OUR LADY OF GOOD COUNSEL S.S.S GAYAZA

S.6 PHYSICAL CHEMISTRY HOLIDAY WORK TERM1, 2024

QN1.

The pH of s 0.001M solution of benzoic acid C₆H₅COOH is 3.59. Calculate

- (i) the dissociation constant of the acid
- (ii) The pK_a value of the acid
- (iii) the degree of dissociation at concentration given

QN2

(a) Write an expression for the acid dissociation constant (K_a) of ethanoic acid in the following equilibrium

CH₃COOH (aq) \leftrightarrow CH₃COO⁻(aq) + H⁺(aq)

- (b) State the relationship between pK_a and K_a
- (c) Given that the approximate value of K_a for ethanoic acid is 1.8x10⁻⁵moldm⁻³, calculate
 (i) The pK_a
 - (ii) the percentage ionization of acid in a 1M aqueous solution
- (d) The p K_a values of (CH₃)₃CCOOH and Cl₃COOH at 20^oC are 5.50 and 0.65 respectively. Which is a stronger acid?

QN3

Chloric (I) (hypochlorous) acid HClO, is a weak acid; $K_{a \text{ of}} \text{HClO} = 3.2 \text{ x } 10^{-8} \text{ moldm}^{-3}$.

- (a) Calculate the [H⁺] and [$^{-}$ OH] in 1.25 x 10 $^{-2}$ M HClO.
- (b) What is the pH of 1.25×10^{-2} M hypochlorous acid?

QN4

(a) At 25°C, ammonia has a base ionization constant $K_b = 1.8 \times 10^{-5} \text{moldm}^3$.

$$K_b = \frac{[NH^+][0H^-]]}{[NH_3]}$$

(b) Calculate the concentration of [⁻OH] in 0.1M ammonia solution at 25^oC. State any assumption

QN5

Calculate the concentration of hydroxide ion in 0.1M NH₄OH (Kb = 1.75×10^{-5} moldm⁻³)

ON6

Calculate the pH of 0.25M NaOH solution.

ON 7

Calculate the basic ionization 4constant for 0.03M ammonia, given that the pH of this ammonia is 10.6.

ON 8

A 0.01M solution of ammonia is 4.0% ionized

- (a) Calculate the pH of the solution, $(K_{w = 10^{-14}} \text{ mol}^2 \text{dm}^{-6} (3 \text{ marks})$ (b) Determine the base dissociation constant (3marks)

ON 9

- (a) Write an expression of pH
- (b) Calculate the pH of a0.05M sodium hydroxide solution, $(K_{w = 10^{-14}} \text{ mol}^2 \text{dm}^{-6})$ (2marks)
- (c) State the effect of dilution on pH of sodium hydroxide solution? give a reason for your answer

ON10

The second dissociation constant of a dibasic acid is $4.39 \times 10^{-5} \text{ mol}^2 \text{dm}^{-6}$ at 25° C.

- (a) Calculate the degree of ionization of 0.01M solution of the acid
- (b) Sketch a graph to show how the degree of dissociation varies with dilution.

ON 11

A solution containing 2.3 x 10⁻⁶ moldm⁻³ of aluminium hydroxide completely ionizes in water, (Kw $=10^{-14}$ mol²dm⁻⁶).

- (a) Write equation for the reaction of aluminium hydroxide $(1 \frac{1}{2} \text{ mark})$
- Calculate the pH of the resultant solution (3marks) (b)

BUFFERS

QN12

- a) Define the term a 'buffer' solution
- b) Calculate the mass of sodium ethanoate that should be added to 1 litre of 0.1M ethanoic acid in order to produce a solution of pH = 4.0. (Ka = $1.8 \times 10^{-5} \text{ moldm}^{-3}$)
- c) State what would happen to the pH of the solution in (b) if small amount of the following were added:
 - i. sodium hydroxide solution
 - ii. hydrochloric acid
- d) State one biological application of a buffer solution

QN 13

- (a) Ethanoic is a weak acid
 - (i) Explain what is meant by a 'weak acid'. (2marks)
 - (ii) Calculate the pH of a 0.05M ethanoic acid solution (Ka = 1.8×10^{-5} moldm⁻³). State any assumption you make
- (b) (i) Explain what is meant by a 'buffer solution'
 - (ii) Discuss the action of a buffer solution (5marks)
- (c) A solution was made by dissolving7.2g of ethanoic acid and 12.0g of sodium ethanoate to make 1 liter of solution. To the solution was added 0.8cm³ of 1M HCl. Calculate the pH of the solution. State any assumption you make.

QN 14

- (a) What is meant by the term buffer solution?
- (b) Calculate the mass of sodium ethanoate that should be added to 1dm^3 of 0.1M ethanoic acid in order to give a solution whose pH is 4. State any assumption made. $K_a(\text{CH}_3\text{COOH} = 1.75 \text{ x } 10^{-5} \text{moldm}^{-3})$ (4marks)

QN15.

 100 cm^3 of a solution containing 1.83g of sodium hydroxide dissolved in 250 cm³ of aqueous solution was added to and thoroughly mixed with 200 cm^3 of 0.2M ethanoic acid.

- (a) Calculate the PH of the resultant solution
- (b) Calculate the PH of the resultant solution if
 - (i) 1.5 cm^3 of 0.2M sodium hydroxide solution were added to the original solution
 - (ii) 2.0 cm^3 of 0.3M ethanoic acid were added to the original solution

HYDROLYSIS OF SALTS

QN16

Sodium benzoate undergoes hydrolysis when dissolved in water

(a) Write an equation for hydrolysis of sodium benzoate

 $C_6H_5COO^-(aq) + H_2O(l) \quad \leftrightarrow \quad C_6H_5COOH(aq) + OH^-(aq)$

(b) Write an expression for the hydrolysis constant K_h .

$$K_h = \frac{[C_6H_5C00H][0H^-]}{[C_6H_5C00^-]}$$

- (c) The hydrolysis constant of sodium benzoate is 1.6×10^{-5} moll⁻¹.
- (i) Calculate the concentration of the hydroxide ions in a 0.10M sodium benzoate at 25° C (Kw = 1 x10⁻¹⁴ mol²dm⁻⁶) (4marks)

QN1 7

Phenylamine hydrochloride, $\bigvee_{i=1}^{NH_3Cl}$ undergoes

hydrolysis when dissolved in water. Write equation for the reaction

- (b) A 0.2M solution of phenylamine hydrochloride has a pH of 3.5. Calculate
 - (i) The molar concentration of hydrogen ions in solution (2marks)
 - (ii) The hydrolysis constant K_h of phenyl hydrochloride.

QN18

Ammonia chloride undergoes hydrolysis when dissolved in water according to the equation

 $NH_4^+(aq) \leftrightarrow NH_3(aq) + H^+(aq)$

If the hydrolysis constant for ammonia hydrochloride, K_h is 5.6 x 10⁻¹⁰, calculate

- (i) The pH of 0.1M solution of ammonium chloride
- (ii) The percentage hydrolysis of 0.1M solution of ammonium chloride

SOLUBILITY OF SPARINGLY SOLUBLE IONIC COMPOUNDS IN WATER

When a sparingly soluble salt such as silver chloride or barium sulphate, is added to water, a little dissolves and produces ions in solution. Equilibrium is established between the ions and the solid salt when the rate at which ions leave the crystal frame work of the solid is equal to the rate at which they are deposited again. Since the solubility is very small, the ions present in the liquid are few in number and are so far apart that they are free from mutual interference. We can therefore say that in the very dilute saturated solution the solution is completely dissociated.

With a solution of a sparingly soluble electrolyte AxBy in contact with the solid the dissociation can be expressed as follows:

 $AxBy + aq \quad \leftrightarrow \qquad xA^{y+} + yB^{x-}$ $K_c = \frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y][aq]}$

Since the salt is only slightly dissociated in water, the $[A_x B_y]$ and [aq] are constant

thus, $K_c[A_xB_y][aq] = K_{sp} = [A^{y+}]^x[B^{x-}]^y$

The constant K_{sp}/K_s is the solubility product of the electrolyte, AxBy. The solubility product of a sparingly soluble electrolyte is the product of the concentration of ions in a saturated solution raised to corresponding Stoichiometric ration in the salt. The higher the K_{sp} is the higher the solubility of the salt.

Example1

The solubility of silver chloride at 18° C is 1.46×10^{-3} gdm⁻³. What is the solubility product (Ag =108, Cl = 35.5)

Solution

Note that in the calculation of solubility products the concentrations are expressed in **moldm**⁻³ or **moll**⁻¹

Mass of 1 mole of AgCl = 108 + 35.5 = 143.5g

Solubility of AgCl = $\frac{1.46 \times 10^{-3}}{143.5}$ = 1.0 x 10⁻⁵ moldm⁻³

Since one 'molecule' of silver chloride furnishes on dissociation one Ag^+ ion and one Cl^- ion, and since the dissolved silver chloride is completely dissociated in ions

$$K_{sp} = [Ag^+][Cl^-] = (1 \ge 10^{-5})(1 \ge 10^{-5})$$

= 1 \times 10^{-10}mol^2 dm^{-6}

Example 2

The solubility of calcium hydroxide in water at 20° C is 2.78gdm⁻³. What is the solubility product? (Ca = 40, O = 16, H = 1)

Solution

Molarity of Ca(OH)₂ = $\frac{2.78}{[40+2(16+1)]} = 0.0376$ moldm⁻³

 $[Ca^{2+}] = 0.0376 \text{moldm}^{-3}$

 $[OH^{-}) = 2 \ge 0.0376 = 0.0752 \text{ moldm}^{-3}$ $K_{sp} = [Ca^{2+}][OH^{-}]^2 = 0.0376 \ge (0.0752)^2$ $= 2.13 \ge 10^{-4} \text{ mol}^3 \text{ dm}^{-9}$

Limitation to the solubility product concept

- 1. Salts like potassium nitrate of relatively high solubility, do not possess solubility products because the law of mass action does not hold in their case. The solubility product concept is only valid for saturated solution in which the total concentration of ions is no more than about 0.01M
- 2. The solubility product constant, like all other equilibrium constants change with temperature; consequently, the temperature at which solubility product is measured should always be specified unless it relates to the standard temperature of 298K or 25° C.

Application of solubility product concept

(a) The common ion effect

This is the reduction in the solubility of a sparingly soluble salt in a solution in which it has a common ion.

Although the solubility product of a particular salt is constant at a constant temperature, the concentrations of the individual ions may vary over a very wide range. When a saturated solution is obtained by dissolving the pure salt in water the concentration of the ions produced are in the ratio determined by the stoichiometry of the compound. E.g. concentration of Ag^+ and CrO_4^{2-} ions in pure saturated silver chromate solution must be in ration 2:1. However, when a saturated solution is obtained by mixing two solutions containing a common ion (such as Ag_2CrO_4 and $AgNO_3$) there may be a big difference in the concentration of the ions in solution.

QN1 9

Calculate the solubility of BaSO₄ in

(i) Water?

(ii) in 0.1M sodium sulphate solution?

 $(K_{sp} = 1 \ge 10^{-10} \text{mol}^2 \text{dm}^{-6})$

QN20

- (a) Describe how the solubility product of magnesium hydroxide in water can be determined (6marks)
- (b) (i) A saturated solution of magnesium hydroxide in water contains 1.44×10^{-4} moles of magnesium hydroxide per liter of solution at 25°C. Calculate the value of the solubility product, K_{sp} , of magnesium hydroxide at 25°C. (3marks)

(ii) Solid magnesium hydroxide was shaken with a 0.1M solution of magnesium nitrate until equilibrium was attained at 25° C. Calculate the amounts of magnesium hydroxide, in grams per liter that dissolved.

(c) Equations of some reaction are given below AgCl(s)

$$\leftrightarrow \qquad \operatorname{Ag}^{+}(\operatorname{aq}) + \operatorname{Cl}^{-}(\operatorname{aq}) K_{1} = 1.7 \times 10^{-10}$$

$$\operatorname{Ag}^{+}(\operatorname{aq}) + 2\operatorname{NH}_{3}(\operatorname{aq}) \leftrightarrow \qquad \operatorname{Ag}(\operatorname{NH}_{3})^{2+} K_{2} = 1.7 \times 10^{7}$$

(i) Derive an expression in terms of K_1 and K_2 for the equilibrium constant for the following reaction:

 $AgCl(s) + 2NH_3(aq) \leftrightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$ (3marks) (ii)Calculate the value of equilibrium constant in (i) (2marks)

QN21

Lead (II) sulphate is sparingly soluble in water.

- (a) Write expression for the solubility product of lead (II) sulphate (1mark)
- (b) 5g of lead sulphate was shaken with 1dm^3 of water. Determine the percentage of lead (II) sulphate that dissolved. ($K_{sp} = 1.6 \times 10^{-8}$, Pb = 207, S= 32, O=16) (4marks)
- (c) If 0.05M sulphuric acid was used instead of water in (b), calculate the percentage of Lead (II) sulphate that dissolved and state any assumption you make (4marks)

QN22

- (a) Write equation for solubility of silver bromide in water at 25^{0} C
- (b) If the solubility product of silver bromide at 25° C is 5.0 x 10^{-13} mol²dm⁻⁶, calculate the solubility in

gdm⁻³ at 25⁰C of silver bromide in:

i) water	(3marks)
(ii) 0.1M hydrobromic acid. (State any assumption made)(c) State two methods that can be used to determine the solubility product	(3marks)
	(2marks)

NOTE: Research and make notes on:

Common ion effect

PH change and PH Curves during titrations of acids with bases of different strengths