Topics in the November 2007 Exam Paper for CHEM1002

Click on the links for resources on each topic.

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- Solubility Equilibrium
- Metal Complexes

2007-N-3:

- Kinetics

2007-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2007-N-5:

- Weak Acids and Bases
- Periodic Trends
- Coordination Chemistry

2007-N-6:

- Alkenes
- Alcohols
- Organic Halogen Compounds

2007-N-7:

- Representations of Molecular Structure
- Stereochemistry

2007-N-8:

- Alcohols
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- Organic Halogen Compounds
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2007-N-9:

- Representations of Molecular Structure
- Stereochemistry
- Carboxylic Acids and Derivatives

2007-N-10:

- Synthetic Strategies

	Marks
• Define what is meant by an "allotrope". Give an example of a *pair* of allotropes involving (i) carbon and (ii) oxygen.	3

Allotropes are different structural forms of the same element. Examples include

- **Carbon: diamond, graphite and the fullerenes**
- **Oxygen: O_2 and ozone O_3**
- **Phosphorus: white and black-phosphorus**

• The K_{sp} of $Fe(OH)_3$ is 2.0×10^{-39} M^4. What is the solubility of $Fe(OH)_3$ in g L^{-1}?	**5**

The solubility equilibrium and constant for the dissolution of $Fe(OH)_3$ are:

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = [Fe^{3+}(aq)][OH^-(aq)]^3$$

If S moles of $Fe(OH)_3$ dissolve, S mol of $Fe^{3+}(aq)$ and $3S$ mol of $OH^-(aq)$ are formed. Thus,

$$K_{sp} = (S) \times (3S)^3 = 27S^4 = 2.0 \times 10^{-39}$$

$$S = 9.3 \times 10^{-11} \text{ M}$$

The formula mass of $Fe(OH)_3$ is $(55.85 \text{ (Fe)} + 3 \times (16.00 \text{ (O)} + 1.008 \text{ (H)}))$ g mol^{-1} = 106.874 g mol^{-1}. Thus, as 9.3×10^{-11} mol dissolves in 1.0 L, the mass which dissolves in 1.0 L is:

mass = number of moles × formula mass
= $(9.3 \times 10^{-11}$ mol$) \times 106.874$ g mol^1 = 9.9×10^{-9} g

Answer: **9.9×10^{-9} g L^{-1}**

What effect does lowering the pH have on the solubility of $Fe(OH)_3$? Explain your answer.

The equilibrium for the reaction:

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$

lies to the left. Addition of H^+ removes the OH^- and hence, from Le Chatelier's principle more $Fe(OH)_3(s)$ will dissolve.

Hence, lowering the pH will increase the solubility.

			Marks

- The following data were obtained for the reaction between gaseous nitric oxide and hydrogen at 1280 °C.

Marks 4

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$
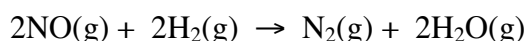
Experiment number	INITIAL [NO] (M)	INITIAL [H$_2$] (M)	INITIAL REACTION RATE (M min^{-1})
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	1.0×10^{-2}	2.0×10^{-3}	5.0×10^{-5}
3	1.0×10^{-2}	4.0×10^{-3}	1.0×10^{-4}

Deduce the rate law for this reaction and calculate the value of the rate constant.

RATE LAW	RATE CONSTANT
Between experiments 1 and 2, [H$_2$] is constant and [NO] is doubled. The rate increases by a factor of four. The reaction is second order with respect to NO.	**Using experiment 1,** **rate = k[NO]^2[H$_2$]** **$1.3\times10^{-5} = k \times (5.0\times10^{-3})^2 \times (2.0\times10^{-3})$**
Between experiments 2 and 3, [NO] is constant and [H$_2$] is doubled. The rate increases by a factor of two. The reaction is first order with respect to H$_2$. **rate = k[NO]^2[H$_2$]**	**k = 260 M^{-2} min^{-1}** **The units of k can be deduced from balancing those of the other terms:** **M min^{-1} = (units of k) × (M)^2 × (M)**
Answer: **rate = k[NO]^2[H$_2$]**	Answer: **260 M^{-2} min^{-1}**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

**Marks
8**

- Solution A consists of a 0.50 M aqueous solution of HF at 25 °C. Calculate the pH of Solution A. The pK_a of HF is 3.17.

As HF is a weak acid, $[H_3O^+]$ must be calculated using a reaction table:

	HF	H₂O	⇌	H₃O⁺	HF
initial	0.50	large		0	0
change	-x	negligible		+x	+x
final	0.50 –x	large		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{x^2}{0.50 - x}$$

As $pK_a = -\log_{10}K_a$, $K_a = 10^{-3.17}$ and is very small, $0.50 - x \sim 0.50$ and hence:

$$x^2 = 0.50 \times 10^{-3.17} \quad \text{or} \quad x = 1.84 \times 10^{-2}\ M = [H_3O^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+] = -\log_{10}[(1.84 \times 10^{-2})] = 1.74$$

pH = **1.74**

ANSWER CONTINUES ON THE NEXT PAGE

At 25 °C, 1.00 L of Solution B consists of 12.97 g of lithium fluoride, LiF, dissolved in water. Calculate the pH of Solution B.

The molar mass of LiF is 6.941 (Li) + 19.00 (F) = 25.941. Hence, the number of moles in 12.97 g is:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{12.97}{25.941} = 0.5000 \, \text{mol}$$

As this is dissolved in 1.00 L, $[F^-]$ = 0.500 M.

F^- is a weak base so $[H_3O^+]$ must be calculated via the calculation of $[OH^-]$ from the reaction table:

	F^-	H_2O	$\rightleftharpoons$	HF	OH^-
initial	0.500	large		0	0
change	-x	negligible		+x	+x
final	0.500 - x	large		x	x

The equilibrium constant K_b is given by:

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{x^2}{0.500 - x}$$

As pK_a + pK_b = 14.00, pK_b = 14.00 − 3.17 = 10..83. As pK_b = $-\log_{10}K_b$, $K_b = 10^{-10.83}$ and is very small. Hence, 0.500 − x ~ 0.500 and hence:

$$x^2 = 0.500 \times 10^{-10.83} \quad \text{or} \quad x = 2.72 \times 10^{-6} \, M = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = -\log_{10}[(2.72 \times 10^{-6})] = 5.57$$

Finally, as pH + pOH = 14.00, pH = 14.00 − 5.57 = 8.43

pH = **8.43**

ANSWER CONTINUES ON THE NEXT PAGE

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C. Calculate the pH of the final solution.

The solution consists of a weak acid (HF) and its conjugate base (F⁻). The Henderson -Hasselbalch equation can be used:

$$pH = pK_a + \log_{10}\left(\frac{[base]}{[acid]}\right)$$

When the two solutions are mixed, the volumes doubles and so the concentrations halve: [base] = [F⁻] = 0.250 M and [acid] = [HF] = 0.25 M. Hence,

$$pH = pK_a + \log_{10}\left(\frac{[base]}{[acid]}\right) = 3.17 + \log_{10}\left(\frac{0.250}{0.25}\right) = 3.17$$

pH = **3.17**

If you wanted to adjust the pH of the mixture of Solution A and Solution B to be exactly equal to 4.00, which component in the mixture would you need to increase in concentration?

pH needs to increase: increase [base] (i.e. [LiF])

	Marks
• Briefly explain why H_2S is a stronger Brønsted acid than H_2O.	**2**

**S is much larger atom than O, so the H–S bond is much longer and weaker than H–O, so H_2O is weaker acid than H_2S.**

	2
• Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Ni^{2+}.	

The Ni atom has the electron configuration [Ar] $4s^2 3d^8$ and the Ni^{2+} ion has the configuration [Ar] $3d^8$ as the two electrons are removed from the 4s orbitals.

The electrons in the d-orbitals are arranged to minimize the repulsion between them. This results in two of the electrons being unpaired.

□	↓↑	↓↑	↓↑	↑	↑

4s   **3d**
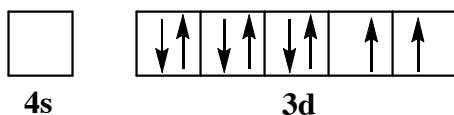
The presence of unpaired electrons leads to paramagnetism.
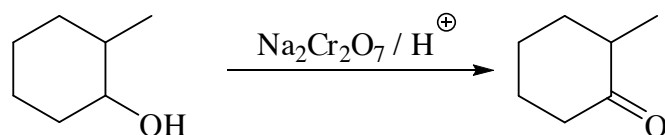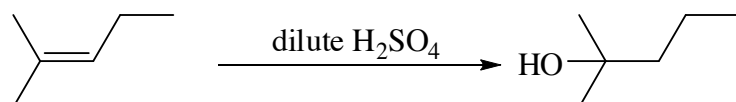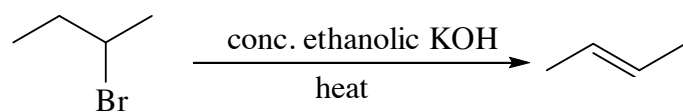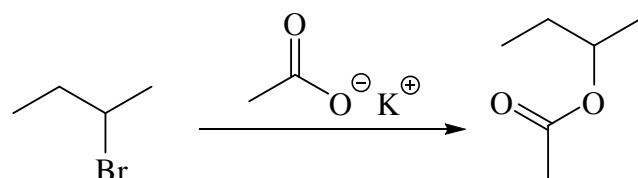
	6
• Complete the following table.	

Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of *d*-electrons in the complex ion	Species formed upon dissolving in water
$K_3[Mn(CN)_6]$	**III**	**6**	**4**	**K^+(aq) $[Mn(CN)_6]^{3-}$(aq)**
$[Ru(NH_3)_5(OH_2)](NO_3)_2$	**II**	**6**	**6**	**$[Ru(NH_3)_5(OH_2)]^{2+}$(aq) NO_3^-(aq)**
$[Cr(en)_3]Cl_3$	**III**	**6**	**3**	**$[Cr(en)_3]^{3+}$(aq) Cl^-(aq)**

en = ethylenediamine = $NH_2CH_2CH_2NH_2$

	Marks
• Give the name of the starting material where indicated and the constitutional formula of the major organic product formed in each of the following reactions.	**8**

$$\xrightarrow[\text{CCl}_4 \text{ (solvent)}]{\text{Cl}_2}$$
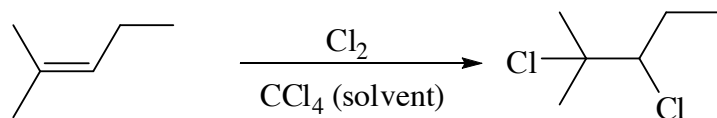
Name: 2-methyl-2-pentene

$$\xrightarrow{\text{dilute H}_2\text{SO}_4}$$

$$\xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7 / \text{H}^{\oplus}}$$

Name: 2-methylcyclohexanol

$$\xrightarrow[\text{heat}]{\text{conc. ethanolic KOH}}$$

Name: 2-bromobutane

Marks
4

• Classify the starting materials for each of the following reactions as nucleophile or electrophile in the boxes provided and indicate with $\delta\oplus$ and $\delta\ominus$ the polarisation of the H–Br and C–Br bonds in the starting materials.
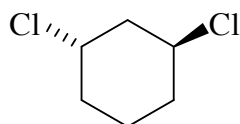
| nucleophile | electrophile |

| nucleophile | electrophile |
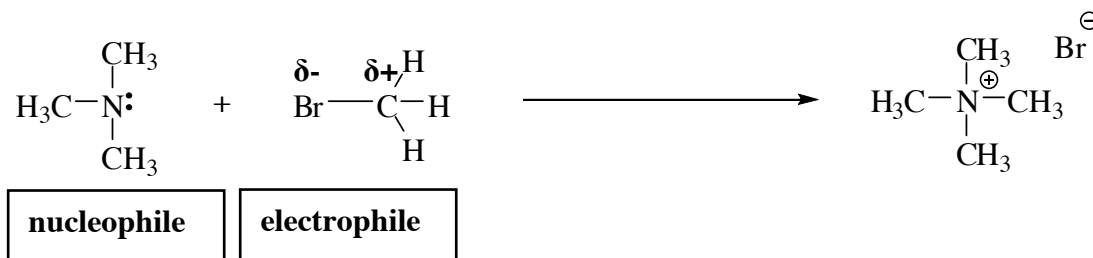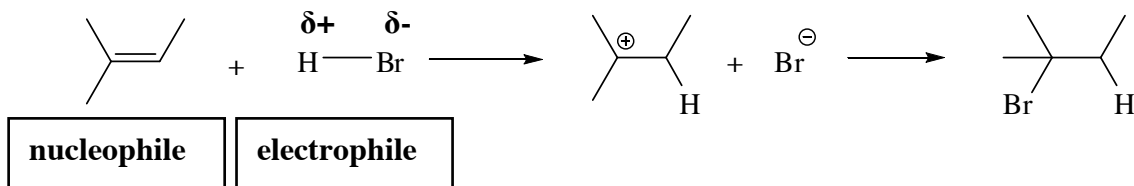
3

• Draw the constitutional formula for each of the following compounds.

(Z)-4-methylhex-2-ene
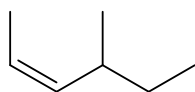
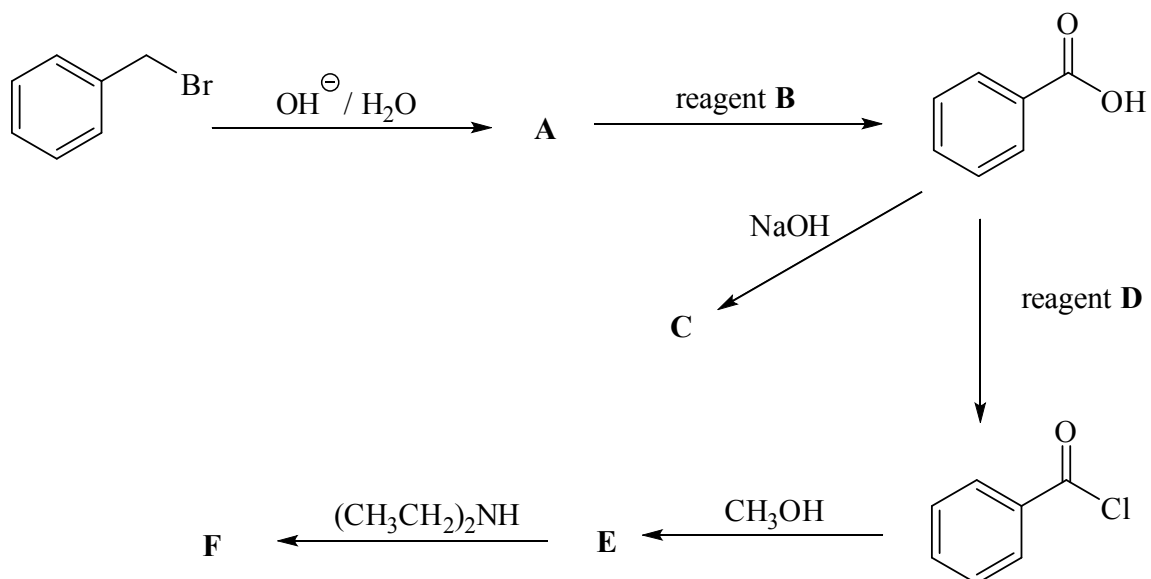*trans*-1,3-dichlorocyclohexane

Cl,,, Cl

(R)-butan-2-ol

OH
H,,,
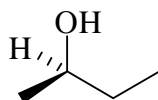
Marks
6

- Consider the following reaction sequence.

Give the reagents **B** and **D** and draw the structures of the major organic products, **A**, **C**, **E** and **F**, formed in these reactions.

A	D
	SOCl₂ / heat
B	E
$Cr_2O_7^{2-} / H^+$	
C	F
	CH₃OH

Marks
7

- Dopa is a non-proteinogenic amino acid used to treat Parkinson's disease. Only the enantiomer (**X**) is effective in restoring nerve function. The other enantiomer is highly toxic.

(**X**)
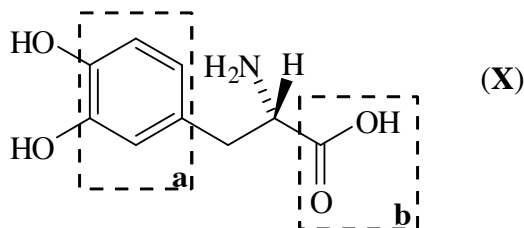
What is the molecular formula of (**X**)?

$C_9H_{11}O_4N$

List the substituents attached to the stereogenic centre in descending order of priority according to the sequence rules.

highest priority   lowest priority

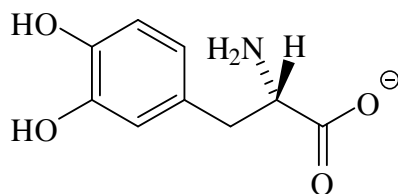| $-NH_2$	$-COOH$		$-H$

What is the absolute stereochemistry of (**X**)? Write (*R*) or (*S*).

(*S*)

Name the functional groups, highlighted by the boxes **a** and **b**, present in (**X**).
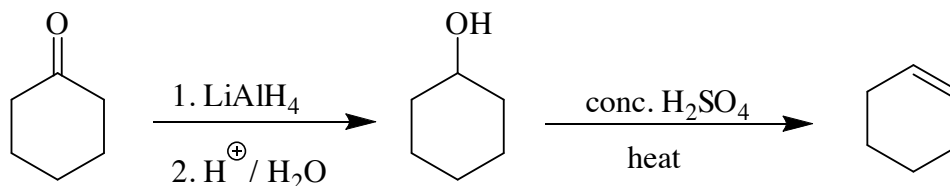
a = arene (aromatic ring)	b = carboxylic acid

Give the constitutional formula of the product obtained when (**X**) is treated with $NaHCO_3$.

Marks
6

- Show clearly the reagents you would use to carry out the following chemical conversion. Exactly one intermediate compound and hence two steps are required. Give the constitutional formula of the intermediate compound.

How could you distinguish between the starting material, the intermediate compound and the final product using infrared spectroscopy?

The starting material shows strong absorbance in the infrared, around 1700 cm^{-1} due to the carbonyl (C=O) group.

The iIntermediate shows strong and broad absorbance in the infrared, around 3500 cm^{-1} due to the alcohol (O–H) group.

The final product has no absorbance in these two regions of the infrared spectrum. (The C=C bond will absorb quite weakly around 1400 cm^{-1}.)