Topic 1: The Mole Concept, Stoichiometry and Redox

1. SRJC/PRELIMS 2011/P3/1(a), (b)

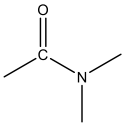
Acrylamide is a compound that is found in many deep fried foods such as French fries and potato chips. It is believed to be carcinogenic.

(a) Acrylamide contains 50.7% by mass of carbon, 7.0% by mass of hydrogen, 19.8% by mass of nitrogen and 22.5% by mass of oxygen. Given that the relative molecular mass of acrylamide is 71.0,

(i) determine the molecular formula of acrylamide.

(ii) Hence, draw a possible structure of acrylamide.

Hint: an amide has the following functional group



(b) Acrylamide is also found in beverages such as prune juice and coffee. Studies show that a person can safely ingest up to 0.5 mg / kg body weight in a day without any observed adverse effects. Given that 1 kg of brewed coffee contains 1.2×10^{-7} mol of acrylamide, calculate the maximum volume of coffee a 50 kg woman can drink per day. You may assume that coffee has the same density as water.

2. RVHS/PRELIMS 2011/P3/4(b)

Chlorine can also be used to synthesize a bromine-containing oxoanion that is mainly used in continuous or batch dyeing processes.

When chlorine is passed through an aqueous solution containing potassium hydroxide and potassium bromide, the bromide ions are oxidised to the bromine-containing oxoanion.

Careful addition of aqueous lead nitrate to the resulting solution precipitates 4.17 g of $PbCl_2$. When this precipitate is filtered off and the resulting filtrate is evaporated, 0.835 g of a white crystalline solid is obtained. The white solid has the following composition by mass: K, 23.4 %; Br, 47.8 %; O, 28.8 %.

(i) Determine the formula of the white crystalline solid.

(ii) Calculate molar ratio of white crystalline solid to lead chloride formed.

(iii) Hence, construct a balanced equation for the reaction between chlorine, potassium bromide and potassium hydroxide.

3. NYJC/PRELIMS 2014/P2/4(b)

In an experiment, H_2S was reacted with 12.00 cm^3 of 0.30 mol dm^{-3} of an unknown bromate ion, BrO_x^- in acidic medium to form sulfur, S, of mass 0.289 g and bromine solution.

Deduce the oxidation state of Br in BrO_x^-, and hence the value of **x**.

Criteria of Success Checklist
For each question, tick if you have
☐ provided clear s_____ for ALL working ☐ presented i_____ answers to 4 s.f. ☐ presented final answers to _____ ☐ provided units, when applicable ☐ presented value of A_r or M_r to _____., when applicable
Things to note: • Conversion of units for volume: 1 dm^3 = _____ cm^3 = _____ m^3 1 cm^3 = _____ dm^3 = _____ m^3 1 m^3 = _____ dm^3 = _____ cm^3 • In the calculation of empirical formula from experimental data, if the following figures are obtained for the number of moles, they are usually multiplied by a factor in order to get the correct simplest ratio. E,g 1.5 (multiply by __), 1.33 (multiply by __), 1.25 (multiply by __), 1.2 (multiply by __)

- In balancing half equations,
    1. balance the atom that is not ___ or ____ first.
    2. Balance O by adding _____
    3. Balance H by adding _____
    4. Balance charge by adding _____

    Continue with step 5 to 7 for basic medium

    5. Add _____ (same number of moles as H^+) to both sides of the equation
    6. For every mole of $H^+ + OH^-$, replace it with 1 mol of _____
    7. Simplify the equation (if necessary) by cancelling out _____ that occurs on both sides of the equation.

- For questions to calculate oxidation number in redox reactions,
    1. Write out one _____ equation for the known species
    2. Work out the _____ ratio of the 2 reactants
    3. Using the mole ratio and the half equation written, determine the number of _____ transferred in the redox reaction. The number of electrons given out by the species that is oxidised will be _____ by the species that is reduced.
    4. Determine the original/final oxidation number by taking into account the final/original oxidation state and the number of electrons taken in/ given out.
- For oxidation state, the sign is written _____ of the number e.g +2, -1.

Topic 2: Atomic Structure

1. (a) JJC/PRELIMS 2004/P2/Q1

Particle	Electric charge	Mass Number	Number of		
			Protons	Electrons	Neutrons
X	0		16		16
Y	-1	81		36	
Z		70	31	28	

Complete the table above.

(b) (i) Using *spdf* notation, give the electronic configuration of particle **Y** and **Z**.

Y: _____

Z: _____

(ii) Compare the ionic size of particle **Y** and $_{37}Rb^{+}$. Give your reason.

_____

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(c) State, with reasons, whether the first ionization energy of element **X** is higher or lower when compared with that of **(i)** phosphorus and **(ii)** selenium.

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Things to note:

- **Criteria of success for electronic configuration include**
  - starting from $1s^2$ ([Ar] $3d^{10}4s^24p^6$ is not acceptable)
  - superscript to represent number of _____in the subshell (1s2 or $1s_2$ are not acceptable)

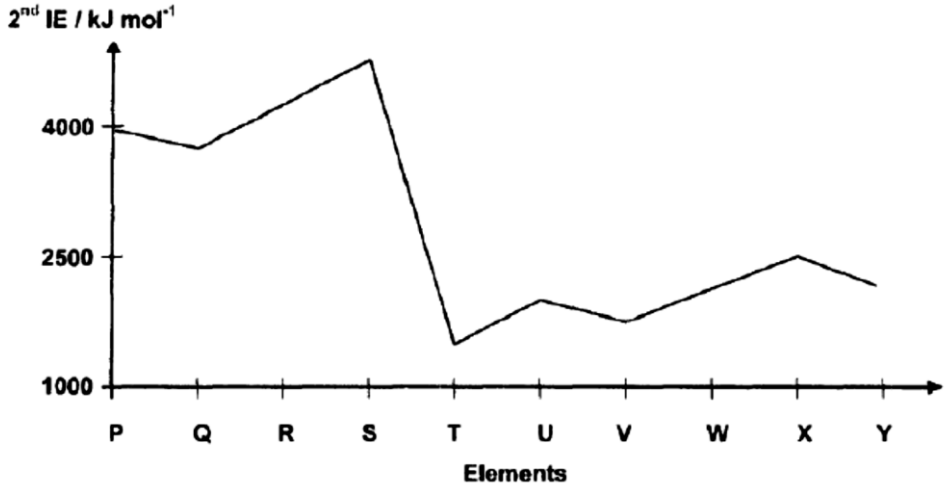
  Note that there should not be commas between subshell ($1s^2$,$2s^2$,$2p^6$ is unacceptable)

- **For comparison of ionic radius of isoelectronic ions, answers should compare**
  - nuclear charge (depends on number of _____)
  - _____ effect (depends on number of inner electrons)
  - _____ nuclear charge
  - conclude that the species with valence electron more strongly _____ would have _____ionic radius

- **Criteria of success for decreasing IE trend down the group, state**
  - Se has a larger number of _____ shells than X, hence _____ effect increases
  - The _____ of the valence electrons from the positively charged nucleus is also greater for Se as compared to X
  - Hence, the valence electrons in Se are less _____ attracted to the nucleus.
  - _____ energy is needed to remove the _____ (state the subshell) electron in Se compared to 2p (state the subshell) electron in X.
  - First ionisation energy of Se is lower.

2. MJC/PRELIMS 2005/P2/Q1

In an analytical chemistry laboratory, the plasma torch is used to ionize a variety of samples. Samples of unknown elements **P** – **Y** (atomic numbers below 20) were passed through the plasma torch and their second ionisation energies were recorded and plotted as shown.



(a) Identify the Group in the Periodic Table element **W** belongs to and write its ground state electronic configuration.

Group: _____

Electronic configuration: _____

(b) Element **W** forms form than one stable chloride. State the formula of one of these chlorides. Draw the dot-and-cross diagram of the chloride of **W** that you have stated and predict its shape.

Shape: _____

(c) There are 2 pairs of elements among the elements **P** – **Y** that belong to the same group. Identify each pair, stating the respective Groups to which they belong.

Pairs	Elements	Group
1		
2		

(d) By considering the appropriate electronic configurations, explain the drastic decrease in second ionisation energy between elements **S** and **T**.

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Things to note:

- **Criteria of Success for dot-and-cross diagram**
  - Using dot and cross only to represent electrons (other symbols such as circle are not acceptable)
  - Showing ALL electrons on the side (Cl) atoms
- **Criteria of Success for drastic decrease in 2nd IE between S and T**
  - Compare difference in number of filled quantum shells and hence _____between _____electrons and nucleus
  - Compare difference in _____ experienced by valence electrons
  - Compare extent of _____ between valence electrons and nucleus
  - Compare amount of _____ required to remove _____electrons.

Topic 3: Chemical Bonding

1. RVHS/PRELIMS 2011/P1/Q5

Phosphorus forms three chlorides, P_2Cl_4, PCl_3 and PCl_5, of which the latter two are most common. PCl_3 is made industrially on a large scale by the direct chlorination of phosphorus, while PCl_5 serves as a valuable chemical intermediate in many processes.

(a) PCl_3 can function as a Lewis base, reacting with boron trifluoride, BF_3, in the molar ratio of 1:1. Using the Valence Shell Electron Pair Theory, draw diagrams to illustrate the molecular shapes of PCl_3 and BF_3 and indicate the bond angles.

(b) Suggest the type of bonding that can take place between PCl_3 and BF_3.

_____

(c) Draw a dot-and-cross diagram of phosphorus pentachloride, PCl_5, predicting the shape of the molecule.

Shape: _____

(d) PCl_5 is molecular in the gaseous phase. However, it adopts an ionic structure in the crystalline phase, with the lattice consisting of $[PCl_4]^+$ and $[PCl_y]^-$ ions.
Suggest a likely identity of the ion $[PCl_y]^-$.

2. MJC/PRELIMS 2013/P3/Q4(c)

Gallium forms many halogen-containing compounds such as gallium(III) chloride which is a reagent for organic synthesis.

(a) The numerical values of lattice energies for the gallium(III) halides are listed in the table below. Two sets of data for the lattice energies are available, as one is determined experimentally, while the other is theoretically calculated.

Compound	experimental value / kJ mol^{-1}	theoretical value / kJ mol^{-1}
$GaCl_3$	5645	5217
$GaBr_3$	5552	4966
GaI_3	5476	4611

Account for the difference in agreement between the experimental and theoretical values of the lattice energies of the gallium(III) halides from $GaCl_3$ to GaI_3.

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(b) Gallium(III) chloride has a melting point of only 78 °C. Conversely, gallium(III) fluoride, GaF_3, is a white solid that melts above 1000 °C. Under room conditions, the molar mass of gallium chloride is 352.4 g mol^{-1}.

(A_r of Ga = 69.7, A_r of Cl = 35.5)

(i) Draw dot-and-cross diagrams of gallium(III) fluoride and gallium(III) chloride.

(ii) Deduce, with reasoning, the shape and bond angle around gallium in gallium(III) chloride.

_____

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HCI PRELIMS 2013/P2/Q3

3 (a) In fast nuclear reactors, the nuclear fission chain reaction is sustained by fast neutrons. They typically operate at a temperature of about 600 °C and so water is unsuitable as a cooling liquid. Instead, liquid metals are used as the cooling agents.

The melting and boiling points of some metals are given in the table below.

Metal	Melting point /°C	Boiling point /°C
Magnesium	650	1090
Sodium	98	884
Mercury	–39	357

(i) From the list of metals, select one metal that can be used as a cooling agent for the nuclear reactor. Explain your choice.

_____

_____

(ii) Explain why the melting point of magnesium is higher than that of sodium.

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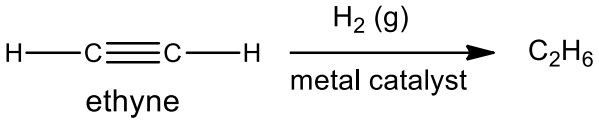
(b) Alkynes are highly versatile compounds that may be utilised for numerous reactions. They can be easily reduced to their alkanes by addition of H_2 over a metal catalyst.



(ii) Describe, in terms of orbital overlap, the bonding of the two carbon atoms of the C≡C bond in ethyne. You may use diagrams to illustrate your answer.

Criteria of Success Checklist of describing bonding using orbitals overlap diagram

Tick if you have

☐ drawn correct shape of hybrid orbitals and unhybridised orbitals
☐ drawn correct orientation of the hybrid orbitals e.g. linear, trigonal planar or tetrahedral
☐ labelled the hydrid orbitals and unhybridised orbitals
☐ labelled sigma bond (head-on overlap of hybridized orbitals)
☐ labelled pi bond (side-ways overlap of unhybridized orbital)

Things to note:

- In drawing dot-cross diagram, electrons to give to the _____ atom for anions; electrons removed from _____ atom in cations. Central atom from period ____onwards can expand its octet and have _____ 8 electrons around it.
- To determine the shape of the molecule, the number of _____ pairs and _____ pairs of electrons around the central atom must be taken into account.
- According to VSEPR, _____repulsion > _____repulsion > _____ repulsion
- Not all metals and non-metals form ionic compound. E.g _____is covalent due to _____ of Al^{3+} which _____ the electron cloud of the anion to a large extent.
- Always use SIA (**s**_____, **i**_____and **a**_____) to answer boiling/melting point questions
- Orbitals (not atoms) _____ in forming covalent bonds.
- In determining the hybridization state,

Total no. of sigma bonds and lone pairs of electrons	hybridisation
4	
3	
2	

Topic 4: The Gaseous State

1. RJC 2011/P1/6

Deuterium, ^{2}H, is an isotope of hydrogen.

In an experiment, 3.7 g of a gas **X** at 25 °C was found to occupy the same volume as 0.368 g of deuterium gas at 17 °C. Both gases were at the same pressure.

What is the relative molecular mass of the gas **X**?

A $\frac{2.0 \times 3.7 \times 25}{0.368 \times 17}$ **B** $\frac{3.7 \times 298}{2.0 \times 0.368 \times 290}$

C $\frac{4.0 \times 3.7 \times 290}{0.368 \times 298}$ **D** $\frac{4.0 \times 3.7 \times 298}{0.368 \times 290}$ ( )

2. AJC 2012/P1/6

Two gas bulbs, **E** and **F**, are connected by a stopcock. Bulb **E** contains argon and bulb **F** contains oxygen gas. The pressure and volume of gas in each bulb at 25 °C is shown below.

	Bulb **E**	Bulb **F**
Volume / dm^3	v	7v
Pressure / kPa	p	5p

The stopcock is then opened and the gases were allowed to mix at 25 °C. Subsequently, the temperature of the mixture is raised and the final pressure is found to be 9p.

What is the temperature of the gases in the mixture that gives a pressure of 9p?

3. CJC 2006/P3/1

(a) **Y** is a gas having a certain mass, *m*. The table below shows the volume occupied by **Y** at different pressures.

Pressure / atm	**Volume / cm^3**	**Temperature / K**
1	1000	273
30	31.2	273
60	14.9	273

Using the provided information, deduce if **Y** shows ideal behavior. You may include relevant calculations to explain your answer.

(b) An organic compound, **Z**, contains carbon, hydrogen and oxygen only. When vaporised at 101 kPa and 373 K, 0.100 g of **Z** occupied a volume of 66.7 cm^3. Calculate the relative molecular mass of **Z**.

4. RVHS 2011/P3/1

(a) It was found that one molecule of haemoglobin combines with four molecules of oxygen. If 2.00 g of haemoglobin combines with 3.06 cm^3 of oxygen at 37.0 °C and 98.7 kPa, what is the molar mass of haemoglobin?

(b) The actual molar mass of haemoglobin is 6.90×10^4 g mol^{-1}. Based on your working in **(a)**, explain why there is a discrepancy in the two values.

_____

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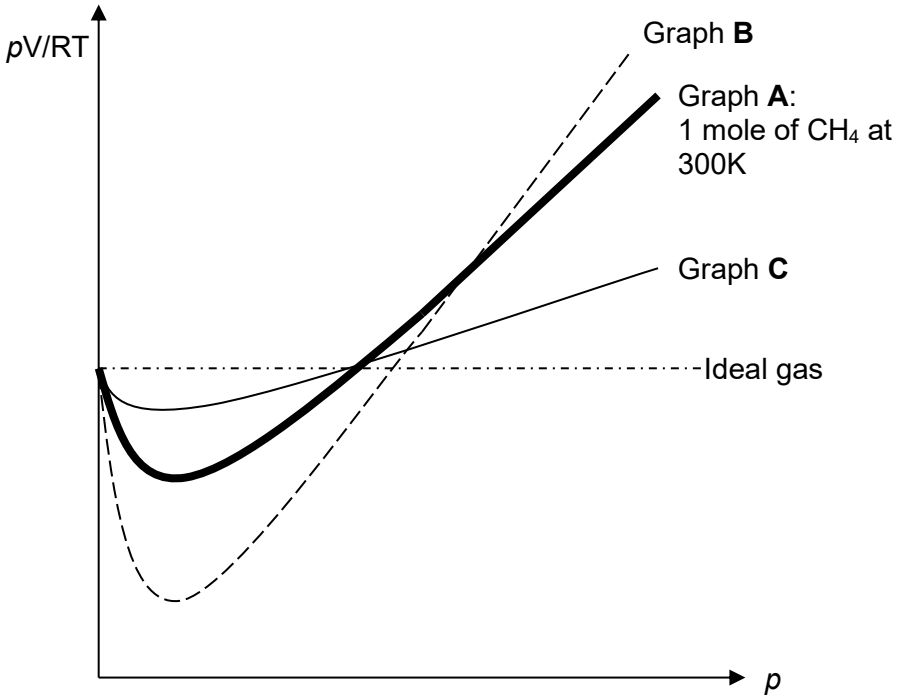
_____

5 The values of pV/RT are plotted against p for one mole of the following gases at the specified temperature:

- One mole of CH_4 at 300K
- One mole of CH_4 at 500K
- One mole of NH_3 at 300K



Given that graph **A** is obtained for 1 mole of CH_4 at 300K, suggest and explain what Graphs **B** and **C** represent.

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Criteria of Success Checklist for calculations
tick if you have
☐ provided clear statements for ALL working ☐ presented intermediate answers to 4 s.f. ☐ presented final answers to 3 s.f. ☐ presented M_r to 1 d.p. ☐ provided units, when applicable

Things to note:

- When using pV = nRT , R = 8.31, P in _____, V in _____, n in _____ and T in ___
  1 atm = 760 mmHg = _____ Pa (approximately)
  1 bar = _____ Pa
  1 dm^3 = _____ cm^3 = _____ m^3
  1 cm^3 = _____ m^3
  T (K) = T (^oC) + _____
- Real gases _____ most from ideal gas behaviour under the following conditions:

1. At very _____ pressure
2. At very _____ temperature

- Gases with _____intermolecular forces of attraction tend to deviate _____ from ideal behaviour

Topic 5: The Periodic Table

1. PJC/PRELIMS 2013/P3/Q4

(a) When magnesium chloride is added to water, a solution of pH 6.5 is formed.
When aluminium chloride is added to water, the resulting solution has a pH of 3. With the aid of equations, explain the difference in the observations.

RI/PRELIMS 2013/P3/Q3

(b) Silicon, phosphorus and sulfur are Period 3 elements.
Arrange these three elements in order of decreasing melting point and account for the order in terms of structure and bonding.

2. YJC/PRELIMS 2013/P2/Q2

Elements **J**, **K**, and **L** are consecutive elements in period 3 of the *Periodic Table*.

The first eight ionisation energies, *I.E.*, of element **K** are as follows.

***I.E.* / kJ mol^{-1}**	1011	1907	2914	4963	6273	21267	25431	29872

(i) With reference to the data above, deduce the Group of the *Periodic Table* to which **K** is likely to belong to.

_____

_____

_____

(ii) Predict, giving your reasoning, whether the first ionisation energy of element **L** will be higher or lower than that of **K**.

_____

_____

_____

_____

(iii) When dissolved in water, the chlorides of elements **J** and **K** produce solutions that turn blue litmus red. Write balanced equations to represent the reactions of these chlorides with water.

_____

_____

Things to note:

- $AlCl_3$ is a covalent chloride although it is a metal chloride due to the _____ charge density of _____.
- Unlike NaCl, the other 2 metal chlorides, $AlCl_3$ and $MgCl_2$ are acidic as they will undergo _____ in water due to the high _____ of the cations.
- Sulfur exists as _____ while Phosphorus exists as _____. Their molecular formula is taken into account when explaining the trend of melting point across Period 3 elements.
- The _____ jump in successive ionisation energies of an element is due to removal of electron from an _____.
- Ionisation energy generally _____ across a period. Anomaly in ionisation energy across the period occurs for the 2 following sets of outer electronic configurations: _____ and _____

Topic 6: Chemical Energetics

1. DHS/PRELIMS 2008/P3/Q4(d)

An experiment is conducted to determine the enthalpy change of neutralisation between methanoic acid (HCOOH) and aqueous sodium hydroxide (NaOH). Some solid methanoic acid is added to sodium hydroxide solution. The changes in temperature and amount of reagents mixed are recorded as follows:

Initial temperature/ ^oC	24.0
Final temperature/ ^oC	34.5
Mass of HCOOH added/ g	1.84
Volume of 1 mol dm^{-3} NaOH(aq) used/ cm^3	50.0

(i) Define *standard enthalpy change of neutralisation.*

_____

_____

(ii) Use the above data to calculate the enthalpy change of neutralisation, assuming that 4.2 J is required to raise the temperature of 1 cm^3 solution by 1 ^oC.

(iii) The magnitude of enthalpy change of neutralisation between aqueous nitric acid and aqueous sodium hydroxide is found to be larger than the value calculated in part **(ii)**. Explain why this is so.

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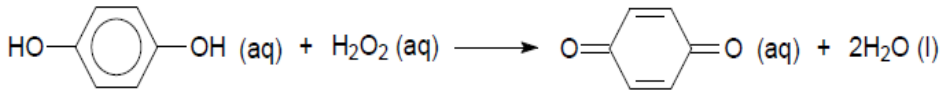
Things to note:

- When using the formula, q = mc∆T, the mass of the solution is taken to be the volume of the solution, as the density of the solution is assumed to be that of water, which is 1 g cm^{-3}. The mass of the solid is not included in the formula as the solid dissolves in the solution.
- If two solutions are added together, the mass in the formula will be the **total** volume of the two solutions, assuming the density of the solution is 1 g cm^{-3}.
- The sign of the enthalpy change is dependent on the temperature change. In this question, ΔH has a negative sign as the final temperature is _____ than the initial temperature.
- The number of moles substituted in the formula, $\Delta H^{\theta} = \pm\frac{q}{n}$, is

  n = number of moles of _____ formed for $\Delta H^{\ominus}_{neut}$
  n = number of moles of _____ burnt for $\Delta H^{\ominus}_{c}$
  n = number of moles of _____ formed for $\Delta H^{\ominus}_{f}$
  n = number of moles _____ _____ for any general $\Delta H^{\ominus}$

2. DHS/PRELIMS 2008/P3/Q1(a), (c) (Modified)

(a) When under attack, the bombardier beetle uses "chemical warfare". It defends itself from attack by mixing together solutions of hydrogen peroxide and hydroquinone ($C_6H_4(OH)_2$) in the presence of enzymes. This reaction releases free oxygen that produce enough energy to bring the mixture to boiling point. An audible explosion occurs as the beetle fires a hot spray at its attacker from its abdomen. Quinone, $C_6H_4O_2$ is one of the products formed.



hydroquinone quinone

(i) State *Hess' Law*.

_____

_____

(ii) Construct an energy cycle and use the following data to calculate the enthalpy change of reaction inside the beetle.

$C_6H_4(OH)_2$ (aq) → $C_6H_4O_2$ (aq) + H_2 (g)	$\Delta H^{\ominus}$ = +177 kJ mol^{-1}
H_2O_2 (aq) → H_2O (*l*) + ½ O_2 (g)	$\Delta H^{\ominus}$ = −95 kJ mol^{-1}
H_2 (g) + ½ O_2 (g) → H_2O (*l*)	$\Delta H^{\ominus}$ = −286 kJ mol^{-1}

Criteria of Success of drawing Energy Cycle:

- All equations are _____
- Equations are _____ by appropriate coefficient (if applicable)
- _____ _____ are written for all species
- _____ _____ is written above the arrow

(iii) Draw a labelled energy profile for the reaction above and indicate clearly the activation energy and enthalpy change of reaction.

Criteria of Success of drawing Energy Profile Diagram/Reaction Pathway

- Axis is correctly labelled with _____
- Correct shape of graph is drawn to show _____ or _____ reaction
- Arrow is drawn with _____ labelled with value (if any)
- Arrow is drawn with _____ labelled with value (if any)
- _____, _____, intermediate (for 2 or more steps) are written with state symbols

(b) Concentrated hydrogen peroxide is a dangerously reactive substance because the decomposition is very exothermic.

$H_2O_2\ (l) \rightarrow H_2O\ (l) + \frac{1}{2}\ O_2\ (g)$ $\Delta H^{\ominus} = -98.1$ kJ mol^{-1}

(i) Given that $\Delta S^{\ominus}$ of the above reaction is +62.8 J mol^{-1}K^{-1}, calculate $\Delta G^{\ominus}$ of the reaction at 298K.

Things to note:

- Values substituted for ΔH and ΔS must be _____ with the units. If the value of ΔH has units of kJ mol^{-1}, the value of ΔS must also be converted to the same units of kJ mol^{-1}K^{-1} for calculation.

(ii) Based on your answer in part **(i)** or otherwise, suggest two precautions for the storage of concentrated hydrogen peroxide.

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3. ACJC/PRELIMS 2008/P3/Q4(a)

The atomisation reaction of 1-chlorobutane, C_4H_9Cl, is

$$CH_3CH_2CH_2CH_2Cl\ (l) \longrightarrow 4C\ (g) + 9H\ (g) + Cl\ (g)$$

The enthalpy change of formation of 1-chlorobutane is −188 kJ mol^{-1} and the enthalpy change of atomisation of carbon is +716 kJ mol^{-1}.

(i) What is meant by the term *standard enthalpy change of formation*?

_____

_____

_____

(ii) Using the above data and suitable data from the *Data Booklet,* construct a **labelled energy level diagram** and calculate the enthalpy change of atomisation of $CH_3CH_2CH_2CH_2Cl$.

Criteria of Success of drawing Energy Level Diagram:

- Axis is correctly labelled with _____
- All equations are _____
- Equations are _____ by appropriate coefficient (if applicable)
- _____ _____ is written for all species
- Arrow drawn pointing upwards for _____ reaction; Arrow

(iii) Calculate another value for the enthalpy change of atomisation of $CH_3CH_2CH_2CH_2Cl$ using **only bond energies** from the *Data Booklet*.

(iv) State **two** reasons for the difference in the values calculated in **(ii)** and **(iii)**.

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Topic 7: Reaction Kinetics

1. YJC/PRELIMS 2009/P2/Q3(b)

The hydrolysis of sucrose can be catalysed by the enzyme invertase, or by dilute acids. The initial reaction of the hydrolysis can be represented by:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The following results were obtained using hydrochloric acid as the catalyst:

Expt	[HC*l*] / mol dm^{-3}	[sucrose] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	0.024
2	0.10	0.20	0.048
3	0.20	0.30	0.144

(i) Use these data to deduce the order of reaction with respect to HC*l* and sucrose.
Hence, give the rate equation for the reaction and calculate the rate constant for the reaction, stating its units.

Things to note:

- Inspection method or mathematical method is acceptable.
- Units of rate constant can be derived from the rate equation.

Criteria of Success for Inspection Method:

- State which _____ experiments that you are comparing
- State which reactant concentration is kept _____
- State which reactant concentration is _____
- Conclude the _____ ____ _____

(ii) Given that the half-life of sucrose in experiment 1 was 3.0 s, predict a value for the half-life of sucrose in experiment 3, giving your reasoning.

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Things to note:

- HC*l* is a catalyst as it is not part of the equation. Hence, it can be taken to be in large excess as catalyst is regenerated.

2. ACJC/PRELIM 2010/P2/Q5a

The reaction between iodide ions, I^-, and persulfate ions, $S_2O_8^{2-}$, is slow.

The reaction can be speeded up by adding a small amount of Fe^{2+} ions.

The initial rate of the slow reaction between iodide ions and persulfate ions can be studied by using thiosulfate ions. The equations for the reactions are as follows.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-} \quad \text{(slow)} \quad \text{reaction } \mathbf{I}$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \quad \text{(fast)} \quad \text{reaction } \mathbf{II}$$

In the presence of a constant amount of thiosulfate ions, the iodine being slowly produced by reaction **I** will immediately react in reaction **II** until all the thiosulfate ions has been used up. At that point, free iodine will be present in the solution, which will cause a sudden appearance of a deep blue colour if starch is present.

A series of experiments was carried out using different volumes of the five reagents. The following results were obtained.

Expt No.	Vol. of $S_2O_8^{2-}$ /cm^3	Vol. of I^- /cm^3	Vol. of $S_2O_3^{2-}$ /cm^3	Vol. of water /cm^3	Vol. of starch /cm^3	Time for the appearance of deep blue colour/s
1	20	20	10	5	5	30
2	20	15	10	10	5	40
3	5	25	10	15	5	t_3
4	10	15	10	20	5	80

(i) If the orders of reaction with respect to persulfate ions and iodide ions are both one respectively, deduce an expression relating the volume of these two reactants and time taken for the appearance of deep blue colour. Explain your reasoning.
Predict the time, t_3, required for the appearance of deep blue color in experiment 3.

(ii) In the Haber process, the rate of formation of ammonia is increased by using an iron catalyst. State the type of catalysis occurring here and describe using the Maxwell-Boltzmann Distribution curve how the iron catalyst can increase the rate of reaction.

Things to note:

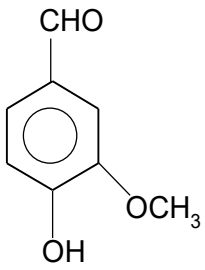
- Iron is a heterogeneous catalysis as it is in _____ physical state as the reactants. Homogeneous catalysis is when the catalyst and reactants are in the _____ physical state.

Criteria of Success of Drawing Boltzmann Distribution Graph:

- Axis is correctly labelled with _____
- _____ is written at the origin
- _____ E_a lines are drawn with the lowered E_a labelled as E_a (with catalyst)
- _____ different sets of shading
- Graph does not touch the _____

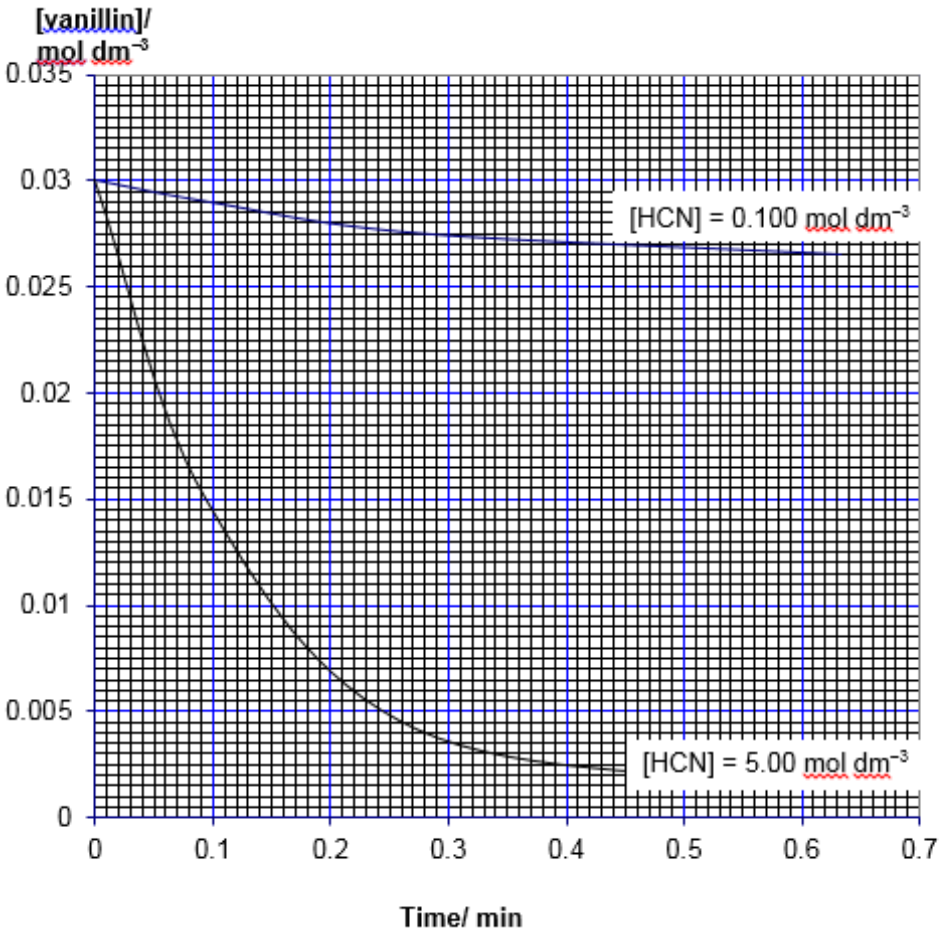
3. JJC/PRELIMS 2009/P2/Q3

Vanillin is used widely as a flavoring, usually in sweet foods such as ice cream and chocolate. It exists as a yellow solid and dissolves readily in water to form a yellow solution.



vanillin

The kinetics of the reaction between vanillin and HCN were investigated using two different initial concentration of HCN. Both experiments were conducted at 25 °C in a buffer solution of pH 9.0.



(a) Assuming that the reaction produces a colourless product, suggest one plausible method by which the concentration of vanillin may be followed during the course of the reaction.

_____

_____

_____

(b) Using the graph, determine the order of the reaction with respect to vanillin. Show workings on the graph.

Criteria of Success of Drawing Half-Life:

- Show _____ half-lives drawn on the graph
- Mark out where half-lives are and indicate the value of $t_{½}$ clearly

(c) In the experiment using 0.100 mol dm^{-3} HCN, the half-life of the reaction is 4.75 min. Hence determine, with explanation, the order of reaction with respect to HCN.

_____

_____

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_____

Topic 8: Chemical Equilibria

1 ACJC/2006/III/1

When solid lead (II) sulfate is added to aqueous sodium iodide, the following equilibrium is established:

$$PbSO_4\,(s) + 2I^-\,(aq) \rightleftharpoons PbI_2\,(s) + SO_4^{2-}\,(aq)$$

The equilibrium constant for this reaction may be determined by adding an excess of lead (II) sulfate to a known volume of standard sodium iodide solution and allowing the mixture to reach equilibrium in a water bath maintained at the desired temperature. Excess iced water is then added and the mixture is titrated with standard silver nitrate solution.

In an experiment, $PbSO_4$ (s) was added to 50.0 cm^3 of 0.100 mol dm^{-3} aqueous sodium iodide solution. 30.00 cm^3 of 0.100 mol dm^{-3} aqueous silver nitrate was needed to precipitate all the iodide ions remaining in solution at equilibrium.

(a) Calculate the number of moles of I^- ions in the original sodium iodide solution.

(b) Calculate the number of moles of I^- and SO_4^{2-} ions in solution at equilibrium.

(c) Write an expression for the equilibrium constant, K_c, for this reaction and calculate its value.

2 Vanadium(V) oxide, V_2O_5, can be used as a heterogeneous catalyst in the manufacture of sulfuric acid. The key step during the Contact Process is the oxidation of sulfur dioxide to sulfur trioxide.

$$SO_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g) \qquad \Delta H = -98\ kJ\ mol^{-1}$$

The operating conditions for the Contact Process are 450°C and 5 atm.

(a) Explain the choice of the operating conditions and the need for a catalyst.

_____

_____

_____

_____

_____

_____

(b) When a 2:1 mixture of SO_2 and O_2 was allowed to reach equilibrium at the operating conditions as stated above, it was found that the percentage conversion of SO_2 is 95.0%. Write an expression for the equilibrium constant, K_p, and hence calculate K_p from the above data.

3 In a gaseous reaction at constant pressure of 1 atm, XY_3 is synthesized from X_2 and Y_2.

$$X_2\,(g) + 3Y_2\,(g) \rightleftharpoons 2XY_3\,(g)$$

A mixture of 4.0 moles of X_2 and 12.0 moles of Y_2 was placed in a vessel of volume 20 dm^3 at 450K. When the system has reached equilibrium, it was found that 4.0 moles of XY_3 was present.

(a) Calculate the partial pressure of each species at equilibrium.

(b) Hence calculate the value of K_p of this reaction.

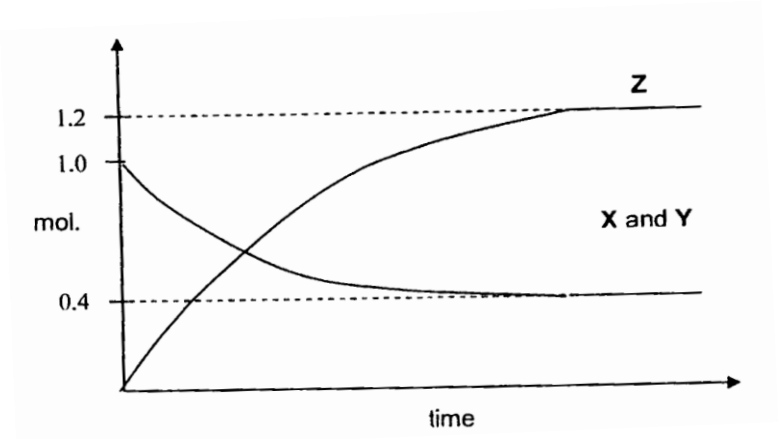
(c) When the volume of the vessel was increased and the system allowed to come to a new equilibrium at the same temperature, 9.0 moles of Y_2 were found to be present. Calculate the new equilibrium pressure of the system.

(d) What effect will the use of a catalyst have on the K_p value? Explain your answer.

4 Two gases, **X** and **Y**, react as follows.

$$\mathbf{X}\,(g) + \mathbf{Y}\,(g) \rightleftharpoons 2\mathbf{Z}\,(g)$$

A mixture containing 1 mole each of **X** and **Y** was heated in a closed vessel of volume 3 dm^3 and the reaction allowed to reach equilibrium at 300K. The graph shows how the number of moles of each gas varies with time.



(a) Calculate the value of the equilibrium constant K_c for this reaction at 300K.

(b) On reaching equilibrium, a further 1 mole each of **X** and **Y** was injected into the vessel and the system allowed to reach the new equilibrium at the same temperature of 300K. Calculate the new equilibrium concentration of **Z**.

(c) Predict, with reasoning, how the position of the equilibrium might change if the volume of the reaction vessel is reduced.

_____

_____

_____

_____

(d) When the temperature was increased to 400K, the K_c value was found to be higher than the value calculated in **(a)**.

Explain whether the forward reaction is exothermic or endothermic.

_____

_____

_____

_____

Things to note:

- K_c should be expressed in terms of equilibrium _____ of reactants and products. Working should show division by volume for 1(c) and 4(a) and not merely substitution in terms of moles.
- K_p should be expressed in terms of _____ of reactants and products at equilibrium. Working should show substitution of partial pressure (and not just moles) in 2(b) and 3(a).

- When applying Le Chatelier's Principle (for Q4c), format of presentation includes
  - State what the change is (i.e. volume decrease, implying pressure increase)
  - Describe how the system will counteract with the change (i.e. _____ the pressure by favouring the side with _____number of _____ molecules)
  - State how the _____ of equilibrium would shift (e.g. right/left/no change)

- K_c only changes with temperature because rate constant of forward and rate of backward reaction increase/decrease to _____ extent. When K_c increase with increasing temperature, it implies that _____ _____of _____reaction _____ to greater extent than rate constant of backward reaction. Forward reaction is favoured with increase in temperature. Hence forward reaction must be endothermic.

Topic 9: Organic Chemistry (Introduction to Org Chem, Isomerism, Alkanes, Alkenes)

1. **A** and **B** are constitutional isomers with molecular formula C_4H_{10}.
   When **A** reacts with chlorine gas in the presence of light, two monochlorinated alkanes **C** and **D** are formed. Only **D** contains a chiral carbon.
   When **B** reacts with chlorine gas in the presence of light, two monochlorinated alkanes **E** and **F** are formed, both do not contain chiral carbon.
   Identify the compounds **A** – **F** by drawing their skeletal formulae.

Hint: To do this question, you need to explore the different constitutional isomers that C_4H_{10} can form via trial and error.

Things to note:

Constitutional isomers are compounds with the same molecular formula but **different** _____.

Enantiomers have the same molecular and structural formulae. They are _____ **mirror images** of each other. Enantiomerism occurs when a molecule has

- a _____**centre** and
- **no** _____

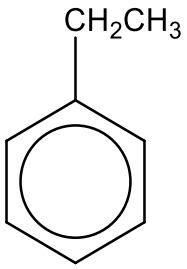
A _____**centre** arises when there is a sp^3 hybridised atom covalently bonded to _____**different groups** (atoms, group of atoms or electron pairs).

_____ occurs when alkane reacts with halogen under UV light. It involves three stages: initiation, propagation and termination.

The mixture of mono-substituted isomeric products occurs at all the _____ that can be substituted in F.R.S. The actual proportion of the isomers depends on the _____of forming the intermediates and the _____of the intermediates.

RJC/PRELIMS 2008/P3/Q1(b) – Modified

2. The structure of ethylbenzene is given below.



ethylbenzene

When ethylbenzene is mixed with limited amounts of chlorine gas and exposed to ultraviolet light, 2 mono-chlorinated isomeric products are formed.

(a) Draw the 2 mono-chlorinated products and state the expected ratio in which they would be formed.

(b) The one which is expected to form in a lesser amount as predicted in **(a)**, however, is the major product. Explain how this is so.

(c) In this reaction, a side product, with molecular formula $C_{16}H_{18}$, is produced. Draw a possible structure of the side product. Using an equation and curly arrows, show how this side product is formed.

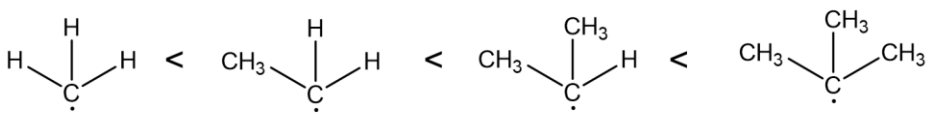
Things to note:

Stability of Radicals

Radicals have different levels of stability based on the **number of _____ groups** attached to the carbon that has an unpaired electron. Alkyl groups are _____ and **reduce the** _____ **on the carbon radical** they are attached to, hence _____ the carbon radical.

Therefore, **more alkyl groups** attached to the carbon radical will **increase the _____ of the carbon radical**.

Example:



Methyl radical **Least stable** | primary radical | secondary radical | tertiary radical **Most stable**

3 When pentane is mixed with chlorine in the presence of uv light, the following reaction takes place:

$$CH_3(CH_2)_3CH_3 + Cl_2 \rightarrow CH_3CHCl/CH_2CH_2CH_3 + HCl$$

(a) Describe the mechanism of this reaction. You may use skeletal structures in your answer.

Criteria of Success:

When 'describing' or 'outlining' a FRS mechanism, one is not expected to write too many words. Remember to include the following:

- _____ **of the mechanism** (Free Radical Substitution)
- _____ in sequential order (Initiation, Propagation, Termination)
- _____ **arrows** (representing the flow of one electron)
- _____(radical species with single dot representing one electron on the _____carbon)
- Do not use condensed molecular formulae in the form C_3H_7, C_4H_9 etc as it is ambiguous which C bears the unpaired electron

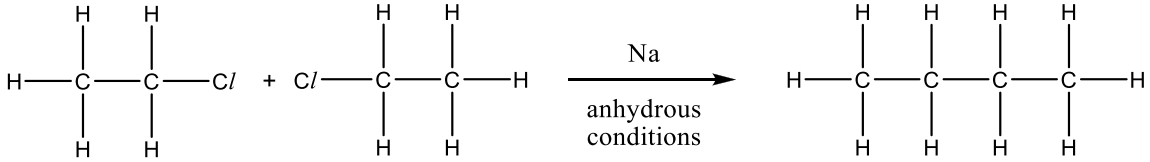
Identify the intermediates if applicable (for multiple substitutions).

(b) The presence of NO is known to slow down the chlorination of pentane.
Draw the dot-and-cross diagram of a molecule of NO. By considering the electron distribution of the NO molecule, suggest how it slows down the reaction.

(c) Draw the skeletal structures of all possible mono-chlorinated products and the ratio in which they would be formed.

(d) Using data from the Data Booklet, explain why pentane is less readily brominated than chlorinated. Your answer should make reference to the process of propagation in your mechanism in (a).
Hint: $\triangle H_r = \sum BE(rxts) - \sum BE(pdts)$

4. Butane can be synthesized via the Wurtz reaction. The Wurtz reaction is a coupling reaction in organic chemistry where two alkyl halides are reacted with sodium to from a new carbon-carbon bond. In the example shown below, chloroethane reacts with powdered sodium metal under anhydrous conditions to give butane.



(a) Explain why the Wurtz reaction must be carried out under anhydrous conditions.

_____

_____

_____

(b) In a separate experiment, an equimolar mixture of chloromethane and chloroethane was used instead. The reaction resulted in a mixture of three organic products, one of which is butane.

Identify **P** and **Q**. State the relative ratios of butane, **P** and **Q.**

Hint: Examine the R groups of each chloroalkane and replicate the pattern shown in the Wurtz reaction. Think about probability of forming each species.

Things to note:

The propane is formed from the combination of two different alkyl portions (mixture of ___C alkyl and ____ C alkyl parts.) Hence, there will be _____ the chance of forming it as compared to ethane which is formed from combining the same type of alkyl parts.

(c) Compound **J** is 1,5-dichlorohexane. When **J** undergoes the Wurtz reaction, **K** is formed. When 0.01 mol of **K** is reacted with excess O_2, 1.44 dm^3 of CO_2 measured at room temperature and pressure is obtained.

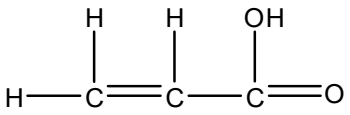
Deduce the identity of **K** and draw its structure.

Hint: Replicate the same pattern shown in Wurtz reaction. Find out the number of carbons in **K** and think of a cyclic structure.

Things to note:
Even though this reaction is unfamiliar, learn to recognize the process and mimic similar process, that is, break the two C – Cl bonds and then combine the two C atoms together.

5 [ACJC/PRELIMS 2013/P2/Q3]

(a) Compound **M**, shown below, reacts with hydrogen bromide. Describe the mechanism for the reaction.



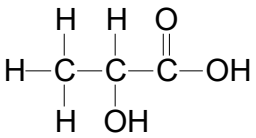
Compound **M**

Criteria of Success:

In describing the electrophilic addition mechanism, you should include:

- N_____ of the mechanism
- Steps in sequential order: (Attack of electrophile by π electrons on _____, attack of _____ by nucleophile (X^-) to form product)
- Curly full arrows (from double bond of C=C to e_____ (e.g. δ+Br), from l_____ on X^- (e.g. Br^-) to C^+)
- Labels (_____, δ+, δ-, _____ on X^-)
- If there are more than 1 possible product and question did not specify a particular product, always draw the m_____product, following Markovnikov's rule.

(b) Compound **M** can be chemically converted into compound **N**, shown below:



compound **N**

Compound **N**, is found in muscle tissues as lactic acid and is optically active whereas when it is chemically synthesized, it is optically inactive. Explain.

_____

_____

_____

_____

_____

_____

Things to note:

When _____ of the two enantiomers present, the rotating power of one enantiomer **exactly** _____ **that of the other**. Such a mixture is known as **racemate/ racemic mixture** and is **optically** _____.

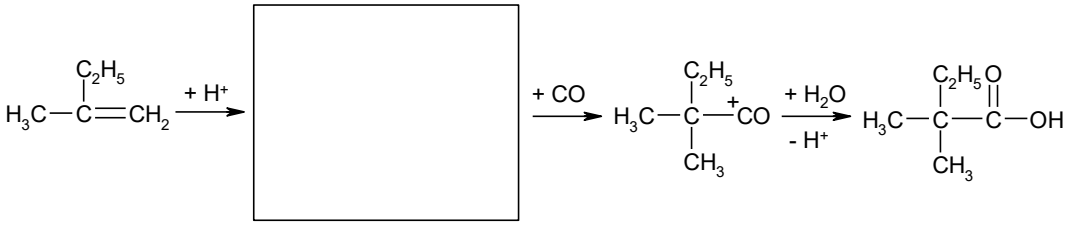
The enantiomers have identical chemical properties except **in their interactions with another molecule**. They have different biological properties, e.g. in drugs action. Many drugs are chiral molecules of which one enantiomer is biologically active and the other has either a different type of activity or none at all.

6. [YJC/PRELIMS 2013/P2/Q4]

(a) Alkenes are susceptible to attack by electrophiles due to the presence of the electron-rich carbon-carbon double bond.

In the Koch reaction, alkenes react with carbon monoxide and water to form certain secondary and tertiary carboxylic acids.

The mechanism steps below shows 2-methylbut-1-ene undergoing the Koch reaction.



2-methylbut-1-ene | intermediate **P** | intermediate **Q** | product **R**

(i) Draw, in the space provided above, the structure of intermediate **P**.

(ii) Give the IUPAC name of the product **R**.

_____

(iii) Deduce the number of electrons around the carbon atom that is bonded to the oxygen atom in intermediate **Q**.

_____

(iv) Draw the displayed formula for the starting alkene that will form $CH_3CH_2CH(CH_3)CO_2H$ after undergoing the Koch reaction.

(b) A cycloalkane with the molecular formula C_5H_{10} gives only **two** mono-brominated products when reacted with bromine in the presence of ultraviolet light. Give the structural formulae of the two bromocycloalkane, and suggest the ratio in which the two products will be formed.

Things to note:

i) The carbocation formed will be the more stable one with m_____ R groups bonded to the C^+.

ii) As all hydrogen atoms in the alkanes (containing 3 or more C atoms) are susceptible to s_____, isomeric products are formed. The ratio they are formed will be the simplified ratio of the number of (same) _____ atoms that the alkane can be substituted to form the products.

7. TPJC/PRELIMS 2014/P2/Q6

Hydrocarbons are economically important chemicals due to their role as the world's main source of fuel, and as starting materials for the synthesis of many useful organic compounds.

The table below gives the boiling point of three organic compounds of similar molecular mass.

Organic compound	**Structural Formula**	**M_r**	**Boiling point/^{0}C**
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86.0	68
2-methylpentane	$CH_3CH(CH_3)CH_2CH_2CH_3$	86.0	60
pentan-2-ol	$CH_3CH(OH)CH_2CH_2CH_3$	86.0	120

Explain the difference in boiling point between

(a) hexane and 2-methylpentane

(b) 2-methylpentane and pentan-2-ol

~ END OF DECEMBER HOLIDAY REVISION PACKAGE~