Our country, our future

525/1

S6 CHEMISTRY

Exam 20

PAPER 1

DURATION: 2 HOUR 45 MINUTES

INSTRUCTIONS TO CANDIDATES

Answer all questions in section A and six questions in section B.
All questions must be answered in the space provided
The periodic table, with relative atomic masses, is supplied at the end of the paper
Mathematical tables (3 figure tables) are adequate or non-programmable scientific electronic calculators may be used.
Illustrate your answers with equations where applicable

For Examiners' use only

For examiner's use only																	Total
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	

SECTION A: (46 MARKS)
Answer all questions in this section

1. (a) (i) Define the term "Osmotic pressure

Osmotic pressure is the minimum pressure that prevents entry of water into the solution through a semipermeable membrane ta given temperature

(ii) State 4 conditions solutions should have in order to obey the laws of osmotic pressure
- Solution should be dilute
- The solute should not dissociate in water.
- Solute should not react with solvent

- Solute should not associate in water

(b) The Osmotic pressure of an aqueous solution containing 3.22g of a polymer Q per 100 cm^3 of a solution is 5.637 x 10^{-2} Pa at 25^0C. Determine the molecular mass of Q

From PV = nRT

$5.637 \times 10^{-2} \times 100 \times 10^{-6} = \frac{3.22}{Mr} \times 8.314 \times (273 + 25)$

$Mr = \frac{3.22 \times 8.314 \times 298}{5.637 \times 10^{-2} \times 100 \times 100^{-6}}$ = 1,415,253,120

2. (a) Explain what is meant by "half life" of a radioactive substance.

Time taken for a radioactive substance to reduce to half its initial concentration.

(b) Complete the following equation for the decay of bismuth

$$^{214}_{83}Bi \rightarrow {}^{0}_{-1}e + {}^{214}_{84}Po$$

(c) The half-life of bismuth is 19.7 minutes. Determine the percentage by mass of bismuth which will be remaining after 16.0 minutes of decay of bismuth.

Solution

Rate constant, $\lambda = \frac{In\ 2}{19.7} min^{-1}$

From $In\frac{N_0}{N} = \lambda t = \frac{In\ 2}{19.7} \times 16$

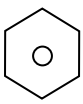
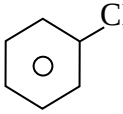
$\frac{N}{N_o} \times 100 = 57\%$

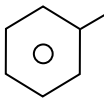
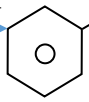
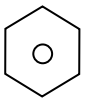
The percentage of remaining mass = 57%

3. Show how the following conversions could be carried out

(a) CH_3CO_2H from methanol

$$CH_2OH + PCl_5 \rightarrow CH_3Cl + KCN \rightarrow CH_3CN \xrightarrow{H^+} CH3COOH$$

(b)  From  CH_2OH

 CH_2OH $\xrightarrow{Cr_2O_7^{2-}/H^+}$  COOH $\xrightarrow{\text{soda lime, heat}}$ 

4. State what is observed and write an equation(s) when the following compounds are reacted

(a) Aqueous potassium dichromate (VI) with hydrogen sulphide

Orange solution turns green with formation yellow precipitate
$Cr_2O_7^{2-}(aq) + 6I^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3I_2(aq) + 7H_2O(l)$

(b) When lead (IV) oxide is heated with sulphur dioxide
White precipitate
$PbO_2(s) + SO_2(g) \rightarrow PbSO_4(s)$

(c) Aqueous copper (II) nitrate with potassium iodide

White precipitate and brown solution
$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$

5. (a) Define
(i) enthalpy of hydration

This is enthalpy change when 1mole of gaseous ions are completely hydrated.

(ii) enthalpy of solution

This is enthalpy change when 1 mole of ionic solution is dissolved in exchange water

(b) The enthalpies of solution and lattice energies of salts AX and BX are given in the table below.

Salt	Enthalpy of solution/$kJmol^{-1}$	Lattice energy/ $kJmol^{-1}$
AX	+20	– 880
BX	– 10	– 790

Calculate the enthalpy of hydration of each salt

AX

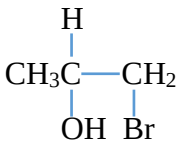
Enthalpy of solution = lattice energy + hydration energy
20 = 880 + hydration energy
Hydration energy = 20 – 880 = $-860kJmol^{-1}$

BX

Hydration energy = -10+ -790 = $-800kJmol^{-1}$

(ii) State the salt which has a larger value of hydration energy
AX

6. Complete the following equations and write the IUPAC name of the major organic product

(a) $CH_3CH = CH_2 \xrightarrow{Br_2/H_2O}$ 

1-bromopropan-2-ol

(b) $C_6H_5NH_2 \xrightarrow[\text{dil HCl } O^oC]{NaNO_2}$ $C_6H_5N^2Cl$ benzene diazonium chloride

(c) $(CH_3)_3\,C\,Br + CH_3\,\bar{O}\,Na^+ \xrightarrow[\text{heat}]{CH_3OH}$ $(CH_3)_2\,C = CH_2$ 2-methylpropene

7. The standard electrode potentials for some systems are given below

$Ca^{2+}(aq) + 2e \longrightarrow Ca(s)\ E^\theta = -2.87V$

$Mg^{2+}(aq) + 2e \longrightarrow Mg(s)\ E^\theta = -2.37V$

(a) Write the convention for the cell

$Ca/Ca^{2+}//Mg^{2+}/Mg$

(b) Write the equation for the overall reaction

$Ca(s) + Mg^{2+}(aq) \rightarrow Ca^{2+}(aq) + Mg(s)$

(c) (i) calculate the cell voltage

$E_{cell} = E_{RHE} - E_{LHE}$

$= (-2.37) - (-2.87) = 0.5V$

(ii) What conclusion can you draw from the e.m.f value in c (i) above

The cell is feasible because e.m.f is positive.

8. (a) (i) Define the term "complex ion"

This a metal ion bonded with small molecules called ligands by dative bonds

(ii) Explain why transition metals form many complexes

- They have high charge density to attract lone pair of electrons from ligands
- The have vacant orbitals to form accommodate lone pair of electrons from ligands to form dative bonds.

(c) (i) Write the structural formulae of the isomers of chromium (III) chloride
$CrCl.6H_2O$
$[Cr(H_2O)_6]^{3+}[Cl^-]_3$
$[Cr(H_2O)_5Cl]^{2+}[Cl^-]_2 .H_2O$
$[Cr(H_2O)_4Cl_2]^+[Cl^-] .2H_2O$

(ii) State one way of distinguishing the isomers

By titration with standard silver nitrate
By electroconductivity.

9. (a) (i) Explain what is meant by boiling point elevation constant

This elevation of boiling points caused by 1 mole of solute in 1000g of solvent.

(ii) 2.8g of cadmium iodide CdI_2 was dissolved in 20g of water. Calculate the boiling point of an aqueous solution of cadmium iodide at normal pressure. (boiling point elevation constant = $0.52^0Cmol^{-1}kg^{-1}$)

Mass of cadmium iodide in 1000g of water
20g of water contains 2.8g of cadmium iodide
1000g of water contains $\frac{2.8\ x\ 1000}{20}$ = 140g

Formula mass of cadmium iodide = 112 + 127 x 2 =366

Boiling point elevation
366g of CdI_2 cause elevation of 0.52^0C
140g of CdI_2 cause elevation of $\frac{0.52\ x\ 140}{366} = 0.2^0C$

Boiling point of solution = boiling point of water + boiling point elevation
= 100 + 0.2 = 100.2^0C

(b) state four assumptions made in the calculation in (a)

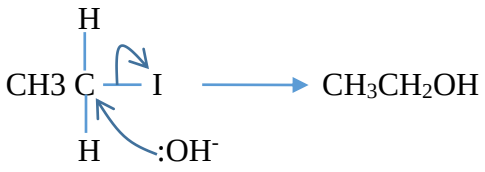
- the solution is dilute
- cadmium iodide does not react with water
- cadmium iodide does not dissociate in water
- cadmium iodide does not associate in water

SECTION B (54 MARKS)
Answer only six questions in this section

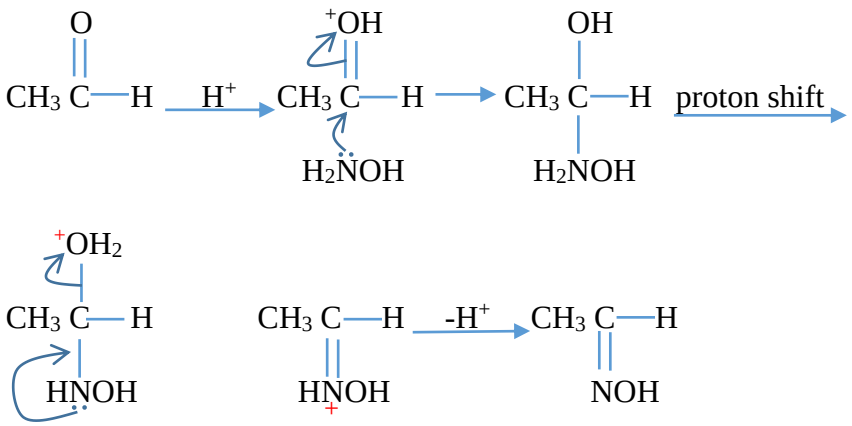
10. Complete the following equations and in each case write the mechanism for the reaction

(a) $CH_3CH_2I + KOH\ (aq) \rightarrow CH_3CH_2OH$

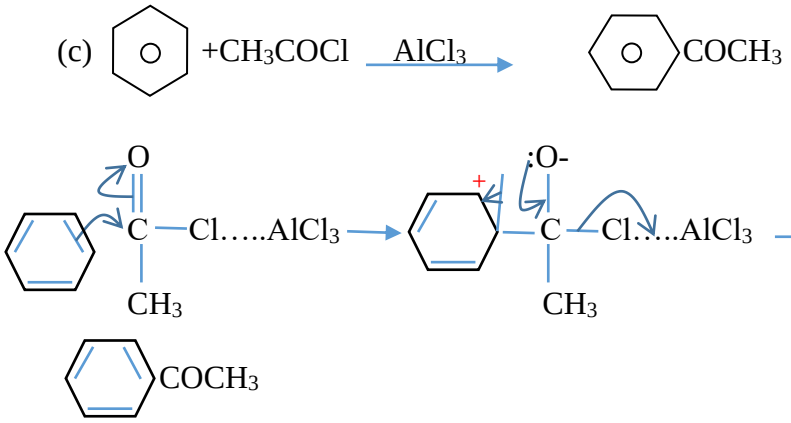
Mechanism



(b) $CH_3CHO + NH_2OH \xrightarrow{H^+(aq)} CH_3CH{=}NOH$



(c)



11. Explain why

(a) The melting point of calcium oxide is much higher than that of calcium chloride

Chloride ion is bigger than oxygen atom. It is easily polarized. Thus calcium oxide is more ionic than calcium chloride.

(b) When solid lead (IV) chloride is added to water, white fumes are observed and a brown precipitate is formed

Lead (IV) chloride hydrolyse in water to produce hydrochloric acid that fumes in moist air and a brown precipitate of lead (IV) oxide
$PbCl_4$ (l) + $2H_2O$(l) → PbO_2(s) + 4HCl(aq)

(c) An aqueous iron (III) chloride solution has a pH < 7

Iron (III) ions hydrolyse to produce hydrogen ions
Fe^{3+}(aq) + $3H_2O$(l) → $F3(OH)_3$(s) + $3H^+$(aq)

12. (a) State
(i) the distribution (partition) law

At constant temperature, a solute distributes itself into immiscible solvents at constant ratio of concentration provided the solute is in the same molecular state in both solvent.

(ii) the conditions under which the distribution law is valid

- none of the solute is saturated
- temperature is constant
- the solute is in the same molecular state in both solvents

(b) 1.00dm^3 of aqueous solution contains 5.00g of butanoic acid. Calculate the mass of butanoic acid extracted when the solution was shaken
(The distribution coefficient of acid between solvent Q and water is 4)
(i) with 500.0cm^3 of solvent Q

Let the mass of butanoic acid extracted be x
The mass of butanoic acid left in water = (5-x)

$$K_D = \frac{[butanoic\ acid]in\ Q}{[butanoic\ acid]in\ water} = \frac{\frac{x}{500}}{\frac{(5-x)}{1000}} = 4$$

$$x = 3.3g$$

(ii) twice with 250.0cm^3 of solvent Q

Let the mass of butanoic acid extracted by the first 250cm^3 be k
The mass of butanoic acid left in water = (5-k)

$$K_D = \frac{[butanoic\ acid]in\ Q}{[butanoic\ acid]in\ water} = \frac{\frac{k}{250}}{\frac{(5-x)}{1000}} = 4$$

$$x = 2.5g$$

The mass remaining in water = 5 – 2.5 = 2.5g

et the mass of butanoic acid extracted by the 2nd 250cm^3 be p
The mass of butanoic acid left in water = (2.5-p)

$$K_D = \frac{[butanoic\ acid]in\ Q}{[butanoic\ acid]in\ water} = \frac{\frac{p}{250}}{\frac{(2.5-p)}{1000}} = 4$$

$$p = 1.25g$$

Total mass extracted = 2.5 + 1.25 = 3.75g

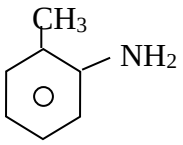
13. Name one reagent that can be used to distinguish between each of the following pairs of compounds and state what would be observed in each case if the reagent is reacted with the compounds

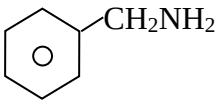
(a) C_6H_5COOH and C_6H_5OH
Reagent: sodium hydrogen carbonate solution

Observation
C_6H_5COOH – effervescence
C_6H_5OH – no observable change

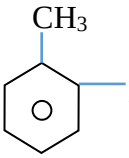
Or

Reagent: neutral solution of iron (III) chloride
C_6H_5COOH – no observable change
C_6H_5OH – purple solution

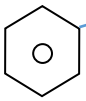
(b) 

and 

Sodium nitrite solution followed by hydrochloric acid at 0-5^{0}C



NH_2 No observable change


CH_2NH_2 - effervescence

(c) CH_3OH and CH_3CH_2OH

Reagent: iodine in sodium hydroxide solution
CH_3OH – no observable change
CH_3CH_2OH – yellow precipitate

14. (a) (i) Write an expression for the acid dissociation constant Ka, for ethanoic acid

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

(ii) Relationship between acid dissociation, Ka, and the degree of ionisation of an acid α

$Ka = \alpha^2C$

(b) The electrolytic conductivity of a 1.6×10^{-2}MCH_3COOH at 20^0C is 1.96×10^{-2} Sm and its molar conductivity at infinite dilution is 3.5×10^{-2} Sm^2mol^{-1} Calculate

(i) the molar conductivity of ethanoic acid at 20^0C

$1.6 \text{ X } 10^{-2}$ $moldm^{-3}$ = $1.6 \times 10^{-2} \times 1000$ $moldm^{-3}$ = $16molm^{-3}$

$\Lambda c = \frac{K}{C} = \frac{1.6 \, x \, 10^{-2}}{16} = 0.001$ Sm^2mol^{-1}

(ii) the degree of ionisation of the acid at 20^0C

$\alpha = \frac{\Lambda_c}{\Lambda_0} = \frac{0.001}{0035} = 0.29$

(iii) the pH of the acid

$[H^+] = \alpha C = 0.29 \times 1.6 \times 10^{-2} = 4.64 \times 10^{-3} moldm^{-3}$
$pH = -\log [H^+] = 2.3$

(c) Besides concentration, state one other factor that can affect the pH of the acid
temperature

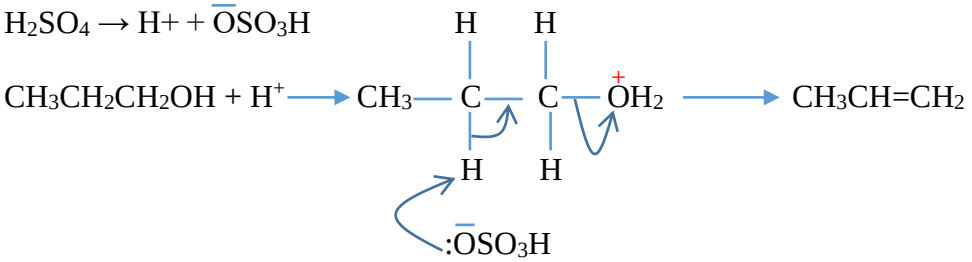
15. (a) Write the structural formulae and names of all possible isomers of an organic compound having the molecular formula C_3H_8O

CH_3CH_2CHOH – propan-1-ol
$CH_3CH(OH)CH_3$ – propan-2-ol

(b) When one of the isomers p in (a) above was reacted with acidified potassium dichromate compound Q was formed. Q reacted with phosphorous pentachloride to form compound R and hydrogen chloride gas
Identify
P- propan-1-ol
Q – propanoic acid
R- propanoylchloride

(c) Write equation and indicate a mechanism for the reaction between P and concentrated sulphuric acid

$H_2SO_4 \rightarrow H^+ + \bar{O}SO_3H$



16. (a) Write an equation for the hydrolysis of sodium ethanoate in water
(b) Write an expression for the hydrolysis constant K_h of sodium ethanoate
(c) Calculate
(i) the value of K_h for sodium ethanoate and indicate its units
(Ka for CH_3 COOH is 1.8 x 10^{-5}, Kw = 1 x 10^{-14})

$$K_h = \frac{K_w}{K_h} = \frac{10^{-14}}{1.8\ x\ 10^{-5}} = 5.6 \text{ x } 10^{-10} \text{moldm}^{-3}$$

(ii) The pH of a 0.1M sodium ethanoate solution

	CH_3COO^- (aq) + H_2O (l) ↔	CH_3COOH +	OH^-(aq)
Initially	0.1	-	-
At eqbm	0.1 – x	x	x

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{X^2}{0.1} = 1.8 \text{ x } 10^{-5}$$

x = 1.34 x 10^{-3}moldm^{-3}

$$[H+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.34\ x\ 10^{-5}} = 7.36 \text{ x } 10^{-10}$$

pH = -log $[H^+]$ = 9.1

(d) State what would be the effect on pH of the solution in (c) (ii) if Icm^3 of 0.IM ethanoic acid was added to it
pH remain unchanged

17. (a) In volumetric estimation of reducing agents, potassium dichromate (VI) is preferred to potassium manganate (VII) as an oxidant.

1. High purity
2. Should be stable in the atmosphere (otherwise it absorbers water from the out)
3. High solubility -Then it dissolves well in the relevant medium and reacts rapidly.
4. Should react rapidly during the titration. Thereby the stoichiometric ratio of the reaction can't be changed.
5. Important to have a higher molecular mass -percentage error of weighing minimizes
   Commonly used reference materials are: $KHC_8H_4O_4$, $Na_2C_2O_4$, $H_2C_2O_4*H_2O$, Na_2CO_3, K_2Cr_2O7, NaCl, $CaCO_3$, metal zinc, etc.

(b) 3.8 of solder containing tin was dissolved in excess hydrochloric acid. The solution was made up to 250cm^3. 25.0cm^3 of this solution required 23.5cm^3 of a 0.01M potassium dichromate (VI) solution for complete reaction

(i) write the half equation for potassium dichromate (VI) acting as an oxidising agent in acid medium
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

(ii) calculate the number of moles of potassium dichromate (VI) used
moles of $Cr_2O_7^{2-}$
1000cm^3 contain 0.01mole
23.5cm^3 contain $\frac{0.01\ x\ 23.5}{1000}$ = 2.35 x 10^{-4} moldm^{-3}.

(iii) Calculate the number of moles of tin in the 250cm^3 of solution

Eqn. $Cr_2O_7^{2-}(aq) + 3Sn^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Sn^{4+}(aq) + 7H_2O(l)$

Mole Sn^{2+} in 25.0cm^3 = 2.35 x 10^{-4} x 3 = 7.05 x 10^{-4} moldm^{-3}

Mole Sn^{2+} in 250cm^3 = 7.05 x 10^{-4} x $\frac{250}{25}$ = 7.05 x 10^{-3}moldm^{-3}

(iv) Determine the percentage, by mass, of tin in the solder
Mass of tin = 7.05 x 10^{-3} x 119 = 0.84g
Percentage of tin = $\frac{0.84}{3.8}$ = 22.1%