activity is the same as the concentration. That means we can straight forward we can use this expression:

$$K_c=\frac{k_1}{k_2}=\frac{[C]^c[D]^d}{[A]^a[B]^b}...............................(11)$$

But in case of concentrated solutions in that case we must consider the activity and activity coefficient. Now some rules to be followed. When you think about the equilibrium expression then you have to follow the follow some rules.

What are the rules?

1) In case of ions and molecules in dilute solution, concentration is expressed in moles per liter. So, it is the aqueous solution. So, there we have to use the concentration of ions in terms of moles per liter.

2) Now in case of solvent in a dilute solution, the concentration is taken as unity.

3) Now when some pure solids or pure liquids is in equilibrium with the solution:

For pure solids or a liquid which is in equilibrium in case of say heterogeneous equilibrium where all are not in the same case, then it is called heterogeneous equilibrium. In that case pure solids or liquids in equilibrium with the solutions then the concentration is taken as unity.

4) When there is a mixture of liquids then the concentration should be expressed in mole fraction.

5) And in case of gases (we have already seen that in case of NO_2 and N_2O_4) we have used the partial pressure. So, in gas phase when the reaction goes on, the concentration we have to use in terms of partial pressure in atmosphere. These are the rules that we have to follow when we develop some equilibrium expression because otherwise everything will be wrong.

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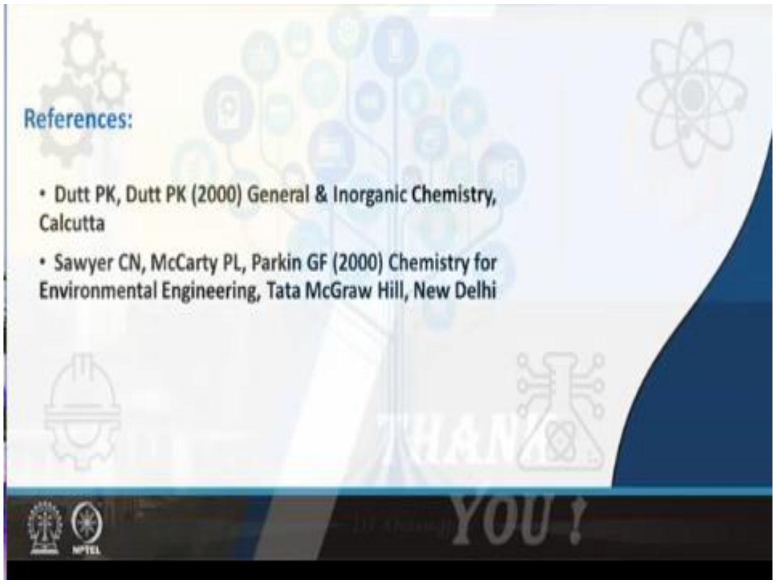

References:

- Dutt PK, Dutt PK (2000) General & Inorganic Chemistry, Calcutta
- Sawyer CN, McCarty PL, Parkin GF (2000) Chemistry for Environmental Engineering, Tata McGraw Hill, New Delhi

Now for this part we have we can use any text books of physical chemistry, text books of inorganic chemistry. I have given two references but you can have these explanations in many books. You can consult these books or other books also. This is from Sawyer McCarty, I have already given these two references in case of acid, bases and salts in the module 1.

I am giving the same reference here and thank you for hearing this first lecture for this module 2, (lecture number 6). Thank you.