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Class 12
Chemistry

Chapter 3

ChemicalEquilibria

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CHEMICAL EQUILIBRIA

Strength of Acids and Bases

The degree to which different Bronsted acids give off protons is called "acid strength". A relatively strong acid is an acid that can give off more protons then another acid. Bases differ in degree to which they accept protons as well. A strong base can accept protons to a greater extent than another base.

- **Strong and Weak Acids:** Strong acids ionize almost completely in water. Weak acids ionize only partially in water. Acid strength can be expressed useing the acid dissociation constant Ka.

  Consider a general acid HX in water;

  $HX + H_2O \rightleftharpoons H_3O^+ + X^-$

  At equilibrium, equilibrium constant is,

  $$K = \frac{[H_3O^+][X^-]}{[HX][H_2O]}$$

  Since water in is large excess, its concentration is considered constant.

  $K[H_2O] = [H_3O^+][X^-]/[HX]$

  $Ka = [H_3O^+][X^-]/[HX]$

  Ka measures how much the acid ionizes at equilibrium. Larger Ka = strong acid. Temperature effects Ka. Alway mention the temperature

  To make numbers easier to work with Ka is converted to pKa. $pKa = -\log Ka$ Lower pKa = stronger acid.

- **Strong and Weak Bases:** The strength of a base is its ability to accept a proton (H^+) from a solvent (usually water). Strong bases ionize almost completely in water, weak bases ionize partially.

  Strong bases for example:

  $NaOH \longrightarrow Na^+ + OH^-$ (sodium hydroxide)

  $KOH \longrightarrow K^+ + OH^-$ (potassium hydroxide)

  For a base B in water:

  $B + H_2O \rightleftharpoons BH^+ + OH^-$

  The base ionization constant K_B measures base strength:

  $K_B = [BH^+][OH^-]/[B]$

  Larger K_B = strong base
  Smaller K_B = weak base

  $pK_B = -\log K_B$
  lower pK_B = stronger base

Buffer Solutions and their Applications

A solution whose pH does not change significantly when a small amount of acid or base is added to it. The pH remains constant. Their are types of buffer solutions: Acidic Buffer, has pH less than 7. Weak acid + salt of weak acid with strong base. For example, $CH_3COOH + CH_3COONa$. Basic Buffer, has pH more than 7. Weak base + Salt of weak base with strong acid. For example, $NH_4OH + NH_4Cl$.

- **Buffer action:** Consider a buffer solution of CH_3COOH and CH_3COONa. The common ion effect helps us to understand how the buffer will work. CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH_3COONa, a strong electrolyte is added to the CH_3COOH solution, the dissociation of CH_3COOH is suppressed due to the common ion effect of CH_3COO^-

  $CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$

  $CH_3COONa_{(s)} \rightleftharpoons CH_3COO^- + Na^+$

  By addition of acid: $HCl \longrightarrow H^+ + Cl^-$

  $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

  $CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$

  By addition of base: $NaOH \longrightarrow Na^+ + OH^-$

  $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

  $H^+ + OH^- \rightleftharpoons H_2O$

- **Calculation of pH of Buffer Solution:** Calculate the pH of an acetic acid-sodium acetate buffer solution containing 1·0 moles of each component.

  $[CH_3COOH] = 1$ mole, $[CH_3COO^-] = 1{\cdot}0$ mole

  $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

  $Ka = [CH_3OO^-][H^+]/[CH_3COOH]$

  $Ka = (1)(H^+)/(1)$

  $Ka = H^+$

$pKa = pH$
$pH = -\log(1.8 \times 10^{-5})$
$pH = 4.745$
What will be the pH of this solution after the adition of 0.01 mole of hydrochloric acid to 1 dm^3 of the solution? Assume that the volume of the solution remains unchanged with the addition of HCl. (Ka for acetic acid is 1.8×10^{-5}).
$HCl \longrightarrow H^+ + Cl^-$
0.01 0.01 0.01
$CH_3COO^- + H^+ \longrightarrow CH_3COOH$
Intial concentration:
$[CH_3COOH] = 1.0$ mole
$[CH_3COO^-] = 1.0$ mole
Final concentration:
$[CH_3COOH] = 1.0 + 0.01 = 1.01$ mole
$[CH_3COO^-] = 1.0 - 0.01 = 0.99$ mole
$Ka = [CH_3COO^-][H^+] / [CH_3COOH]$
$[H^+] = Ka[CH_3COOH]/[CH_3COO^-]$
$[H^+] = 1.8 \times 10^{-5}(1.01)/0.99$
$[H^+] = 1.83 \times 10^{-5}$
$pH = -\log(1.83 \times 10^{-5})$
$pH = 4.736$

- **Applications of Buffer Solutions:** Buffers play a crucial role in various everyday applications, helping to maintain stability and prevent abrupt changes in different systems.

The buffer system in blood plasma: The bicarbonate ion (HCO_3) plays a crucial role in maintaining blood pH through the bicarbonate buffer system. The normal blood pH range is approx. 7.35 – 7.45, a value higher than 7.8 or lower than 6.8 can be lethal. Bicarbonate buffer solution is basically a reversible reaction of carbon dioxide and bicarbonate ions in the blood.

Formation of carbonic acid:
$CO_2 + H_2O \rightleftharpoons H_2CO_3$
Decomposition of carbonic acid into bicarbonate and hydrogen ions.
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

Carbonic anhydrase are catalysts for this buffer solution and they are found in red blood cells.

Neutrallization of acids: The H^+ ion produced by an acid is absorbed by bicarbonate to form carbonic acid.
$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$
Neutrallization of bases: The OH^- ion produced by a base is neutrallized by using H^+ ion of deionized carbonic acid.
$OH^- + H_2CO_3 \rightleftharpoons HCO_3^- + H_2O$

Topic 3.4 and 3.3 are not included

The Partition Coefficient

When two immiscible liquids (like ether and water) are mixed and allowed to stand, they form two separate layers. Ether is less dense, so it forms the upper layer and the water settles down. If a solute X can dissolve in both liquids, it will distribute itself between them. A solution of solute X in water is shaken with ether in separatory funnel. After standing, the concentration of X in water decreases. This is because some solute moves into the ether layer. Thus, the solute is distributed between both solvents. After some time, a dynamic equilibrium is established. At equilibrium, the ratio of concentrations of the solute in the two solvents becomes constant at a fixed temperature. The constant ratio of solute concentrations in two immisicible solvents is called partition coefficient. (Kpc). It has a constant value at constant temperature. Sine it is a ratio, it has no units.

$$Kpc = \frac{\text{Conc. of ~~solvent~~ solute in solvent 1}}{\text{Conc. of solute in solvent 2}}$$

The distribution of a solute between two immiscible solvents follow the Nernst Distribution Law.

- **Factors affecting the numerical value of partition coefficient:** The partition coefficient shows how a solute distributes itself between two imisicible solvents, usually a polar solvent (water) and a non-polar solvent (organic solvent).

Polarity of the Solute: Polar solutes dissolve better in polar solvents. This is due to dipole-dipole interactions or hydrogen bonding. For example, Ethanol is polar because of its -OH group. It is more soluble in water than in octanol. Hence, its Kpc favors the polar phase.
Polarity of the Solvent: The nature of the solvent strongly affects solute distribution. Non-polar solutes prefer non-polar solvents. Polar solutes prefer polar solvents. For example, Benzene is non-polar. It dissolves better in octanol than in water. Therefore its Kpc is higher in the non-polar phase.
Temperature: Partition coefficient depends on temperature. Changing temperature affects, solubility of solute and kinetic energy of molecules. For example, Aspirin (polar solute), at higher temperature, it becomes more soluble in water than in octanol. Hence its Kpc changes with temperature.
Molecular Structure and Size: Larger molecules interact differently with solvents than smaller ones. Functional groups and molecular size affect solubility. For example, Ethyl acetate (smaller) and Butyl acetate (larger), Butyl acetate may have a lower partition coefficient due to steric hindrance.

- **Calculation of Partition Coefficient:** When $100\,cm^3$ of a $0.150\ mol\,dm^{-3}$ solution of a aqueous methylamine (CH_3NH_2) is shaken with $75.0\,cm^3$ of an organic solvent in the separating funnel to allowed to come to equilibrium. Only $25\,cm^3$ of the aqeous layer is run off and titrated against 0.2825M HCl $7.05\,cm^3$ of HCl was used.

Data: Volume of aqeous methylamine solution: $100\,cm^3$
Initial Concentration of methylamine: $0.150\ mol\,dm^{-3}$
Volume of organic solvent: $75.0\,cm^3$
Volume of aqeous layer titrated: $25.0\,cm^3$
Volume of HCl used for titration: $7.05\,cm^3$
Concentration of HCl: $0.225\ mol\,dm^{-3}$
Calculate the partition coefficient of methylamine in the organic solvent and water.
Solution: Equilibrium equation:
$CH_3NH_2 \rightleftharpoons CH_3NH_2$ (organic solvent)
Kpc expression:
$K_{pc} = [CH_3NH_2]_{organic\ layer} / [CH_3NH_2]$
Total moles of methylamine in the orginal solution
Total moles $CH_3NH_2 = 0.100 \times 150/1000 = 0.015\ mol$ (These moles are distributed in two lyer)
No. of moles methylamine in the aqeous layer:
$CH_3NH_2 + HCl \rightarrow CH_3NH_3Cl$
$25cm^3$ of aqeous layer reacted with $7.05\,cm^3$ of 0.225M HCl
1 mol of CH_3NH_2 is: 1 mol of HCl
$n = M \times V\,dm^3$
$n = 0.225 \times 7.05/1000$
$n = 0.001586\ mol$
As $25cm^3$ of the aqeous layer was titrated, the 0.001586 mol of methylamine was present in $25cm^3$ of the aqeous layer
So, the moles of methylamine present in $100\,cm^3$ of aqeous layer=
$0.001586 \times 100/25 = 0.00634\ mol$
Number of moles of CH_3NH_2 present in organic layer:
Mol CH_3NH_2 (organic layer) = mol(CH_3NH_2 (total) − mol(CH_3NH_2 (aqeous layer)
$= 0.015 - 0.00634$
$= 0.00867\ mol$
Change the number of moles into concentrations:
Conc. (CH_3NH_2 in aqeous layer) $= 0.00634 \times 1000/100 = 0.0634\ mol\,dm^{-3}$
Conc. (CH_3NH_2 in organic layer) $= 0.0866 \times 1000/75 = 0.116\ mol\,dm^{-3}$
Substitute the values into Kpc expression:
$K_{pc} = 0.116/0.0364 = 1.83$
Since the value of Kpc is larger than 1, methylamine is more soluble in organic solvent than in water.

SHORT QUESTIONS

Explain the common ion effect with a suitable example.
The common ion effect is the suppression of ionization of a weak electrolyte when a strong electrolyte containing a common ion is added to the solution. Consider a weak acid such as acetic acid: $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$. It ionizes only slightly in water. When sodium acetate (CH_3COONa), a strong electrolyte, is added, it dissociates completely: $CH_3COONa \rightarrow Na^+ + CH_3COO^-$. The increased solution of the common ion CH_3COO^- shifts the equilibrium to the left, thereby reducing the ionization of acetic acid. For example, in a buffer solution of acetic acid and sodium acetate, the ionization of acetic acid is suppresed due to the pressence of the common acetate ion. Thus, the common ion effect explains why the addition of a common ion decreases the degree of ionization of a weak electrolyte.
Differentiate between strong and weak acids using the extent of ionization and Ka.
Strong acids ionize almost completely in aqeous solution, producing a high concentration of hydrogen ions. Because their extent of ionization is very large, they have a large value of the acid dissociation constant Ka. Weak acids, on the other hand, ionize only partially in water. Their extent of ionization is small, so they have a small value of Ka. Thus, the greater the extent of ionization, the larger the value of Ka and the stronger the acid. Conversly acids with low ionization have low Ka values and are weak acids.
Differentiate between strong and weak bases using the extent of ionization and Kb
Strong bases ionize almost completly in ageous solution, producing a high concentration of hydrogen~~oxide~~ ions (OH^-). Due to their large extent of ionization, they have a large value of the base dissociation constant Kb. Weak bases ionize partially in water and produce fewer hydroxide ions. Therefore their extent of ionization is small, and they have a small value of Kb. Hence, a larger extent of ionization corresponds to a higher Kb, and a stronger base, while smaller extent of ionization correspondes to a lower Kb and a weaker base.
Define buffer solution and provide an example of how it can be made.
A buffer solution is a solution that resists change in pH where small amounts of acid or base are added. For example, an acidic buffer can be prepared by mixing a weak acid with its salt containing a common ion. Like, a buffer solution is made by mixing acetic acid (CH_3COOH) with sodium acetate (CH_3COONa) in water.
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
$CH_3COONa \rightleftharpoons Na^+ + CH_3OO^-$
The presence of the common ion CH_3COO^- helps maintain a nearly constant pH.
How does a buffer solution ~~and~~ control pH? Include chemical equations in your answer.
A buffer solution controls pH by neutrallizing small amounts of added acid or base and thus resists changes in pH. It usually consists of a weak acid and its salt, or a weak base and its salt. Equilibrium in acetic-acid-sodium buffer:
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$
When a small amount of acid (HCl) is added: $HCl \rightarrow H^+ + Cl^-$
The added H^+ ions are removed by acetate ions: $CH_3COO^- + H^+ \rightarrow CH_3COOH$
When a small amount of base (NaOH) is added: $NaOH \rightarrow Na^+ + OH^-$
The OH^- ions are neutallized by H^+ from the weak acid: $H^+ + OH^- \rightarrow H_2O$ (More acetic acid dissociates to replace the lost H^+).
Explain how HCO^- plays a role in controlling pH in the blood.
The pH of human blood is maintained at about 7.4 by the bicarbonate buffer system, which consists mainly of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-). Equilibrium in blood: $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
When acid is added (increase in H^+):
Extra H^+ ions combine with bicarbonate ions: $H^+ + HCO_3^- \rightarrow H_2CO_3$
Carbonic acid then breaks down into CO_2 and water: $H_2CO_3 \rightarrow CO_2 + H_2O$
CO_2 is then removed by the lungs, preventing a fall in pH.
When base is added (increase in OH^-):
OH^- ions react with carbonic acid: $OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O$
This prevents a rise in pH.

CONCEPT ASSESSMENT

When 2 grams of a solute is shaken with a mixture of 150cm^3 of water and 20cm^3 of chloroform. After shaking, 1·5 grams of the solute is found in the chloroform layer. Calculate the partition coefficient.

Mass of solute shaken: 2.0 gram
Volume of water layer: 150 cm^3 = 0·150 dm^3
Volume of Chloroform layer: 20cm^3 = 0.020 dm^3
Mass of solute in chloroform: 1·5gram
Mass of solute in water: 2·0 - 1·5 = 0·5 gram
Kpc of the solute between chloroform and water: ?

Formula: $K_{pc} = \frac{\text{Concentration of solute in chloroform}}{\text{Concentration of solute in water}}$

Conc. in chloroform: 1·5/0·020 = 75gdm^{-3}
Conc. in water: 0·5/0·150 = 3·33gdm^{-3}
Kpc = 75/3·33
Kpc = 22·5

∵ unit dont matter, just have same units so no need to convert in $mddm^{-3}$.

Since the partition coefficient is larger, the solute is much more soluble in chloroform than in water.