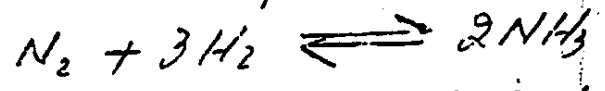


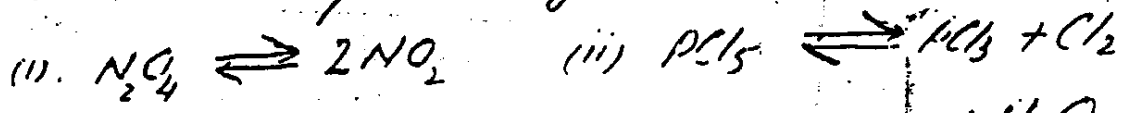
Q. WHAT ARE REVERSIBLE REACTIONS. DISCUSS AN EQUILIBRIUM STATE IN A REVERSIBLE REACTION.

ANS: The chemical reactions which proceed both in forward and reverse direction are called reversible reactions. In these reactions reactants give rise to products and products react back to give reactants again. These reactions never go to completion because as soon as some products are formed, they are converted back into reactants.

These are represented by two arrows " $\rightleftharpoons$ ". For example consider synthesis of  $NH_3$



Nitrogen and hydrogen react to produce " $NH_3$ ".  
Rate  $NH_3$  decomposes into  $N_2$  and hydrogen.  
Some more examples are given below.



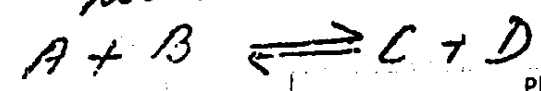
EQUILIBRIUM STATE:-

In a reversible reaction the state at which rate of forward reaction becomes equal to rate of backward reaction is called an equilibrium state.

At equilibrium state Rate Forward = Rate reverse

The concentration of reactants and products become constant at equilibrium. It does not change with the passage of time at given set of conditions of temperature, pressure, volume etc.

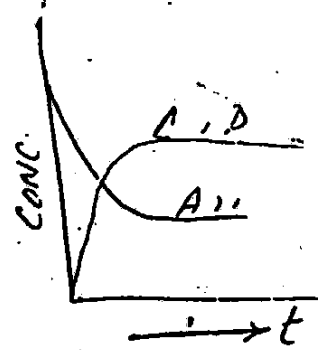
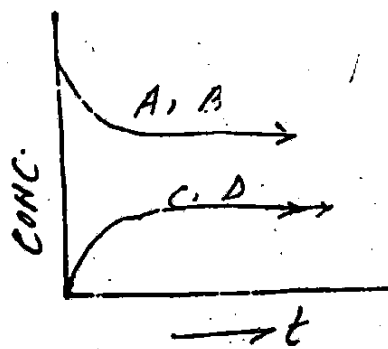
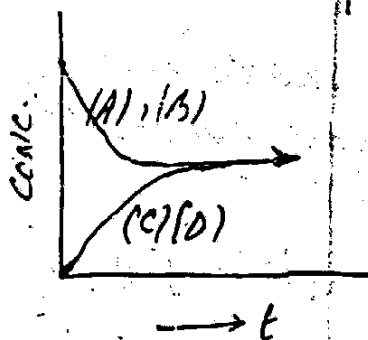
Let us consider a reversible reaction



At the beginning the conc. of reactants decreases and concentration of products increases but at equilibrium state conc. of reactants and products becomes constant.

At equilibrium state it seems as if the reaction has stopped but actually rate of forward and reverse reaction become exactly equal.

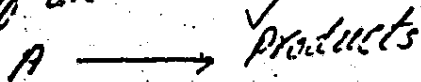
At equilibrium, conc., temp., pressure, volume becomes constant. It is not a static equilibrium. It is a dynamic equilibrium. Both forward and reverse reactions are taking place. Let us consider following graphs.



These graphs show that at equilibrium conc. of reactants and products must be constant not always equal.

STATE & EXPLAIN LAW OF MASS ACTION. DERIVE AN EQUILIBRIUM CONSTANT EXPRESSION FOR A REVERSIBLE REACTION, "A + B  $\rightleftharpoons$  C + D" (3)

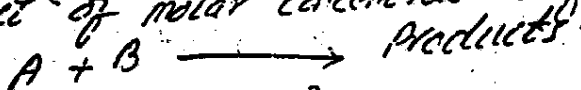
ANS:- Guldberg and Waag proposed Law of Mass Action. According to Law of Mass Action, "The rate of reaction is directly proportional to molar concentration (Active Mass) of reactant (if there is only one reactant)



$$\text{Rate} \propto [A]$$

$$\text{Rate} = k[A]$$

Square bracket indicates molar concentration of "A". If there are more than one reactants then the Law is stated as "The reaction is directly proportional to the product of molar concentrations of reactants."



$$\text{Rate} \propto [A][B]$$

$$\text{Rate} = k[A][B]$$

If there are some co-efficients with reactants then Rate of reaction is directly proportional to molar conc. of reactants raise to power their co-efficients.



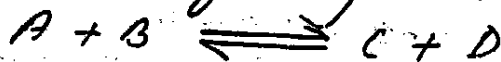
$$\text{Rate} \propto [A]^a [B]^b$$

$$\text{Rate} = k[A]^a [B]^b$$

"k" is called Rate constant

4

DERIVATION OF EQUILIBRIUM CONSTANT:  
Let us consider following reversible reaction at equilibrium.



According to law of mass action,

Rate of forward Reaction  $\propto [A][B]$

$$\text{Rate of forward Reaction} = k_f [A][B] \quad \text{--- (1)}$$

Rate of reverse Reaction  $\propto [C][D]$

$$\text{Rate of Reverse Reaction} = k_r [C][D] \quad \text{--- (2)}$$

" $k_f$ " is rate constant for forward reaction and  
" $k_r$ " is rate constant for reverse reaction.

Since reaction is at equilibrium, so rate of forward reaction is equal to rate of reverse reaction.

$$\text{Rate (forward)} = \text{Rate (Reverse)}$$

From equation (1) & (2)

$$k_f [A][B] = k_r [C][D]$$

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$K_c = \frac{[C][D]}{[A][B]} \quad \text{(3)}$$

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" $K_c$ " is called Equilibrium constant. The subscript "c" indicates that reactants and products have been expressed in molar concentration. The equation (3) is called equilibrium constant expression. For a more general reaction



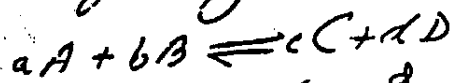
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{OR} \quad \frac{C_c \times D_d}{A^a \times B^b}$$

If reactants and products are gases then equilibrium constant expression can be written in terms of their partial pressures.

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

## RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANTS. 5

The expression for equilibrium constant depends upon units of concentration used. Let us consider following reversible reaction at equilibrium state



If reactants and products are expressed in moles/dm<sup>3</sup> (molar conc) then equilibrium constant is written as "K<sub>c</sub>".

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\textcircled{1} - K_c = \frac{C_c^c \times C_D^d}{C_A^a \times C_B^b}$$

If reactants and products are ideal gases, the molar conc. of each gas is proportional to partial pressure. Then for such a gaseous reaction equilibrium constant is written as

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \quad \text{---} \textcircled{2}$$

RELATION BETWEEN "K<sub>c</sub>" and

K<sub>p</sub> is written as

$$K_p = K_c (RT)^{\Delta n} \quad \text{---} \textcircled{3}$$

"Δn" is change in number of moles going from reactant to products

$$\Delta n = (c+d) - (a+b)$$

If Δn = 0

$$K_p = K_c \quad \text{---} \textcircled{4}$$

R = General gas constant

T = Absolute Temperature

When reactants and products are written in terms of mole fractions Equilibrium constant could be written as

$$K_x = \frac{X_C^c X_D^d}{X_A^a X_B^b} \quad \text{---} \textcircled{5}$$

X<sub>A</sub>, X<sub>B</sub>, X<sub>C</sub>, X<sub>D</sub> are mole fractions of components A, B, C, D.

Relation between "K<sub>p</sub>" and "K<sub>x</sub>" is

$$K_p = K_x (P)^{\Delta n} \quad \text{---} \textcircled{6}$$

If Δn = 0

$$K_p = K_x \quad \text{---} \textcircled{7}$$

If reactants and products are written in the form of number of moles then equilibrium constant could be written as

$$K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}$$

Relation between  $K_p$  and  $K_c$  could be written as

$$K_p = K_c \left(\frac{P}{N}\right)^{\Delta n} \quad \text{--- (8)}$$

If  $\Delta n = 0$

$$K_p = K_c \left(\frac{P}{N}\right)^{0}$$

$$K_p = K_c \quad \text{--- (9)}$$

It is clear from above expressions that  $K_c = K_p = K_x = K_n$  for those reactions in which there is no change in number of moles going from reactants to products.

### APPLICATIONS OF EQUILIBRIUM CONSTANT

#### 1) DIRECTION OF REACTION

Direction of a chemical reaction at a particular instant can be predicted by determining ratio of conc. of products and reactants. There are three possibilities:

(1) If the value  $\frac{[\text{PRODUCT}]}{[\text{REACTANT}]}$  is less than " $K_c$ " then it means that there should be more products to attain equilibrium. It means reaction proceeds "forward" direction.

$$K_c > \frac{[\text{PRODUCT}]}{[\text{REACTANT}]}$$

(2) If  $K_c < \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$  then it means there are more products than required for equilibrium state. Hence reaction will proceed in reverse direction to attain equilibrium state.

(3) When ratio of conc. is equal to " $K_c$ " then reaction is in equilibrium state.

# APPLICATIONS OF " $K_c$ " VALUE

6-B

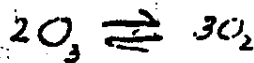
## $K_c$ USED TO DETERMINE EXTENT OF REACTION.

The value of " $K_c$ " can be used to determine extent of chemical reaction. There are three possibilities in this respect.

(i) VERY LARGE " $K_c$ " VALUE: Very large " $K_c$ " value indicates that reactants are quite unstable and products are very much stable. It means reactants are quite reactive but products are quite unreactive. Thus almost all reactants are converted into products. At equilibrium there will be high concentration of products but low conc. of reactants. The reaction is almost complete in forward direction.

### EXAMPLE

Decomposition of ozone ( $O_3$ )



$$K_c = \frac{[O_2]^3}{[O_3]^2} = 1 \times 10^{55} \text{ at room temp.}$$

- It means
- (i) " $O_3$ " is quite unstable.
  - (ii) At equilibrium there is very high conc. of oxygen and very low conc. of ozone.
  - (iii) Reaction is almost complete in forward direction i.e. almost all ozone is converted into oxygen.

### EXAMPLE 2



$$K_c = \frac{[Cl_2]}{[Cl]^2} = "K_c" = 10^{38}$$

It means almost all chlorine atoms combine to form molecules. Chlorine atoms are unstable and  $Cl_2$  molecules are stable. When chlorine atoms are used as starting material, reaction is almost complete in forward direction.

(ii) "VERY SMALL VALUE OF " $K_c$ " Very small value of " $K_c$ "

indicates that reactants are very much stable and products are unstable. Thus very few reactant molecules are converted into products. There is high conc. of reactants and low concentration of reactants, products at equilibrium.

### EXAMPLE:



$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 1 \times 10^{-30} \text{ at } 25^\circ C$$

It means " $N_2$ " and " $O_2$ " are much stable and NO (products) are unstable. The reaction will not occur to appreciable extent. The equilibrium mixture contains almost entirely " $N_2$ " and " $O_2$ ". There are traces of (NO) at equilibrium stage. The backward reaction is almost complete.

(ii)  $K_c$  NEITHER VERY LARGE NOR VERY SMALL:

If " $K_c$ " is neither very large nor very small then it means that there will be appreciable amounts of reactants and products at equilibrium stage. None of the reactants or products is very much reactive or unreactive. The reaction is not complete in any direction.

EXAMPLE  $N_2 + 3H_2 \rightleftharpoons 2NH_3$   $K_c = 10$  at  $300^\circ C$

It means there is almost equal conc. of reactants and products at equilibrium stage. The reactants and products are almost equally stable.

$K_c$  USED TO DETERMINE DIRECTION OF REACTION.

If value of " $K_c$ " is known, we can determine whether a reaction will prefer proceed FORWARD or BACKWARD to attain equilibrium state. Consider reaction  $A+B \rightleftharpoons C+D$

written as  $K_c = \frac{[C][D]}{[A][B]}$ . (The equilibrium constant expression is written as  $K_c = \frac{[C][D]}{[A][B]}$ ). There are three possibilities.

(i) If  $K_c > \frac{[\text{Initial conc. of C}][\text{Initial conc. of D}]}{[\text{Initial conc. of A}][\text{Initial conc. of B}]}$

(The values of initial concentrations of reactants and products are placed in equilibrium constant expression. If answer is less than actual value of  $K_c$  (given) then reaction will proceed in forward direction to attain equilibrium state.)

(ii) If  $K_c < \frac{[\text{Initial conc. C}][\text{Initial conc. of D}]}{[\text{Initial conc. A}][\text{Initial conc. B}]}$

In this case reaction will proceed in BACKWARD to attain equilibrium state.

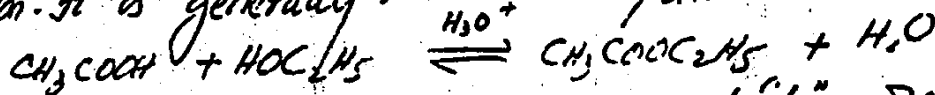
(iii)  $K_c = \frac{[\text{Initial conc. C}][\text{Initial conc. D}]}{[\text{Initial conc. A}][\text{Initial conc. B}]}$

In this case reaction has already attained equilibrium state. - Rate of forward and backward reaction is equal.



## Equilibrium Constant Expression For Esterification 8

The reaction of an organic acid with Alcohol is called esterification. It is generally written as follows



Let us consider "a" moles of acid and "b" moles of alcohol mixed together in a flask of volume "V" litre.

The progress of reaction is studied by finding amount of acid after definite intervals. Let at equilibrium stage conc. of acid is "a-x". The amount of alcohol at equilibrium will be b-x.

Concentration of acid at equilibrium state =  $\left(\frac{a-x}{V}\right) \frac{\text{mole}}{\text{dm}^3}$   
 " " Alcohol " " =  $\left(\frac{b-x}{V}\right) \frac{\text{mole}}{\text{dm}^3}$   
 Concentration of ester at equilibrium =  $\frac{x}{V} \frac{\text{mole}}{\text{dm}^3}$   
 " " WATER at equilibrium =  $\frac{x}{V} \frac{\text{mole}}{\text{dm}^3}$

The equilibrium constant expression could be written as  $K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{HOC}_2\text{H}_5]}$

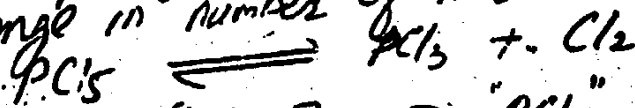
$$K_c = \frac{\left(\frac{x}{V}\right) \left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right) \left(\frac{b-x}{V}\right)}$$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

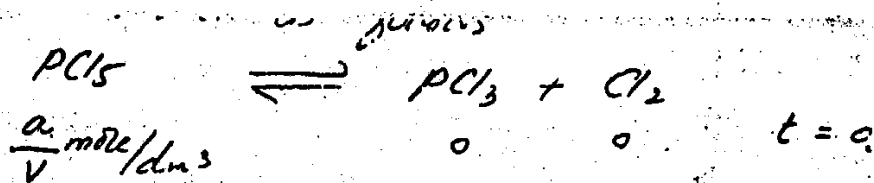
In the final expression volume has been cancelled out indicating that equilibrium constant value is independent of volume changes.

## 2) DISSOCIATION OF PCl<sub>5</sub> (Thermal decomposition of PCl<sub>5</sub>)

is an example of homogenous gaseous phase reaction with change in number of moles



Let us consider "a" moles of "PCl<sub>5</sub>" is decomposed in a flask of volume "V" litre. Let "x" is degree of dissociation. Then at equilibrium conc. of each comp-



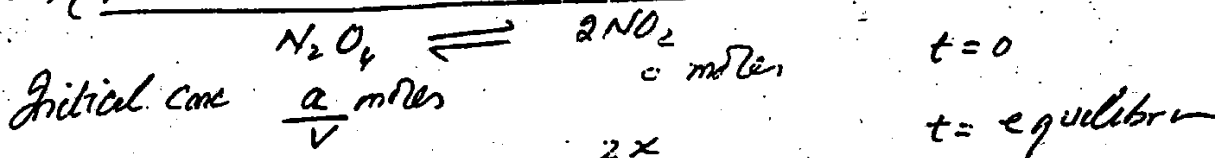
At equilibrium  $\left(\frac{a-x}{V}\right) \rightleftharpoons \left(\frac{x}{V}\right) \left(\frac{x}{V}\right) \frac{\text{moles}}{\text{dm}^3}$   $t = \text{equilibrium}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$K_c = \frac{\left(\frac{x}{V}\right) \left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

The final expression for " $K_c$ " depends upon volume change. Thus equilibrium composition will change with change in vol.

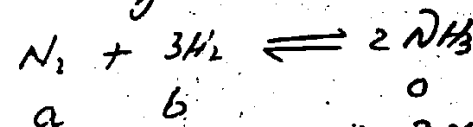
### (3) THERMAL DECOMPOSITION OF $\text{N}_2\text{O}_4$



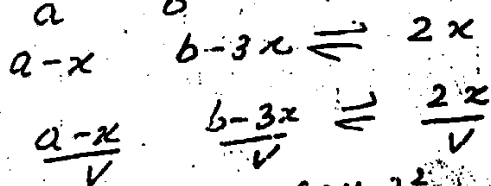
$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)} = \frac{4x^2}{(a-x)V}$$

Thus " $K_c$ " depends upon volume changes.

### 4) SYNTHESIS OF AMMONIA



Let us consider " $a$ " moles of  $\text{N}_2$  and " $b$ " moles of  $\text{H}_2$  mixed together. At equilibrium " $x$ " moles of nitrogen have been decomposed. Then eq.



moles of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  will be  $\left(\frac{a-x}{V}\right)$ ,  $\left(\frac{b-3x}{V}\right)$  and  $\frac{2x}{V}$  respectively. The final expression for " $K_c$ " involves  $V^2$  in numerator.

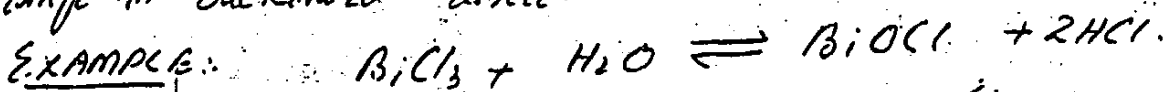
$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right) \left(\frac{b-3x}{V}\right)^3}$$

$$K_c = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

LE-CHATLIER'S PRINCIPLE If a system at equilibrium is <sup>10</sup> disturbed by any change the system will shift itself so as to undo or minimize the effect of change. This is called Le-Chatlier's Principle

EFFECT OF CHANGE IN CONCENTRATION: If concentration of reactants is increased or conc. of products is decreased at equilibrium, reaction will shift in forward direction to nullify this change. And if conc. of products is increased and conc. of reactants is decreased, reaction will shift in backward direction.

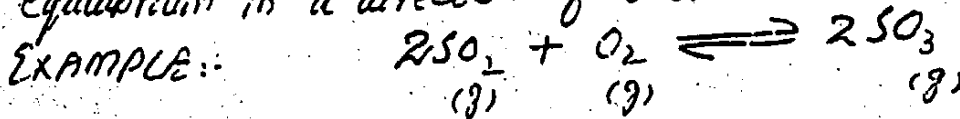


$$K_c = \frac{[\text{BiOCl}][\text{HCl}]^2}{[\text{BiCl}_3][\text{H}_2\text{O}]}$$

Aq. sol. of  $\text{BiCl}_3$  is cloudy due to formation of  $\text{BiOCl}$ . If some  $\text{HCl}$  is added solution becomes clear because reaction is shifted in backward direction. However if some water is added, solution once again becomes cloudy due to formation of  $\text{BiOCl}$  by shift of equilibrium in forward direction. Thus % yield of products can be increased by removing one of the products from reaction mixture.

EFFECT OF CHANGE IN PRESSURE OR VOLUME: - The change in pressure or volume effects only those reactions in which there is change in number of moles going from reactants to products.

According to Le-Chatlier's Principle increase in pressure or decrease in volume will shift equilibrium in a direction of decrease in number of moles.



When this reaction reaches equilibrium state volume of product equilibrium mixture is less than initial vol. of reactants. If volume is further decreased, the reaction

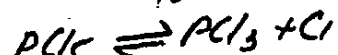
will shift in forward direction. Equilibrium constant expression for this reaction could be written as  $K_c = \frac{4x^2}{(a-2x)(b-x)}$

If volume is decreased then the reaction should proceed forward to produce some more products "x" so that "K<sub>c</sub>" becomes constant.

$$K_c > \frac{4x^2}{(a-2x)(b-x)}$$

Similarly by increasing pressure volume decreases, and system must be shifted in forward direction to maintain value of K<sub>c</sub>.

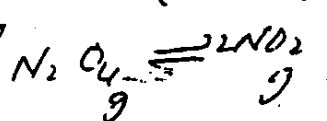
Similarly consider following two systems



$$K_c = \frac{x^2}{v(a-x)}$$

In both these system reaction should be shifted in forward

direction by increase in volume, because due to increase in volume  $K_c > \frac{x^2}{v(a-x)}$



$$K_c = \frac{4x^2}{v(a-x)}$$

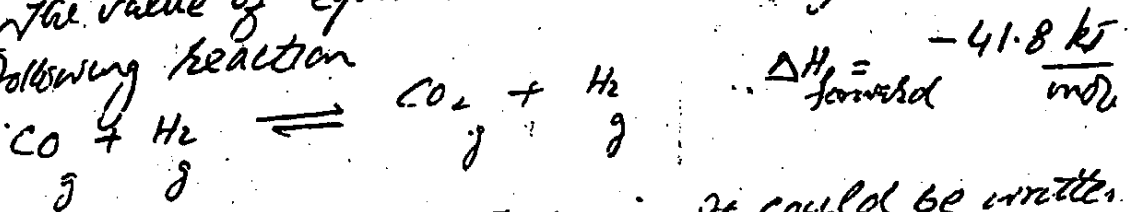
Some more products should be produced to keep value of "K<sub>c</sub>" constant.

The reactions in which number of moles of reactants and products are equal, these are not affected by change in pressure or volume. The reactions in which reactants and products are liquids or solids are not effected by pressure or volume changes.

### EFFECT OF TEMPERATURE CHANGE

According to Le-Chatelier's principle, increase in temperature favours endothermic reaction while decrease in temp. favours exothermic reaction. The value of equilibrium constant changes with Temp.

Consider following reaction

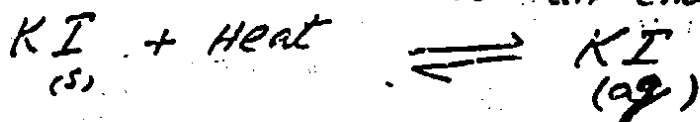


Forward reaction is endo exothermic. It could be written as  $CO + H_2 \rightleftharpoons CO_2 + H_2 + \text{Heat}$

If heat is removed from system by cooling, the reaction will shift in forward direction to compensate loss of

Loss of heat. On the other hand if heat is <sup>12</sup> added to the system it will move in backward direction.

SOLUBILITY OF SALT IN WATER:- The solubility of most of the salts in water is an endothermic process



Thus if saturated solution of KI is heated, more salt could be dissolved in water. On the other hand crystallization of salt takes place on cooling saturated sol.

The solubility of some salts in water is not endothermic (heat of solution is close to zero) the solubility of such salts in water is not much affected by change in temp. For example solubility of NaCl in water is not much affected by temperature.

### EFFECT OF CATALYST

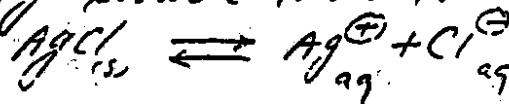
The chemical substances which speed up the rate of reaction but they are recovered after completion of reaction are called catalyst. The equilibrium position is not affected by use of catalyst. It only decreases the time required to reach equilibrium state. It increases both the rate of forward as well as backward reaction.

WRITE A NOTE ON SOLUBILITY PRODUCT.

The product of molar concentrations of oppositely charged ions in saturated solution of sparingly soluble salt when they are in equilibrium with solid salt is called solubility product. It is denoted by  $K_{sp}$ .

Let us consider saturated solution of  $AgCl$  which is sparingly soluble salt. It has following equilibrium

According to law of Mass Action



$$K_c = \frac{[Ag^{+}][Cl^{-}]}{[AgCl]}$$

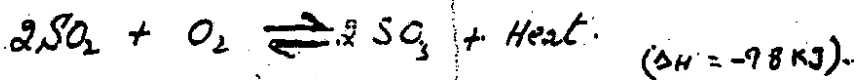
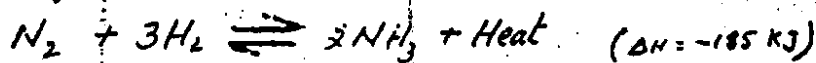
Since  $AgCl$  is sparingly soluble so  $[AgCl]$  concentration of solid  $AgCl$  almost remains constant. So above equation could be written as

$$K_c [AgCl] = [Ag^{+}][Cl^{-}]$$

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

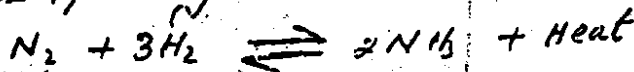
' $K_{sp}$ ' is called solubility product constant. It is equal to product of molar conc. of oppositely charged ions in saturated solution of sparingly soluble salt.

Q:- Discuss conditions of temperature, concentration, pressure and catalyst for maximum yield of  $NH_3$  and  $SO_3$  by following reactions.



Synthesis of Ammonia by Haber process:

Ammonia  $NH_3$  is very important chemical used widely in fertilizer industry. Most of ammonia is synthesized by Haber process. The equation for Haber process is given as



For maximum yield of Ammonia following changes are brought about, keeping in view Le-Chatelier's principle. Le-Chatelier states, "When a system in equilibrium is disturbed by any change, the system will shift itself so as to undo or minimize the effect of change."

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Effect of Concentration:- According to Le Chatelier's principal there are two methods to shift equilibrium in forward direction by changing concentration. These are

- (i) By increasing concentration of reactants ( $N_2, H_2$ )
- (ii) By decreasing concentration of products ( $NH_3$ )

So for maximum yield of ammonia by Haber process the concentration of  $N_2, H_2$  is kept high while conc. of  $NH_3$  is kept low by removing it from reaction mixture.  $NH_3$  is continuously removed from reaction mixture.

Effect of Pressure:- According to Le-Chatelier's principal

Increase in pressure shifts equilibrium in a direction of decrease in volume, and vice versa. For synthesis of ammonia by Haber process eq. of reaction is  $N_2 + 3H_2 \rightleftharpoons 2NH_3$

There is decrease in number of moles (decrease in volume) in forward direction so for maximum yield of  $NH_3$  by Haber process pressure should be kept high to shift in forward direction. In actual practice a pressure of 200-600 atm is used during preparation of ammonia.

Effect of Temperature:- According to Lechatelier's principal

"Increase in temperature favours endothermic reaction while decrease in temperature favours exothermic reaction."

The synthesis of ammonia by Haber process is governed by following exothermic reaction  $N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{Heat}$

So for maximum yield of ammonia temperature must be kept low because forward reaction is exothermic. In actual practice temperature of  $400-450^\circ C$  is used. No doubt it's reasonably high temperature but it decreases time taken to reach equilibrium state.

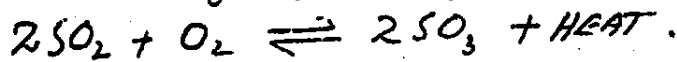
Effect of Catalyst:- catalyst speeds up a chemical reaction but is recovered after completion of reaction. The catalyst actually decreases energy of activation. So it speeds up rate of forward and reverse reaction, so it decreases time taken to reach equilibrium.

In synthesis of ammonia by Haber process, Iron and aluminium oxide are used as catalyst for maximum yield of ammonia.

VOLUME CHANGE:- The volume decreases in forward direction so formation of  $NH_3$  is favoured at low volume.

## SYNTHESIS OF $SO_3$ BY CONTACT PROCESS.

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This reaction is of prime importance in synthesis of  $H_2SO_4$ . For maximum yield of  $SO_3$  following conditions are applied.

Concentration: - According to Le-Chatelier's principle reaction is favoured in forward direction by increasing conc. of reactants and decreasing conc. of products. So for maximum yield of  $SO_3$  conc. of  $SO_2$  and  $O_2$  is kept high while " $SO_3$ " is continuously removed.

Pressure: - Increase in pressure shifts equilibrium in the direction of decrease in volume. There is decrease in volume (number of moles) in forward direction. So for maximum yield of " $SO_3$ " high pressure must be used. In actual practice a pressure of 1.5 atmospheres is used.

Temperature: - According to Le-Chatelier's principle increase in temperature favours endothermic reaction while decrease in temperature favours exothermic reaction.

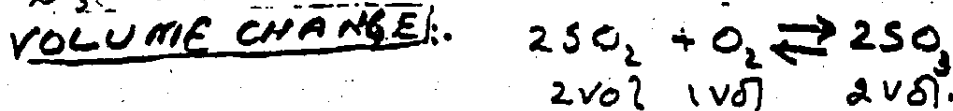
Since synthesis of  $SO_3$  is exothermic so for maximum yield of  $SO_3$  low temperature must be used. The yield of  $SO_3$  is maximum at  $300^\circ C$  and very low at  $700^\circ C$ . In actual practice temperature is gradually decreased from  $650^\circ C$  to  $200^\circ C$ .

Catalyst: - Catalyst decreases time taken to reach equilibrium state by speeding forward and reverse reaction.

For maximum yield of  $SO_3$  in contact process Vanadium pentoxide and "Platinum" are used as catalyst.

In lead chamber process  $NO$ , and  $NO_2$  gases are used as catalyst for maximum yield of  $SO_3$  by above reaction.

### VOLUME CHANGE:



There is decrease in volume in forward direction. So decrease in volume of container will (formation) favour formation of  $SO_3$ . So high pressure and low volume should be used for max. yield of  $SO_3$ .



COMMON ION EFFECT / The decrease in degree of ionization of a less soluble electrolyte by addition of another stronger electrolyte having some common ions is called COMMON ION EFFECT. The concentration of un-ionized species increases and it may precipitate out as solid. 16

FOR EXAMPLE CONSIDER PURIFICATION OF SODIUM CHLORIDE BY PASSING HCl GAS.

In a saturated solution of sodium chloride following equilibrium is established

$$\text{NaCl}_{(s)} \rightleftharpoons \text{Na}^{+}_{(aq)} + \text{Cl}^{-}_{(aq)}$$

The equilibrium constant expression can be written as follows

$$K_c = \frac{[\text{Na}^{+}_{(aq)}][\text{Cl}^{-}_{(aq)}]}{[\text{NaCl}_{(s)}]}$$

When HCl gas is passed through this sol<sup>n</sup> [NaCl] it ionizes as follows

$$\text{HCl} \rightleftharpoons \text{H}^{+} + \text{Cl}^{-}$$

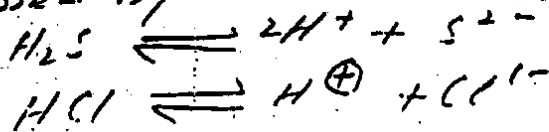
The conc. of  $\text{Cl}^{-}$  ions is increased and eq. No 1 is shifted backward. Thus pure NaCl is precipitated.

EXAMPLES OF COMMON ION EFFECT

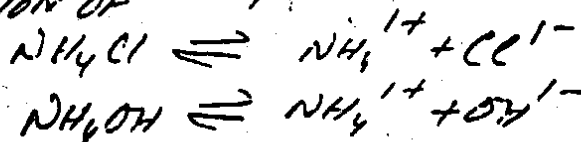
The solubility of  $\text{KClO}_3$  in water is suppressed by addition of more soluble salt KCl by common ion effect

$$\text{KClO}_3 \rightleftharpoons \text{K}^{+} + \text{ClO}_3^{-}$$

(2) DISSOCIATION OF WEAK ACID  $\text{H}_2\text{S}$  IS SUPPRESSED BY ADDITION OF HCl.



(3) DEGREE OF DISSOCIATION OF  $\text{NH}_4\text{OH}$  IS SUPPRESSED BY ADDITION OF  $\text{NH}_4\text{Cl}$ .



$\text{NH}_4^{+}$  ION suppress degree of dissociation of  $\text{NH}_4\text{OH}$

Common ion effect has wide range of applications in qualitative analysis and preparation of Buffers.

pH and pOH OF SOLUTION? PROVE THAT  $pH + pOH = 14$   
 pH of a solution may be defined as logarithm of reciprocal  
 of hydrogen ion conc. of a solution. OR the negative  
 log of hydrogen ion concentration

$$pH = \log \frac{1}{[H^+]} \text{ or } pH = -\log [H^+]$$

EXPLANATION: - pure water ionizes to very little extent  
 $H_2O \rightleftharpoons H^+ + OH^-$  The equilibrium constant can be  
 written as  $K_c = \frac{[H^+][OH^-]}{[H_2O]}$  OR  $K_c [H_2O] = [H^+][OH^-]$

Water is in large excess, therefore  $K_w = [H^+][OH^-]$  -  
 " $K_w$ " is called ionic product of water. Its value at 25  
 has been determined experimentally. It is  $1 \times 10^{-14}$   
 Thus  $1 \times 10^{-14} = [H^+][OH^-]$  since  $[H^+] = [OH^-]$  Thus  
 $1 \times 10^{-14} = [H^+][OH^-]$

$$1 \times 10^{-14} = [H^+]^2$$

$$1 \times 10^{-7} = [H^+] \text{ and } [OH^-] = 10^{-7}$$

ACIDITY OR ALKALINITY of a solution depends upon  
 $[H^+]$  ion concentration. A solution which contains  $10^{-7} M$   
 $[H^+]$  ion is NEUTRAL solution.

ACIDIC solution contains more than  $10^{-7} M [H^+]$  ion concentration.  
 ALKALINE solution has  $[H^+]$  ions less than  $10^{-7}$ .

The concentration of  $[H^+]$  and  $[OH^-]$  can vary from  $1 - 10^{-14}$ .  
 SORENSON DEvised a convenient method for expressing  
 power of hydrogen ion concentration in terms of pH.

$$pH = \log \frac{1}{[H^+]} \text{ or } pH = -\log [H^+]$$

For example pH of water can be calculated as

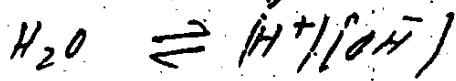
$$pH = -\log 1 \times 10^{-7} \text{ and } pOH = -\log [OH^-]$$

$$pH = 7 \quad pOH = -\log 10^{-7}$$

For neutral solution  $pH = 7$  A solution which has

pH greater than "7" is Alkaline solution and a solution whose pH is less than 7 is acidic solution.

PROOF  $pH + pOH = 14$ .



$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K_c [H_2O] = [H^+][OH^-]$$

$$K_w = [H^+][OH^-]$$

$$1 \times 10^{-14} = [H^+][OH^-]$$

Taking  $-ve$  log of both sides

$$14 = -\log[H^+] + (-\log[OH^-])$$

$$14 = pH + pOH$$

$[H^+]$	pH	RESULT
$10^0$	0	ACIDIC
$10^{-1}$	1	
$10^{-2}$	2	
$10^{-3}$	3	
$10^{-4}$	4	
$10^{-5}$	5	NEUTRAL
$10^{-6}$	6	
$10^{-7}$	7	BASIC
$10^{-8}$	8	
$10^{-9}$	9	
$10^{-10}$	10	
$10^{-11}$	11	
$10^{-12}$	12	
$10^{-13}$	13	
$10^{-14}$	14	

This sum of pH and pOH for aqueous sol. is always 14 at 25°C.

(See example No. ~~10~~ Text Book)

DETERMINATION OF pH OF SOLUTION.

There are two methods of determination of pH of solutions

(1) By use of indicators (2) By electrometric method.

2) BY INDICATORS The indicators may be used in solution

form or in the form of pH papers. However pH papers cannot be used for colored solutions.

ELECTROMETRIC METHOD It is more accurate method of

measuring pH of solution. The solution of unknown pH is separated from solution of known pH by thin glass membrane.

A potential difference is generated across membrane. This is amplified and measured directly with potentiometer. The pH is read directly from scale.

SIGNIFICANCE OF pK<sub>a</sub>

The equilibrium constants such as  $K_a$ ,  $K_b$ ,  $K_w$  and conc. of  $[H^+]$  and  $[OH^-]$  ions are usually very small numbers. Such numbers are usually written in exponential form. For example  $[H^+]$  in water =  $1 \times 10^{-7}$ .

$K_a$  for  $CH_3COOH = 1.8 \times 10^{-5}$ ,  $K_a$  for  $COOH = 5.4 \times 10^{-2}$

$K_a$  for  $H_2CO_3 = 4.4 \times 10^{-7}$

But such numbers are difficult to work out in some mathematical problems. Therefore these are usually expressed in terms of negative logarithm. To express a numerical value as negative log symbol "p" is used. When a symbol "p" precedes a symbol then it means take negative log of that value.

For example pK<sub>a</sub> means negative log of K<sub>a</sub> (acid diss constant)

pK<sub>b</sub> means " " " K<sub>b</sub> (base diss constant)

pH means negative log of  $[H^+]$  ion conc.

For example for formic acid  $K_a = 1.8 \times 10^{-4}$   
 $pK_a = -\log(1.8 \times 10^{-4}) = 3.74$

The smaller quantity the value of negative logarithm the larger the value of that quantity. For example

pH = 7 means  $[H^+] = 10^{-7}$

pH = 6 means  $[H^+] = 10^{-6}$

pH = -4 means  $[H^+] = 10^4$  larger value of  $[H^+]$

Similarly the larger the value of pK<sub>a</sub> the lesser is the value of K<sub>a</sub> and weaker is the acid. For example pK<sub>a</sub> of formic acid is 3.74 and pK<sub>a</sub> of acetic acid is 4.75 which means formic acid is stronger acid than acetic acid. Very strong acids have pK<sub>a</sub> value in negative which means they have v. large K<sub>a</sub>

pK<sub>a</sub> of  $HClO_4 = -10$   $K_a = 10^{+10}$

pK<sub>a</sub> of  $HBr = -9$   $K_a = 10^9$

Similarly smaller the value of  $K_b$  the larger is the value of  $K_a$  and stronger the base and vice versa. The symbol "p" is especially useful for expressing acidity or basicity of a solution. For example a solution having pH less than 7 has  $[H^+]$  ions greater than  $10^{-7}$  (i.e. water) hence it is acidic solution. A solution having pOH greater than 7 have high conc. of  $[OH^-]$  ions than water hence it is basic sol.

$pH + pOH = 14$  For aqueous solution.  
 If pH is known we can calculate pOH and vice versa.  
 If  $pH$  or  $pOH$  is known we can calculate  $[H^+]$  and  $[OH^-]$  conc. in solution  $pH = -\log[H^+]$

$$\text{Antilog}(-pH) = [H^+]$$

$$\text{Antilog}(-pOH) = [OH^-]$$

Q1-

WHAT ARE BUFFER SOLUTIONS? DISCUSS THEIR COMPOSITION, BUFFERING MECHANISM, pH AND APPLICATIONS OF BUFFERS.  
 Ans. - In laboratory a solution of definite pH is often required. The preparation of a solution at a definite pH is often difficult if solution comes in contact with water it absorbs  $CO_2$  and becomes acidic. If solution is stored in glass bottle alkaline impurities leached out from glass alters pH of solution.

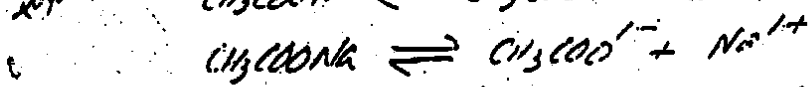
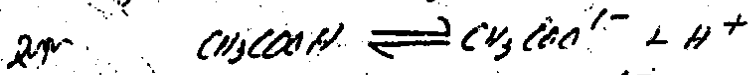
A solution which can keep its pH constant is called Buffer solution. It has following characteristics:  
 1) Its pH remains constant for fairly long time  
 2) Its pH remains constant on addition of small amount of acid or small amount of base.  
 3) Its pH remains constant on dilution.

This property of such a solution is called Buffer action. The capability of a buffer solution to maintain definite pH is called Buffer Capacity. The range of pH over which a buffer will function is called Buffer Range.

## BUFFER COMPOSITION

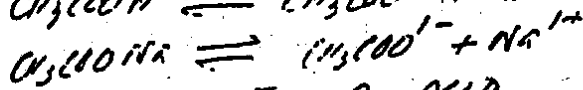
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1) A weak acid and its salt with strong base - e.g.  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  OR  $\text{H}_2\text{CO}_3$  and  $\text{NaHCO}_3$



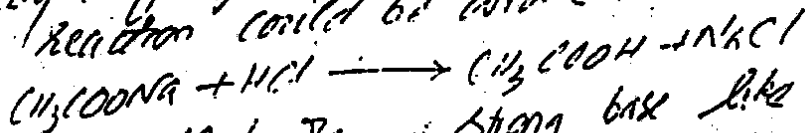
2) A weak base and its salt with strong acid e.g.  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$

BUFFERING MECHANISM / Let us consider how does a buffer solution maintain its pH almost constant

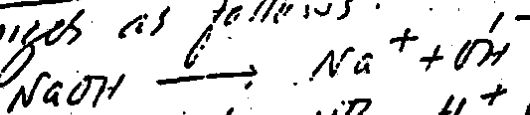


ADDITION OF SMALL AMOUNT OF ACID  
When a strong acid such as  $\text{HCl}$  is added it ionizes almost 100%  $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$

The conc of  $\text{H}^+$  ions in solution is temporarily increased. According to Lechatliers principle eq. no. 1 is shifted backward. The decrease in conc of  $\text{CH}_3\text{COO}^-$  is compensated by shifting eq. no. 2 in forward direction. The net reaction could be written as

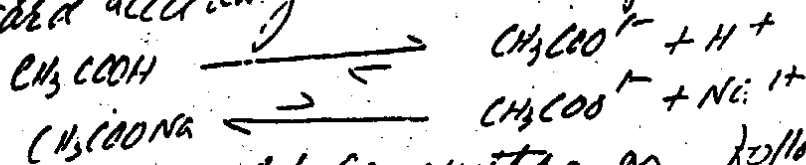


ADDITION OF BASE / When a strong base like  $\text{NaOH}$  is added it ionizes as follows

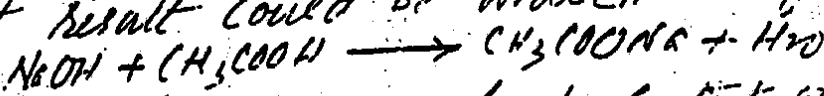


The  $\text{OH}^-$  produced react with  $\text{H}^+$  to form  $\text{H}_2\text{O}$

The conc of  $\text{H}^+$  ions is decreased temporarily. The eq. no. 1 is shifted forward and eq. no. 2 is shifted backward according to Lechatliers principle



The net result could be written as follows



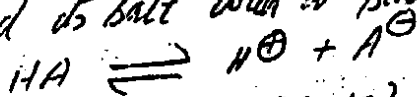
Thus pH of solution remains almost constant on addition of small amount of acid or base.

## pH OF BUFFER SOLUTION AND HENDERSON HASSSELBALCH EQUATION

The pH of buffer solution is mainly determined by two factors

- (i) The value of  $K_a$  of weak acid or  $K_b$  of weak base
- (ii) The ratio of concentration of weak acid and its conjugate base or conc. of weak base and its conj. acid

Let us consider a weak buffer solution produced by weak acid and its salt with a strong base:



$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} \quad \text{--- (1)}$$

$K_a \frac{[HA]}{[A^{\ominus}]} = [H^{\oplus}]$       by taking negative log of both sides

$$-\log K_a \frac{[HA]}{[A^{\ominus}]} = -\log [H^{\oplus}]$$

or  $pH = -\log K_a + \left( -\log \frac{[HA]}{[A^{\ominus}]} \right)$

$$pH = pK_a - \log \frac{[HA]}{[A^{\ominus}]}$$

$$pH = pK_a + \log \frac{[A^{\ominus}]}{[HA]} \quad \text{--- (2)}$$

Equation "2" is known as Henderson Hasselbalch equation

Since weak acid ionizes to a very little extent so this equation could be written as

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{Acid}]} \quad \left[ \begin{array}{l} \text{Anions are mostly} \\ \text{produced by salt} \end{array} \right] \quad \text{--- (3)}$$

Similarly a buffer solution produced by weak base and its salt with strong acid will produce solution of pH given by following eq

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]} \quad \text{--- (4)}$$

It is clear from above equations (3) & (4) that buffer solution can keep its pH and pOH constant but all buffer solutions do not have equal pH. The pH

of buffer solution will depend upon nature of weak acid  
i.e.  $K_a$  or the nature of weak base ( $K_b$ ) and <sup>relative</sup> conc. of weak  
acid and its salt or weak base its salt.

Example: - For example a buffer solution made by mixing  
0.5molar sodium acetate and 0.5m acetic acid has  $pH = 4.75$   
while a buffer solution of some conc. of carbonic acid  
and sodium bicarbonate will have  $pH = 6.4$  Similarly a  
buffer sol of weak base and its salt will have different pH.

BUFFER CAPACITY

The buffer capacity refers to the amount  
of acid or base that can be added to the buffer solution  
without changing its pH appreciably. The capacity of buffer  
solution depends upon absolute quantity of acid and salt  
used to prepare buffer solution. However pH of buffer sol.  
depends upon the relative conc. of acid and its salt.

MAXIMUM CAPACITY

The buffer has its maximum capacity at  
 $pH = pK_a$  or  $pOH = pK_b$  (i.e.  $\frac{[salt]}{[Acid]} = 1$  or  $\frac{[Base]}{[salt]} = 1$ )  
Whenever ratio of weak acid or weak base to salt conc. is  
less than 0.1 or greater than 10, the buffer solution  
loses its effectiveness. Since  $\log 0.1 = -1$  and  $\log 10 = 1$   
this means buffer range is about one pH unit on either  
side of  $pK$ .

"pH Range of buffer =  $pK_a \pm 1$

pOH range of buffer =  $pK_b \pm 1$

For example (acetic acid) buffer,  $pH$  effective range

is  $[Sodium\ acetate]$   
EFFECTIVE RANGE =  $4.74 \pm 0.1$   
= 4.374 To 5.174

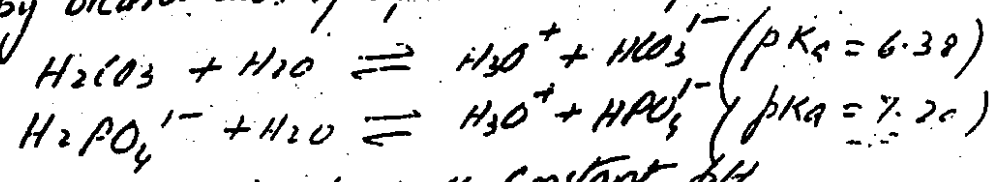
BUFFER RANGE It is defined as range of pH value  
over which a particular buffer system will function.

APPLICATIONS OF BUFFER SOLUTIONS

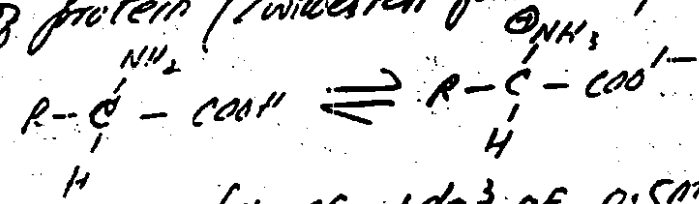
- 1) Buffer solutions are used in electroplating, manufacture  
of leather, photographic materials and dyes. These processes  
are greatly effected by pH changes.



- 2) Buffer solutions are used to calibrate pH of solution.
- 3) The bacteriological research, culture media are generally buffered to maintain constant pH required for growth of bacteria.
- 4) Buffers are very important in biological systems. The biochemical reactions in living things are very sensitive to pH changes. The rates of reactions mostly depend upon the pH of medium. For example human blood is buffered to pH = 7.4 by bicarbonates, phosphates and complex protein systems.



- 5) The study of reaction rates requires constant pH.
- 6) The protein study makes use of buffers. Solution, the degree of ionization of protein (zwitterion formation) depends upon pH of medium.



EXAMPLE WHAT IS EFFECT ON pH OF 1 dm<sup>3</sup> OF 0.5M CH<sub>3</sub>COOH - 0.5 M CH<sub>3</sub>COONa BUFFER SOLUTION BY ADDING 0.1 MOLE OF H<sub>3</sub>O<sup>+</sup> (STRONG ACID)  $K_a = 1.8 \times 10^{-5}$  FOR ACETIC ACID.

$K_a = 1.8 \times 10^{-5}$

$pK_a = -\log K_a$

$= -\log 1.8 \times 10^{-5} = 4.75$

$pH = pK_a + \log \frac{[SALT]}{[ACID]}$

$pH = 4.75 + \log \frac{0.5}{0.5}$

$pH = 4.75$

Thus initial pH of buffer sol. is 4.75.

When 0.1 mole of H<sub>3</sub>O<sup>+</sup> is added it will react with

CH<sub>3</sub>COO<sup>-</sup> ions to form acetic acid

$$H_3O^+ + CH_3COO^- \rightleftharpoons CH_3COOH + H_2O$$

0.1	0.5	0.5	zero
(0.1-0.1)	(0.5-0.1)	0.5+0.1	0+0.1
zero	0.4	0.6	0.1

$pH = pK_a + \log \frac{[SALT]}{[ACID]}$

$pH = 4.75 + \log \frac{0.4}{0.6}$

$pH = 4.57$

Thus there is very little change in pH of solution by addition of strong acid.