

**Topics in the June 2009 Exam Paper for CHEM1102**

Click on the links for resources on each topic.

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- [Periodic Trends in Aqueous Oxide](#)
- [Coordination Chemistry](#)

2009-J-3:

- [Strong Acids and Bases](#)
- [Kinetics - Catalysis](#)
- [Physical States and Phase Diagrams](#)
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2009-J-4:

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2009-J-5:

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- Explain in terms of their electronic configurations **and** ionisation energies why the halogens (Group 17) are powerful *oxidising* agents.

**Marks**  
**2**

**Oxidising agents are themselves reduced (*i.e.* they gain electrons).**

The electronic configuration of the halogens (Group 17) is  $np^5$ . They are small atoms (atomic size decreases across a period as the nuclear charge increases). In each period, the halogen is the element with the highest number of protons in the nucleus that also has an incomplete shell.

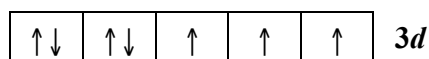
As a result, they will readily gain a single electron to form the  $X^-$  ion.

Similarly, the high nuclear charge and small size means that they have high ionisation energies. Hence halogens are poor reducing agents.

- 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**

A cobalt atom has 9 valence electrons: it is in Group 9 of the Periodic Table. A  $Co^{2+}$  cation has lost 2 electrons so has  $(9 - 2) = 7$  valence electrons. The configuration of  $Co^{2+}$  is  $3d^7$ . These occupy the five *d*-orbitals to maximize the number of unpaired electrons (to minimize the electron-electron repulsion):



$Co^{2+} (d^7)$

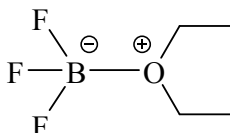
Paramagnetism arises as a result of the presence of 1 or more unpaired electrons.  $Co^{2+}$  has 3 unpaired electrons and so is paramagnetic.

- $\text{BF}_3$  is a Lewis acid in its reaction with diethyl ether. Explain what is meant by a Lewis acid and draw the product of this reaction.

**Marks**  
**2**

**A Lewis acid is an electron pair acceptor.**

$\text{BF}_3$  possess an empty  $p$ -orbital on B.  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  possess a lone pair on O.  $\text{BF}_3$  reacts with  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  by accepting this pair of electrons:  $\text{BF}_3$  acts as a Lewis acid and  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  acts as a Lewis base.

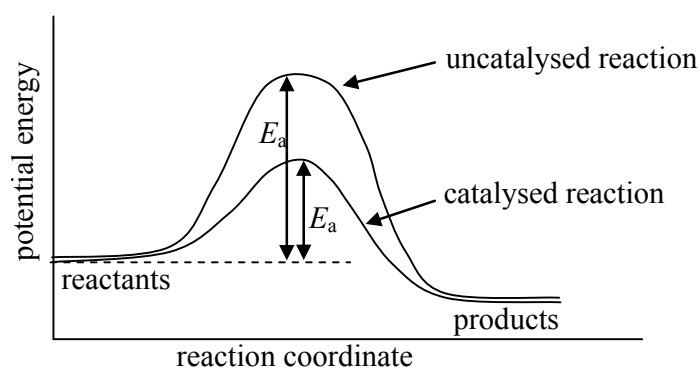


- What is a catalyst and, in general terms, how does it work? Make reference to an energy level diagram in your answer.

**2**

**A catalyst is a substance that increases the rate of a reaction without being consumed in the reaction.**

**A catalyst works by providing an alternative reaction pathway of lower activation energy,  $E_a$ .**



- The gas methane,  $\text{CH}_4$ , has a critical point at  $-82^\circ\text{C}$  and 46 atm. Can methane be liquefied at  $25^\circ\text{C}$ ? Explain your answer.

**2**

**The critical temperature ( $T_c$ ) is the temperature above which a substance cannot exist as a liquid. Thus, methane cannot be liquefied above  $-82^\circ\text{C}$  and so cannot be liquefied at  $25^\circ\text{C}$ .**

- Define what is meant by an “allotrope”. Give an example of a pair of allotropes involving (i) oxygen and (ii) a pair not involving oxygen.

**2**

**Allotropes are different structural forms of the same element.**

**(i) Dioxygen,  $\text{O}_2$ , and ozone,  $\text{O}_3$ , are allotropes of oxygen.**

**(ii) Examples include (a) white and red phosphorus, (b) graphite, diamond and fullerene for carbon and (c) rhombic, monoclinic and amorphous sulfur.**

- Complete the following table. (en = ethylenediamine =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ )

**Marks**  
**9**

Formula	$\text{K}_2[\text{CoCl}_4]$	$\text{Na}_3[\text{FeBr}(\text{CN})_5]$	$[\text{Zn}(\text{en})_2(\text{NO}_3)_2]$
Oxidation state of transition metal ion	<b>+2 (II)</b>	<b>+3 (III)</b>	<b>+2 (II)</b>
Coordination number of transition metal ion	<b>4</b>	<b>6</b>	<b>6</b> <b>(4 × N from en and 2 × O from <math>\text{NO}_3^-</math>)</b>
Number of <i>d</i> -electrons in the transition metal ion	<b>7</b> <b>(Co is in Group 9 so <math>\text{Co}^{2+}</math> has 9 – 2 = 7)</b>	<b>5</b> <b>(Fe is in Group 8 so <math>\text{Fe}^{3+}</math> has 8 – 3 = 5)</b>	<b>10</b> <b>(Zn is in Group 12 <math>\text{Zn}^{2+}</math> has 12 – 2 = 10)</b>
Charge of the complex ion	<b>2–</b> <b><math>[\text{CoCl}_4]^{2-}</math></b>	<b>3–</b> <b><math>[\text{FeBr}(\text{CN})_5]^{3-}</math></b>	<b>0</b> <b><math>[\text{Zn}(\text{en})_2(\text{NO}_3)_2]</math></b>
Geometry of the complex ion	<b>tetrahedral</b>	<b>octahedral</b>	<b>octahedral</b>
List all the ligand donor atoms	<b>4 × Cl</b>	<b>1 × Br and 5 × C</b>	<b>4 × N and 2 × O</b>

- Solution A consists of a 0.020 M aqueous solution of propionic acid,  $\text{C}_3\text{H}_6\text{O}_2$ , at 25 °C. Calculate the pH of Solution A. The  $\text{p}K_a$  of propionic acid is 4.87.

**Marks**  
**8**

As  $\text{C}_3\text{H}_6\text{O}_2$  is a weak acid,  $[\text{H}^+]$  must be calculated by considering the equilibrium:

	$\text{C}_3\text{H}_6\text{O}_2$	$\rightleftharpoons$	$\text{C}_3\text{H}_5\text{O}_2^-$	$\text{H}^+$
initial	0.020		0	0
change	-x		+x	+x
final	$0.020 - x$		x	x

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[\text{C}_3\text{H}_5\text{O}_2^-][\text{H}^+]}{[\text{C}_3\text{H}_6\text{O}_2]} = \frac{x^2}{(0.020 - x)}$$

As  $\text{p}K_a = 4.87$ ,  $K_a = 10^{-4.87}$ .  $K_a$  is very small so  $0.020 - x \sim 0.020$  and hence:

$$x^2 = 0.020 \times 10^{-4.87} \quad \text{or} \quad x = 0.000519 \text{ M} = [\text{H}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}[0.000519] = 3.28$$

Answer: **pH = 3.28**

At 25 °C, 1.00 L of Solution B consists of 2.24 g of potassium propionate ( $\text{KC}_3\text{H}_5\text{O}_2$ ) dissolved in water. Calculate the pH of Solution B.

The molar mass of  $\text{KC}_3\text{H}_5\text{O}_2$  is:

$$\begin{aligned} \text{molar mass} &= (39.10 \text{ (K)} + 3 \times 12.01 \text{ (C)} + 5 \times 1.008 \text{ (H)} + 2 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} \\ &= 112.17 \text{ g mol}^{-1} \end{aligned}$$

Thus, 2.24 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{2.24 \text{ g}}{112.17 \text{ g mol}^{-1}} = 0.0200 \text{ mol}$$

If this is dissolved in 1.0 L,  $[\text{C}_3\text{H}_5\text{O}_2^-]_{\text{initial}} = 0.0200 \text{ M}$ .

As  $\text{C}_3\text{H}_5\text{O}_2^-$  is a weak base,  $[\text{C}_3\text{H}_5\text{O}_2^-]$  must be calculated by considering the equilibrium:

ANSWER CONTINUES ON THE NEXT PAGE

	$\text{C}_3\text{H}_5\text{O}_2^-$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{C}_3\text{H}_6\text{O}_2$	$\text{OH}^-$
<b>initial</b>	<b>0.0200</b>	<b>large</b>		<b>0</b>	<b>0</b>
<b>change</b>	<b>-y</b>	<b>negligible</b>		<b>+y</b>	<b>+y</b>
<b>final</b>	<b><math>0.0200 - y</math></b>	<b>large</b>		<b>y</b>	<b>y</b>

The equilibrium constant  $K_b$  is given by:

$$K_b = \frac{[\text{C}_3\text{H}_6\text{O}_2][\text{OH}^-]}{[\text{C}_3\text{H}_5\text{O}_2^-]} = \frac{y^2}{(0.0200 - y)}$$

For an acid and its conjugate base:

$$\text{p}K_a + \text{p}K_b = 14.00$$

$$\text{p}K_b = 14.00 - 4.87 = 9.13$$

As  $\text{p}K_b = 9.13$ ,  $K_b = 10^{-9.13}$ .  $K_b$  is very small so  $0.0200 - y \sim 0.0200$  and hence:

$$y^2 = 0.0200 \times 10^{-9.13} \text{ or } y = 0.000000385 \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}[0.000000385] = 5.41$$

Finally,  $\text{pH} + \text{pOH} = 14.00$  so

$$\text{pH} = 14.00 - 5.41 = 8.59$$

Answer: **pH = 8.59**

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

Combining the two solutions will double the overall volume, to 2.00 L. As a result, the concentration of both the acid and base will halve: [acid] = 0.010 M and [base] = 0.0100 M.

The solution contains a weak acid and its conjugate base. The pH of this buffer solution can be calculated using the Henderson-Hasselbalch equation:

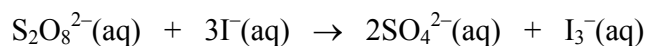
$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.87 + \log \frac{0.0100}{0.010} = 4.87$$

Answer: **pH = 4.87**

If you wanted to adjust the pH of Solution C to be exactly equal to 5.00, which component in the mixture would you need to increase in concentration?

**More base is needed: add  $\text{KC}_3\text{H}_5\text{O}_2$**

- Peroxydisulfate and iodide ions react according to the following equation.



The following rate data were collected at room temperature.

Experiment	$[\text{S}_2\text{O}_8^{2-}(\text{aq})]_0$ (M)	$[\text{I}^-(\text{aq})]_0$ (M)	Initial rate ( $\text{mol L}^{-1} \text{s}^{-1}$ )
1	0.080	0.034	$2.2 \times 10^{-4}$
2	0.080	0.017	$1.1 \times 10^{-4}$
3	0.160	0.017	$2.2 \times 10^{-4}$

Determine the rate law for the reaction.

Between experiments (1) and (2),  $[\text{S}_2\text{O}_8^{2-}(\text{aq})]_0$  is constant and  $[\text{I}^-(\text{aq})]_0$  is halved from 0.034 M to 0.017 M. This halves the initial rate. The rate is directly proportional to  $[\text{I}^-(\text{aq})]$ : the reaction is first order with respect to  $[\text{I}^-(\text{aq})]$ .

Between experiments (2) and (3),  $[\text{I}^-(\text{aq})]_0$  is constant and  $[\text{S}_2\text{O}_8^{2-}(\text{aq})]_0$  is doubled from 0.080 M to 0.160 M. This doubles the initial rate. The rate is directly proportional to  $[\text{S}_2\text{O}_8^{2-}(\text{aq})]$ : the reaction is first order with respect to  $[\text{S}_2\text{O}_8^{2-}(\text{aq})]$ .

Hence:

$$\text{rate} = k[\text{S}_2\text{O}_8^{2-}(\text{aq})][\text{I}^-(\text{aq})]$$

Calculate the value of the rate constant at room temperature.

From experiment (1), the rate =  $2.2 \times 10^{-4} \text{ M s}^{-1}$  when  $[\text{S}_2\text{O}_8^{2-}(\text{aq})] = 0.080 \text{ M}$  and  $[\text{I}^-(\text{aq})] = 0.034 \text{ M}$ . Hence:

$$2.2 \times 10^{-4} \text{ M s}^{-1} = k(0.080 \text{ M})(0.034 \text{ M})$$

$$k = 0.081 \text{ M}^{-1} \text{s}^{-1}$$



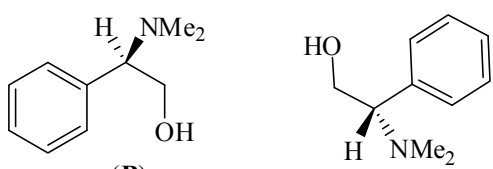
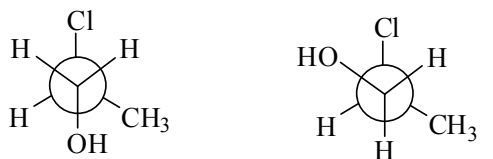
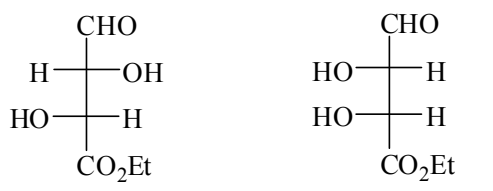
(Note that the units are worked out by requiring that the units on the two sides of the rate law are the same.)

Answer:  $0.081 \text{ M}^{-1} \text{s}^{-1}$

**Marks**  
**3**

- Consider the following pairs of compounds. Indicate the isomeric relationship that exists between the compounds in each set.

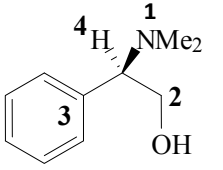
**Marks**  
**8**

	<b>constitutional isomers</b> <b>(different connectivity)</b>
 <b>(A)</b>	<b>diastereoisomers</b> <b>(same connectivity but different 3D arrangement)</b>
 <b>(B)</b>	<b>enantiomers</b> <b>(non-superimposable mirror images)</b>
	<b>conformational isomers</b> <b>(can be interconverted by rotation of the central C-C bond)</b>
 <b>(C)</b>	<b>diastereoisomers</b> <b>(same connectivity but different 3D arrangement. Not enantiomers)</b>

Give the full name of compound **(A)** that unambiguously describes its stereochemistry.

**(E)-2-pentene. (The alkyl groups are on opposite sides of the C=C hence (E)).**

What is the configuration of the stereogenic centre in compound **(B)**?

 <b>(B)</b>	<p>The priorities are indicated on the figure. With the lowest priority at the back, the sequence 1-2-3 is in a clockwise direction: <b>(R)</b>.</p>
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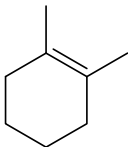
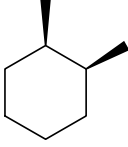
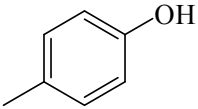
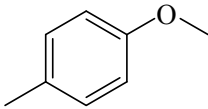
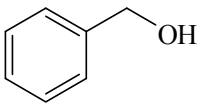
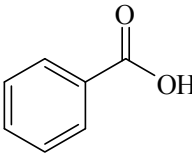
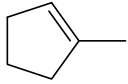
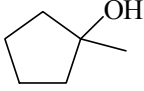
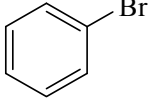

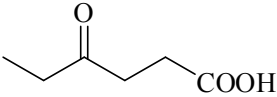
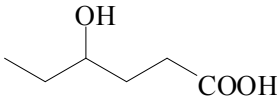
Is compound **(C)** a *meso* isomer? Give a reason for your answer.

**No. C does not have a plane of symmetry so is optically active.**

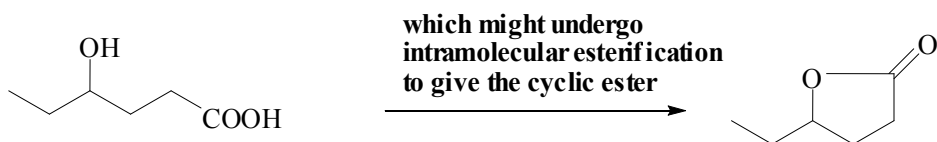


- Complete the following table. Make sure you indicate any relevant stereochemistry.

**Marks**  
**6**

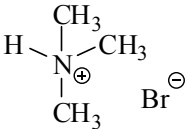
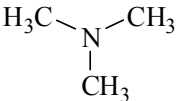
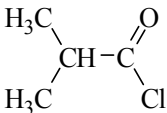
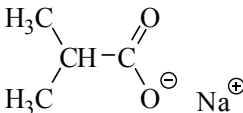
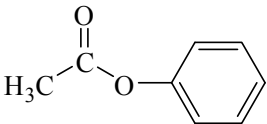

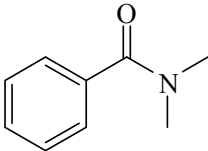
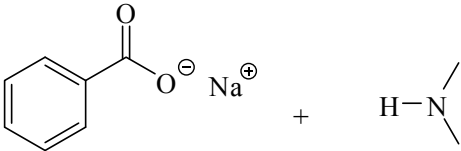
STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	$\text{H}_2/\text{Pd/C}$ (catalyst)	
	1. dilute NaOH 2. $\text{CH}_3\text{Br}$	
	$\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$	
	aqueous $\text{H}_2\text{SO}_4$	
	1. Mg / dry ether 2. $\text{H}_2\text{O}$	
	1. $\text{NaBH}_4$ 2. $\text{H}^+/\text{H}_2\text{O}$	

The final product may react further:



- Give the constitutional formula(s) of the organic product(s) formed when each of the following compounds is treated with 4 M sodium hydroxide. The first three reactions proceed at room temperature; the last two require heating.

**Marks**  
**7**

COMPOUND	ORGANIC PRODUCT(S)
$\text{CH}_3\text{CH}_2\text{COOH}$	$\text{CH}_3\text{CH}_2\text{CO}_2^\ominus$
	
	
	
	

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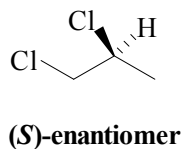
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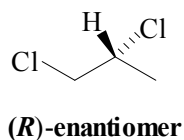
- 1,2-Dichloropropane can exist in two enantiomeric forms, compounds I and II. In the boxes below draw structures of the two enantiomers of 1,2-dichloropropane clearly showing the stereochemistry at the chiral carbon.

**Marks  
5**

compound I



compound II

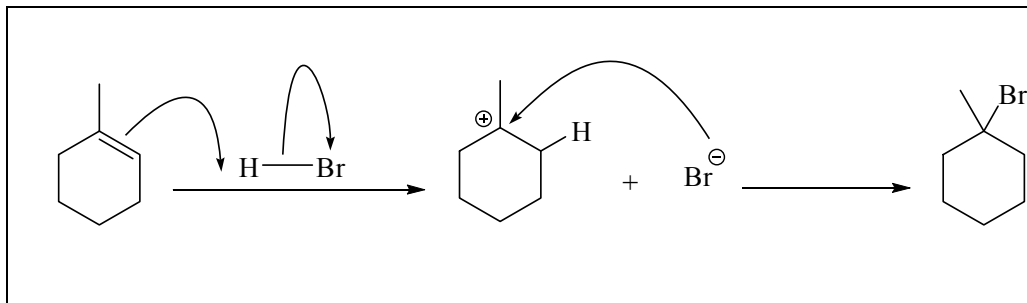


There are three other compounds, III, IV and V with molecular formula  $C_3H_6Cl_2$ . In the boxes below, give the constitutional formulas and names of these compounds.

Structure	Name
compound III 	<b>2,2-dichloropropane</b>
compound IV 	<b>1,1-dichloropropane</b>
compound V 	<b>1,3-dichloropropane</b>

Compounds I, II, III, IV and V are isomers. From the list <i>enantiomers</i> , <i>diastereomers</i> , <i>conformers</i> , <i>constitutional isomers</i> complete the following table.		<b>Marks 4</b>
PAIR OF COMPOUNDS	ISOMERIC RELATIONSHIP BETWEEN PAIR OF COMPOUNDS	
I and III	<b>constitutional isomers</b>	
I and IV	<b>constitutional isomers</b>	
II and IV	<b>constitutional isomers</b>	
1,2-Dichloropropane can be synthesised in the laboratory by treatment of propene with chlorine as is shown in the following equation.		
$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array} \xrightarrow{\text{Cl}_2} \begin{array}{c} & \text{CH}_3 \\ & / \\ \text{Cl}-\text{CH}_2-\text{C}-\text{Cl} \\ & \diagdown \\ & \text{H} \end{array}$		
Which of the following best describes the product: ( <i>R</i> )-enantiomer, ( <i>S</i> )-enantiomer, racemate?		<b>racemate (equal amounts of (<i>R</i>) and (<i>S</i>) will be formed)</b>

- Give the mechanism of the reaction that occurs when 1-methylcyclohexene is converted to 1-bromo-1-methylcyclohexane by the addition of HBr. Give the structure of the intermediate carbocation that is formed and indicate (with curly arrows) all the bonding changes that occur.

**Marks**  
**3**

- Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step will be required. Indicate all necessary steps and the constitutional formulas of any intermediate compounds.

**Marks**  
**6**