Topics in the June 2014 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2014-J-2:

- Crystal Structures
- Coordination Chemistry
- Kinetics
- Kinetics - Influences
- Kinetics - Catalysis

2014-J-3:

- Weak Acids and Bases

2014-J-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2014-J-5:

- Coordination Chemistry

2014-J-6:

- Solubility Equilibrium

2014-J-7:

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

2014-J-8:

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

2014-J-9:

- Stereochemistry
- Carboxylic Acids and Derivatives

2014-J-10:

- Stereochemistry
- Alkenes
- Alcohols

2014-J-11:

- Alcohols
- Organic Halogen Compounds

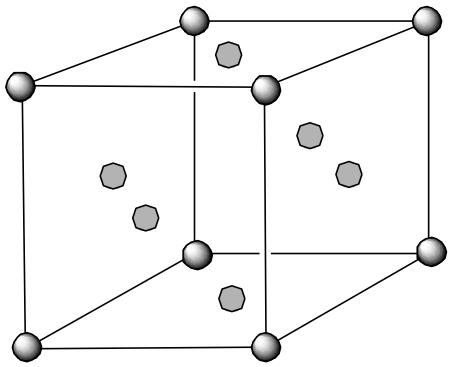
2014-J-12:

- Carboxylic Acids and Derivatives

- Alcohols
- Aldehydes and Ketones
- Synthetic Strategies

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**



= Au = Cu

What is the chemical formula of the alloy?

There are 8 Au atoms on the corners: each contributes 1/8 to the unit cell so the net number of Au atoms is 8 × 1/8 = 1.

There are 6 Cu atoms on the faces: each contributes 1/2 to the unit cell so the net number of Cu atoms is 6 × 1/2 = 3.

Answer: **Cu_3Au**

- 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**

Co^{2+} has a $3d^7$ configuration: ↑↓ | ↑↓ | ↑ | ↑ | ↑

Co^{2+} is a d^7 system, so must have at least 1 unpaired electron. Consequently it must be paramagnetic.

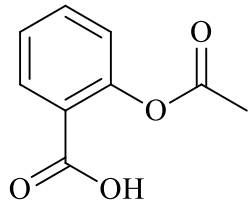
- Briefly explain how a catalyst works. **2**

A catalyst provides an alternative reaction pathway that has a lower activation energy. This allows the reaction to proceed at lower temperatures or under milder conditions. The catalyst is not consumed during the reaction and does not affect the final position of equilibrium.

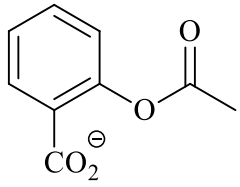
Marks 5

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

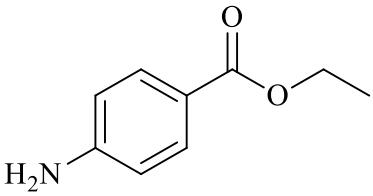
  (a) Draw the conjugate base of aspirin and the conjugate acid of benzocaine.
  (b) *Circle* the form of each that will be present in a highly acidic environment.



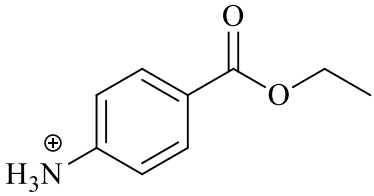
aspirin



conjugate base of aspirin



benzocaine



conjugate acid of benzocaine

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** / benzocaine
Drug absorbed in the intestine:	aspirin / **benzocaine**

Aspirin is absorbed in the stomach as it remains in the neutral uncharged form in the acidic environment.

Benzocaine is absorbed in the intestine as it remains in the neutral uncharged form in the basic environment.

Aspirin, $C_9H_8O_4$ is not very soluble in water. "Soluble aspirin", the sodium salt $NaC_9H_7O_4$, is often administered instead. 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.

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

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:

	$C_9H_8O_4(aq)$	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:

$$K_a = \frac{[H_3O^+][C_9H_7O_4^-(aq)]}{[C_9H_8O_4(aq)]} = \frac{x^2}{0.010-x}$$

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**

Ammonia, NH_3, is a weak base in water. Write the equation for the acid/base reaction between aspirin and ammonia.

$$C_9H_8O_4(aq) + NH_3(aq) \rightarrow C_9H_7O_4^-(aq) + NH_4^+(aq)$$

What is the expression for the equilibrium constant, *K*, for this reaction?

$$K = \frac{[NH_4^+(aq)][C_9H_7O_4^-(aq)]}{[NH_3(aq)][C_9H_8O_4(aq)]}$$

Rewrite this expression in terms of the K_a of aspirin and the K_a of NH_4^+. (Hint: multiply by $[H^+]/[H^+] = 1$) Hence calculate the value of *K*. The pK_a of NH_4^+ is 9.2.

For $C_9H_8O_4$, K_a ($C_9H_8O_4$) = $\frac{[H_3O^+][C_9H_7O_4^-(aq)]}{[C_9H_8O_4(aq)]} = 10^{-3.5}$

For NH_3, K_a (NH_4^+) = $\frac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]} = 10^{-9.2}$

$$K = \frac{[NH_4^+(aq)][C_9H_7O_4^-(aq)]}{[NH_3(aq)][C_9H_8O_4(aq)]} = \frac{[NH_4^+(aq)]}{[NH_3(aq)][H^+(aq)]} \times \frac{[H^+(aq)][C_9H_7O_4^-(aq)]}{[C_9H_8O_4(aq)]}$$

$$= \quad (1 / K_a(NH_3)) \quad \times \quad K_a(C_9H_8O_4)$$

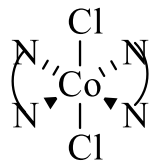
$$K = (1 / 10^{-9.2}) \times (10^{-3.5}) = 10^{5.7} = 5.0 \times 10^5$$

Answer: 5.0×10^5

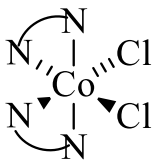
Would aspirin dissolve in a solution of ammonia? Explain your answer.

The equilibrium constant for the reaction of ammonia and aspirin is very large: aspirin will dissolve.

• Name the complex $[CoCl_2(en)_2]$. en = ethylenediamine = $NH_2CH_2CH_2NH_2$	**Marks 4**
dichloridobis(ethylenediamine)cobalt(II)	
Draw all possible isomers of this complex.	



trans isomer



cis isomers

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 8

- A solution is prepared that contains sodium chloride and sodium chromate (both 0.10 M). When a concentrated solution of silver nitrate is added slowly, white AgCl(s) begins to precipitate. After most of the Cl^-(aq) has been consumed, red Ag_2CrO_4(s) starts to precipitate.

  Ignoring dilution, what is the concentration of silver ions when silver chloride solid first starts to precipitate? K_{sp} (AgCl) is 1.8×10^{-10}.

K_{sp} refers to the dissolution reaction: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$K_{sp}(AgCl) = [Ag^+(aq)][Cl^-(aq)]$

As $[Cl^-(aq)] = 0.10$ M, the minimum concentration of $Ag^+(aq)$ required to ensure AgCl(s) is present is given by:

$[Ag^+(aq)] = K_{sp}(AgCl) / [Cl^-(aq)] = (1.8 \times 10^{-10} / 0.10)$ M $= 1.8 \times 10^{-9}$ M

Answer: **1.8×10^{-9} M**

Ignoring dilution, what is the concentration of silver ions when silver chromate solid first starts to precipitate? K_{sp} (Ag_2CrO_4) is 3.6×10^{-12}.

K_{sp} refers to the dissolution reaction: $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^-(aq)$

$K_{sp}(Ag_2CrO_4) = [Ag^+(aq)]^2[CrO_4^-(aq)]$

As $[CrO_4^-(aq)] = 0.10$ M, precipitation of Ag_2CrO_4(s) will occur when:

$[Ag^+(aq)]^2 = K_{sp}(Ag_2CrO_4) / [CrO_4^-] = (3.6 \times 10^{-12} / 0.10)$ M $= 3.6 \times 10^{-11}$ M

$[Ag^+(aq)] = 6.0 \times 10^{-6}$ M

Answer: **6.0×10^{-6} M**

What is the concentration of chloride ions when silver chromate solid first starts to precipitate?

As $[Ag^+(aq)] = 6.0 \times 10^{-6}$ M when silver chromate starts to precipitate, the concentration of Cl^-(aq) is given by:

$[Cl^-(aq)] = K_{sp}(AgCl) / [Ag^+(aq)] = (1.8 \times 10^{-10} / 6.0 \times 10^{-6})$ M $= 1.8 \times 10^{-9}$ M

$= 3.0 \times 10^{-5}$ M

Answer: **3.0×10^{-5} M**

ANSWER CONTINUES ON THE NEXT PAGE

What percentage of the chloride ion is precipitated before any silver chromate is precipitated?

When silver chromate first precipitates, $[Cl^-(aq)] = 3.0 \times 10^{-5}$ M. Initially, $[Cl^-(aq)] = 0.10$ M so the percentage that has precipitated as AgCl(s) at this point is:

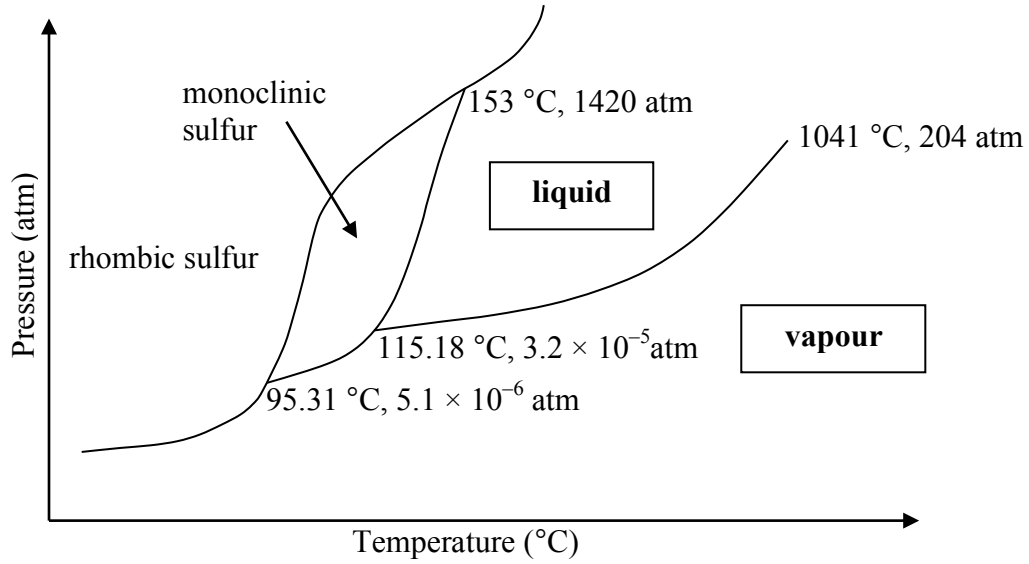
$$\textbf{percentage precipitated} = \frac{(0.10 - 3.0 \times 10^{-5})}{0.10} \times 100\% = 99.97\%$$

Answer: **99.97%**

Marks 6

- Solid sulfur can exist in two forms, rhombic sulfur and monoclinic sulfur. A portion of the phase diagram for sulfur is reproduced schematically below. The pressure and temperature axes are not drawn to scale.

  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 the triple points?

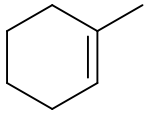
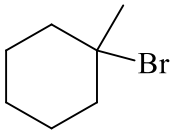
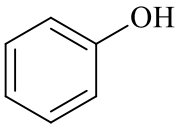
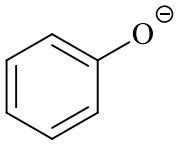
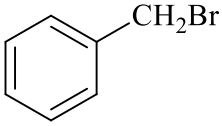
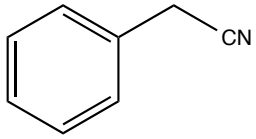
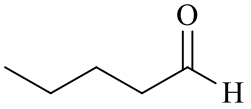
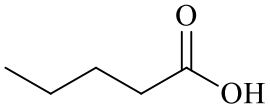
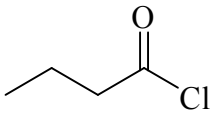
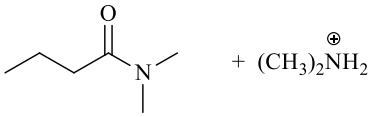
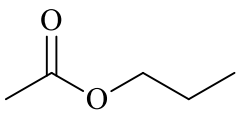
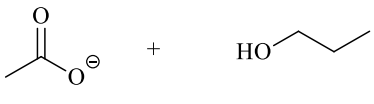
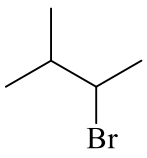
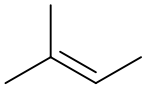
- **rhombic, monoclinic and vapour (at 95.31 °C and 5.1 × 10^{-6} atm);**
- **monoclinic, liquid and vapour (at 115.18 °C and 3.2 × 10^{-5} atm);**
- **rhombic, monoclinic and liquid (at 153 °C and 1420 atm);**

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

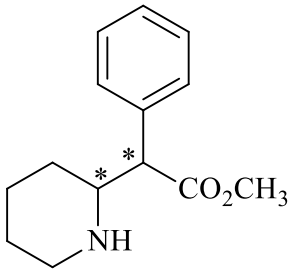
- Complete the following table. Make sure you give the name of the starting material where indicated.

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

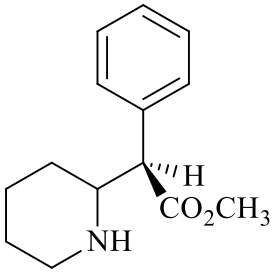
Marks 7

- 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.

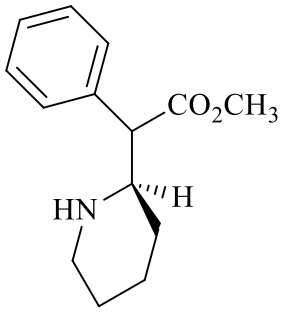
methylphenidate



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



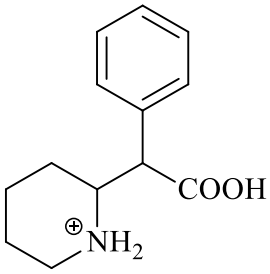
or



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

4 isomers: there are 2 pairs of enantiomers:
Each isomer has 1 enantiomer and 2 diastereoisomers

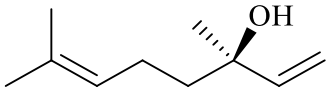
Give the products formed when methylphenidate is hydrolysed with 4 M HCl.



+ CH_3OH

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

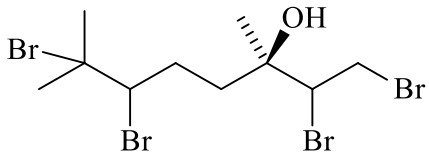
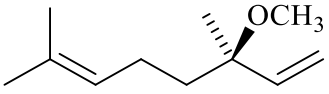
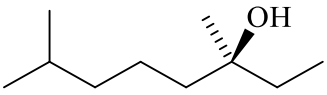
What functional groups are present in (–)-linalool?

Tertiary alcohol and alkene

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

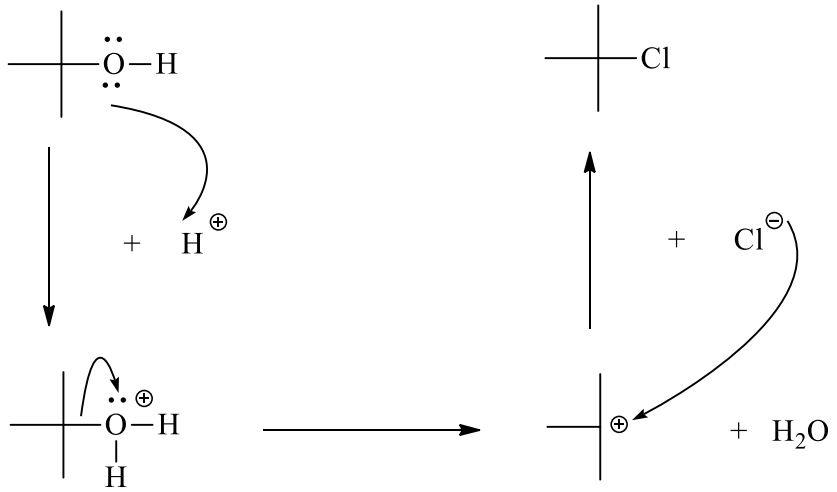
No. One end of each double bond has two identical groups (methyl or hydrogen) attached to it.

Give the structural 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	Structural 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 4

- Concentrated HCl reacts with 2-methyl-2-propanol in an S_N1 reaction to give 2-chloro-2-methylpropane as shown below. Complete the reaction mechanism by adding curly arrows and formal charges on the intermediates as appropriate.



Explain what each part of the abbreviation S_N1 means.

S = **substitution**

N = **nucleophilic**

1 = **unimolecular**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 6

- Show clearly the reagents you would use to carry out the following chemical conversions. More than one step is required in each case. Give the structure of any intermediate compounds formed.