

**MODULE 111 – PRINCIPLES OF PHYSICAL AND INORGANIC CHEMISTRY**  
**UNIT 2 – CHEMICAL EQUILIBRIUM**

**COURSE OUTLINE**

What is chemical equilibrium? How can we write expressions for and deduce the values of  $K_c$  and  $K_p$ , and how can  $K_c$  and  $K_p$  be interconverted? What is Le Chatelier's principle and why is it useful?

What are heterogeneous equilibria? How can we write expressions for and deduce the values of  $K_{sp}$ , and how is this linked to solubility? What is the common ion effect?

What are acid-base equilibria? What is meant by the auto-ionisation, and ionic product, of water? How can we calculate the pH of strong and weak acids and bases from their molarity and vice versa? What is salt hydrolysis and how can we calculate the pH of salts from their molarity and vice versa? What are buffer solutions, how can we prepare them, how can we calculate their pH and why are they useful? What are acid-base indicators and how do they work? How can we choose suitable indicators for use in acid-alkali titrations?

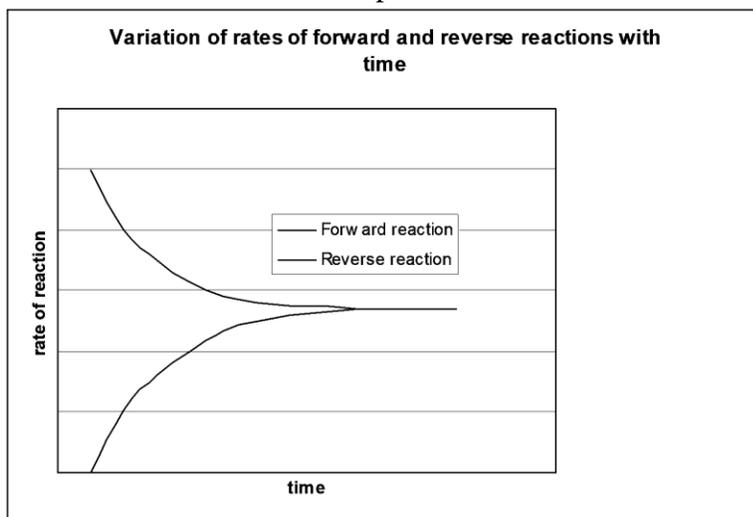
**CONTENTS**

1.	<i>Principles of chemical equilibrium; dynamic equilibrium, <math>K_c</math>, related calculations</i>
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3.	Gaseous equilibria, mole fraction, partial pressure and $K_p$ , relationship between $K_p$ and $K_c$ , related calculations
4.	Heterogeneous equilibria, solubility constants and solubility
5.	Introduction to acid-base equilibria; acid-base pairs, auto-ionisation of water, acids and bases in water
6.	pH and pOH of strong and weak acids and bases
7.	Salt hydrolysis and salt pH
8.	Buffer solutions
9.	Indicators and acid-base titrations
10.	Volumetric analysis: acid-base titrations

*Items in Italics are covered in SS Chemistry*

## 1. Principles of Chemical Equilibrium

- Reversible reactions are indicated by the sign  $\rightleftharpoons$ ; a reversible reaction is one in which the reverse reaction is able to take place to a significant extent
- Consider a reversible reaction  $A + B \rightleftharpoons C + D$ ; initially the rate of the reverse reaction is zero as the concentration of products is zero; as the reaction proceeds, the rate of the forward reaction decreases and the rate of the reverse reaction increases; eventually, the reaction will reach a stage where both forward and backward reactions are proceeding at the same rate; at this stage a dynamic equilibrium has been reached; the forward and reverse reactions are proceeding at the same rate and so there is no further change in the concentration of reactants and products:



- All reactions are reversible in theory; in some cases the reverse reaction is insignificant; in others, it is not allowed to take place because the product is removed as soon as it is formed; this is often the case in open systems, so dynamic chemical equilibria are most commonly found in closed systems

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## 2. Equilibrium Constants

- If the following reaction:  $wA + xB \rightleftharpoons yC + Zd$ , the relative concentrations of reactants and products in the system can be given by:

$$\frac{[C]^y[D]^z}{[A]^w[B]^x} = K_c$$

$K_c$  is a constant for a given equation at a given temperature and is known as the **equilibrium constant** of the reaction; if  $K_c$  and the initial amount of each reactant is known, the equilibrium concentration of each reactant and product can be calculated and vice versa, provided that the reaction is taking place at constant volume

- $K_c$  does depend on the stoichiometric coefficients; if the equation  $n(wA + xB \rightleftharpoons yC + Zd)$  were used, the equilibrium constant for the reaction  $K_c^1 = (K_c)^n$ ; in addition,  $K_c$  for the reverse reaction ( $K_c^r$ ) and the forward reaction ( $K_c^f$ ) are related as follows:  $(K_c^r) = (K_c^f)^{-1}$
- The units of the equilibrium constant vary, depending on the relative number of reactant and product species in the equation number of species involved; in general the units can be given by  $(\text{mol dm}^{-3})^{\Delta n}$ , where  $\Delta n$  is the change in the total number of species during the reaction
- In some cases, reactions take place at constant pressure, rather than at constant volume; in such cases the equilibrium constant at constant pressure ( $K_p$ ) should be used instead:
  - $K_p = \frac{p_C^y p_D^z}{p_A^w p_B^x}$  where  $p_A$  = partial pressure of A =  $\frac{n_A}{n_T} P$ , where P is the total pressure and  $n_T$  is the total number of moles
  - So  $K_p = \frac{\left(\frac{n_C}{n_T}\right)^y \left(\frac{n_D}{n_T}\right)^z}{\left(\frac{n_A}{n_T}\right)^w \left(\frac{n_B}{n_T}\right)^x}$  but  $P = \frac{n_T RT}{V}$  from the ideal gas equation (R = molar gas constant, T = temperature)
  - So  $K_p = \frac{\left(\frac{n_C RT}{V}\right)^y \left(\frac{n_D RT}{V}\right)^z}{\left(\frac{n_A RT}{V}\right)^w \left(\frac{n_B RT}{V}\right)^x} = \frac{[C]^y [D]^z}{[A]^w [B]^x} RT^{(y+z-w-x)} = K_c RT^{(y+z-w-x)}$
  - $y + z - x - w$  is the total change in the number of particles during the reaction, or  $\Delta n$
  - so  $K_p = K_c RT^{\Delta n}$
- If  $K_c$  or  $K_p$  is close to 1, it means that the position of equilibrium lies close to the middle of the reaction, which means that the equilibrium mixture contains similar quantities of reactants and products; if  $K_c$  or  $K_p \gg 1$ , it means that the position of equilibrium lies to the right of the reaction, which means that the equilibrium mixture contains significantly more products than reactants; if  $K_c$  or  $K_p \ll 1$ , it means that the position of equilibrium lies to the left of the reaction, which means that the equilibrium mixture contains significantly more reactants than products
- For reactions which are not at equilibrium, the value of  $\frac{[C]^y [D]^z}{[A]^w [B]^x}$  or  $\frac{p_C^y p_D^z}{p_A^w p_B^x}$  is called the reaction quotient  $Q_c$  or  $Q_p$ ; if  $Q < K$ , Q needs to increase before equilibrium is reached and the reaction will move to the right to reach equilibrium; if  $Q > K$ , Q needs to decrease before equilibrium is reached and the reaction will move to the left to reach equilibrium

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### 3. Le Chatelier's Principle

- If the conditions are changed after equilibrium has been established, the system may no longer be at equilibrium and may move in one direction or another to re-establish equilibrium; the direction in which the system will move to re-establish equilibrium can be predicted by Le Chatelier's principle: "If a constraint is imposed on a system at equilibrium, then the system will respond in such a way as to counteract the effect of that constraint"; such constraints can be the addition or removal of one of the reactants or products, a change in pressure, a change in temperature or the addition of a catalyst.
- If a reactant or product is added to or removed from a system at equilibrium, the system will no longer be at equilibrium and the concentrations will change until equilibrium is restored; Le Chatelier's principle predicts that if a reactant's concentration in a system is increased, the system will move to the right in order to decrease the concentration of that reactant, and vice versa; this can also be deduced by considering the effect on the reaction quotient  $Q$  of adding or removing a species; at equilibrium,  $K = Q$ , but if a change is then made which increases  $Q$ , the reaction will move to the left until  $Q$  has decreased back to the value of  $K$ , but if but if a change is then made which decreases  $Q$ , the reaction will move to the right until  $Q$  has increased back to the value of  $K$
- If the pressure is changed when a system is at equilibrium, the system may no longer be at equilibrium and the concentrations will change until equilibrium is restored; Le Chatelier's principle predicts that if the pressure in a system is increased, the system will move to decrease the pressure by moving in whichever direction reduces the total number of gas molecules, and vice versa; this can also be deduced by considering the effect on the reaction quotient  $Q$  of changing the pressure; if  $V$  in the  $K_c$  term is replaced by  $nRT/P$ , then  $P$  will appear in the equilibrium expression as  $P^{\Delta n}$ , so an increase in pressure will increase  $Q$  if  $\Delta n$  is positive and decrease  $Q$  if  $\Delta n$  is negative; the reaction will respond accordingly
- If the temperature is changed when a system is at equilibrium, the system may no longer be at equilibrium and the concentrations will change until equilibrium is restored; if the forward reaction is exothermic, then the temperature of the system will rise if the forward reaction takes place; the reverse reaction will therefore be endothermic, and the temperature of the system will fall if the reverse reaction takes place; Le Chatelier's principle therefore predicts that an increase in temperature will favour the endothermic reaction, and that a decrease in temperature will favour the exothermic reaction; if the forward reaction is exothermic, then an increase in temperature will cause the system to shift to the left, and a decrease in temperature will cause the system to shift to the right, and vice versa; changes in  $Q$  cannot be used to predict the effect of a change in temperature because  $K$  itself varies with temperature
- The addition of a catalyst will have no effect on the position of equilibrium; it will increase the rate of the forward and reverse reactions, but by the same amount. The position of equilibrium will thus be unchanged

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#### **4. Heterogeneous Equilibria**

- A heterogeneous equilibrium is one in which the reactants and products are not all in the same phase; this can be a gaseous mixture with some solid or liquid species, or an aqueous or liquid mixture with some solid species
- In aqueous and liquid equilibria, the concentration terms for solids can be considered to be independent of the quantity of solid present; they can therefore be included in the value of the equilibrium constant and are not included in the equilibrium expression
- This is significant when considering the solubility of sparingly soluble ionic compounds, which set up an equilibrium with the aqueous solution as follows:  $A_xB_y(s) \rightarrow xA^{m+}(aq) + yB^{n-}(aq)$ ; the equilibrium constant for such an equilibrium system would be given by  $K_{sp} = [A^{m+}]^x[B^{n-}]^y$ ;  $K_{sp}$  is known as the solubility product of the compound; this can be used to predict the solubility of different ionic compounds under different circumstances
- It can be concluded from the  $K_{sp}$  expression that the solubility of a compound in aqueous solution will be significantly reduced if one or other of the ions is already present in solution; this is known as the common ion effect
- In gaseous equilibria, the concentration terms for both solids and gases can be considered to be independent of the quantity of those substances present; they can therefore be included in the value of the equilibrium constant and are not included in the equilibrium expression; the  $K_p$  expression for heterogeneous reactions should therefore include the partial pressures of the gaseous terms only

## 5. Acid-base equilibria

### (a) Bronsted-Lowry theory

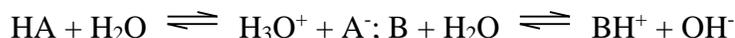
- Bronsted-Lowry definition for acids and bases is the most useful one for considering reversible reactions between acids and bases; an acid is a substance which can behave as a proton ( $\text{H}^+$ ) donor - any species containing H attached to an electronegative atom can behave as an acid;  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ ; **a base is a substance which can behave as a proton acceptor**; any species which has a lone pair of electrons can thus behave as a base;  $\text{B} + \text{H}^+ \rightleftharpoons \text{BH}^+$

- The species formed when an acid gives up a proton can accept a proton and thus behave as a base, and the species formed when a base accepts a proton can give up a proton and behave as an acid:



HA and  $\text{A}^-$ , and  $\text{BH}^+$  and B, are conjugate acid-base pairs; HA and  $\text{BH}^+$  are the conjugate acids of  $\text{A}^-$  and B respectively;  $\text{A}^-$  and B are the conjugate bases of HA and  $\text{BH}^+$  respectively; thus every acid-base reaction can be considered to reach an equilibrium with one acid and one base on each side; and the conjugate acids and bases on the other side:  $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{BH}^+$

- Not all acids are equally good proton donors; in fact some give up their protons very reluctantly; conversely, some bases accept protons readily whereas others accept protons very reluctantly; acids and bases can be classified as strong or weak based on their ability to donate and accept protons respectively; the stronger the acid, the weaker its conjugate base and vice versa
- Most common acid-base reactions take place in aqueous solution, and thus acids and bases are generally defined by the way in which they react with water; the Arrhenius definition of acids and bases can be considered a special case of the Bronsted-Lowry definition – when Arrhenius acids react with water, water behaves as a base; when Arrhenius bases react with water, water behaves as an acid:



In strong acids and bases, this dissociation is complete; in weak acids and bases, this dissociation is partial; the dissociation of Arrhenius acids in water is often simplified to  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ ;

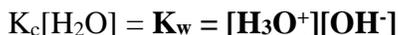
- Water is an example of a species which can behave as an acid and a base; such species are said to be **amphoteric**; amphoteric species have a conjugate acid and a conjugate base and can undergo acid base reactions with themselves:  $\text{AH} + \text{AH} \rightleftharpoons \text{A}^- + \text{AH}_2^+$

Water reacts with itself as follows:  $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ ; this is known as the auto-ionisation of water and is a feature of every aqueous solution, including pure water

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**(b) Auto-ionisation of water**

- The equilibrium constant for this dissociation can be written as follows:  $K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$ ; the concentration of water in aqueous solution ( $55 \text{ mol dm}^{-3}$ ) is not changed significantly by this dissociation, since the proportion of water which dissociates into its ions is small; the water concentration can thus be assumed to be constant and it can be incorporated into  $K_c$  as follows:



This expression is known as the **ionic product of water** and has a value of  $1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$  at  $25^\circ\text{C}$ ; this value is a constant at a given temperature; the ionic product of water is slightly higher at higher temperatures, suggesting that the dissociation is endothermic;  $[\text{H}_3\text{O}^+]$  is often simplified to  $[\text{H}^+]$

- The pH of pure water can be calculated from this expression:  
in pure water  $[\text{H}^+] = [\text{OH}^-]$  so  $K_w = [\text{H}^+][\text{OH}^-] = [\text{H}^+]^2$  so  $[\text{H}^+] = \sqrt{K_w} = 1 \times 10^{-7} \text{ mol dm}^{-3}$  and  $\text{pH} = 7.0$
- The value of  $K_w$  can be used to calculate  $[\text{OH}^-]$  if  $[\text{H}^+]$  is known, and the value of  $[\text{H}^+]$ , and hence the pH, if  $[\text{OH}^-]$  is known; this can be used to calculate the pH of strong bases

**(c) Dissociation constants for weak acids and bases**

- Weak acids dissociate partially in water and reach an equilibrium as follows:

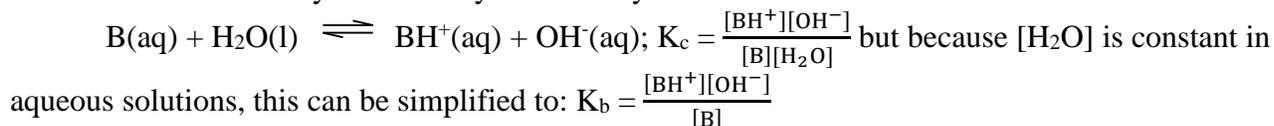


The equilibrium expression for the dissociation of a weak acid is as follows:  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$

$K_a$  is known as the **acid dissociation constant** for the acid and has units of  $\text{mol dm}^{-3}$ ; it is often quoted as  $\text{p}K_a = -\log_{10}K_a$ ; the larger the  $K_a$ , the greater the degree to which the acid dissociates into its ions and the stronger the acid

- The pH of weak acids can be calculated if the  $K_a$  and molarity of the acid are known; the calculation can be simplified by ignoring the auto-ionisation of water, and hence assuming that all of the  $\text{H}^+$  has come from the acid; this means that  $K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$ ; the calculation can be further simplified by assuming that  $x$  is small and hence  $\text{C(1-x)} \approx \text{C}$ ; substituting  $\text{C}$  and  $\text{x C}$  into the  $K_a$  expression gives  $K_a = \frac{\text{x}^2\text{C}}{\text{C}}$ ; therefore  $\text{x} = \sqrt{\frac{K_a}{\text{C}}}$ ; note that  $x$  decreases as  $\text{C}$  increases – this is consistent with Le Chatelier's principle;  
 $[\text{H}^+] = \text{x C} = \text{C}\sqrt{\frac{K_a}{\text{C}}} = \sqrt{K_a\text{C}}$ ; this expression means that if any two of  $[\text{H}^+]$ ,  $K_a$  and  $\text{C}$  are known, the other can be calculated, as well as the pH; these calculations can be done without making the  $\text{C(1-x)} \approx \text{C}$  approximation but it is then necessary to solve a quadratic; this is necessary if  $x$  is appreciable

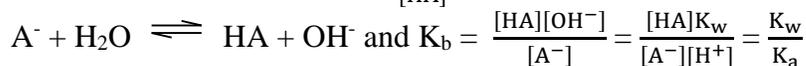
- Weak bases can be analysed in a very similar way:



$[\text{OH}^-] = \text{x C} = \text{C}\sqrt{\frac{K_b}{\text{C}}} = \sqrt{K_b\text{C}}$ ; this expression means that if any two of  $[\text{OH}^-]$ ,  $K_b$  and  $\text{C}$  are known, the other can be calculated, as well as the pH

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- The  $K_a$  of a weak acid can be directly related to the  $K_b$  of its conjugate base by considering the following equations:  $HA \rightleftharpoons H^+ + A^-$  and  $K_a = \frac{[H^+][A^-]}{[HA]}$



This means that if the  $K_a$  of weak acid is known,  $K_b$  of its conjugate base can be deduced and vice versa

**(d) Salt hydrolysis**

- Salts are composed of the conjugate acid and base of the base and acid which were neutralised to make them
  - Salts which are made from strong acids and strong bases have no significant acid-base properties of their own; this is because the  $K_a$  and  $K_b$  values of the strong acid and the strong base respectively are so high that the  $K_a$  and  $K_b$  values of the conjugate acid and base respectively extremely small and can be ignored; such salts can be considered neutral
  - If a salt is made from a weak acid; the conjugate base of the weak acid will have a  $K_b$  value sufficiently large to cause a significant reaction with water; such salts are alkaline and have pH values greater than 7; similarly is the salt is made from a weak base, the conjugate acid of the weak base will have a  $K_a$  value sufficiently large to cause a significant reaction with water; such salts are acidic and have pH values lower than 7; the tendency of cations or anions in salts to react with water resulting in acidic or alkaline solutions is known as **salt hydrolysis**; in salts of weak acids and weak bases, both cation and anion will hydrolyse; the resulting pH of the solution will depend on the relative magnitude of  $K_a$  and  $K_b$  of the cation and the anion in the salt

**(e) Very dilute solutions**

- In all the calculations considered so far, the  $H_3O^+$  present due to the auto-ionisation of water has been ignored. This is normally a reasonable assumption, since water only ionises very slightly ( $[H^+] = 1 \times 10^{-7} \text{ mol dm}^{-3}$  in pure water); in very dilute solutions, however, the  $H^+$  present due to the auto-ionisation of water is significant and cannot be ignored; in strong acids and bases it is relatively easy to calculate the effect of the dissociation of water: consider a strong acid of molarity  $C$ , which will dissociate to give  $H^+$  ions of concentration  $C$ ; consider also the dissociation of water to give  $[H^+] = [OH^-] = x$   
 In total,  $[H^+] = C + x$  and  $[OH^-] = x$ , so  $[H^+][OH^-] = K_w = x(C + x)$ , so  $x^2 + Cx - K_w = 0$

So  $x = \frac{\sqrt{(C^2 + 4K_w)} - C}{2}$ ; if  $C$  is significant,  $C^2 + 4K_w \approx C^2$  and  $x \approx 0$ ; if  $C = 0$ ,  $x = \sqrt{K_w}$ ; if  $C$  is small but not 0,  $x$  can be calculated and the pH calculated from  $[H^+] = C + x$

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**(f) Polyprotic acids and bases**

- Some acids are capable of donating more than one proton and some bases are capable of accepting more than one proton; these are known as polyprotic acids and bases respectively:



- In such acids and bases, each successive dissociation will have its own  $K_a$  or  $K_b$  value:



- $K_{a1}$  is always greater than  $K_{a2}$ , which is always greater than  $K_{a3}$ ; furthermore, the dissociations are not independent of each other but the  $H^+$  from the first dissociation suppresses the subsequent dissociations, so in many cases only the first dissociation is significant; an analogous situation occurs in polyprotic bases
- Polyprotic acids and bases form more than one salt, depending on how many protons have been accepted or lost; salts formed from the partial neutralisation of polyprotic acids are called acid salts; they still have available protons and their own  $K_a$  value ( $K_{a2}$  or  $K_{a3}$ ); they will also have a  $K_b$  value resulting from the  $K_{a1}$  or  $K_{a2}$  of their conjugate acid; they are thus amphoteric and will set up a variety of equilibria in water; their net behaviour will depend on the relative magnitude of  $K_a$  and  $K_b$ ; salts formed from the partial neutralisation of polyprotic bases are called base salts; they will have their own  $K_b$  value but also a  $K_a$  value resulting from the  $K_b$  of the conjugate base; salts formed from the complete neutralisation of polyprotic acids will be polybasic and vice versa; most salts formed from polyprotic acids and bases are likely to undergo some form of salt hydrolysis
- Polyprotic acids, bases and their salts form several equilibria simultaneously with water and their pH calculations are complex

**(g) Buffer Solutions**

- A buffer solution is a solution which can resist changes in pH on addition of small quantities of acid or alkali or on dilution; buffer solutions are a mixture of a weak acid and a weak base; the weak acid neutralises any  $OH^-$  added and the weak base neutralises any  $H^+$ , but the acid and the base must both be sufficiently weak not to react significantly with each other; most buffer solutions are mixtures of weak acids and their conjugate bases ( $HA$  and  $A^-$ ) or weak bases and their conjugate acids ( $B$  and  $BH^+$ ); these mixtures are easy to analyse because they only form a single equilibrium
- Buffer solutions form the following equilibrium in water:  $HA \rightleftharpoons H^+ + A^-$
- $K_a = \frac{[H^+][A^-]}{[HA]}$ ,  $[H^+] = \frac{K_a[HA]}{[A^-]}$ ,  $pH = pK_a + \log \frac{[A^-]}{[HA]}$  (Henderson-Hasselbalch equation)
- For basic buffers,  $K_b = \frac{[BH^+][OH^-]}{[B]}$ ,  $[OH^-] = \frac{K_b[B]}{[BH^+]}$ ,  $pOH = pK_b + \log \frac{[BH^+]}{[B]}$  so  $pH = pK_w - pK_b - \log \frac{[BH^+]}{[B]}$
- unlike in weak acids, both  $[HA]$  and  $[A^-]$  are similar and much larger than  $[H^+]$ ; the simplification  $[H^+][A^-] = [H^+]^2$  therefore no longer applies, the same is true with  $[B]$  and  $[BH^+]$  in basic buffers

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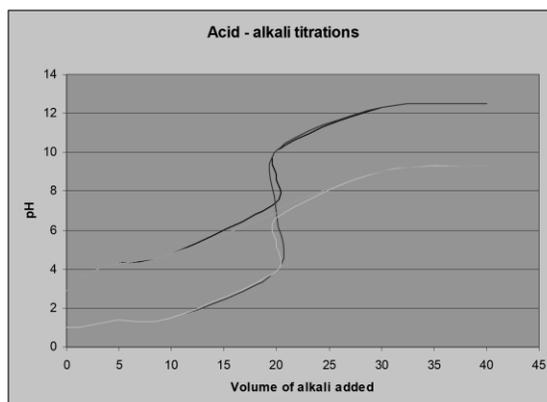
- The reaction is therefore able to proceed in both directions to a significant extent; on addition of  $H^+$ , the reaction moves left to reduce  $[H^+]$ ,  $[HA]$  will increase slightly and  $[A^-]$  will decrease slightly, causing only a slight decrease in pH; the addition of  $OH^-$  removes  $H^+$  so the reaction moves right to replace  $H^+$ ,  $[HA]$  will decrease slightly and  $[A^-]$  will increase slightly, causing only a slight increase in pH
- this works until the amount of  $H^+$  added exceeds the amount of  $A^-$  present, or the amount of  $OH^-$  added exceeds the amount of  $HA$  present, in which case the buffering capacity of the solution has been exceeded and the solution is no longer able to behave as a buffer
- basic buffers work in a very similar way
  
- On dilution, the pH does not change significantly because the ratio  $\frac{[A^-]}{[HA]}$  does not change; both  $A^-$  and  $HA$  dissociate more to compensate for the dilution
  
- A buffer does not have to a mixture of a weak acid and its conjugate base; any mixture of a weak acid and a weak base will have the same effect; any amphoteric substance with significant values of both  $K_a$  and  $K_b$  can behave as a buffer
  
- Buffers are extremely useful whenever the pH needs to be kept within certain limits, as is the case with many biochemical processes; blood is buffered within pH limits of 6.8 – 7.4 by a mixture of dissolved  $CO_2$  ( $H_2CO_3$ ) and its conjugate base  $HCO_3^-$ ; the precise pH can be set by choosing an acid with a  $pK_a$  value close to the desired pH and mixing it with its conjugate base in the ratio required to achieve the required pH
  
- Buffer solutions can be prepared either by mixing the weak acid with the weak base, or by partial neutralisation of the weak acid or base

### **(h) Titrations and Indicators**

- During titrations between acids and alkalis, the pH of the solution changes very sharply within two drops on either side of the equivalence point as the solution changes from acidic to alkaline (or vice versa); the equivalence point of the titration is the mid-point of the steep section of the titration curve
  
- The pH of the mixture can be calculated at any point during a titration; how this is done depends on whether the acid and base are strong or weak:
  - If both acid and alkali are strong, then the pH can be deduced by considering the number of moles of  $H^+$  or  $OH^-$  remaining, assuming that they react completely until one runs out; this method should also be used when a strong acid or base is in excess
  - If a strong acid is added to a weak base, or a strong base is added to a weak acid, so that the weak base or weak acid are in excess and therefore only partially neutralised, a buffer solution is established and its pH can be calculated by considering the relative amounts of  $HA$  and  $A^-$  (or  $B$  and  $BH^+$ ) in the mixture; a particularly useful situation occurs at half-neutralisation, when  $[HA] = [A^-]$  and therefore  $pH = pK_a$ ; this means that the  $pK_a$  of the acid can be directly read from the pH titration curve
  - The pH at the equivalence point can be deduced from consideration of any salt hydrolysis taking place
  - Weak acid-weak base titrations result in multiple equilibria existing simultaneously and are not easily analysed

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- The titration curves for all the different possible titrations can be sketched on the same graph as follows:



Type of titration	pH at equivalence point	pH change at equivalence point
Strong acid - strong base	7.0	4 to 10
Weak acid - strong base	Approx 8.5	7 to 10
Strong acid - weak base	Approx 5.5	4 to 7
Weak acid - weak base	Approx 7	No sudden change

- The pH and the pH changes at the equivalence point are guidelines only; for strong acids and strong bases, the pH depends on the molarities; for weak acids and weak bases, the pH depends on the molarities and the dissociation constants

- An acid-base indicator is a weak acid which dissociates to give an anion of a different colour; consider a weak acid HIn: 
$$\text{HIn(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{In}^-(\text{aq})$$

Colour 1 Colour 2

HIn and its conjugate base In<sup>-</sup> are different colours; the colour of the indicator depends on the relative concentrations of the two species, which in turn depends on the pH; if the solution is strongly acidic, the above equilibrium will be shifted to the left and HIn (colour 1) will dominate; if the solution is strongly alkaline, the above equilibrium will shift to the right and In<sup>-</sup> (colour 2) will dominate

- The pH at which HIn and In<sup>-</sup> are present in equal amounts is called the end-point of the indicator; it depends on the indicator dissociation constant K<sub>In</sub> as follows:

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \text{ so } [\text{H}^+] = [\text{H}^+] = \frac{K_{\text{In}}[\text{HIn}]}{[\text{In}^-]}, \text{ so when } [\text{HIn}] = [\text{In}^-], [\text{H}^+] = K_{\text{In}} \text{ and } \text{pH} = \text{p}K_{\text{In}}$$

Typically, one colour will dominate the other if its concentration is more than 10 times the other, which would happen if  $\text{pH} < \text{p}K_{\text{In}} - 1$  (Colour 1) or  $\text{pH} > \text{p}K_{\text{In}} + 1$  (Colour 2); in between these pH values, when  $\text{pH} = \text{p}K_{\text{In}} \pm 1$ , an intermediate colour would appear; this serves as a general rule only; the exact pH range over which an indicator changes colour depends on the relative intensity of the two colours and varies from indicator to indicator

**MODULE 111 – PRINCIPLES OF PHYSICAL AND INORGANIC CHEMISTRY**  
**UNIT 2 – CHEMICAL EQUILIBRIUM**

- Indicators are used in acid - alkali titrations in order to find the equivalence point of the titration; if they are to determine the equivalence point accurately, they must undergo a complete colour change at the equivalence point; this means that the pH range of the colour change (ie the end-point of the indicator) must fall completely within the pH range of the equivalence point; not all indicators can therefore be used for all titrations, and indicators must be chosen carefully so that the end-point of the indicator matches the pH range at the equivalence point