Topics in the November 2008 Exam Paper for CHEM1002

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- Weak Acids and Bases

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- Kinetics

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Marks

- The nickel(II) ion exists as the $[Ni(OH_2)_6]^{2+}$ complex ion in aqueous solution. Define the term complex. **4**

A complex is a species that consists of a central metal ion which acts as a Lewis acid surrounded by a number of ligands that act as Lewis bases. The charge on the complex may be positive, negative or neutral depending on the charge on the cation and the number and charge of all the ligands.

What is the name of this complex ion?

hexaaquanickel(II) ion

Why is such a solution acidic?

H_2O donates a lone pair to form a coordinate bond to Ni^{2+}. The pull of the cation on these electrons weakens the O–H bonds as the oxygen has to pull electron density form these bonds.

Write a balanced equation for the corresponding reaction.

$$[Ni(OH_2)_6]^{2+} + H_2O \rightleftharpoons [Ni(OH_2)_5OH]^{+} + H_3O^{+}$$

- You have completed a number of titrations during your laboratory work. What is the difference between the 'end point' and the 'equivalence point' in a titration? **4**

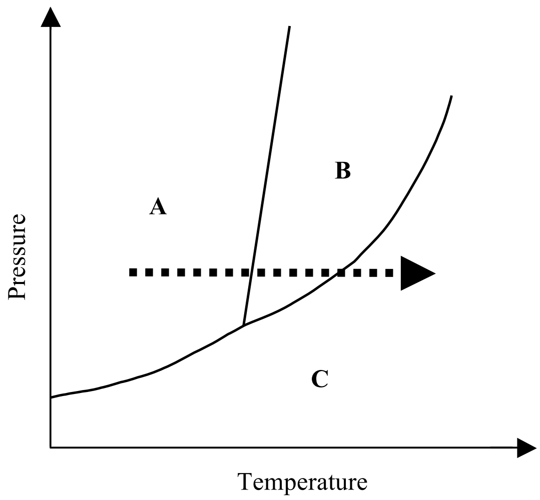
The equivalence point is the point where the reaction stoichiometry is exactly satisfied. For an acid base reaction, it corresponds to the point at which the amount of acid added is exactly equal to the amount of base initially present (or *vice versa*).
The endpoint is where the indicator changes colour and the reaction is observed to be completed.

How do you need to consider that distinction when you chose an indicator for a particular titration?

The endpoint and equivalence point need to be as close to one another as possible.

Marks
6

- Examine the following pressure/temperature phase diagram for a one component system.



Which phase exists in the fields labelled **A**, **B** and **C**?

A: **solid**	**B**: **liquid**	**C**: **gas**

Explain your assignment of these phases.

The dotted arrow on the phase diagram above passes through all three regions. It represents an increase in temperature at constant pressure. At low temperature, the particles in the system have low energy and so exist as a solid in phase A. As the temperature is increased, they gain energy and pass from solid to liquid, in phase B. At even higher temperature, they have sufficient energy to pass to gas, in phase C.

What do the lines in the diagram represent?

The lines represent the boundaries between phases. At each temperature and pressure on a line, both of the phases to the left and to the right of that point are in equilibrium and co-exist.

What happens when you move across a line either by changing temperature or pressure?

Moving across a line corresponds to a phase change.

ANSWER CONTINUES ON THE NEXT PAGE

For a compound with this phase diagram, would the solid be denser than the liquid or vice versa? Explain your answer.

The solid is denser.

The gradient of the line between A and B is positive. If the system is at the phase change between solid and liquid (i.e. a point on the line) then increasing the pressure (moving vertically upwards on the diagram) will move the system to the solid phase.

This is because the solid takes up less volume: increasing the pressure favours the solid over the liquid. If the solid takes up less volume, it must be denser.

Marks 4

- The data given in the table below were obtained for the reaction between nitric oxide and chlorine at 1400 K.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

Experiment number	INITIAL $[Cl_2]$ (mol^{-1} L^{-1})	INITIAL [NO] (mol^{-1} L^{-1})	INITIAL REACTION RATE (mol^{-1} L^{-1} s^{-1})
1	0.10	0.10	0.18
2	0.20	0.10	0.36
3	0.10	0.20	0.72

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

RATE LAW	RATE CONSTANT
Between experiments (1) and (2), [NO] is fixed and $[Cl_2]$ is doubled. This leads to the rate doubling: **rate α $[Cl_2]^1$.** **Between experiments (1) and (3), $[Cl_2]$ is fixed and [NO] is doubled. This leads to the rate increasing by a factor of 4:** **rate α $[NO]^2$.** **Overall,** **rate = $k[NO]^2[Cl_2]$.**	**Using this rate law and the rate from experiment (1),** **$0.18\ M\ s^{-1} = k(0.10\ M)^2(0.10\ M)$** **Hence,** **$k = 180\ M^{-2}\ s^{-1}$** **The units of k are such that the units of the left and right hand sides of the equation are the same:** **$M\ s^{-1}$ = (units of k)$(M^2)(M)$** **units of $k = M^{-2}\ s^{-1}$**
Answer: **rate = $k[NO]^2[Cl_2]$**	Answer: **rate constant = 180 M^{-2} s^{-1}**

Marks

- Calculate the pH of a 0.020 M solution of $Ba(OH)_2$. 1

$Ba(OH)_2$ is a strong base so it will completely dissociate in solution:

$Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$

As each $Ba(OH)_2$ dissociates to make $2OH^-$, a 0.020 M solution has $[OH^-(aq)]$ = 0.040 M.

By definition, pOH = $-\log_{10}[OH^-(aq)]$ so pOH = $-\log_{10}(0.040)$ = 1.40.

As pH + pOH = 14.00,

pH = 14.00 – 1.40 = 12.60

pH = **12.60**

- Calculate the pH of a 0.150 M solution of HNO_2. The pK_a of HNO_2 is 3.15. 3

As HNO_2 is a weak acid, $[H_3O^+]$ must be calculated using a reaction table:

	HNO_2	H_2O	$\rightleftharpoons$	H_3O^+	NO_2^-
initial	**0.150**	**large**		**0**	**0**
change	**$-x$**	**negligible**		**$+x$**	**$+x$**
final	**$0.150 - x$**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{0.150 - x}$$

As pK_a = $-\log_{10}K_a$, $K_a = 10^{-3.15}$ and is very small, $0.150 - x \sim 0.150$ and hence:

$x^2 = 0.150 \times 10^{-3.15}$ or $x = 1.03 \times 10^{-2}$ M = $[H_3O^+]$

Hence, the pH is given by:

pH = $-\log_{10}[H_3O^+] = -\log_{10}(1.03 \times 10^{-2})$ = 1.987

pH = **1.987**

ANSWER CONTINUES ON THE NEXT PAGE

- Calculate the pH of a solution that is 0.080 M in acetic acid and 0.160 M in sodium acetate. The pKa of acetic acid is 4.76.

2

The solution contains both a weak acid (acetic acid) and its conjugate base (the acetate ion). This is a buffer and its pH can be calculate using the Henderson-Hasselbalch equation. With [acid] = 0.080 M and [base] = 0.160 M,

$$\mathbf{pH = p\mathit{K}_a + \log\left(\frac{[base]}{[acid]}\right) = 4.76 + \log\left(\frac{0.160}{0.080}\right) = 5.06}$$

pH = **5.06**

Marks

- Hydrogen bonding is important for the physical properties of water and consequently the very existence of life on earth. What effect does the formation of hydrogen bonding have on the density of solid water (ice) compared to liquid water. Explain. **4**

In liquid water, each molecule is involved in four H-bonds: two via the H atoms and two via the lone pairs. In ice, the molecules are arranged in a regular 3D network with holes in the lattice - each O is at the centre of a distorted tetrahedron and each molecule is involved in only 2 H-bonds. Water has the greater number of H-bonds, so the molecules are held closer together and it is denser than ice.

Predict the physical form of water under ambient conditions if no hydrogen bonds existed. Explain that prediction.

It would probably be a gas.

H_2O has the same number of electrons are CH_4 so dispersion forces would be of similar strength.

H-bonding is not possible in CH_4 and it is a gas. It is therefore likely that, without hydrogen bonding, water would be too.

- $BaSO_4$ is used as a contrast agent for X-ray images of intestines. What is the solubility product constant, K_{sp}, for $BaSO_4$, given that a maximum of 1.2×10^{-3} g dissolves in 500 mL of water. **4**

The formula mass of $BaSO_4$ is:

$$137.34\ (\text{Ba}) + 32.07\ (\text{S}) + 4 \times 16.00\ (\text{O}) = 233.44\ \text{g mol}^{-1}$$

A mass of 1.2×10^{-3} g therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{1.2 \times 10^{-3}\ \text{g}}{233.44\ \text{g mol}^{-1}} = 5.14 \times 10^{-6}\ \text{mol}$$

The equation for the dissolution is:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

If 5.14×10^{-6} mol dissolves, then the number of moles of $Ba^{2+}(aq)$ and $SO_4^{2-}(aq)$ will also be 5.14×10^{-6} mol. As these amounts are present in 500 mL of water:

$$[Ba^{2+}(aq)] = [SO_4^{2-}(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{5.14 \times 10^{-6}\ \text{mol}}{0.500\ \text{L}} = 1.03 \times 10^{-5}\ \text{M}$$

Finally, the solubility product constant is:

$$K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)] = (1.03 \times 10^{-5})(1.03 \times 10^{-5}) = 1.1 \times 10^{-10}$$

Answer: **1.1×10^{-10}**

Ba^{2+} ions are toxic. Comment on the suitability of $BaSO_4$ as a contrast agent.

As $BaSO_4$ has a very low solubility, $[Ba^{2+}(aq)]$ will be low and so very few of the toxic Ba^{2+} are actually dissolved into the blood stream.

What advantage would there be in administering $BaSO_4$ as a slurry which also contains 0.5 M Na_2SO_4?

The equilibrium,

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

will be shifted to the left by the addition of additional SO_4^{2-} from Na_2SO_4. This is an example of Le Châtelier's principle and is called the 'common ion effect'.

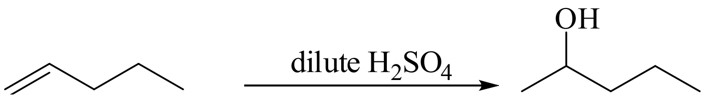
By shifting the reaction to the left, even less $BaSO_4$ will dissolve, reducing $[Ba^{2+}(aq)]$ to:

$$[Ba^{2+}(aq)] = K_{sp} / [SO_4^{2-}(aq)] = (1.1 \times 10^{-11})/(0.5) = 2 \times 10^{-10} \text{ M}$$

This can be compared to the much higher value of 1×10^{-5} M calculated above.

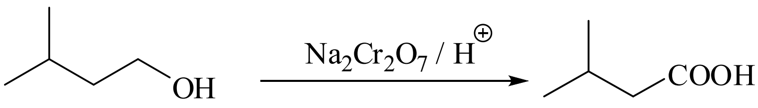
Marks 8

- 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.



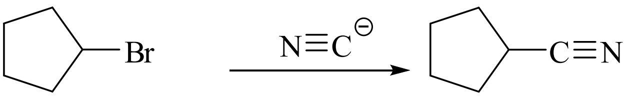
Name: 1-pentene

(Acid catalysed addition of H-OH across a C=C double bond, following Markovikov's rule)



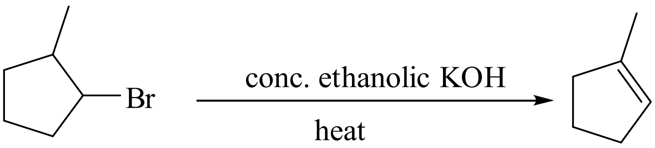
Name: 3-methyl-1-butanol

(Oxidation of a primary alcohol to a carboxylic acid)

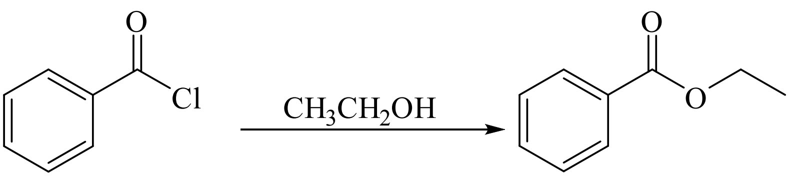


Name: bromocyclopentane

(Nucleophilic substitution by Br^- by CN^-)



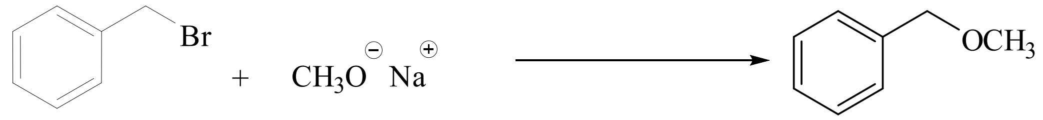
(Base catalysed elimination of H-Br to form a C=C, following Zeitsev's rule).



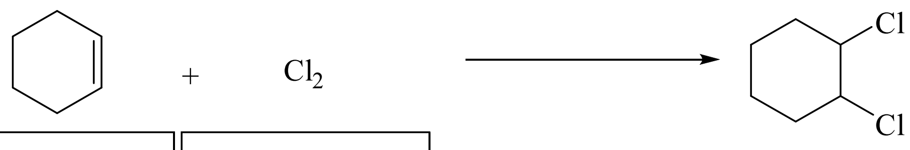
(Formation of an ester from an acid chloride).

Marks 6

- Classify the starting materials for each of the following reactions as nucleophile and electrophile in the boxes provided and draw the structure of the product.



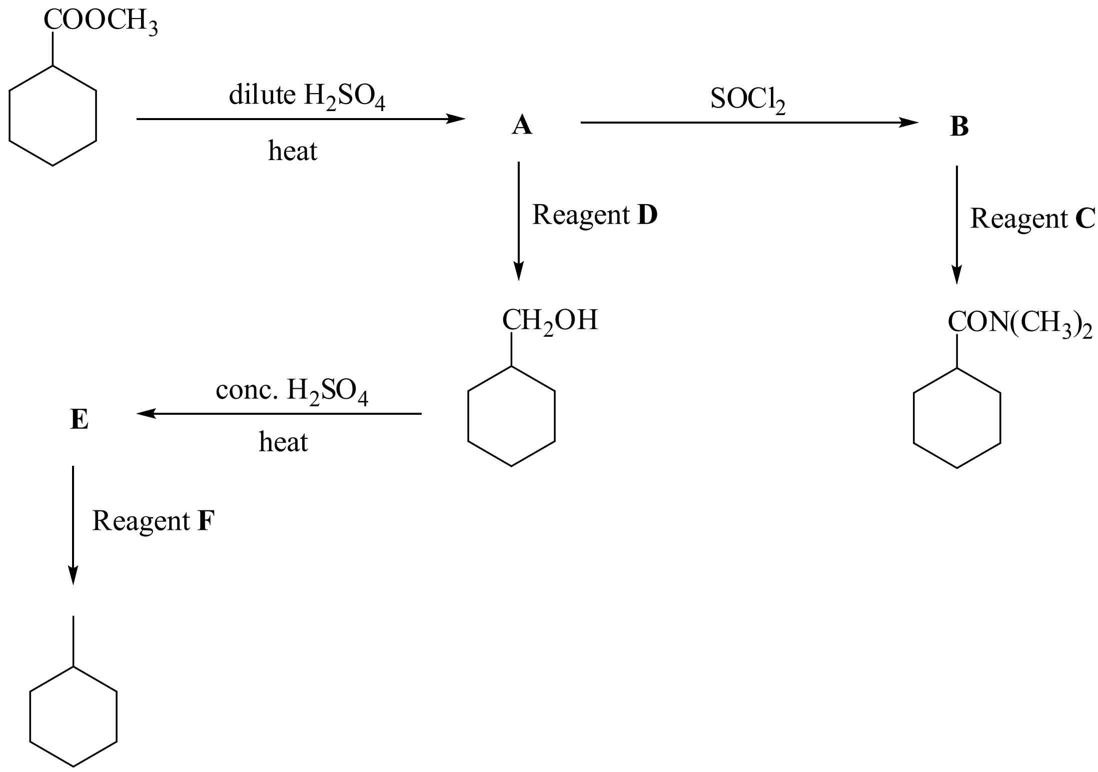
electrophile	**nucleophile**



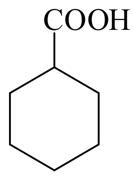
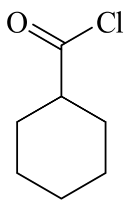
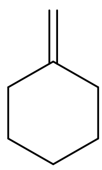
nucleophile	**electrophile**

Marks 6

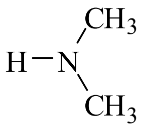
- Consider the following reaction sequence.



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

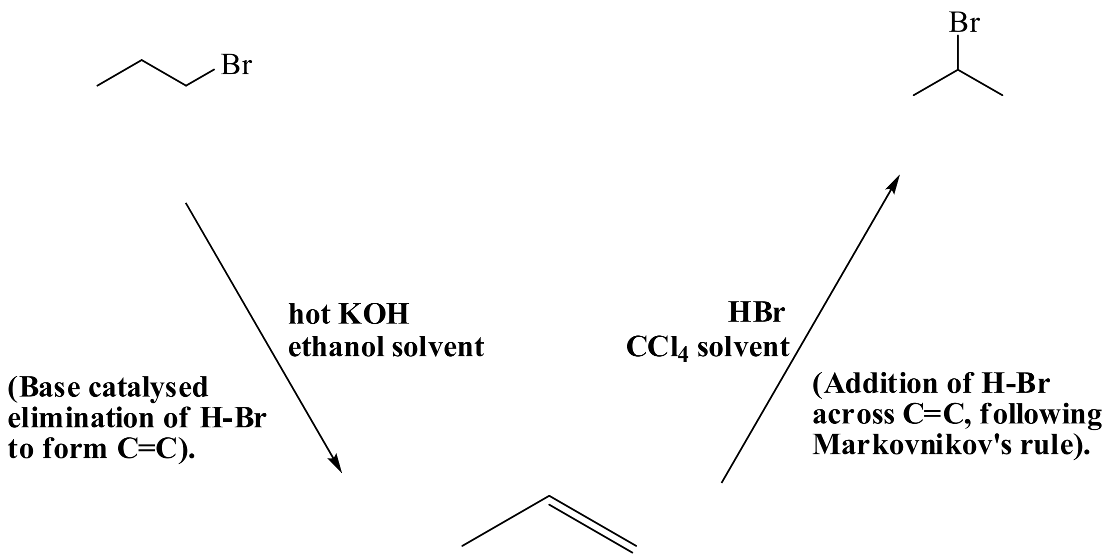
A  **(Hydrolysis of an ester to a carboxylic acid).**	**D** **(1). $LiAlH_4$ / dry ether** **(2). H^+ / H_2O** **(Reduction of carboxylic acid to primary alcohol).**
B  **(Formation of an acid chloride from a carboxylic acid).**	**E**  **(Acid catalysed elimination of H-OH ("dehydration") to form C=C).**

ANSWER CONTINUES ON THE NEXT PAGE

C	**F**
 **(Formation of amide from acid chloride).**	**H_2 / Pd/C** **(Reduction of alkene to alkane).**

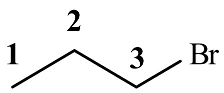
Marks 5

- Show clearly the reagents you would use to carry out the following chemical conversion. Two steps are required. Give the structure of the intermediate compound.

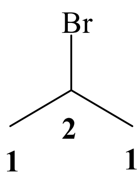


How could you distinguish between the starting material and the product by ^{13}C NMR spectroscopy?

The starting material has 3 different carbon environments so will give 3 resonances in the ^{13}C NMR.



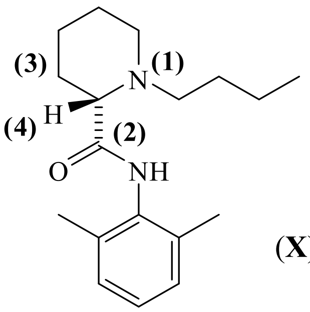
The produt has 2 different carbon environments so will give 2 resonances in the ^{13}C NMR.



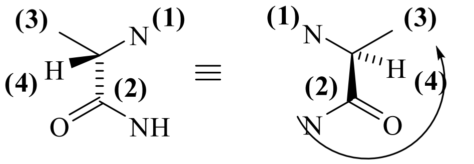
The two carbon atoms labelled as '1' are equivalent.

Marks
7

- Bupivacaine is the active molecule in some local anaesthetics. Of the two enantiomers, the one shown below (**X**) is the more effective.



(**X**)



counter-clockwise

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

$C_{18}H_{28}ON_2$

Calculate the m/z value for the major peak you would expect to see for the molecular ion in the high resolution mass spectrum.
[Atomic masses: $^{1}H = 1.0078$; $^{12}C = 12.0000$; $^{16}O = 15.9949$; $^{14}N = 14.0031$]

The molecular ion has *m* = molar mass:

Molar mass = (18 × 12.0000 (C) + 28 × 1.0078 (H)
+ 15.9949 (O) + 2 × 14.0031 (N)) g mol^{-1} = 288.2195 g mol^{-1}

Answer: **288.2195 g mol^{-1}**

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

highest priority lowest priority

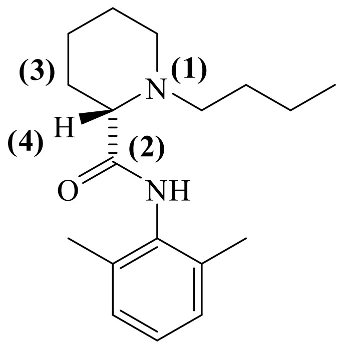
$-N(R_1)R_2$	$-CONHR$	$-CH_2-$	$-H$

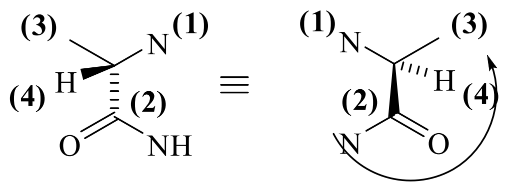
What is the absolute stereochemistry of **(X)**? Write (R) or (S).

(*S*)
(see above)

Name the functional groups present in (**X**).

(tertiary) amine, amide, aromatic ring

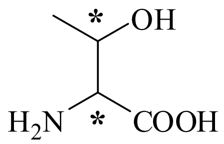




counter-clockwise

Marks
4

- Threonine (**Y**) is an amino acid. On the structure of (**Y**) below, identify all stereocentres in threonine with an asterisk (*).

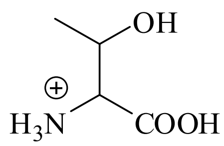
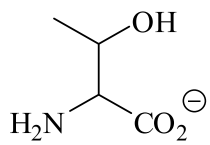


(**Y**)

How many possible stereoisomers of threonine are there?

Two chiral centres so 4 possible stereoisomers (*RR*, *SS*, *RS* and *SR*)

Give the structures of the products obtained when threonine is treated with the following reagents.

1 M HCl	1 M NaOH
 **(HCl is a strong acid so will protonate the amine – a weak base. It will not protonate the very, very weakly acidic oxygen atoms at this concentration).**	 **OH^- is a strong base and will deprotonate the carboxlic acid – a weak acid. It will not deprotonate the very, very weakly acidic N-H or alcohol O-H groups.**