Topics in the November 2013 Exam Paper for CHEM1002

Click on the links for resources on each topic.

2013-N-2:

- Crystal Structures
- Metal Complexes
- Coordination Chemistry
- Kinetics

2013-N-3:

- Weak Acids and Bases

2013-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2013-N-5:

- Strong Acids and Bases
- Solubility Equilibrium

2013-N-6:

- Intermolecular Forces and Phase Behaviour
- Physical States and Phase Diagrams

2013-N-7:

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

2013-N-8:

- Stereochemistry

2013-N-9:

- Representations of Molecular Structure
- Alkenes
- Alcohols

2013-N-10:

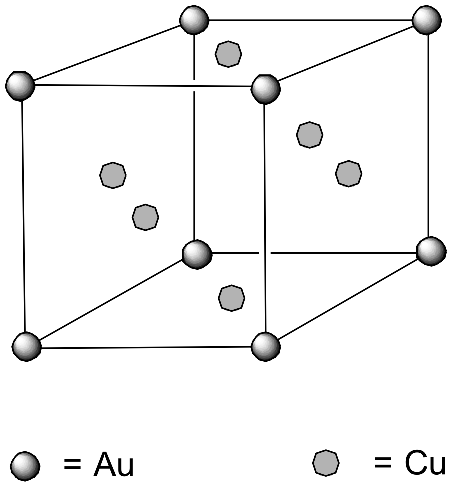
- Carboxylic Acids and Derivatives

2013-N-11:

- Synthetic Strategies
- Stereochemistry

Marks

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. **2**



What is the chemical formula of the alloy?

There are 8 Au atoms on the corners, each contributes 1/8 to the cell. The total number of Au atoms is 8 × 1/8 = 1.

There are 6 Cu atoms on the faces, each contributes 1/2 to the cell. The total number of Cu atoms is 6 × 1/2 = 3

Answer: **Cu_3Au (or $AuCu_3$)**

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

Cobalt is in group 9 so Co^{2+} has (9 – 2) = 7 valence electrons: its configuration is $3d^7$. These electrons occupy the five 3*d* orbitals according to Hund's rule to minimise electron – electron repulsion.

↑↓	↑↓	↑	↑	↑

It has 3 unpaired electrons and so it is paramagnetic.

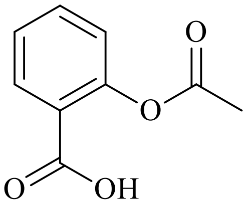
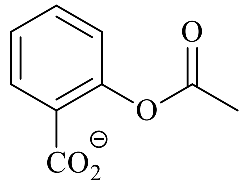
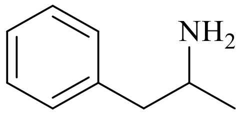
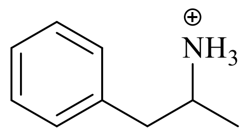
- Briefly explain how a catalyst works. **2**

A catalyst provides a different reaction pathway which has a lower activation energy.

Marks
7

- The structures of the drugs aspirin and amphetamine are shown below.

  (a) Draw the conjugate base of aspirin and the conjugate acid of amphetamine.
  (b) *Circle* the form of each that will be present in a highly acidic environment.

 aspirin	 conjugate base of aspirin
 amphetamine	 conjugate acid of amphetamine

Ions are less likely to cross cell membranes than uncharged molecules. One of the drugs above is absorbed in the acid environment of the stomach and the other is absorbed in the basic environment of the intestine. Identify which is absorbed in each environment below and *briefly* explain your answers.

Drug absorbed in the stomach:	**aspirin** / amphetamine
Drug absorbed in the intestine:	aspirin / **amphetamine**

Aspirin is absorbed in stomach. In this acidic environment, it is mainly in its protonated uncharged form.

Amphetamine is absorbed in the basic environment of the intestine where it exists as uncharged unprotonated molecule.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks 7

Calculate the pH of a 0.010 M solution of aspirin at 25 °C. The pK_a of aspirin is 3.5 at this temperature.

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

	$C_9H_8O_4$	H_2O	$\rightleftharpoons$	H_3O^+	$C_9H_7O_4^-$
initial	**0.010**	**large**		**0**	**0**
change	**$-x$**	**negligible**		**$+x$**	**$+x$**
final	**$0.010 - x$**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][C_9H_7O_4^-]}{[C_9H_7O_4]} = \frac{x^2}{0.010 - x}$$

As pK_a = $-\log_{10}K_a$, $K_a = 10^{-3.5}$ and is very small, $0.010 - x \sim 0.010$ and hence:

$$x^2 = 0.010 \times 10^{-3.5} \quad \text{or} \quad x = 1.8 \times 10^{-3}\text{ M} = [H_3O^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}(1.8 \times 10^{-3}) = 2.8$$

pH = **2.8**

Aspirin, $C_9H_8O_4$ is not very soluble. "Soluble aspirin" can be made by reacting aspirin with sodium hydroxide. Write the chemical equation for this reaction.

$$C_9H_8O_4(s) + OH^-(aq) \rightarrow C_9H_7O_4^-(aq) + H_2O(l)$$

Is a solution of "soluble aspirin" acidic or basic? Briefly explain your answer.

Basic. The $C_9H_7O_4^-$(aq) ion reacts with water (*i.e.* undergoes hydrolysis) to generate a small amount of OH^- ions. The $C_9H_7O_4^-$(aq) ion is a weak base, so the following equilibrium reaction lies very much in favour of the reactants.

$$C_9H_7O_4^-(aq) + H_2O(l) \rightleftharpoons C_9H_8O_4(aq) + OH^-(aq)$$

Marks 8

- The concentration of iron in the ocean is one of the primary factors limiting the growth rates of some basic life forms. Write the chemical equation for the dissolution reaction of $Fe(OH)_3$ in water.

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

What is the solubility of $Fe(OH)_3$ in mol L^{-1}? K_{sp} ($Fe(OH)_3$) is 2.8×10^{-39} at 25 °C.

From the chemical equation, $K_{sp} = [Fe^{3+}(aq)][OH^-(aq)]^3$.

If x mol of $Fe(OH)_3$ dissolve in one litre, then $[Fe^{3+}(aq)] = x$ and $[OH^-(aq)] = 3x$. Hence,

$$K_{sp} = (x)(3x)^3 = 27x^4 = 2.8 \times 10^{-39}$$

$$x = 1.0 \times 10^{-10} \text{ M}$$

Answer: **1.0×10^{-10} M**

Before the Industrial Revolution, the concentration of $OH^-(aq)$ in the oceans was about 1.6×10^{-6} M. What pH corresponds to this concentration at 25 °C?

If $[OH^-] = 1.6 \times 10^{-6}$ M, then be definition

$$pOH = -\log_{10}[OH^-(aq)] = -\log_{10}(1.6 \times 10^{-6}) = 5.8$$

As pH + pOH = 14.0,

$$pH = 14.0 - 5.8 = 8.2$$

Answer: **pH = 8.2**

What is the solubility of $Fe(OH)_3$ in mol L^{-1} at this pH?

As $[OH^-(aq)] = 1.6 \times 10^{-6}$ M and $K_{sp} = [Fe^{3+}(aq)][OH^-(aq)]^3$:

$$\begin{aligned}[Fe^{3+}(aq)] &= K_{sp} / [OH^-(aq)]^3 \\ &= 2.8 \times 10^{-39} / (1.6 \times 10^{-6})^3 \text{ M} \\ &= 6.8 \times 10^{-22} \text{ M}\end{aligned}$$

Answer: **6.8×10^{-22} M**

ANSWER CONTINUES OVER THE PAGE

Industrialisation has led to an increase in atmospheric CO_2. Predict the effect that this has had on the amount of Fe^{3+}(aq) in sea water and briefly explain your answer.

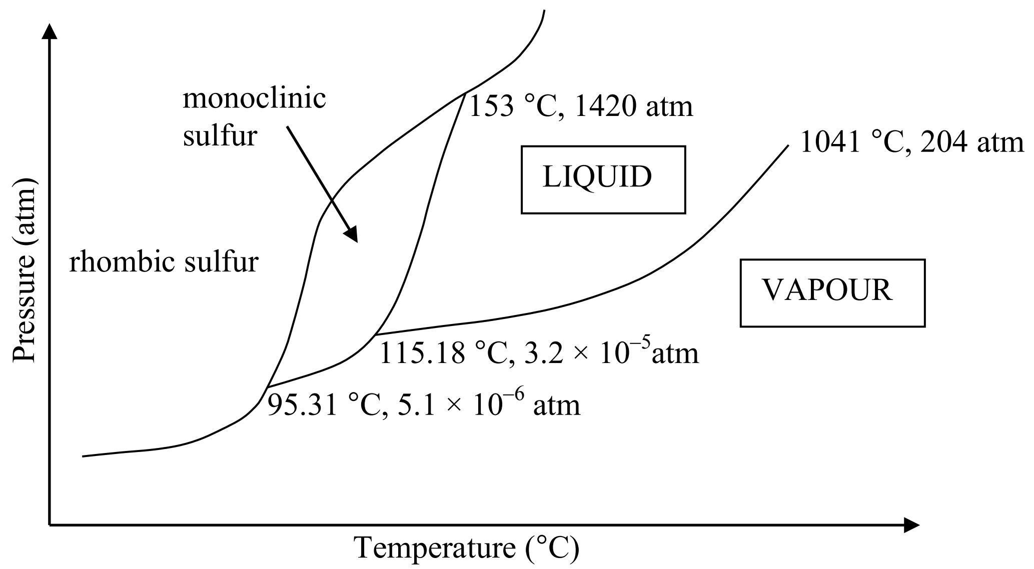
Dissolved CO_2 reacts with water to form H_2CO_3 which is slightly acidic.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The increase in [H^+(aq)] results in a decrease in [OH^-(aq)] and hence (from Le Chatelier's principle) more $Fe(OH)_3$(s) will dissolve.

Marks 9

- Solid sulfur can exist in two forms, rhombic sulfur and monoclinic sulfur. A portion of the phase diagram for sulfur is reproduced schematically below. Complete the diagram by adding the labels "vapour" and "liquid" to the appropriate regions.



Which form of solid sulfur is stable at 25 °C and 1 atm? **rhombic**

Describe what happens when sulfur at 25 °C is slowly heated to 200 °C at a constant pressure of 1 atm.

It changes into the monoclinic form and then it melts.

How many triple points are there in the phase diagram? **3**

What phases are in equilibrium at each of the triple points?

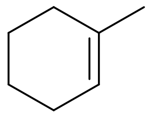
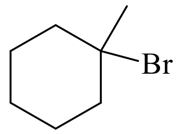
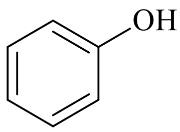
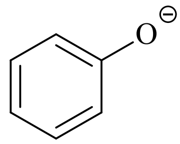
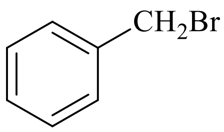
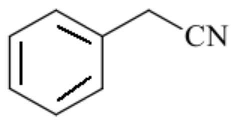
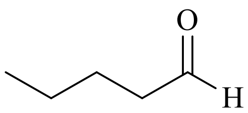
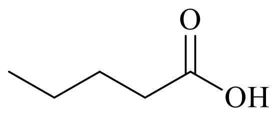
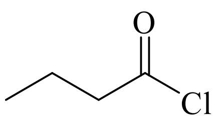
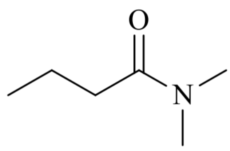
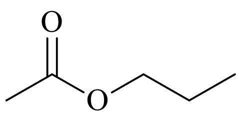
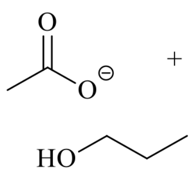
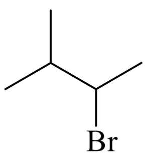
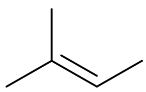
- **rhombic, monoclinic and vapour (at 95.31 °C and 5.1×10^{-6} atm);**
- **monoclinic, liquid and vapour (at 115.18 °C and 3.2×10^{-5} atm);**
- **rhombic, monoclinic and liquid (at 153 °C and 1420 atm);**

Which solid form of sulfur is more dense? Explain your reasoning.

Rhombic is denser. If you start in the monoclinic region and increase the pressure at constant temperature *(i.e.* draw a vertical line upwards) you move into the rhombic region. Rhombic is thus the more stable form at higher pressures, so must be denser.

Marks
11

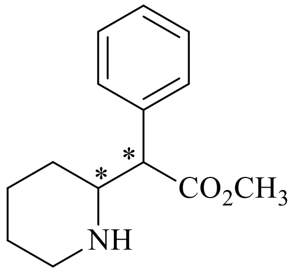
- Complete the following table. Make sure you give the name of the starting material where indicated.

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
 **Name: 1-methylcyclohexene**	HBr / CCl_4 (solvent)	
	NaOH	
	KCN / ethanol (solvent)	
 **Name: pentanal**	$Cr_2O_7^{2-}$ / H^+	
	excess $(CH_3)_2NH$	 + $(CH_3)_2\overset{\oplus}{N}H_2$
	hot 3 M NaOH	
	**hot conc. KOH in ethanol solvent**	

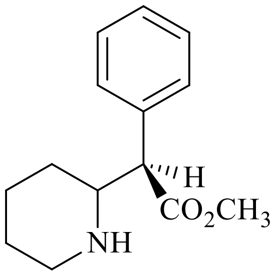
Marks
7

- Methylphenidate, also known as Ritalin, is a psychostimulant drug approved for the treatment of attention-deficit disorder. Identify all stereogenic (chiral) centres in methylphenidate by clearly marking each with an asterisk (*) on the structure below.

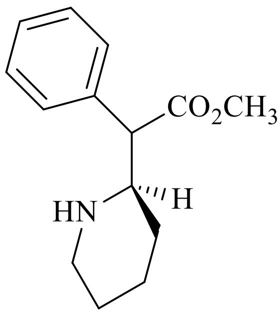
methylphenidate



Using a stereogenic centre you have identified, draw the (*R*)-configuration of that centre.



or



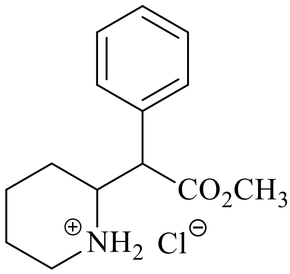
How many stereoisomers are there of methylphenidate? Describe the relationships between these isomers.

4: each isomer has 1 enantiomer and 2 diastereoisomers

Ritalin is generally sold as the hydrochloride salt, formed when methylphenidate is treated with dilute hydrochloric acid. Draw the structure of this salt and suggest why this is the preferred compound for sale.

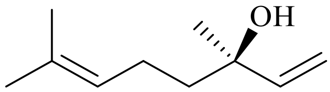
The hydrochloride salt is soluble in water, which generally means better bioavailability.

Salt will have better stability - amines are prone to aerial oxidation.



Marks 8

- The structure of (–)-linalool, a commonly occurring natural product, is shown below.



What is the molecular formula of (–)-linalool?

$C_{10}H_{18}O$

Which of the following best describes (–)-linalool?
achiral compound, racemic mixture,
(*R*)-enantiomer, or (*S*)-enantiomer

(*R*)-enantiomer

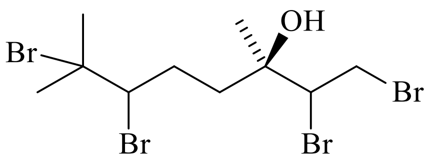
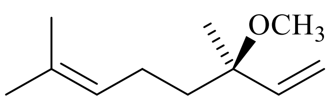
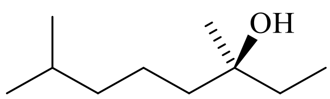
What functional groups are present in (–)-linalool?

Tertiary alcohol and alkene.

Is it possible to obtain (*Z*) and (*E*) isomers of (–)-linalool? Give a reason for your answer.

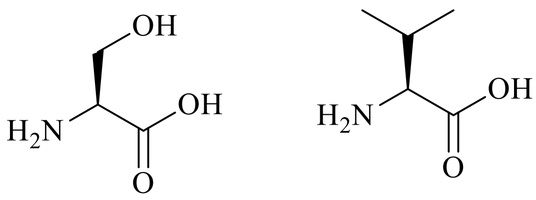
No. One end of each double bond has two identical groups (methyl or hydrogen) attached to it.

Give the constitutional formula of the organic product formed from (–)-linalool in each of the following reactions. NB: If there is no reaction, write "no reaction".

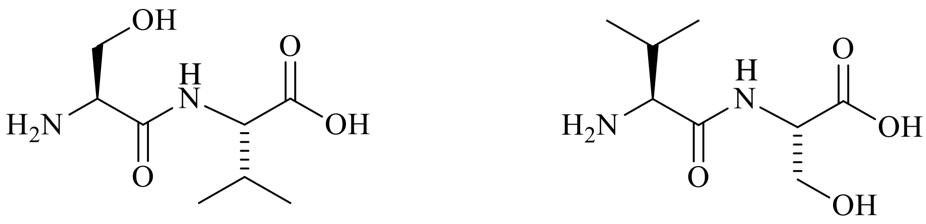
Reagents / Conditions	Constitutional Formula of Product
Br_2 (in CCl_4 as solvent)	
$Na_2Cr_2O_7$ in aqueous acid	**no reaction**
Na, then CH_3Br	
H_2 / Pd-C catalyst	

Marks 3

- The amino acids serine and valine can be reacted together to form 2 dipeptides. Draw the structures of the 2 possible dipeptides.



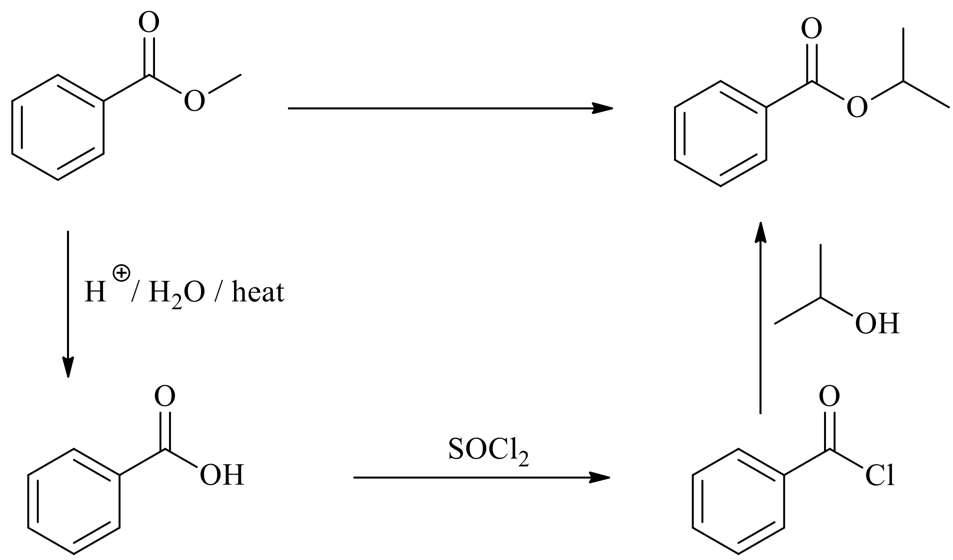
serine valine



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

- Show clearly the reagents you would use to carry out the following chemical conversion. More than one step is required. Give the structure of any intermediate compounds formed. **3**



- Convert the following structure into a Fischer projection. **3**