TITLE

Chemical Equilirium -1

COURSE NAME

CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

PAPER

CHEMISTRY – DSC 2B: CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

COURSE (as per CBCS):

Semester - II: **BSc. Chemistry**

BSc. Physical Science
(Physics, Chemistry, Mathematics)

Introduction

Welcome you all to a fascinating world of chemical equilibrium. This is an important branch of science not only from the understanding point of view; it has lots of applications in industry, biological science, other branch of science and metallurgy etc. It touches our life in many ways. It has an application in the understanding of the chemical reaction, which we see around and the processes which takes place around us.

I'm going to cover in the present lecture; what is Chemical Equilibrium, laws of Mass action, Gibb's free energy and equilibrium, Thermodynamic treatment of Chemical equilibrium.

First we have to understand that why we have to study this equilibrium? The first incidents which goes for any known reversible reaction, is due to Claude Louis Berthollet. He was trying to study the sodium carbonate and its formation around the edges of the Salt Lake and he found that the simple reactions like sodium carbonate (Na_2CO_3) with calcium chloride($CaCl_2$) can give you calcium carbonate ($CaCO_3$) . This is a well-known reaction, but on the sea sore, he found the reactant in a large quantity that is sodium carbonate, which can be only due to the reversal of the above reaction which is well known to be performed in the lab.

The second incidence or the support of this theory, goes to the Cato Guldberg and Peter Waage, when they were trying to establish that the reversible reaction is really a known phenomenon and they try to study the behaviour of such type of reversible reaction forward as well as backward reaction.

Law of Mass Action

The law of mass action can be stated that the driving force of a chemical reaction which is proportional to the active mass of the reacting substance. Assuming that the driving force to determine the reaction rate and the active mass is the equivalent to concentration, the law may be stated as follows:

"the rate of a chemical reaction is directly proportional to the concentration of reacting substance"

Gibbs free energy and Chemical Equilibrium

Guldberg and Waage showed that for a reaction

$$aA + bB \rightleftharpoons cC + dD$$

which is also a reversible reaction and they showed that the reaction in either direction is proportional to what they are called the active masses of various components.

The rate of forward reaction which is going to be proportional to the, the rate constant k_f and the concentration of [A] raised to power 'a' and [B] raised to power 'b', respectively, there is a proportionality constant k_f, which represent the forward rate constant, similarly rate of the reverse reaction will be proportional to the concentration of [C] raised to power 'c' and [D] raised to exponent 'd' and the proportionally constant is represented by k_r.

We had to understand that the quantity in the square bracket represented by concentration, and in a special case when rate of forward reaction = rate of reverse reaction which is represented by the equation

$$K_f [A]^a [B]^b = k_r[C]^c [D]^d$$

rearranging this equation, we are going to get the two rate constant ratio which we are going to represent by $K_{eq} = [C]^c [D]^d / [A]^a [B]^b$

The new constant, which you get, is commonly called as equilibrium constant of the reaction. We have to remember that even the equilibrium looked like, there is no change taking place, indeed the change is taking place. It is macroscopically static, but in a way it is very dynamic in nature, the both forward and the reverse reaction is taking place.

The one of the fundamental property that has to be understood to understand chemical equilibrium is Gibb's free energy. We can define the Gibb's free energy as

"The Gibb's free energy is the maximum useful work excluding PV work associated with the volume change of the system, that a system can do on the surrounding when the process occurs reversibly at constant temperature and pressure".

and we have to know that this is an important property to find out the direction in which the chemical reaction is going to move and to find out the composition of each reactant and product at equilibrium.

If we tried to look at the $\Delta G < 0$, the reaction can spontaneously proceed to right, when $\Delta G > 0$, the reaction can spontaneously proceed to the left, and when $\Delta G = 0$, the reaction is at equilibrium. These are the important criteria which determined in which way the reaction is going to move.

For example, if I have a reactant which is at position one and I have a put that at position two, this in the line from where the reaction is going through as that $\Delta G<0$, it has to go spontaneously towards product. But we have to look at this curve, the energy is decreasing, but it reaches a smaller or the minimum point and then after that it increases. So both the forward reaction and backward reaction is seen in the curve and to state that the spontaneous reaction is taking place at least >50% of the reactant is to convert into product.

In another case, when $\Delta G>0$, the reactant is at position one and product at position two, we can see that the energy of product is higher than the energy of reactant and $\Delta G>0$, so as the reaction proceed it has to go in the reverse direction it has to move from this direction, the energy comes down and which is the minimum point and then the movement it goes further the energy increases and these values are ΔG, the values are at different positions and the equilibrium composition which correspond to an extent of reaction >0 , but <0.5 . So, we have to look at such type of situation.

For example if you take a dinitrogen tetraoxide decomposition is $N_2O_4 \rightleftharpoons 2NO_2$ and in a curve is N_2O_4 having energy 97.3 and the NO_2 has energy under 2.6, but difference between these two energy is 5.3 kJ. But if there is no equilibrium they proceed in a direct manner they have to go through this path straight line, the movement they are following is an actual path have to go through this minimum and then the reaction goes up and the point 3 here, represent the equilibrium concentration of N_2O_4 which is 0.814 M and 0.372M of NO_2 , so this composition is fixed, if we are at the equilibrium position.

Similarly there is exponential curve which shows that there is no possibility to have the pure NO_2 or no possibility to have pure N_2O_4. As the reaction proceed if you try to go to the pure form of this two reactant and product. It goes exponentially toward infinity, but at some point where this extent of reaction is written this point represents reaction, where they are presenting fix concentration and that is equilibrium concentration.

Thermodynamic treatment of Chemical Equilibrium

Now this is the basic qualitative understanding how ΔG changes or affect the equilibrium. Now we have to go to the thermodynamic way to find out the relationship. Before that we have to understand one term that is the extent of the reaction, represented by (xi) ξ , the reaction which we're going to look at is

$$\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_C C(g) + \nu_D D(g)$$

'g' represents the gas, all these reactant and product are in gaseous form and the ξ can be represented as the change in the number of moles by the stoichiometric coefficient or stoichiometric number of the i^{th} reactant. It can be defined as-

the amount of substance that is being change in an equilibrium reaction and it is unit is moles and it was introduced by the Belgian Scientist Theophile de Donder.

Let us look at how the reactant and the product are going to change, I am going to represent (i) for the reactant and (j) for the product. Looking that any reactant 'i' which has an initial concentration of $n_{i,o}$ there will be a decrease in the concentration due to the movement of ξ which is the extent of the reaction and this is for the product the concentration has increased because as the reaction moves the amount of product increase and carrying out the differentiation on this equation, we are going to get $-\nu_i d\xi$ and for the product side $d_{nj} = +n_j d\xi$, the term are like that because the $n_{i,0}$, $n_{j,0}$ are constant, now this reaction has to depend upon the parameters and Gibb's free energy is known to depend upon temperature, pressure and number of moles. So, in our case there are two parameters like temperature and pressure and the for number of moles n_A, n_B, n_C, n_D . To know the change which is taking place we have to do a partial derivative of this equation,

So,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_j \left(\frac{\partial G}{\partial n}\right)_{P,T,n_{j\neq i}}$$

and this term basically represents the four term and (j) is representing A, B, C & D, the four terms i.e. two reactants and two products, so the partial derivative of this going to give me $(\partial G/\partial n)_{P,T,nj}$ and all other parameters which are not there.

So, if I try to find out what this term is equal to? I will see that the dG = VdP-SdT, a very well-known equation, so if I compare this the $(\partial G/\partial T)_P = -S$; from this equation $(\partial G/\partial P)_T = V$; and the last term = $(\partial G/\partial n_i)_{P,\ T,\ nj} = \mu_I$ which is known as chemical potential.

The chemical potential is a very important term which tells you about the change in Gibb's free energy when 1 mol of the substances is added at constant pressure and temperature.

Now substituting all these values and imposing a condition of constant temperature and pressure, we are going to modify the earlier equation; the first two terms goes away we have left with the last term that is $\Sigma\mu_l \, dn_i$

So, this can be written by using the earlier expression, where

$$(\nu_A\mu_A - \nu_B\mu_B + \nu_C\mu_C + \nu_D\mu_D)\, d\xi \, .$$

Now the dG has only dependence on the extent of reaction and this can be written in a partial derivative form as

$$(\partial G/\partial \xi)_{T,P} = \nu_A\mu_A - \nu_B\mu_B + \nu_C\mu_C + \nu_D\mu_D$$

and this term is known as Gibb's free energy of reaction represented by $\Delta_r G$ and it is important parameters to know if you want to understand where the reaction is going with the change in Gibb's free energy.

There is another well-known expression related with the chemical potential the μ_i depend upon temperature and pressure and this is standard chemical potential at a given temperature, this term for an ideal gas depend upon RT ln P_i/P^o this P^o represent the standard pressure at 1 bar this is 1. This term can be taken as 1, when you are measuring the pressure in bar for other this has to be converted for atmosphere and millimeter pressure of Hg.

Now the Gibb's free energy of reaction is represented by $(\partial G/\partial \xi)_{T,P}$ = Σ of all stoichiometric coefficient into the chemical potential that is $\nu_j\mu_j$, j is representing the product - $\nu_i\mu_i$, where the Σ is all the reactant and this an expression we're talking about, it is written again so that you can understand what are the terms being used. $\Delta_r G$ Gibb's free energy of the reaction = $\nu_D\mu_D$ but remember that standard chemical potential + $\nu_C\mu_C^o$ - $\nu_B\mu_B^o$ and $\nu_A\mu_A^o$ plus all the term now plugged in this equation, so we got a RT[ν_D ln P_D/P^o + ν_C ln P_C/P^o - ν_B ln P_B/P^o - ν_A ln P_A/P^o] , the term representing standard pressure and it is 1 in bar. There is a one important quantity need to be introduced that is reaction quotient and reaction quotient if you try to look at we have a 'ln' term here, anything multiplied by 'ln' term in goes to an exponent of the term after ‘ln’, so this term can be compared with the expression that we have write this equation, so we have

$$(P_C/P^o)^{\nu C}\,(P_D/P^o)^{\nu D}\ \ /\ (P_A/P^o)^{\nu A}\,(P_B/P^o)^{\nu B}$$

This full term which represent the product as well as reactant raise to the power, which is the stoichiometric coefficient multiplied in the reaction, is equal to ‘reaction quotient’ and as we compared this with the upper expression we are going to have the Gibb’s free energy of the reaction and that should be = standard Gibb’s free energy which includes these four terms which is having a standard chemical potential + RTlnQ. Q is the reaction quotient. We can write that the Gibb’s free energy of a reaction = 0, as this term the numerator is 0, so $(\partial G/\partial \xi)$ at constant temperature has to be 0 at equilibrium, the movement we put that 0, in the expression we are going to have $\Delta_r(G)^O$ that is standard Gibb’s free energy of a reaction. It should be equal to the – sign because the term has to be taken equal to that side left to right and the – sign seen here, RTln, the term which represent the pressure and P^O can be taken equal to 1, as they can be taken in bar and now this term is in equilibrium we have represented this Q_{eq} and the whole expression termed out to be $\Delta_r(G)^O$ standard Gibb’s free energy of a reaction = - $RTlnQ_{eq}$ and this Q_{eq} we are going to represent by a another term that is K_P that is equilibrium constant expressed in pressure unit and we got the final expression that $\Delta_r(G)^O$ standard Gibb’s free energy of a reaction = $-RTlnK_P$ which is a function of temperature and when we write rearrange this term, we are going to get $K = e^{-\Delta(G)^\circ/RT}$, this is a very important expression and it relate the chemical composition of a chemical reaction to the measurable physical properties of reactant and product like concentration can be determined, pressures can be determined and if the entropy and enthalpy of formation of a given substance are known, it is also possible to predict the equilibrium constant and the mechanism of some of the reaction.

This equilibrium constant along with K_P , which is the equilibrium constant in terms of pressure, can be in the terms of the concentration that is K_C can be in terms of K_X that is mole fraction and K_n number of moles.

So this are the various way of representing the concentration of reactant product in the chemical equilibrium expression. But when we are talking about the ionic solution it is better to write it in the terms of activity. When we try to look at what is the relationship between the different types of chemical equilibrium? like K_P and K_X. In an ideal gaseous, mixture, we know that the partial pressure = the mole fraction into the total pressure i.e. p_i the partial pressure and X_i is a mole fraction and p represent the total pressure of the reaction mixture. So, if we have this expression of the reaction where

$$\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_C C(g) + \nu_D D(g)$$

are the stoichiometric coefficient x different types of reactant and product, but remember that all are in the gaseous phase, we are going to write each term in term of the partial pressure which

$$p_A = x_A P,\ p_B = x_B P,\ p_C = x_C P,\ p_D = x_D P$$

P represents the total pressure

p represent the partial pressure of that component

Substituting this value in the chemical equilibrium expression and we're going to get

$$P_C^{\nu_C} P_D^{\nu_D} / P_A^{\nu_A} P_B^{\nu_B}$$

and when we try to substitute with the expression of mole fraction we're going to get $X_C^{\nu_C}$ $X_D^{\nu_D}$ where X represents the mole fraction of C and D respectively and when you look at the denominator $X_A^{\nu_A}$ $X_B^{\nu_B}$ and because the total pressure is common in all the terms we are going to have $\nu_C + \nu_D - \nu_A + \nu_B$ the first term represent the stoichiometric coefficient of the product and the second term represent the stoichiometric coefficient of reactant and this in a short notation as represented as Δn , so we got a relationship that K_P which is the equilibrium constant under a unit of pressure and K_X is the equilibrium constant with the mole fraction unit but they are related by a pressure term $P\Delta n$, well Δn represent the difference in the stoichiometric coefficient of product and reactant.

We are trying to look at another relationship between two equilibrium constants like K_P and K_C. For that that we have to look at the ideal gas equation that is $P_iV = n_iRT$ and trying to rearrange this expression that we can be crossed multiplied and it is in the denominator, so we got a ratio of n_i/V (RT) and this term can be represented as concentration because we know that number of moles by volume is concentration so we are representing it as C_iRT. When we try to write this expression of pressure and concentration for all the components of the reaction, like n_AA , n_BB n_CC n_DD , we are going to have a partial pressure of $p_A= C_ART$, $p_B = C_BRT$, $p_c = C_cRT$, $p_D = C_DRT$.

When we try to look at the expression of the chemical equilibrium having the pressure unit like $P_C{}^{v}{}_C\ P_D{}^{v}{}_D\ /\ P_A{}^{v}{}_A\ P_B{}^{v}{}_B$ this can be converted in the concentration terms of the product having the stoichiometric coefficients as their exponent, we are going to have this expression there, the RT is common in all the four terms which is going to be raise with the $\nu_C + \nu_D$ which is the stoichiometric coefficients of the product and the stoichiometric coefficient of the reactant. So we can get a relationship that is $K_P=K_C(RT)^{\Delta n}$ where R is a universal gas constant, T is the temperature in Kelvin.

Numerical examples on chemical Equilibrium

Try to understand this equilibrium constant with the help of numerical. We have to have a simple expression like, the H^+ and OH^- in aqueous phase react and give the water, so this can be represented by different thermodynamic parameter, the H^+ do not have any of this ΔH or ΔS. This two term having a numerical values and we are going to use the data provided here to find out the equilibrium constant or we can proceed further. First we have to find the ΔH a standard condition and we substituted the value of product and the substituted value of reactant and the got expression of this two terms and the final valued termed out to be -55.8 kJmol and we have to find the standard entropy value the same way the entropy standard product – standard entropy of reactant and this two values are subtracted and we got a value that is 80.8 and we can find out the standard Gibb's free energy at 25^{O}C by using the expression ΔH-$T\Delta S$ which give a value of -79900 J mol^{-1} and we have this expression to determine the equilibrium constant $K=e^{-\Delta G° /RT}$

substituted all the values we got in the expression the -79900/8.314 x 298

this give exponent $e^{-32.2}$ and the

K = 1.01×10^{-14}

Similarly we can do another numerical where we have a gas like phosgene which can breakdown and give carbon monoxide and chlorine, for that we have to know the K_P and this is aim of this numerical to find out the composition of each of the components. For that we have to draw a table for the components. Like the reactant and the product, initially there is 0.124 atm of $COCl_2$ (Phosgene) , but there's no product. The movement the change takes place, for example -X moles atmosphere has changed the similar there will be increase in the pressure of CO and Cl_2. At equilibrium this value had changed by -X and this value remained X and we had to put in the equilibrium expression and we are going to get

$$X^2 /0.124 – X ,$$

this is a simple expression which has to be solved using a quadratic equation and which can be solved and we get the two values -0.0247.The negative value should be neglected and 0.0206 which is an acceptable value and the value of X can give you the values of partial pressure of $COCl_2$ 0.104 atm and 0.0206 atm for CO and Cl_2, respectively.

Conclusion

This bring us to the end of this lecture that we have covered a fundamental of the chemical equilibrium, what is chemical equilibrium, how it affect the reaction, we have also looked at Law of mass action, which is a precursor of chemical equilibrium. Gibbs free energy and equilibrium relationship we try to look at, so that we understand it better. Then we carried out the thermodynamic treatment of chemical equilibrium. To bring a mathematical form of chemical equilibrium, this covers the basics of equilibrium.

Now we have to move further and we are going to cover in the next episode about the factors which can affect the chemical equilibrium and how to change it in the favour of the reaction or application. Thank you.

TITLE

Chemical Equilirium -2

COURSE NAME

CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

PAPER

CHEMISTRY – DSC 2B: CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

COURSE (as per CBCS):

Semester - II: **BSc. Chemistry**

BSc. Physical Science
(Physics, Chemistry, Mathematics)

Introduction

Hello viewer, I welcome you to the second e-content on chemical equilibrium. In the first e-content we talked about the various aspects of chemical Equilibrium, why we have to study it and what is the mathematical equation, which can help us to calculate the various parameter and its relationships with chemical equilibrium. In this e-content we are going to talk about a very fundamental principle Le Chatelier's Principle and how to treat this Le Chatelier's Principle Thermodynamically, then the temperature dependence of chemical equilibrium i.e. van't Hoff factor, what is van't Hoff isotherm and we are going to talk about the Clapeyron Equation as the last part of this e-content.

Le Chatelier's's Principle

First we have to look at the one of the famous scientist who has brought about the effect of various parameters on a chemical equilibrium. He has tried to state that if an equilibrium is subjected to a stress the equilibrium shifts in such a way as to reduce a stress or in other words if a system equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change. Basically what we want to know from these statements are that if thermo dyne equilibrium is there and we change any of these parameters the equilibrium like to go in direction where it can nullify or reduce the effect of the stress, which is applied on the system.

Now try to look at the various parameters how the system move when a parameter is changed, first look at the given reaction $CO_2 + H_2 \rightarrow H_2O(g) + CO$, if a drying agent is added to absorb water so the concentration of product is decreasing, so the direction of reaction will be shifting to right because there is a decrease in the concentration of product, if you look at the second example $H_2\,(g) + I_2\,(g) \rightarrow 2HI(g)$

and if you add any other gas, which is not a part of this reaction, there is going to be no change in the equilibrium, if you look at the third example the reaction is carried out in an open container as there is a gas involved and the reaction is carried out in an open container which shifts to the right. There are many such example which can be quoted where a stress is applied or a parameter has changed and the system has to react to these type of parameter or stimuli like:

$H_2O(l) \rightarrow H_2O(g)$,

if water evaporates from open container there is a decrease in the concentration, so there will be a movement to the right because it want to compensate the loss of this water molecule and there may be such similar example where you can have a shift to the left or right depending upon the condition but the system always moves in a direction where it can nullify the effect it has taken place. In a specific case, I want to stress that if have a Fe^{2+} and SCN^- it can form a complex. The color of the reactant and the color of the product are different, so if I increase the Fe^{2+} ion concentration, naturally the reaction wants to compensate, the equilibrium want to shift in a direction where it can consume the excess of Fe^{2+} ion , so it will move in the forward direction, as the product color is brown, so the overall the solution will so intense dark brown color and if a given concentration of sulphocyanite salt, which is colorless again it will go towards the product side because the reactant have increased and if by any change we can increase the concentration of this complex, it will go in the backward direction and the overall solution will show a decrease in the intensity of color. To take an example of temperature change and its effect on the equilibrium a very well-known example of Haber's process reaction $of\ N_2(g)\ +\ 3H_2(g)$ which give NH_3 ammonia, which is also in gaseous form, the enthalpy of this reaction is 92.38 kJ. It is exothermic process, so when a system is exothermic process and the change in temperature effect the reaction. The increase in the temperature, the system want to go in a direction where it can consume the excess energy so it will go in a direction in the backward way where it can consume, a yield will decrease because more of the reactant will formed, if I decrease the temperature so the reaction will move in a direction where it can increase the temperature by expulsion of some amount of heat. So this is exothermic reaction which is moving in this direction.

Looking at other parameter which can undergo a change, so that it effects the equilibrium, can be studied. If you take a simple example of N_2O_4 gas which decompose and give $2NO_2$ gas, as the number of moles of gas which is coming out can play a role on the pressure, so we can have a look if the pressure is increased the system like to go in a direction where it can nullify the effect of that increased in the pressure, so if pressure is increased there is more number of moles of NO_2 this side, less number of molecule of gas this side , they would like to go in a direction where it can decrease the pressure, so backward direction is favorable when we have a decrease in pressure overall it will like the direction where more number of molecules are produced which result in the higher pressure, so the forward direction will be prepared. We have to understand that if no gaseous reactant is there we cannot have this effect seen in the equilibrium. If you try to understand the effect of catalyst in the equilibrium. Equilibrium is not shifted by the catalyst so we can say that the catalyst do not affect the overall equilibrium and it increases the rate of forward reaction and the rate of backward reaction by the same amount, so that there is no effect on the equilibrium due to catalyst, if you add the inert gas, if the inert gas is added it increases the pressure but the partial pressure of the reactants and products both increase by the same amount and therefore the equilibrium do not change. On the other hand if the inert gas is added keeping the pressure of the reaction system constant then the equilibrium concentration is affected in the case of reaction for which the volume of the product minus the volume of the reactant will be zero.

The Haber's process is the best example which give us an idea that how important and how useful this principle this. This is a standard Haber's process which can be used for the generation of ammonia basically and this suggests that to maximize the product ammonia we have to use at high pressure and low temperature, this is the condition under which it should be synthesize but to get an better yield, this you can be compromise and that is the way it is done and this has a direct impact on the economical social impact and that is the reason which is the most important or celebrated law.

Thermodynamic treatment of Le Chatelier's's principle

If you try to understand the Le Chatelier's principle from thermodynamic treatment we have to look at this equation

$\nu_A A(g) + \nu_B B(g) \rightarrow \nu_C C(g) + \nu_D D(g)$

The free energy change is going to depend upon the temperature, pressure and extent of the reaction, extent of the reaction we had already discussed in the earlier classes, so extent of the reaction is dependent on the ΔG. If you look at differentiation of this term, taking the partial derivative of all the three terms i.e called ΔG and other two parameters constant and when we do a partial derivative of second term of G with P and partial derivative of G with (ξ)Xi, which is extent of the reaction. We are going to get an expression, this expression is already been seen G/ξ is the reaction which gives free energy and if we do a double derivative of that we are going to represent it by G" , we already known that this G is related to the pressure and the temperature change by this relationship we are going to represent the whole expression by this term where $\frac{\partial G}{\partial T}$ is $\Delta_r V$ but to represent it, it is a volume of reaction that Δ_r is given here and this is volume and entropy of reaction there $\Delta_r S$ is given, substituting these value in the expression we got this term d (Δ_rG) where Δ_rG gives free energy of the reaction, Δ_rS entropy of reaction Δ_rV volume change of the reaction and this is the double derivative of the change of this free energy with the extent of the reaction. This term is represented by this at equilibrium we know that ΔG of reaction is zero, so the terms which contains the ΔG goes away and on the left hand side is equal to zero, on the right hand side we have three terms and entropy is related to the *Xi* by temperature by we can represent heat by the enthalpy of the reaction and i.e. seen here in place of Δ_rS, we can write Δ(RH/ T) and all other terms remains the same and this is explained G''_{eq} and G has a minimum value at equilibrium, to have a minimum value G" must be positive. If you do a thermodynamic treatment of Le Chatelier's principle.

In case when the Xi is changing temperature at constant pressure P can represented by dP=0 and there are only two terms remaining dP=0 makes the dE terms disappear, so we have left with $-\Delta_rH/T$, dT at constant pressure + G"(dξ) at constant pressure = 0 and then we try to rearrange the term we are going to have (∂ξ/∂T) at constant pressure = Δ_rH/ TG" since G" is a positive quantity, the sign of (∂ξ/∂T) at constant pressure will depend upon the sign of ΔH. The term here will depend upon this term then because G" is a positive quantity and temperature always is a positive quantity, so there is direct dependency of the enthalpy on the change in extent of reaction with temperature, so if table can be plotted where the reaction which type of reaction we are talking about is isothermic and enthalpy we know that isothermic enthalpy is negative, this term has to be positive, if change the temperature is increasing and the concentration of the reactant will increase, so it is going in a backward direction, if we have a exothermic the enthalpy is negative this term (∂ξ/∂T) is positive and change in temperature is there, so concentration of product will increase in forward direction, then if you are looking at a endothermic processes, where there is a positive value of enthalpy, this value is going to be negative which respect

to change in temperature if it increases or it decreases they will direct effect on the direction in which the reactant or the product move, if you try to look at the other way possible where ∂ will change with pressure at constant temperature, so he represent the constant temperature by $dT = 0$ so have left with the term which contains dT disappear from the equation and we got $\Delta_r V\ dP$ at constant temperature $+G''(d\xi)$ at constant pressure = 0 and we try to rearrange this expression. In this expression the G" is a positive quantity. So the direct dependency of ΔV or the volume change with the term in the bracket $(\partial\xi/\partial P)$ at constant temperature, so this can be plotted if the volume of reactant and product are always same there is no change
$\Delta V = 0$, so we don't expect any change in the equilibrium i.e. seen by the first line, all this term there will be no effect, if the volume change is positive, so because it contain a negative sign it has to be negative and the change in pressure, if it increases shifts backward towards reactant side, if ΔV is positive, this term has to be negative and the pressure has to be negative or decrease that shifts towards the forward side, negative ΔV, positive $(\partial\xi/\partial P)$ and there is decrease in pressure that shifts backwards towards the reactant side and the same way it happens in the last one.

If we know that there is a parameter which need to be understood with respect to the equilibrium constant i.e. temperature, so if temperature is changing what is the effect on the Gibbs free energy. We can look at this expression we have already derived this expression. What we do we rearrange the term and differentiate it with respect to temperature because that is our aim to understand the effect of temperature on the expression and you can have d/dT, R is a constant so it has come out from the differentiation and I have left with $d\ln K_p/dT$ and I am differentiating $\Delta G°/dT$, we already know that Gibbs Helmholtz equation is termed $= -\Delta H°/T^2$. so we have to compare these two expression the left hand side of both the equation is same so it means that right hand side has to be equal that lead to an very important expression that $d\ln K_p/dT$ should be = $-\Delta H°/RT^2$. This is a well-known equation known as van't Hoff equation or van't Hoff isopore equation. If you try to integrate this van't Hoff equation so that we are in position to find the equilibrium constant at two different pressure or find a two different temperature, what we can do we can take the integration on the left hand side $d\ln K_p = -\Delta H°/R$ integration from the limit Kp_1 - Kp_2 and T_1 -T_2 so this will lead to the expression $1/T_1 - 1/T_2$ and we can take a note of that from natural logarithm to log and we get this 2.203 R is a universal gas constant and all the temperature R in Kelvin. So this is an integrated van't Hoff equation which can help you to find out the chemical equilibrium at two different temperature.

Van't Hoff isotherm

What is van't Hoff isotherm? The Gibbs free energy can change with the change of the temperature and pressure of the thermodynamic system. The van't Hoff isotherm can be used to determine the Gibbs free energy for non-standard state reaction at a constant temperature and this expression represent the van't Hoff isotherm $(\partial G/\partial \xi)$ at constant temperature pressure = $-\Delta_r G$ which gives free energy of reaction + $RT\ln Q_r$ where Q_r represent the reaction quotient and this is free energy of the reaction. So these term can help you to determine in which direction the equilibrium going to shift. When $\Delta_r G$ is less than zero the reaction moves in the forward direction, when $\Delta_r G$ is greater than zero the reaction moves in the backward direction.

Clausius-Clapeyron equation

One of the most important equation we have for a two phase single component system is Clapeyron equation and it is also developed by Clauses independently, so in some cases it is known by Clausius-Clapeyron equation and we can use the Gibbs-Helmholtz equation to derive it. What are different types of phases possible like you can have a water present in a liquid phase and water present in a vapour phase, so there is equilibrium between these two and that is going to happen at the boiling point of the liquid. The second equilibrium can be between solid and liquid at the melting point. The third possible is solid and vapour the sublimation. There is also one more equilibrium possible between one crystalline form to another crystalline form i.e. Rhombic Sulphur to monoclinic Sulphur both are Sulphur but they can exists in two different crystalline form, so the equilibrium can be between these type of systems.

How to derive this Clapeyron equation? Suppose we have a pure substance A and which is in phase A there is another same substance in phase B at a given temperature and pressure we can write G_A as a free energy per mole of the substance in the initial phase A and G_B is the free energy per mole in the final phase B. At equilibrium these two terms has to be equal because ΔG has to be equal to zero and if we take that system is subjected to some amount of change and that change is in the temperature. The temperature has gone from T + dT, there will be effect on the pressure, the pressure is also undergone a change i.e. it is gone from P to P + dP, dP represent a very small change in the pressure. We are going to have an effect on the overall Gibbs free energy i.e. the Gibbs free energy of A is going to change from $G_A + dG_A$ and for phase B: $G_B + dG_B$ but as the equilibrium is already established even after the change is incorporated, so these two term need to be equal and we already know that $G_A = G_B$ before it is disturbed so we can have an expression i.e. $dG = VdP – SdT$ for both the phases and this term already inform you that this two has to be equal, so what we left with the change in this free energy for substance A and the change the change in this free energy for substance B and we can write the expression $V_A\, dP – S_AdT = V_BdP – S_BdT$, try to rearrange the term so that we can get dP and dT on one side, so we are going to get this expression dP/dT = the change of the entropy of B minus entropy of A , volume of B minus volume of A and this can be written as the $\Delta S/\Delta V$ because they represent the final minus initial, it is already known that $\Delta S = Q_{rev}/T$ so when you plug in these values in the Clapeyron equation we are going to have $dP/dT = Q_{rev}/T$, in place of ΔS here we have Q_{rev}/T, ΔV was already there. So this is well known Clapeyron equation when we have to talk about a single component two phase system we have to use this expression. We have to get it at two different phases. Look at the different cases which is possible like water can exists in two different phases we can have the change in pressure, change in temperature and this represent the enthalpy of vaporization and this is $V_{gas} - V_{liquid}$ and g is going to represent the gas and L is going to represent the liquid and this is the expression which we got. We want to have an integrated form of this expression at freezing point we are going to have like ΔH_f which is molar heat of fusion of ice and the expression remains the same, the final i.e. the liquid – solid. The integrated form can be obtained if we assume that in the denominator the $V_{gas} - V_{liquid}$ the gas is very large in volume as compared with the volume of liquid, so we can safely neglect this V_{liquid} and keep only the V_{gas} and this is the modified form where the liquid term is removed from the denominator and this can be easily be integrated and we have to use the ideal gas expression where PV = RT (1 mol) and when we put these values here which is a gas RT/P there is going to $dP/dT = \Delta H_v$ molar heater vaporization by the temperature and the V_{gas} is replaced by RT/P, so it has to go in a reversible manner. So P/RT and we got an expression $P\ \Delta H_v/RT^2$ or we can rearrange the term the P is cross multiplied and we can carry out the integration with limits so pressure can change from (P_1-P_2)dP/dT and the temperature is going from T_1-T_2 and this can be written in the natural *ln* P_2/P_1 = this term is going to give -1/T and when we put the upper and lower limits, I have taken out the negative sign but in the final expression this sign has incorporated inside and that lead to the expression, this is the integrated form of Clapeyron-Clausius equation and natural logarithm has been changed with the log. If you look at the application of Clapeyron-

Clausius equation, the first application which can be thought about is the calculation of molar heat vaporization and if the pressures are known we are in position to get the temperature and vice-versa, if the temperature are known the pressure can be calculated using the integrated form of Clapeyron-Clausius equation.

We would like to take a another case of a simple system solid vapour where there is an equilibrium and the $V_{gas} - V_{solid}$ we know that this solid volume is negligible as compared with gas . so it can be treated in the same manner for liquid gas and we can get the similar Clapeyron-Clausius equation but remember that this is the ΔH of sublimation but in the third case where solid – liquid are there in the system they cannot be integrated easily because the volume of solid cannot be neglected with respect to liquid, so they have to be use in this form both the volume together. If you look at one numerical to understand it better, if we have ether which boils at this temperature at one atmospheric pressure, we have to find out the temperature at which it boils when the pressure is 750 mm, the heat of vaporization is given so we can use the integrated form of Clapeyron-Clausius equation. If you try to look at the solution of the numerical we can get it from the integrated form of Clapeyron clausius equation and there is a pressure terms which is the P_2/P_1 and the ΔH_v heat of vaporization term which is in gm, so it has to converted into mole and only unknown we have the temperature to be determine and if we solve this numerical we are in position to get log T_2 and after solving the T_2 we get a temperature i.e. 634.3 K.

Conclusion

This completed the topic and in today's e-content we have discussed about the Le Chatelier's's Principle and the thermodynamic treatment of the Le Chatelier's Principle. How it can be governed? and the temperature dependence of equilibrium, i.e. Van't Hoff factor, then reaction isotherm and Clapeyron Equation and the various types of Clapeyron equation.

Overall we in these two e-contents we got information about the chemical equilibrium. How chemical equilibrium can play a role. How this can be controlled for application and what are the different types of chemical equilibrium we have. So I hope you will be able to understand and appreciate the reaction which goes towards to and fro and equilibrium exists in them and how to manipulate and to control these types of equilibrium processes.

TITLE

Ionic Equilibria - 1

<u>COURSE NAME</u>

CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

<u>PAPER</u>

CHEMISTRY – DSC 2B: CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

<u>COURSE (as per CBCS):</u>

<u>Semester - II:</u> **BSc. Chemistry**

BSc. Physical Science (Physics, Chemistry, Mathematics)

Introduction

Hello viewers, now we will start a new unit of physical chemistry that is ionic equilibria. This unit is very important in industrial chemistry as well as in chemistry of all living beings. E-content plan for this episode will be based on the chemistry of electrolytes, degree of ionization, factors affecting degree of ionisation and then ionisation constant, we will also discuss about common ion effect which is very important, solubility equilibrium and solubility product, we will also learn about ionic product and its role in precipitation along with solubility product, we will also discuss applications of solubility product principle in qualitative analysis and at the end we will also discuss some numerical problems based on common ion effect and solubility product.

Introduction of Electrolyte

Now to start with electrolytes. As we know water-soluble substances can be distinguished as electrolyte or non-electrolyte, so if a substance is soluble in water it may be electrolyte or it may not be a electrolyte. Electrolytes are basically the electrovalent substances which can be dissociated into ions in solution because of the presence of ions they can conduct electricity. Here we can see the example of electrolyte

$$AB = A^{+} + B^{-}$$

it can be dissociated into A^{+} and B^{-} when it is dissolved in water.

Sodium chloride, cupric sulphate and potassium nitrate, these are the very important and common examples of electrolytes. Non-electrolytes, these are basically covalent substances so they will furnish neutral molecules because ionic bonds are not present in these compounds so they will not conduct electricity. Sugar, alcohol and glycerol are the typical examples of non-electrolytes. Here we can see

$$ROH \text{ dissociate } R^{+} + OH^{-}$$

we cannot dissociate alcohol into alkyl ion and hydroxyl ion when we dissolve it in the water.

Strong electrolytes where almost all the molecules are present in the ionic form, these are the strong electrolytes. Examples of strong acids: like HCl, H_2SO_4, HNO_3, $HClO_4$, HBr and HI they are all considered under the category of strong electrolyte. Examples of strong bases: like NaOH (sodium hydroxide) KOH (potassium hydroxides) and many more. They are almost all ionised in the solution and then many salts like NaCl (sodium chloride), KCl (potassium chloride) they are all considered as strong electrolytes.

Weak electrolytes here only a small proportion of the solute molecule is ionized. Weak acids: as we know all the organic acids are considered to be the weak acids, so they are considered under the category of weak electrolytes. Like oxalic acid, citric acid acetic acid and many inorganic acids also like sulphurous acid, this is again a weak acid, so it is also a weak electrolyte. Many weak bases again organic bases like alkyl amines and then few salts, such as mercury chloride, lead acetate they are weak electrolytes.

Degree of Dissociation

Now what is the meaning of the degree of dissociation? This term is very important when we are studying the ionic equilibrium. We know when we dissolve a certain amount of electrolyte in water very small fraction of it will go into the solution to form the ions

$$AB \text{ equilibrium } A^+ + B^-$$

now when the equilibrium has been reached, as we know rate of the forward reaction means dissociation of AB to give A^+ and B^- and rate of the backward reaction means combination of A^+ and B^- to give AB. So, these two rates become equal then we can say that equilibrium has been reached, so it is act this equilibrium that the fraction of the amount of the electrolyte in solution present as free ions is called the degree of the dissociation.

We can further understand this like

$$X = \text{amount dissociated (mol/l)} / \text{initial concentration (mol/l)}.$$

Value of X can be calculated by applying the law of mass action to the ionic equilibrium just discussed.

$$K' = [A^+] [B^-] / [AB]$$

Here we can see this equilibrium constant will be equal to the product of the concentration of the products upon concentration of the reactant that is AB. If the value of the equilibrium constant K is given then we can calculate the value of X, means concentration of the A^+ or concentration of the B^- at equilibrium.

Degree of dissociation of an electrolyte present in a solution depends upon many factors. First of all most important factor is the nature of the solute. Like strong acids and strong basis. These are the salts obtained by their interactions; they are almost completely dissociated in solution, hence degree of dissociation will also be higher. On the other hand, weak acid and weak bases and their salts, they are feebly dissociated in solutions, therefore degree of dissociation will also be low.

Next factor which influences the degree of dissociation is nature of the solvent, in which solvent we are dissolving our solute is very important. Basically, it is the solvent which is weakening the electrostatic forces between the oppositely charged ions and because of this weakening of electrostatic forces, ions gets separated. This effect of solvent is measured by its `dielectric constant' which is very high in case of water, it is 80. In case of ether it is 4.1 very low and in case of ethyl alcohol it is 25, so we can see water very effectively can dissociate any salt into its ion.

We can further understand this thing with the help of this figure. Here it is the example of sodium chloride present as a solute in the water, so here water molecules will separate it into sodium ion and chloride ion, so they will surround sodium ion, so it is the power of the water molecule which is capable of separating the sodium chloride into sodium ion and chloride ion.

Now next factor is concentration. Concentration the extent of dissociation of any electrolyte is inversely proportional to the concentration of the solution, means more the concentration less will be the dissociation, why it happens? As we have just discussed the role of the solvent into dissociating the solute molecule, so we can very easily understand it is basically the ratio of the solvent molecule to the solute molecule which is playing the very important role. So as the ratio is more so degree of dissociation will be more.

Next factor is the temperature, as we already know at higher temperatures molecular velocities increases, so because of the more vibration, more molecular velocity, molecules will be easily dissociated.

Common Ion Effect

Now very important concept is the common ion effect we will discuss this in detail. When an electrolyte like A^+ C^- is added to solution of another weak electrolyte, here weak electrolyte is very important A^+ and B^-. So these two electrolytes are having a common ion A^+, so because of the presence of common ion dissociation of the weak electrolyte is suppressed, this happens as per the Le Chatelier's principle. Here we can see

$$AB \text{ equilibrium } A^+ + B^-$$

this is the equilibrium of weak electrolyte AB, it is being dissociated into A^+ and B^- , now we add another electrolyte A^+ and C^- , so because of the concentration of A^+ it is rising because of the addition of this salt, so here this equilibrium will be disturbed, so some of the A^+ and B^- will combine with each other to give AB therefore this is the reduction of the degree of the dissociation of the weak electrolyte and it happens because of the addition of a common ion and therefore it is called common ion effect.

Now we will further understand this thing with the help of an example.

$AgCl^{(s)}$ equilibrium $Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

In a saturated solution of silver chloride, we have the equilibrium silver chloride at saturation it will be dissociated into silver ion and chloride ion and an equilibrium is established. Now we add another electrolyte having a common ion sodium chloride it is having a common ion chloride ion, so concentration of chloride ion will increase. Now here this is the weak electrolyte, AgCl being the weak electrolyte its equilibrium is being disturbed, so therefore some of the silver ion and chloride ion will combine and will give back silver chloride, so we can see the role of the common ion.

We can further understand this with the help of another example. Addition of solid NH_4Cl (ammonium chloride) to NH_4OH (ammonium hydroxide). Here we can see ammonium hydroxide being the weak electrolyte

NH_4OH equilibrium $NH_4^+ + OH^-$

it's dissociation will be suppressed, so equilibrium shifts to the left and therefore concentration of the hydroxide ion will be decreased. Why, due to the presence of common ion which is coming from the ammonium chloride, now this is applied for the qualitative analysis of ferric ion, aluminium ion and chromium ion.

Now we will discuss a numerical problem based on above concepts. Find the degree of the dissociation of hydrogen fluoride in one molar aqueous solution, the value of equilibrium constant for the ionic equilibrium is 7.2×10^{-4} . Here we can see HF, this this hydrogen fluoride will be dissociated like this.

HF equilibrium $H^+ + F^-$

On reaching the equilibrium concentration of these three will be at equilibrium stage. Now, suppose initially we have taken one mole of the HF and concentration of the H^+ and concentration of the fluoride will be 0, when equilibrium has been reached then concentration of the hydrogen ion and concentration of the fluoride ion will be the same, because here we can see from this reaction one mole is being dissociated to give one mole of hydrogen ion and one mole of fluoride ion, so if degree of dissociation is X then 1-X will be the remaining concentration of the HF at equilibrium and X will be the concentration of hydrogen ion and again X will be the concentration of the fluoride,

$$[HF] = 1\text{-}x \text{ mol/l}; [F] = x \text{ mole/l}; [H^+] = x \text{ mole/l};$$

so at equilibrium we can see these are the concentrations. So here we can see we will substitute these values into equilibrium expression

$$K = 7.2 \times 10^{-4} = x^2/1.00\text{-}x \text{ (x very small, neglected)}$$

K which is given as 7.2×10^{-4} will be equal to concentration of products hydrogen ion and fluoride ion so therefore it will be x^2 / concentration of reactant that is 1-x, these are the equilibrium concentrations. Now x being very small it can be neglected so equation becomes

$$x^2 = (7.2 \times 10^{-4})\ (1.00) = 7.2 \times 10^{-4}$$

Therefore,

$$x = \sqrt{7.2} \times 10^{-4} = 2.7 \times 10^2$$

Thus we can see that degree of dissociation,

$$x = 2.7 \times 10^{-2}$$

Now coming to the another problem based on the common ion effect. 0.1 mole of sodium formate was added to one litre of 0.2M solution of formic acid having K_a 1.8 x 10^{-4}. How will the concentration of acid diminish assuming the salt to be completely ionised. Now we can see sodium formate this is the salt of sodium ion and formate ion and formic acid, this is a weak electrolyte giving formate ion and hydrogen ion, so here because of the presence of common ion that is formate ion in these two ionisation of the formic acid will be suppressed.

Now we will discuss its solution, we can see the sodium formate and formic acid. Both are having a common ion formate ion and formic acid being the weak electrolyte its ionisation will be suppressed after the addition of sodium formate. Now we will find first of all the concentration of hydrogen ion before the addition of the salt means when common ion effect was not playing any role, so we can see

$$HCOOH \text{ equilibrium } H^+ + HCOO^-$$

prior to the addition of the sodium formate at equilibrium this was the equation and
K_a = concentration of product/reactant

Ka, we can calculate with the help of this expression.

Now as we know

$$[H^+] = K_a \times [HCOOH] / [HCOO^-]$$

H^+ will be equal to K_a x concentration of the product / concentration of the formate ion.

$$[H^+] = [HCOO^-]$$

Now since in this equation one mole of the formic acid being dissociated to give one mole of the hydrogen ion and one mole of the formate ion therefore concentration of the hydrogen ion and concentration of the formate ion both will be the same so we can substitute this and finally we can derive this expression

$$[H^+] = \sqrt{} K_a \times [HCOOH]$$

where we can calculate the concentration of hydrogen ion by square root of K_a and concentration of the acid. Now putting these value finally we can calculate

$= \sqrt{}1.8 \times 10^{-4} \times 0.2 = 6 \times 10^{-3}$ mole per litre

the concentration of the hydrogen ion 6×10^{-3} mol per litre so that was the concentration prior to the addition of sodium formate. Now we will see after the addition of sodium formate salt but happens because of the common ion effect. Now we will calculate the concentration of hydrogen ion with the help of this equation

$$[H^+] = K_a [acid] / [salt] = 1.8 \times 10^{-4} \times 0.2/0.1 = 3.6 \times 10^{-4} \text{ mole per litre}$$

this is the equation which is used in the common ion effect for the calculation of concentration of hydrogen ion. Now putting values in this expression we get the value of H^+ as 3.6×10^{-4} mole per litre. So here we can compare this concentration this was prior to the addition of salt and this concentration this was after the addition of the salt, so we can see overall concentration of hydrogen ion has been decreased by the ratio of 1/16.6 of its original value, so it shows suppression.

Solubility Product

Now coming to the another very important concept of the ionic equilibria which is the solubility product this concept is studied in the solubility equilibrias. Now as we know when we add an electrolyte to the water, some of the electrolyte gets dissociated into ions. Now after some of the ions gets dissociated into ions, now after some time we add more salt then some more will be dissociated into ions. So after some time if keep on adding more and more solid AgCl then what will happen? It will stop dissociating into the ions, so after sometime an equilibrium will be established between ionic solid and saturated solution, so at this stage this system is said to be saturated. So a saturated solution in which the dissolved and undisolved, both are present in equilibrium.

This is the measure of solubility of a solute. The solubility of a substance in a solvent is the concentration in the saturated solution. Molar solubility is defined as the number of moles of the substance per litre of the solution.

Now applying the Law of Mass action to the about equilibrium for AgCl we can get this expression

$$K = [Ag^+] [Cl^-] / [AgCl]$$

now in this expression AgCl that is the amount of the solid in contact with saturated solution this remains same. Thus, the equilibrium expression becomes like this

$$K_{sp} = [Ag^+] [Cl^-]$$

so this K_{sp} is nothing but the solubility product constant which is basically the product of the ionic concentrations at solubility equilibria.

The value of K_{sp} for a particular solubility equilibrium is constant at a given temperature. Now if we rise the temperature then we can dissolve some more solid, so it is dependent on the temperature so at a particular temperature it is constant. Now in general, at any temperature product of the ionic concentrations is known as ionic product which is denoted by Q, so this Ionic product we can see this is also product of the ionic concentrations and solubility product this is also product of the concentration of the ion, but there is a big difference between these two K_{sp} is at saturation. So here we can further understand these things with the help of different type of cases.

Different Cases of Solubility Product

Now in case of salt like A^+ and B^- , calculation of K_{sp} from solubility. Equilibrium reaction as we already discussed, now if S moles per litre with the solubility of the AgCl then the equilibrium concentration of silver ion and chloride ion both will also be S moles per litre, because we know

$$AgCl_{(s)} \text{ equilibrium } Ag^+ + Cl^-$$

one mole is being dissociated to give one mole of silver ion and one mole of chloride ion, so if S mole is the solubility then S mole of the silver ion and S moles per litre of the chloride ions will be present now.

Now we will substitute these values in the expression of solubility product and finally we can obtain solubility product as S^2 means concentrations of the reactants will be multiplied together.

Now Q being the ionic product as we have just learnt, $Q > K_{sp}$

when Q is greater than solubility product, then precipitation will occur means in any saturated solution if we add a slight or very little amount of that electrolyte then Ionic product will be more than the solubility product, so once it crosses, precipitation will take place.

$$Q = K_{sp}$$

Now when Q is equal to the solubility product then solution is said to be saturated and when

$$Q < K_{sp}$$

Q is less than the solubility product then no precipitation will take place and we can add more solid.

Now we will discuss another type of case. Salt like A^{m+} and B^{n-} . For example solubility of calcium fluoride in water at 18°C is 2.05×10^{-4} moles per litre. Calculate its solubility product.

$$CaF_2 \text{ equilibrium } Ca^{2+} + 2F^{-}$$

Now calcium fluoride is ionised as per this equation Ca^{2+} and $2F^{-}$, Now it is being given

$$[Ca^{2+}] = 2.05 \times 10^{-4} , [F^{-}] = 2x[2.05 \times 10^{-4}]$$

concentration of calcium ion 2.05×10^{-4} , since this upon ionisation is giving one mole of this and 2 moles of this, therefore concentration of fluoride will be twice of the concentration of the calcium. Now putting values in the expression we can calculate

$$K_{sp} = 3.45 \times 10^{--11}$$

the solubility product which will come to be $3.45 \times 10^{--11}$

Now another type of problem. Calculation of the K_{sp} for Bismuth sulphide (Bi_2S_3) which has solubility of 10^{-15} mol per litre at 25°C. Now here we can see

$$Bi_2S_3 \text{ equilibrium } 2Bi^{3+} + 3S^{2-}$$

the equilibrium reaction is Bismuth sulphide which is being dissociated into the Bismuth ion and sulphide ion, now it is very clear from this equation these three are present in the ratio of 1:2:3. Thus 1.0 x 10^{-15} mole will give 2(1.0 x 10^{-15} mole) of Bi^{3+} and 3 times of sulphide ion, so we can write the equilibrium concentrations of Bi^{3+} and S^{2-} as like this

$$[S^{2-}] = 3.0 \times 10^{-15} \text{ mol/l}$$

$$[Bi^{3+}] = 2.0 \quad 10^{-15} \text{ mol/l}$$

Substituting these values in the K^{sp} expression, we will get

$$K_{sp} = [Bi^{3+}]^2 [S^{2-}]^3$$

square of the concentration of the Bismuth ion and cube of the concentration of the sulphide ion these two will be multiplied together to get the solubility product and finally value of the solubility product comes to be $K_{sp} = (1.08 \times 10^{-73})$

Now we will discuss the third type of case. Whether precipitation will occur on mixing of solutions or not. When two reacting solutions are mixed, calculate the concentration of each ion in the solution in which precipitation is to be produced. The ionic product *Q*, is then calculated as we already know that K_{sp} is the ionic product at saturation , therefore, the precipitation will occur for any higher ion concentrations than the K_{sp}. So we can also say it like that precipitation will take place when ionic product will exceed the solubility product.

We can further understand this theory with the help of this problem. A 200ml of 1.3 x 10^{-3} M $AgNO_3$ is mixed with 100ml of 4.5 x 10^{-5} M Na_2S solution. Will Precipitation occur? Solubiility product has been given like this $K_{sp} = 1.6 \times 10^{-49}$

Now the reaction that would cause precipitation is :

$$2Ag^{+} + S^{2-} = Ag_2S\ (s)$$

$2Ag^{+}$ ions + sulphide ions they will combine together to give silver sulphide

The ionic product is

$$Q = [Ag^{+}]^{2}\ [S^{2-}]$$

Concentration of these ions will be multiplied and taking in mind their number of moles also.

Now we will calculate the concentrations of silver ion and sulphide ion. So as we know we are mixing the 100ml solution and 200ml solution, so finally we will get the 300 ml solution, so concentration of the silver ion will be the 2 / 3 times of the concentration of the original silver ions coming from the silver nitrate solution. So we can calculate this with the help of this relationship

$$[Ag^{+}] = 1.3 \times 10^{-3} M \times 200ml/300ml = 8.6 \times 10^{-4} M$$

1.3×10^{-3} mol which was the concentration of the silver nitrate multiplied by 200 then divided by 300 ml since we have mixed with 200 ml and we have finally got the 300 ml of the solution, so therefore concentration of the silver ion will be like this. Now coming to the sulphide ions

$$[S^{2-}] = 4.5 \times 10^{-5} M \times 100ml/300ml = 1.5 \times 10^{-5} M$$

which we are getting from the sodium sulphide, so we are mixing the 100 ml of the sodium sulphide and finally we are getting the 300 ml, so concentration will be the one third of the original concentration, so it will be 1.5×10^{-5} molar.

Now we will put these values into the expression for ionic product,

$$Q = (8.6 \times 10^{-4})^2 (1.5 \times 10^{-5}) = 12.9 \times 10^{-13}$$

so Q will be equal to 12.9×10^{-13} , as we have been given the solubility product value K_{sp} for the reaction is = 1.6×10^{-49} (given)

so we can easily see that Q is very very large than the K_{sp}, therefore precipitation will take place, so here we have very easily understood that whether precipitation will take place in a particular equilibria or not, once the ionic product is higher than the solubility product, precipitation will take place.

Conclusion

Now at the end of this e-content we will revise whatever we have learnt so far. So in this unit based on the ionic equilibria first of all we learnt about the electrolytes, the basic principle of the electrolytes weak electrolytes, strong electrolytes we discussed many examples then we learnt the degree of ionisation and ionisation constant, we discussed very important concept of the physical chemistry that is the common ion effect, common ion effect together with solubility product has been very important in the analytical chemistry which is very important in the field of industrial chemistry, we also learnt about the ionic product and how it is related with solubility product and what role it plays in the precipitation, so that was about criteria of precipitation, we discussed many numerical problems based on the important concepts of common ion effect and solubility product. So I hope you have understood very well all these concepts and we will further discussed more about the solubility product and its applications in the quantitative analysis also in the coming e-content thank you.

TITLE

Ionic Equilibria - 2

COURSE NAME

CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

PAPER

CHEMISTRY – DSC 2B: CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

COURSE (as per CBCS):

Semester - II: **BSc. Chemistry**

BSc. Physical Science
(Physics, Chemistry, Mathematics)

Introduction

Hello viewers, now we will start the second e-content of the ionic equilibria, in the last e-content we learnt about some fundamental principles of ionic equilibria, we discussed about types of electrolytes and then very important fundamental concepts of common ion effect and solubility product. Now in this e-content we will be discussing further the applications of the solubility product principles and many other things. Now e-content plan for this is first of all we will be discussing about selective precipitation, we will learn about salt hydrolysis it's basically about cationic and anionic hydrolysis, so we will take the examples of both of these two types, we will learn about degree of hydrolysis and hydrolysis constant and then we will take examples of various salts, we will also discuss quantitative aspects of hydrolysis and then relationship between various constants.

Selective Precipitation

Now to start with selective precipitation. Selective precipitation is basically the application of solubility product principle to qualitative analysis of basic group radicals. Basic group radicals or cations, it involves precipitation of cations from solutions one at a time, so we are able to separate mixtures of cations, we can understand this with the help of this picture, if we are having a mixture of silver ion cupric ion and ferric ion then in the presence of dilute HCl we can separate these three ions with the help of solubility product principle, how? First of all silver will form silver chloride this will be insoluble, so we can filter it out and filtrate will contain Cupric ion and ferric ion. Now among these two we will pass the H_2S gas, since we are passing H_2S gas in the presence of dilute HCl which we had added in the first step, so in the acidic medium Cupric ion will be precipitated as cupric sulphide. Now we will separate these two again and we will get ferric ion which will remain in filtrate. Now we will add ammonium hydroxide and finally we will be able to precipitate out the iron also in the form of ferric hydroxide, so here we can see we have been able to separate mixtures of these three cation one by one, so this is selective precipitation.

Now we can further understand the selective precipitation with the help of qualitative analyses. In the qualitative analysis we have to separate common cations. Now these cations have been divided into various groups based on their solubility product. In this figure, we can see group-I cations possess silver ion Pb^{+2} and mercurous ion, in the group two cations Arsenic, bismuth, cadmium, and many more ions are present, so in this way we have divided all these cations into five groups. Now we will add dilute HCl, then what will happen? First of all group-I will precipitate as chloride, and all these three chlorides are insoluble, therefore they can be separated. Now in the filtrate, we will be getting cations of second, third, fourth and fifth group. Now we will add H_2S gas , H_2S in the presence of dilute HCl it will precipitate the cations of second group in the form of insoluble sulphides, these sulphides will be separated as precipitates.

Now in the filtrate, we will be having third, fourth and fifth group cations. We will add aqueous NaOH or ammonia and we can precipitate out the third group in the form of sulphide and in the form of hydroxide depending upon the type of reagent we are using. These sulphides are base insoluble sulphides and these hydroxides are also insoluble, so these can be easily separated. Now we will be having with group 4 and 5 cations. In the group 4 and five, we will add sodium carbonate or ammonium hydrogen phosphate, so these reagent will be able to precipitate out magnesium, calcium, strontium and barium in the form of insoluble carbonates, so finally we have been able to separate all the cations one by one, this was possible because of the solubility product principle, the principle we have already learnt in the last e-content.

Salt Hydrolysis

Now we will discuss salt hydrolysis, now salt hydrolysis according to Bronsted-Lowry concept of hydrolysis. HA and A^{-} are conjugate acid-base par. Now what is the meaning of conjugate acid base pair? We can understand with the help of this reaction

HA and A^- are conjugate acid-base pair, now what is the meaning of conjugate acid-base pair, we can understand with the help of this reaction

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

this acid is being added to the water, so since this is acid this will lose proton and this proton will be taken up by the water which is acting as a base here and remaining A^- is present here. If acid is weak then remaining A^- this will be a strong conjugate base, so conjugate base this must be relatively strong, if we have started with a strong acid then we will get a weak base as conjugate but if we have started with a weak acid then we will get a strong conjugate base.

Now how we will identify the conjugate acids and bases, with the help of this figure it is very clear that acid after losing a proton is being converted to the conjugate base. So if we are having HCl then Cl^- will be the conjugate base and if we're having acetic acid then acetate ion will be the conjugate base.

$$HCl \rightarrow Cl^-$$

$$NH_3 \rightarrow NH_4^+$$

Now the case of base, base is able to accept the proton from any acid, so after accepting proton we are getting the conjugate acid. Now ammonia which is a base after accepting the proton from any acid, it is being converted to the ammonium ion so here its ammonium ion which is the conjugate acid of the base.

Now what is hydrolysis? Hydrolysis is nothing but interaction of salt ions B^+ A^- with H^+ (hydrogen ion) and OH^- (hydroxyl ion) of water. As we know water molecule H_2O, so H_2O can be broken into H^+ and OH^- , so it's the interaction between B^+ and OH^- and A^- and H^+ that's all about the hydrolysis.

Now we will further understand the meaning of anionic hydrolysis and cationic hydrolysis. Now salt of weak acid that is HA and a strong base gives anion A^- , this A^- will be interacting with the water molecule and it will break down this bond from here and we will be getting OH^- , so in case of anionic hydrolysis, anion is acting upon the water molecule and finally it is giving the hydroxyl ion. Now after anionic hydrolysis we will discuss the case of cationic hydrolysis. In the case of salt of the weak base that is the BOH and a strong acid it will be releasing finaly B^+ , now this B^+ will be acting upon here on the water molecule so since it is carrying the positive charge, so it will be reacting with the hydroxyl ion, so bond will be broken from this point and we will be getting the proton here, so this is called the cationic hydrolysis. Here we can easily observe that in case of cationic hydrolysis, we are getting proton and in case of anionic hydrolysis we were getting hydroxyl ion.

Now we will see the various types of cases of the salts. Now first of all we will take case of strong acid and strong base. In case of the salt of the strong acid with a strong base no hydrolysis takes place, because interaction between the salt and water molecule are not taking place, we can understand this thing and we will also discuss here the effect on pH. Now suppose we are dissolving the NaCl (sodium chloride), sodium chloride is the case of strong acid and strong base salt. NaCl, so if we are assuming that it is dissolving in water giving sodium ion and chloride ion. Now this chloride ion as we know that is it constitutes an acid-base conjugate pair with HCl.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

Since we already know that HCl is a strong acid, therefore, its conjugate base this chloride ion will be a weak base.

$$Cl^- + H_2O \rightarrow HCl + OH^-$$

Since this is the weak base, it will not have a tendency to take up the proton from the water molecule, so second reaction will not take place at all. Therefore no releasing of hydroxyl ion and no change in the pH will be observed.

Now we will discuss the second type of case that is salts of weak acid and strong base. We will take the example of CH_3COONa (sodium acetate), sodium acetate is the salt made up acetate ion and sodium ion, it is made up from the acetic acid and sodium hydroxide, acetic acid is a weak acid and sodium hydroxide is a strong base. Now hydrolysis reaction

$$Na^+ + CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

sodium ion and acetate ion will be reacting with the water molecule and we will be getting acetic acid and sodium hydroxide. Since sodium hydroxide is a strong base it will be in dissociated form, its degree of dissociation will be quite high, but acetic acid being a weak acid it will remain largely undissociated. Hence it will be present in the combined form. Now if observe this reaction then we can easily see that

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

sodium ion is common on both sides, therefore overall reaction remains acetate ion + water molecule being converted to acetic acid and hydroxyl ion, so we can very easily conclude from this reaction then that in case of salts of weak acid and strong base overall pH will be on alkaline side because of the presence of excess OH^- .

Now we will take the case of salt of weak base and strong acid. Here is the example of ammonium chloride NH_4Cl which is made up of weak base that is ammonium hydroxide and strong acid that is hydrogen chloride. Now according to this reaction we can again see that

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

chloride ion is common on both sides, therefore overall we can see that this reaction is leading to the release of proton, therefore, overall pH will be on the acidic side.

Now we will take the last example that is the case of salt of weak bases and weak acid.

Ammonium acetate, CH_3COONH_4 which is made up of acetic acid, a weak acid and ammonium hydroxide a weak base. Now overall reaction here

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \quad .... (1)$$

we can divide this reaction into two-part: anionic hydrolysis and cationic hydrolysis, in the anionic hydrolysis as we have already seen here. OH^- are being released therefore as per this equation 1, pH will be on the alkaline side.

But per the cationic hydrolysis this reaction 2

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \quad ....(2)$$

pH will be on the acidic side. Now overall hydrolysis we can represent this like this.

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Now it depends whether pH is increasing or pH is decreasing it depends on the relative extent of cationic hydrolysis or anionic hydrolysis. If any one of these one reaction is dominating then pH will be changed as per that reaction, if anionic hydrolysis is more than pH will go on the alkaline side and if cationic hydrolysis is more as per the second equation then pH will be on the acidic side.

Quantitative aspect of Hydrolysis

Now we will discuss about the quantitative aspect of hydrolysis. The equilibrium constant obtained after applying law of mass action is called the hydrolysis constant it is represented by K_h.

Now we will understand this constant by taking the case of salt of weak acid and strong base. As we have already learnt in case of weak acid and strong base overall reaction take place like this

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

A^- + H_2O they are giving HA and OH^- . Applying law of mass action to this equation we can see

$$\boldsymbol{K_h} = [\boldsymbol{HA}][\boldsymbol{OH^-}] \,/\, ([\boldsymbol{A^-}]\,[\boldsymbol{H_2O}])$$

Concentration of product / concentration of reactants, so we have put HA X OH^- concentration and A- x concentration of water.

Since concentration of water is very large so it remains practically constant , therefore we can finally derive this equation

$$K_h = [HA][OH^-]/([A^-]) \qquad \ldots\ldots\ldots\ldots.(1)$$

K_H is equal to concentration of HA x OH^- concentration and divided by concentration of the A^- .

Now we will derive relationship between hydrolysis constant and K_w and K_a. Now what is K_w? K_w is the ionic product of water and we can express it

$$K_w = [H^+]\,[OH^-] \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

concentration of hydrogen ion multiplied with the concentration of OH^- . Now for the dissociation of a weak acid HA, we know this reaction

$$HA \rightleftharpoons [H^+] + A^-$$

HA being ionised to the H^+ and A^-

Now we will again apply the law of mass action here and we already know that

$$K_a = [H^+]\,[A^-] / [HA] \ldots..(3)$$

Dissociation constant for the acid will be like this. Now if we divide equation to just arrived for the K_w by the equation 3 just arrived for the K_a, so

$$K_w/K_a = [OH^-][HA] / ([A^-]) = K_h \quad \text{.........(by equation 1)}$$

K_w/K_a it will be equal to $[OH^-]$ $[HA]$ / $[A^-]$, so that was nothing but hydrolysis constant, so we have derived here that

$$K_w/K_a = K_h \quad \text{........................(4)}$$

hydrolysis constant is equal to ionic product of the water divided by equilibrium constant of the acid. Therefore, weaker the acid greater is the hydrolysis constant of the salt. Here we can see very clearly from this equation.

Now relations between hydrolysis constant and degree of hydrolysis. Degree of hydrolysis is represented by α, it is basically fraction of the salt that has undergone the hydrolysis. For one mole of the salt dissolved in V litres of the solution. Then the equilibrium concentration can be shown with the help of this reaction

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

Now initially one mole of the salt is present and initial concentration of HA and OH^- will be 0, but as soon as the equilibrium is established, since degree of dissociation is α, so

α / V, V is the volume this will be the concentration of HA and same will be the concentration of OH^- , because here we can see they are reacting in the equimolar quantities and remaining concentration of the A^- at equilibrium will be $1-\alpha$ / V.

Now we will apply law of mass action once again and we can easily derive this formula for the hydrolysis constant

$$K_h = [HA]\,[OH^-] / ([A^-] = \alpha/V \times \alpha/V / 1- \alpha/V = \alpha^2/(1- \alpha)V$$

α/V, α/V being the concentrations of acid and hydroxyl ions divided by concentration of the A^- , now we will cancel one of the V term from this and overall equation becomes this. If α is very small than 1- α can be taken as 1, so reaction will become

$$K_h = \alpha^2/V$$

$K_h = \alpha^2/V$ converting this two,

$$\alpha^2 = K_hV = K_w/K_a\ V$$

$\alpha^2 = K_hV$ and putting the value of K_h , K_w/K_a and finally

$$\alpha = \surd K_wV / K_a = \surd K_w/K_aC$$

which is the reverse of the V.

Now we will derive pH.

$$pH = 1/2\ pK_w + ½\ pK_a + 1/2 \log C$$

value of the pK_w is 14, so $1/2\ pK_w = 7$

$$pH = 7 + 1/2\ pK_a + 1/2 \log C$$

this we have obtained by doing negative of the logarithm in this equation. From this equation, it is very clear that for aqueous solution of salt of weak acid and strong base pH will be always more than 7, because we are getting a quantities 7+ , so solution will be alkaline.

Now we will take the another case that is salt of weak base and strong acid. We have already learnt its hydrolysis and now we know

$$K_h = [H^+]\,[BOH] / [B^+]$$

$K_h = [H^+]\,[BOH] / [B^+]$ and finally we will get,

$$K_h = K_w/K_b$$

$K_h = K_w/K_b$. Therefore weaker the base greater will be the hydrolysis constant of the salt, why? They are having inverse relation between them.

Now we can see here this is the case of weak acid and strong base example of sodium acetate we discussed and hydrolysis constant is given here, degree of hydrolysis is given here and pH of the solution is given here, in case of strong acid and weak base that is the case of ammonium chloride, hydrolysis constant will be K_w / K_b , degree of hydrolysis like this and pH of the solution will be 1/2 pK_w^-, here we have put – sign, so pH < 7, we already know $pK_w = 14$, therefore 1/2 $pK_w = 7$, 7- this much quantity means overall pH < 7, therefore on acidic side. In third case, we can calculate all the quantities with the help of these formulas and case of sodium chloride as we already learnt it does not undergo hydrolysis.

Numerical Problems

Now we will discuss some problems based on these principles. Calculate the pH of 0.2 molar solution of ammonium chloride having equilibrium constant $K_b = 1.8 \times 10^{-5}$, so first of all we will calculate its hydrolysis constant. As we know ammonium chloride is a salt of weak base and strong acid HCl, therefore

$$K_h = K_w/K_b = 1.0 \times 10^{-14}/ 1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

now putting the values in this formula K_h becomes 5.56×10^{-10}. Now we will calculate the pH. Hydrolysis of ammonium chloride NH_4Cl at equilibrium as we have already discussed can be represented with the help of this equation

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

this is the case of cationic hydrolysis, here we know initial concentration of ammonium chloride is given as 0.2 molar. So at equilibrium 0.2-x , x being the degree of dissociation, x will come here because we're getting 1 mole and 1 mol from the 1 mole of ammonium chloride. So now equation becomes

$$K_h = [NH_4OH]\,[H^+] / [NH_4^+]$$

concentration of ammonium hydroxide x the concentration of hydrogen ion / concentration of ammonium ion. Now we will put the values

$$K_h = x.x. / 0.20 - x$$

x for the ammonium hydroxide and x for hydrogen ion and 0.2 for the ammonium ion, since x is very small we can neglect this. So

$x^2 = K_h \times 0.20 = (5.56 \times 10^{-10}) \times 0.20$

As we have just calculated hydrolysis constant as this, so we will multiply these two quantities and

$x = \sqrt{1.11 \times 10^{-10}} = [H^+] = 1.053 \times 10^{-5}$ mol/l

Will take the under root this quantity and we will get the x. x is the concentration of hydrogen ion. Now to calculate pH

$$pH = -\log [H^+] = -\log (1.053 \times 10^{-5}) = 4.9775$$

We will take negative of the log of the H^+ ion. After solving the value comes out to be 4.9775, so we can see here pH is on the acidic side.

Now we will take another example. Calculate the pH of a solution of ammonium acetate. Dissociation constant of acid

$K_a = 1.75 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$ $K_w = 1.0 \times 10^{-14}$

This is ionic product of the water it is always 10^{-14} . Now we know that

$$pH = 1/2\ pK_w + 1/2\ pK_a – 1/2\ pk_b$$

So now we will put values in this equation,

$½\ pK_w = ½ \log (1.0 \times 10^{-14}) = 7$

So half of that means negative of the logarithm of this quantity divided by two, so it will come 7.

$\frac{1}{2}\ pK_a = -\ 1/2 \log Ka = -\frac{1}{2} \log (1.75 \times 10^{-5})$

we have been given the value of K_A , so we will again take negative logarithm of this quantity and then divide it by 2. This comes out to be 2.3785. In the same way we will calculate half log K_b. Putting these values in the equation

$$pH = 7 + 2.3785 - 2.3723 = 7.006$$

pH becomes 7.006 , this is just above the neutral pH.

Conclusion

Now we will review what we have learnt in this e-content, first of all we learnt about the principles of the selective precipitation and its application in the qualitative analysis, how it is helpful in separation of the mixture of cations then we discussed about the salt hydrolysis, cationic hydrolysis, anionic hydrolysis, degree of hydrolysis and hydrolysis constant K_h, we discussed examples of various salts like salt of weak acid, strong base and salt of strong base weak acid, we also discussed about the quantitative aspects of the hydrolysis and we also derived the relationship between various constant like pH, K_W , K_a, K_b and K_h hydrolysis constant, so we can see how helpful these concepts are to understand many principles of the qualitative and quantitative analysis.

TITLE

Ionic Equilibria - 3

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PAPER

CHEMISTRY – DSC 2B: CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY

COURSE (as per CBCS):

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BSc. Physical Science
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Introduction

Hello viewers, now in the third lecture we will move further and we will learn some more concepts of the ionic equilibria, so far we have learnt about the basic principles, about the electrolytes about the degree of dissociation, common ion effect, solubility product, its applications, hydrolysis constant. Now in this lecture, we are going to discuss about the very important concept of the chemistry that is pH concept, we will also discuss about the pH scale and role of the pH, we will calculate the pH for different type of salts then we will discuss very important fundamentals buffer solutions and action of the buffer. We will also discuss some numerical problem based on these concepts to make our understanding very clear.

pH Concept

Now to start with the pH concept of the solutions pH concept was introduced by Sorensen in 1909 that was used basically to express hydrogen ion concentrations in a more convenient and simple way. As we know hydrogen ion concentrations are typically very small numbers, therefore they are reported in terms of pH. pH can be defined as the negative of base 10 logarithm of the hydrogen ion concentration, so

$$pH = -\log [H^+]$$

H^+ is the concentration of hydrogen ion, we can also write it as

$$[H^+] = 10^{-pH}$$

hydrogen ion concentration = 10^{-pH} .

In the same way concentration of hydroxyl ion in aqueous solution of a base can be represented with the help of this equation

$$p[OH] = -\log [OH^-]$$

Now we already know equilibrium constant for water is represented by

$$pK_w = -\log [K_w]$$

so we can see for any quantity X we can write

$$pX = -\log X$$

The p in these expression means minus log of the quantity. So we can represent K_a in the form of pK_a which will be equal to $-\log K_a$. Since

$$K_w = [H^+][OH^-] = 10^{-14}$$

K_w being the ionic product of the water, $H^+ \times OH^-$ it is always 10^{-14} , therefore

$$pK_w = pH + pOH = 14$$

pK_w taking negative logarithm of these two quantities, it will be pH + pOH = 14.

pH can be measured by addition of a pH indicator into the solution.

Here this is the colour key. So we can match the colour of the solution with this key and then we're able to tell the pH of the solution. pH can be measured by using a pH meter together with pH- selective electrodes, for example many type of electrodes like pH glass electrode, hydrogen electrode, quinhydrone electrodes they are being used for this purpose. pH can also be checked with the help of pH paper. Here again we will match the colour of the paper.

pH Scale

Now pH scale, As we know in the neutral solution

$$\text{Neutral solution} \rightarrow [H^+] = [OH^+]$$

concentration of the hydrogen ion will be equal to the concentration of the hydroxyl ion.

$$\text{Acidic solution} \rightarrow [H^+] > [OH^+]$$

In the acidic solution, hydrogen ion concentration will be more than concentration of the hydroxyl ion and

$$\text{Basic solution} \rightarrow [H^+] < [OH^+]$$

In basic solution concentration of the hydroxyl ion will be more than the concentration of the hydrogen ion.

We can see this picture which is showing the pH range of the many type of solutions and many natural liquids. Like pH of the hydrogen chloride hydrogen chloride is a very strong acids, so its pH is in the range of 1 that is concentration of hydrogen ion concentration will be 10^{-1} moles per litre, pH of the lemon juice, it will be higher than the pH of hydrochloric acid it will be around more than 2 then pH of the vinegar that is acidic acid will be even more than that then many other type of juices like orange juice, tomato juice pH is rising, so it is coming to the neutral site and here it's the pH of pure water which will be 7, absolutely neutral pH. Pure water means it is not containing any other ions than hydrogen ion and hydroxyl ion, so no impurities at all hence pH will be 7. Now if we move further then on the alkaline side, there are so many things like eggs, milk of magnesia, detergents then pH will be in the range of 10 then soap more alkaline than ammonia solution and finally NaOH which is supposed to be the very strong base it is having the pH of 13.

Now we will understand interpretation of the pH with the help of this problem. The hydrogen ion concentration of a fruit juice is $3.3x10^{-2}$ molar. What is pH of the juice? Is it acidic or basic? Now we know the definition of the pH is minus -log H^+, and we have been given hydrogen ion concentration as this. Now substituting this into the definition of pH we will get the pH value as 1 .48. So we can see this 1.48 lies very much on the acidic side. Therefore this solution will be acidic.

Role of pH in our life and environment

Now what is the role of the pH? We can see hydrangea macrophylla blossom in pink colour or blue colour that depends on the pH of the soil. In the alkaline soil at the pH is more than 7 flowers are pink but in the acidic soils flowers are blue, so here we can see how the pH affects the colour of the flowers.

Enzymes and many other biological molecules including macromolecules will hydrogen bonds like DNA, RNA, haemoglobin is these functions only at specific pH. So in our body also pH is maintained.

Now will discuss a very important and related topic that is acid rain. Acid rain, form of air pollution in which airborne acids produced by electric utility plants and other sources fall to earth in distant regions. The corrosive nature of acid rain causes widespread damage to the environment. The problem begins with the production of sulphur dioxide and nitrogen oxides from the burning of fossil fuels, such as coal, natural gas and oil, and from the industrial processes. In cities, acid pollutants corrode almost everything they touch, accelerating natural wear and tear on structures such as buildings and statues. Acids combine with other chemicals to form urban smog, which attacks the lungs, causing illness and premature deaths. Places significantly impacted include most of eastern Europe, coast of China and Taiwan United States, and south-eastern Canada.

Buffer Solutions and Concept

Now we will take another very important topic that is buffer solutions. A buffer solution contains a weak acid mixed with its conjugate base or weak base and conjugate acid. This resist changes in pH when a small amount of a strong acid or base is added to it. Here we can see weak acid and its conjugate base, therefore it will be a strong base they are being added. Buffers in the body, absorb H_3O^+ or OH^- from foods and many other cellular processes to maintain pH because we know in our body many metabolic changes are taking place and they are occurring only at specific pH, therefore, it’s very important to maintain pH. Buffers are important in the proper functioning of cells and blood. In the blood pH remains close to 7.4 therefore buffer has the role of maintaining it to it’s the proper value. A change in the pH of the blood affects the uptake of oxygen therefore all the cellular processes and our metabolism.

Now among the blood buffer systems, four major buffer systems are

- Protein buffer systems
- Amino acids
- Hemoglobin buffer system
- Phosphate buffer system
- Bicarbonate-carbonic acid buffer system

Now we will see what are the various components of a buffer. Buffer solution contains a combination of acid-base conjugate pairs. It may be a pair of weak acid and its conjugate base. Resulting in the formation of the salt or a weak base and it salt with the conjugate acid, concentration of these two components should be equal.

Here we will see the case of acetic acid (weak acid) and its salt with a strong base that is sodium acetate.

$$CH_3COOH \quad \text{equilibrium} \quad H^+ + CH_3COO^-$$

We know acidic acid being ionized like this and

CH_3COONa equilibrium Na^+ CH_3COO^-

sodium acetate is being ionized like this. Here since anions means acetate ions are coming from the salt its concentration is taken as the concentration of salt only because we know acetic acid being a very weak acid it will be dissociated very less.

Now we will further understand how a buffer works? Here is the buffer of acetic acid and sodium acetate. As we have already learnt that these to be present in the equal proportions, so their concentrations should be the equal. Now suppose we are adding a little amount of acid then we will see how it resist change in the pH, now upon addition of acid, what will happen here from this reaction, this acid will combine with the acetate ion and will be converted to the acidic acid. Acetic acid being a very weakly dissociated acid, concentration of hydrogen ion will not be much affected. Here we can see upon mixing hydrogen ion concentration of acetic acid have risen slightly and concentration of acetate ion has slightly worn down. So we can see pH of the solution will not be much affected. Now coming to the addition of hydroxyl ion now we can see the second reaction where acetic acid is being treated with a hydroxyl ion and we're getting acetate ion, so concentration of acetate ion is increasing slightly here and concentration of acetic acid is decreasing slightly here. But here also from this reaction it is very clear that

$$CH_3COOH + OH \rightarrow CH_3COO^- + H_2O$$

OH^- being added to it, but they are not able to release any of the OH^- , therefore pH will not increase, so we can see how the buffer of the acetic acid and sodium acetate is able to maintain the pH.

Henderson Hasselbach Equation and its applications

Now we will further learn pH of the buffer with the help of dissociation expression of weak acid that is

$$K_a = [A^-][H^+] / [HA]$$

As we had already learnt that $K_a = [A^+][H^+] / [HA]$

Now this expression can be rearranged to solve for the concentration of hydrogen ion like this.

Now using properties of the log concept and then taking negative of the logarithm we can convert this equation in the form of

$$pH = pK_a + \log [A^-] / [HA] = pK_a + \log [salt]/[acid]$$

$pH = pK_a + \log [A^-]$ that is concentration of the salt because as we already discussed that A^- is mainly coming from the salt and divided by concentration of the acid. In the same way we can derive the equation for the pOH also

$pOH = pK_b + \log [B^+] / [B\,OH] = pK_b + \log [salt] / [base]$

since here B^+ is also coming from the salt so we will write it as

$$pOH = pK_b + \log [salt] / [base]$$

This equation is very important for the calculation of pH and pOH for the buffers and it is called Henderson-Hasselbalch equation

This graph shows the region of the maximum buffering capacity this is at pH is equal to pK_a , here we can see examples of blood buffer composed of carbonic acid and bicarbonate ion, this is the concentration of bicarbonate ion, this is increasing from 0 to 25 here, so 75% will be the concentration of carbonic acid. Now at equal concentration 50-50, this is actually the buffer action takes place. So this region around this pH where $pH = pK_a$. Here capacity of the buffer will be the maximum and slight change in the pH will be resisted. It is at this pH at this pK_a value, if we are adding acid or we are adding a base then it will resist the change in the pH.

Now we will further understand this concept with the help of some numerical problems. We need to produce a buffer solution that has a pH of 5.27. We have already given a solution that contains 10.0 mmol (millimoles) of acetic acid weak base. How many mmoles of sodium acetate its salt with conjugate base you can see, so how many mmoles of sodium acetate will be required to add to this solution? The pK_a of acetic acid is being given as 4.75.

Now we will substitute into the Henderson-Hasselbalch equation the various values we have been given, we have been given the pH value here 5.27 and we have been given the pKa value also and we have already been given the concentration of the acetic acid that is HA, so we need to calculate only A^- that is concentration of the sodium acetate.

So if we take x be the required concentration and we will put all the values here in the equation then x will come out to be 33.1 mmol of sodium acetate.

Now another problem now aspirin has a pK_a of 3.4. What is the ratio of A^- to HA in the blood, as we now pH of the blood is 7.4. You have to find the ratio between A^- and HA so we don't need the concentrations.

Now

$pH = pK_a + \log [A^-] / [HA]$

$7.4 = 3.4 + \log [A^-]/ [HA]$

$7.4 - 3.4 = 4 = \log [A^-]/ [HA]$

pH we have been given is 7.4, pK_a 3.4, so this quantity

log A^-/HA will come out to be the 4, now taking in the form of

$10^4 = 10000 = [A^-]/ [HA]$

This will come out to be the ratio of the A^- and HA that is acid that is what we have to calculate, ratio of the A^- to HA. So we can see this is the 10000 times of the sodium acetate ion concentrations or any A^- salt it was the example of aspirin, so concentration of A- and concentration of HA should be in the ratio of 10:1.

Now another problem fifty percent of a weak acid is in an ionized form in a solution with pH of 5.000, what is the pK_a value for the weak acid?

Now let us suppose the acid is HA and its ionic anion is A^-. As it has been already given 50% of the acid is in ionized form, so 50% in the A^- , therefore, concentration of the HA remaining will be again 50%, now using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log [A^-]/[HA]$$

at half-neutralization, $[HA]/[A^-] = 1$.

Both are 50-50, therefore at half-neutralization log(1) = 0, therefore at half-neutralization pH will be the pK_a that is the pH at which we will get the maximum buffering capacity.

Conclusion

Now at the end of this lecture we will summarise what we have discussed. We discussed about the pH concept and its interpretation and its role in many biological processes, we also learnt to calculate pH for different type of salts, we also discussed about the buffer solutions, action of the buffer, how it controls that changes in the pH, we also solved many numerical problems based on these concepts. So at the end of this unit we can easily understand the various concepts of ionic equilibria many ionic reactions which are taking place in the solution and many concepts of the qualitative analysis and quantitative analysis.