ANSWERS TO 2024 DECEMBER HOLIDAY REVISION PACKAGE

Topic 1: The Mole Concept and Redox Reaction

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

(a)

	C	H	N	O
% by mass	50.7	7.0	19.8	22.5
A_r	12	1	14	16
Mole Ratio	4.225	7	1.414	1.406
Simplest Ratio	3	5	1	1

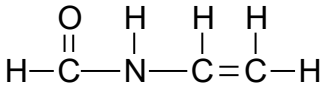
Let the molecular formula of acrylamide be $C_{3n}H_{5n}N_nO_n$.

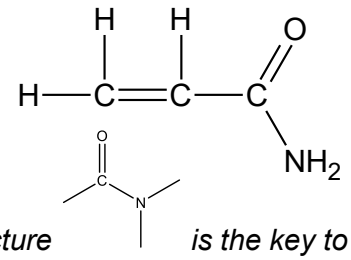
M_r of acrylamide = 71.0 = n (3 × 12.0 + 5 × 1.0 + 14.0 + 16.0)

n = 1

Hence, the molecular formula of acrylamide is $\underline{C_3H_5NO}$.

Possible structures of acrylamide:





Comments: *Knowing the amide structure* *is the key to derive the possible structures.*

(b) Maximum mass of acrylamide the woman can take in per day

= $0.5 \times 10^{-3} \times 50 = 0.025$ g

Mass of acrylamide in 1 kg of coffee = $1.2 \times 10^{-7} \times 71.0$

= 8.520×10^{-6} g per kg of coffee

Maximum mass of coffee the woman can drink per day

= $0.025 \div (8.520 \times 10^{-6}) = 2934$ kg

Since coffee has the same density as water, maximum volume of coffee the woman can drink per day = 2934 ÷ 1 = 2934 dm^3

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

(i)

Element	K	Br	O
Mass ratio	23.4	47.8	28.8
Mole ratio	$\frac{23.4}{39.1}$=0.598	$\frac{47.8}{79.9}$=0.598	$\frac{28.8}{16}$=1.8
Simplest ratio	1	1	$\frac{1.8}{0.598}$=3.01= 3

Formula of white solid is $KBrO_3$

(ii) No of moles of $KBrO_3$= $\frac{0.835}{167}$= 0.00500 mol

No of moles of $PbCl_2$ = = $\frac{4.17}{278}$=0150 mol

$$\frac{n_{KBrO_3}}{n_{PbCl_2}} = \frac{0.00500}{0.0150} = \frac{1}{3}$$

(iii)

$2e + Cl_2 \rightarrow 2Cl^-$	X 3	
$3H_2O + Br^- \rightarrow BrO_3^- + 6H^+ + 6e$	[acidic medium]	
$6OH^- + + Br^- \rightarrow BrO_3^- + 3H_2O + 6e$	[alkaline medium]	

K^+ ions are participating ions – Balance accordingly.

$3Cl_2 + KBr + 6KOH \rightarrow 6KCl + KBrO_3 + 3H_2O$

3. $H_2S \rightarrow S + 2H^+ + 2e$

Amount of BrO_x^- = (12.00/1000) x 0.300 = 0.0036 mol

Amount of S = Amount of H_2S = 0.289 / 32.1 = 0.009 mol

Mole ratio of BrO_x^- : H_2S = 1 : 2.5 = 2 : 5

1 H_2S lost 2 e.

5 H_2S lost 10 e.

10 e gained by 2 BrO_x^-.

1 BrO_x^- gains 5 e.

Final oxidation state of Br in Br_2 = 0

Initial oxidation state of Br in BrO_x^- is +5

$5 + (-2)x = -1$

<u>x = 3</u>

Criteria of success checklist:

☐ 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:

- Conversion of units for volume:

  $1\ dm^3 = 1000\ cm^3 = 10^{-3}\ m^3$
  $1\ cm^3 = 10^{-3}\ dm^3 = 10^{-6}\ m^3$
  $1\ m^3 = 1000\ dm^3 = 10^{6}\ cm^3$

- 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 2), 1.33 (multiply by 3), 1.25 (multiply by 4), 1.2 (multiply by 5)
- In balancing half equations,
  1. balance the atom that is not O or H first.
  2. Balance O by adding H_2O
  3. Balance H by adding H^+
  4. Balance charge by adding electrons

  Continue with step 5 to 7 for basic medium

  5. Add OH^- (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 H_2O
  7. Simplify the equation (if necessary) by cancelling out H_2O that occurs on both sides of the equation.
- For questions to calculate oxidation number in redox reactions,
  1. Write out one half equation for the known species
  2. Work out the mole ratio of the 2 reactants
  3. Using the mole ratio and the half equation written, determine the number of electrons transferred in the redox reaction. The number of electrons given out by the species that is oxidised will be taken in 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 in front of the number e.g +2, -1

Topic 2: Atomic Structure

1(a)

Particle	Electric charge	Mass Number	Number of		
			Protons	Electrons	Neutrons
X	0	32	16	16	16
Y	-1	81	35	36	46
Z	+3	70	31	28	39

(b)(i) **Y**: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$

Z: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

(ii) Ionic size of **Y** is larger than that of Rb^+. **Y** and Rb^+ are isoelectronic (same no of electrons) hence the shielding effect is the same. The nuclear charge of **Y** is lower than Rb^+ as it has fewer protons. Therefore effective nuclear charge of **Y** is lower than Rb^+. The valence electrons are thus less strongly attracted towards the nucleus of **Y**, hence **Y** has a larger ionic radius than Rb^+.

(c) **X**: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

Se: [Ar] $3d^{10}\ 4s^2\ 4p^4$

(i) **X** has lower 1st ionisation energy than of P. This is because the presence of inter-electronic repulsion between the paired electrons in the 3p orbital outweighs the effect of increased nuclear charge from P to **X**, hence less energy required to remove an electron from the paired 3p electrons in **X**.

(ii) Comparing **X** and Se, Se has one additional principal quantum shell, thus distance between valence electron and nucleus is greater. The valence electron also experience greater shielding. This leads to weaker attraction between valence electron and nucleus thus less energy is required to remove valence electron from Se. Hence Se has a lower first ionisation energy than **X**.

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 electron 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)

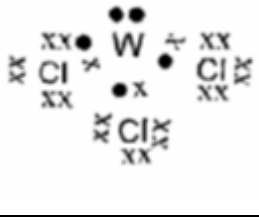
- **For comparison of ionic radius of isoelectronic ions, answers should compare**
  - nuclear charge (depends on number of protons)
  - shielding effect (depends on number of inner electrons)
  - effective nuclear charge
  - conclude that the species with valence electron more strongly attracted would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

- **Criteria of success for decreasing IE trend down the group, state**
  - Se has a larger number of filled quantum/electronic shells than X, hence shielding/screening effect increases
  - The distance 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 strongly attracted to the nucleus.
  - Less energy is needed to remove the 4p (state the subshell) electron in Se compared to 2p (state the subshell) electron in X.
  - First ionisation energy of Se is lower

2(a) Group 15

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

(b)

Either WCl_3	Or WCl_5
	
Trigonal pyramidal	Trigonal bipyramidal

(c)

Pair 1:	**P** & **X**	Group 16
Pair 2:	**Q** & **Y**	Group 17

(d) $\mathbf{S}^+$: $1s^2\ 2s^2\ 2p^6$
$\mathbf{T}^+$: $1s^2\ 2s^2\ 2p^6\ 3s^1$

Comparing $\mathbf{T}^+$ and $\mathbf{S}^+$, $\mathbf{T}^+$ has a higher nuclear charge but with one additional principal quantum shell, distance between valence electron and nucleus is greater. The valence electron experience greater shielding and hence weaker attraction between valence electron and nucleus, resulting in much lower energy required to remove the 3s electron in $\mathbf{T}^+$ than 2p electron in $\mathbf{S}^+$.
2nd IE of **T** is lower than that of **S**.

Things to note:

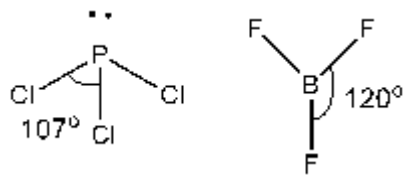
- **Criteria of Success for dot-and-cross diagram**
  - Using dot and cross only to represent electrons (other symbols such as circle are not acceptable)
  - Showing all electrons on the side (Cl) atoms

- **Criteria of Success for drastic decrease in 2nd IE between S and T**
  - Compare difference in number of filled quantum shells and hence distance between valence electrons and nucleus
  - Compare difference in shielding experienced by valence electrons
  - Compare extent of attraction between valence electrons and nucleus
  - Compare amount of energy required to remove valence electrons.

Topic 3: Chemical Bonding

1. RVHS/PRELIMS 2011/P1/Q5

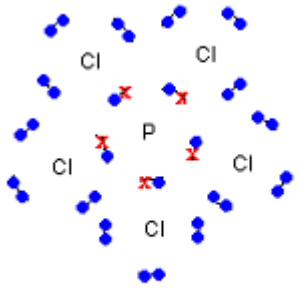
(a)



(b) Dative bond / coordinate bond

Comment: *PCl_3 can donate the lone pair electrons to BF_3 and B has empty orbital to accept this lone pair electrons, hence forming dative bonding.*

(c)

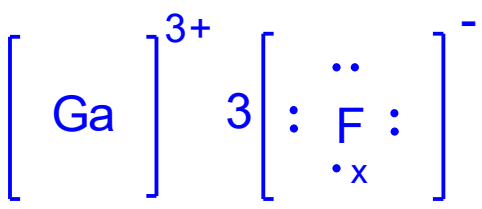


Shape: Trigonal bipyramidal

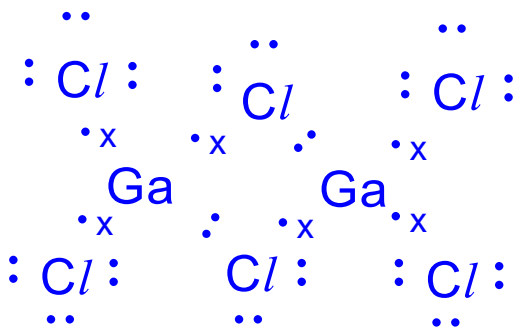
(d) $[PCl_6]^-$

2. (a) Polarisability / extent or ease of polarisation : Cl^- < Br^- < I^- . Hence, covalent character : $GaCl_3$ < $GaBr_3$ < GaI_3 leading to greater difference between experimental and theoretical value.

(b)(i)



gallium(III) fluoride



gallium(III) chloride

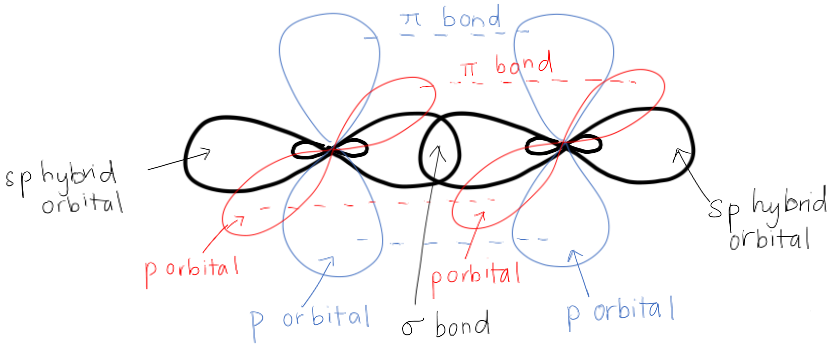
(ii) Shape around each Ga is tetrahedral with bond angle of 109.5° as there are 4 bond pairs and no lone pairs around Ga.

3 (a) (i) Sodium. At 600°C, sodium is <u>still a liquid</u>.

(ii)
- Both have <u>giant metallic lattice structure</u> with <u>strong electrostatic forces of attractions between cations and sea of delocalized electrons.</u>
- <u>Number of delocalised electrons in magnesium is greater than sodium.</u>
- <u>More energy</u> is required to overcome the <u>stronger metallic bonding in Mg</u>, hence melting point of magnesium is higher than sodium.

(ii)
- C≡C consists of 1 α bond and 2 π bonds.
- The α bond is formed from a <u>head on</u> overlap of the <u>sp hybridised</u> orbitals
- The π bonds are formed from a <u>side on</u> overlap of the <u>unhybridised p</u> orbitals.

If a diagram is drawn, diagram must be labeled to show the orbitals involved in each overlap.



<u>Things to note:</u>
- In drawing dot-cross diagram, electrons to give to the more electronegative atom for anions; electrons removed from less electronegative atom in cations. Central atom from period 3 onwards can expand its octet and have more than 8 electrons around it.
- To determine the shape of the molecule, the number of bond pairs and lone pairs of electrons around the central atom must be taken into account.
- According to VSEPR, lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion
- Not all metals and non-metals form ionic compound. E.g $AlCl_3$ is covalent due to high charge density of Al^{3+} which polarizes the electron cloud of the anion to a large extent.
- Always use SIA (**<u>s</u>**tructure, <u>i</u>nteraction and **<u>a</u>**mount of Energy) to answer boiling/melting point questions
- Orbitals (not atoms) overlap in forming covalent bonds.
- In determining the hybridization state,

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

Topic 4: The Gaseous State

1. Step 1: Convert temp to K,
   Gas **X** – 25 + 273 = 298 K
   Deuterium – 17 + 273 = 290 K

Step 2: Modify the ideal gas equation to include relative molecular mass M_r

$pV = nRT$

$$pV = \frac{mass \times RT}{M_r}$$

Since both gases are at the same pressure and volume,

$$pV = \frac{mass \times RT}{M_r} = \frac{mass\ (\mathbf{X}) \times RT}{M_r(\mathbf{X})} = \frac{mass\ (Deuterium) \times RT}{M_r(Deuterium)}$$

Step 3: Insert the known values for each gas

Deuterium gas is similar to hydrogen gas H_2, it is a diatomic molecule D_2 with M_r of 4 as each deuterium atom has a mass of 2.

$$\frac{mass\ (\mathbf{X}) \times RT}{M_r(\mathbf{X})} = \frac{mass\ (Deuterium) \times RT}{M_r(Deuterium)}$$

$$\frac{3.7 \times R \times 298}{M_r(\mathbf{X})} = \frac{0.368 \times R \times 290}{4}$$

Simplifying the equation gives us

$$M_r(\mathbf{X}) = \frac{4 \times 3.7 \times 298}{0.368 \times 290}$$

2. It is necessary to find the pressure after mixing at 25 °C first, then find how temperature affected the pressure to change it to 9p.

   Making use of the expression,
   $p_1V_1 = p_2V_2 + p_3V_3$, where V_1 is the total volume (v + 7v) = 8v,
   $p_1 = (p_2V_2 + p_3V_3) / V_1 = (p \times v + 5p \times 7v) / 8v = 36pv / 8v = 4.5pV$

   Since temperature then changed to result in a final pressure of 9p, we can apply
   $\frac{p_1}{T_1} = \frac{p_2}{T_2}$
   25 °C = 298 K
   p_1 is 4.5p, p_2 is 9p, T_1 is 298 K
   $T_2 = (p_2 \times T_1) / p_1 = 596$ K

3. **(a)** If gas exhibits ideal gas behaviour, pV = constant
   $p_1V_1 = (1)(1000) = 1000$ atm cm^3
   $p_2V_2 = (30)(31.2) = 936$ atm cm^3
   $p_3V_3 = (60)(14.9) = 894$ atm cm^3

   Since pV is not constant for all 3 cases or $P_1V_1 \neq P_2V_2 \neq P_3V_3$, **Y** does not show ideal gas behaviour.

(b) $pV = nRT = (m/M_r)RT$

M_r of Z = $(mRT)/pV$

$= (0.100 \times 8.31 \times 373) / (101000 \times 66.7 \times 10^{-6}) = 46.0$

Note: *need to convert to SI units when using ideal gas equation*

4. (a) $pV = nRT$

$(98.7 \times 10^3)(3.06 \times 10^{-6}) = n(8.31)(37+273)$

$n = 1.172 \times 10^{-4}$ mol

No. of moles of haemoglobin = $n/4 = 2.930 \times 10^{-5}$ mol

Molar mass of haemoglobin = $2.00/(2.930 \times 10^{-5}) = 6.83 \times 10^4$ g mol^{-1}

(b) Oxygen is not an ideal gas as it possesses significant intermolecular instantaneous dipole-induced dipole interactions between its molecules.

5. **B** is NH_3 at 300K while **C** is CH_4 at 500K.

NH_3 at 300K deviates more from ideal gas behaviour than CH_4 at 300K. This is because NH_3 molecules are held by stronger hydrogen bonding as compared to weaker instantaneous dipole-induced dipole interactions between CH_4 molecules.

CH_4 at 500K deviates less from ideal gas behaviour than CH_4 at 300K. This is because at higher temperature, the molecules possess higher kinetic energy and is more able to overcome the instantaneous dipole-induced dipole interactions between them, so these interactions become less significant.

Things to note:

- When using pV = nRT , R = 8.31, P in Pa, V in m^3, n in mol and T in K

  1 atm = 760 mmHg = 101325 Pa (approximately)

  1 bar = 1 x 105 Pa

  1 dm^3 = 1000 cm^3 = 10^{-3} m^3

  1 cm^3 = 10^{-6} m^3

  T (K) = T (^oC) + 273
- Real gases **deviate** most from ideal gas behaviour under the following conditions:

1. **At very high pressure**
2. **At very low temperature**

- Gases with **stronger intermolecular forces of attraction** tend to **deviate more** from ideal behaviour

Topic 5: The Periodic Table

1(a)

$MgCl_2$ undergoes hydration and slight hydrolysis.

$$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$$
$$[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H_3O^+$$

$AlCl_3$ undergoes hydration and appreciable hydrolysis.

$$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$$
$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$$

Al^{3+} has higher charge density than Mg^{2+}, polarises the electron cloud of water molecules. It weakens the O-H bond to a greater extent to release more H^+.

Thus, its solution is more acidic (lower pH).

(b) $Si > S_8 > P_4$ or Si, S_8, P_4

Si has a giant molecular structure. It has the highest melting point because a lot of energy is required to break the strong Si–Si covalent bonds between Si atoms.

Both P and S have simple molecular structures, with P existing as non-polar P_4 molecules and S existing as non-polar S_8 molecules.

S_8 has a lower melting point than Si because less energy is needed to overcome the weaker instantaneous dipole-induced dipole interactions between the S_8 molecules than breaking the covalent bonds between Si atoms.

P_4 has the lowest melting point among the three elements because the intermolecular instantaneous dipole-induced dipole interactions present are even weaker than those in S_8 since the P_4 molecule has a smaller and less polarizable electron cloud electrons than the S_8 molecule.

2.

(i) Group 15

The 6th IE is much higher than the 5th IE, which implies that the 6th electron is in the inner shell and there are 5 valence electrons in **K**.

(ii) Lower

The electronic configuration of element **L** is [Ne] $3s^2\ 3p^4$, hence there will be inter-electronic repulsion between the paired electrons in the p-orbital. This effect outweighs the increase in nuclear charge and less energy is required to remove the valence electron from **L**.

(iii) $\mathbf{J}Cl_4 + 2H_2O \rightarrow \mathbf{J}O_2 + 4HCl$ or $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

$\mathbf{K}Cl_5 + 4H_2O \rightarrow H_3\mathbf{K}O_4 + 5HCl$ or $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

Things to note:

- $AlCl_3$ is a covalent chloride although it is a metal chloride due to the high charge density of Al^{3+}.
- Unlike NaCl, the other 2 metal chlorides, $AlCl_3$ and $MgCl_2$ are acidic as they will undergo partial hydrolysis in water due to the high charge density of the cations.
- Sulfur exists as S_8 while Phosphorus exists as P_4. Their molecular formula is taken into account when explaining the trend of melting point across Period 3 elements.
- The largest jump in successive ionization energies of an element is due to removal of electron from an inner quantum shell.
- Ionisation energy generally increases across a period. Anomaly in ionisation energy across the period occurs for the 2 following sets of outer electronic configurations: ns^2 to ns^2 np^1 and ns^2 np^3 to ns^2 np^4

Topic 6: Chemical Energetics

1. **(i)** The standard enthalpy change of neutralisation, $\Delta H_{neut}^{\ominus}$, is the enthalpy change when an acid reacts with a base to form one mole of water in dilute aqueous solution at 298 K and 1 bar.

(ii) q = mcΔT = 50.0 x 4.2 x (34.5-24.0) = 2205 J = 2.205 kJ

$HCOOH + NaOH \rightarrow HCOO^-Na^+ + H_2O$

Limiting reagent is HCOOH

No of moles of HCOOH = $\frac{1.84}{46}$ = 0.04 mol

No of moles of NaOH = $\frac{50}{1000}$ x 1 = 0.05 mol (excess)

No of moles of H_2O formed = No of moles of HCOOH (limiting reagent) = 0.04 mol

$\Delta H_{neut} = -\frac{q}{nH2O} = -\frac{2.205}{0.04}$ **=** – 55.1 kJ mol^{-1}

(iii) HCOOH is a <u>weak acid</u> and hence <u>does not dissociate fully</u>. Some energy is required to <u>fully ionise the undissociated weak acid</u>, hence <u>ΔH_{neut} is less exothermic</u> (or has a smaller magnitude).

Things to note:

- When using the formula, q = mcΔT , the mass of the solution is taken to be the volume of 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 eventually.
- If there are two solutions added together, the mass in the formula will be the total volume of the two solutions, assuming density of solution is 1 g cm^{-3}.
- The sign of enthalpy change is dependent of the temperature change. In this question, ΔH has a negative sign as the final temperature is **higher** than the initial temperature.
- The number of moles substituted in the formula, $\Delta H^{\ominus} = \pm\frac{q}{n}$, is
  n = number of moles of **water** formed for $\Delta H^{\ominus}_{neut}$
  n = number of moles of **substance** burnt for $\Delta H^{\ominus}_{c}$
  n = number of moles of **compound** formed for $\Delta H^{\ominus}_{f}$
  n = number of moles **limiting reagent** for any general $\Delta H^{\ominus}$

2. (a)(i) Hess' Law states that the enthalpy change for a chemical reaction is the same, regardless of the pathway taken, provided the initial states of the reactants and final states of the products are the same.

(ii) $C_6H_4(OH)_2$ (aq) + H_2O_2 (aq) $\xrightarrow{\Delta H_{rxn}}$ $C_6H_4O_2$ (aq) + $2H_2O$ (l)

+177

$C_6H_4O_2$ (aq) + H_2 (g) + H_2O_2(aq) – 286

– 95

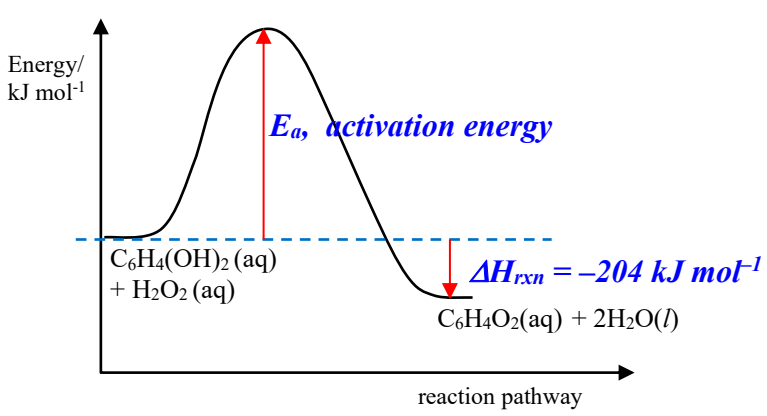
½ O_2 (g) + H_2O(l) + H_2(g) + $C_6H_4O_2$ (aq)

ΔH_{rxn} = +177 + (– 95) + (– 286) = –204 kJ mol^{-1}

Criteria of Success of drawing Energy Cycle:

- All equations are **balanced**
- Equations are **multiplied** by appropriate coefficient (if applicable)
- **State symbols** are written for all species
- Value of **enthalpy change** is written above the arrow

(iii)



Criteria of Success of drawing Energy Profile Diagram/Reaction Pathway

- Axis is correctly labelled with **units**
- Correct shape of graph is drawn to show **exothermic** or **endothermic** reaction
- Arrow is drawn with **ΔH** labelled with value (if any)
- Arrow is drawn with **E_a** labelled with value (if any)
- **Reactants**, **products**, intermediate (for 2 or more steps) are written with state

(c)(i) $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$

$= (-98.1) - (298)(62.8 \times 10^{-3}) = -117 \text{ kJ mol}^{-1}$

Things to note:

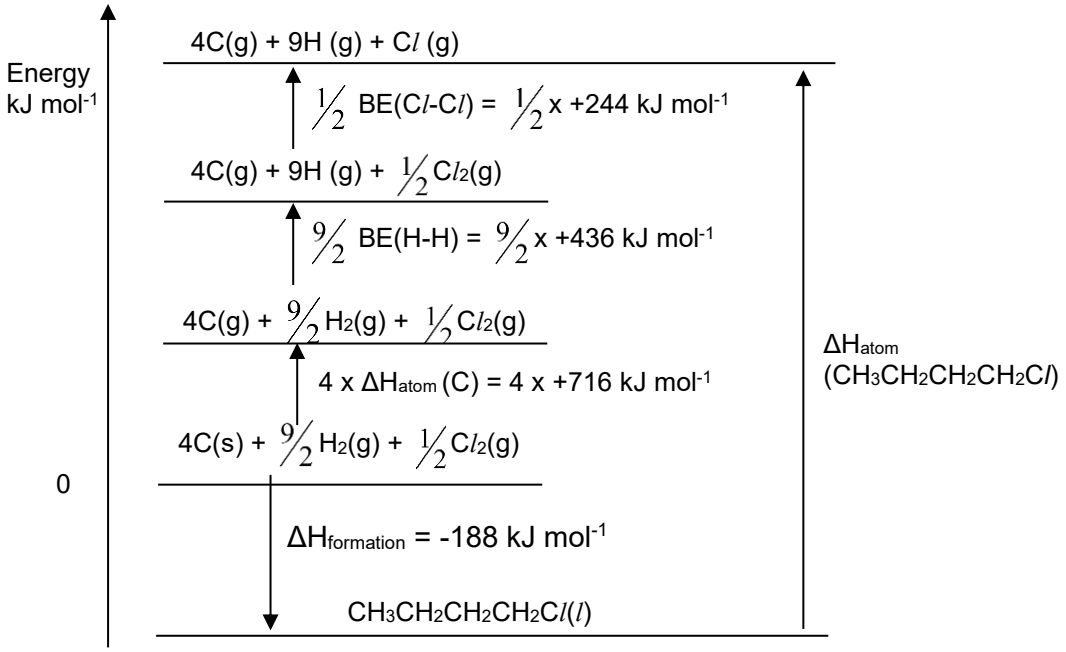
- Values substituted for ΔH and ΔS must be **consistent** with the units. If the value of ΔH has units of kJ mol^{-1}, the value of ΔS must also be converted to the same units of kJ mol^{-1}K^{-1} for calculation.

(ii)

- Store concentrated H_2O_2 at low temperature and in dark bottles to prevent decomposition to form O_2 gas.
- Allow O_2 gas to escape to prevent build up of pressure
- Ensure that the containers used to store H_2O_2 are free from impurities as they can act as catalysts for decomposition

3. **(i)** Enthalpy change of formation is the enthalpy change when one mole of compound is formed from its constituent elements in their standard states are at 298 K and 1 bar.

(ii)



$\Delta H_{atom}(CH_3CH_2CH_2CH_2Cl) = -(-188) + 4(716) + \frac{9}{2}(436) + \frac{1}{2}(244)$

$= +5140 \text{ kJ mol}^{-1}$ (3.s.f)

Criteria of Success of drawing Energy Level Diagram:

- Axis is correctly labelled with **units**
- All equations are **balanced**
- Equations are **multiplied** by appropriate coefficient (if applicable)
- **State symbols** is written for all species
- Arrow drawn pointing upwards for **endothermic** reaction; Arrow drawn pointing downwards for **exothermic** reaction
- Value of **enthalpy change** is written above the arrow

(iii) ΔH_{atom} ($CH_3CH_2CH_2CH_2Cl$) = BE(C-Cl) + 3BE(C-C) + 9BE(C-H)
= 340 + 3(350) + 9(410)
= +5080 kJ mol^{-1}

(iv) 1. Bond energy values from the Data Booklet are only average values.
2. For **(ii)**, enthalpy change of vapourisation of $CH_3CH_2CH_2CH_2Cl(l)$ is not taken into account.

Topic 7: Kinetics

1. YJC/PRELIM2009/P3/Q3(b)

(i) Let the rate equation be: rate = k [HCl]^x[sucrose]^y

Comparing experiment 1 and 2, when [HCl] is constant,

[sucrose] is doubled, and initial rate is doubled.

Hence order of reaction with respect to [sucrose] is 1.

Comparing experiment 2 and 3:

$$\left(\frac{0.10}{0.20}\right)^x\left(\frac{0.20}{0.30}\right)^1 = \frac{0.048}{0.144} \Rightarrow x = 1$$

Hence order of reaction with respect to [HCl] is 1.

Hence rate = k [HCl][sucrose]

Using experiment 1:

$$k = \frac{0.024}{(0.10)(0.10)} = 2.40\ mol^{-1}dm^3s^{-1}$$

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 **two** experiments that you are comparing
- State which reactant concentration is kept **constant**
- State which reactant concentration is **varied**
- Conclude the **order of reaction**

(ii) Rate = k [HC*l*][sucrose]

= k' [sucrose] where k' = k[HC*l*]

$t_{1/2} = \left(\frac{\ln 2}{k'}\right) = \left(\frac{\ln 2}{k[HCl]}\right)$

Since [HC*l*] is doubled in experiment 3, half-life will be halved.

Half-life of sucrose in experiment 3 = 1.5 s

> **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/PRELIM2010/P3/Q5a

(i) ∗ Since total volume of solution is constant,

concentration of a reactant ∝ volume of reactant

∗ rate ∝ 1/time

rate = k $[S_2O_8^{2-}][I^-]$

$\frac{1}{t} = k\,(V_{S_2O_{8^{2-}}})(V_{I^-})$

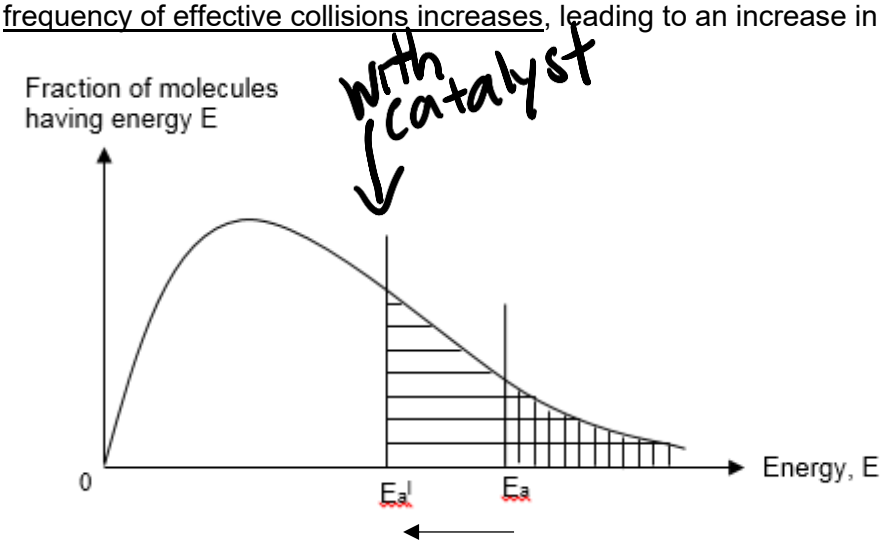
$t = \frac{1}{k\,(V_{S_2O_{8^{2-}}})(V_{I^-})}$

$\frac{t_3}{80} = \frac{\frac{1}{k\,(5)(25)}}{\frac{1}{k\,(10)(15)}}$ (Can also compare expt 3 with either expts 1 or 2)

t_3 = 96 s

(ii) Heterogeneous catalysis

The catalyst (Fe) provides an alternative pathway with a lower activation energy. The number of molecules with energy greater than or equal to the activation energy is greater. Hence the frequency of effective collisions increases, leading to an increase in rate of reaction.



Things to note:

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

Criteria of Success of Drawing Boltzmann Distribution Graph:

- Axis is correctly labelled with **units**
- **Zero** is written at the origin
- **Two** E_a lines are drawn with the lowered E_a labelled as E_a (with catalyst)
- **Two** different sets of shading
- Graph does not touch the **x-axis**

3. JJC/PRELIM2009/P2/Q3

(a) Concentration of vanillin may be followed by measuring the colour intensity of vanillin using a colorimeter.

Comment: *Since vanillin is yellow solution while the product is colourless, the yellow colour intensity will decrease as the reaction proceeds. The colour intensity will be proportional to the concentration of vanillin left in the mixture.*

(b) Using the graph [HCN] = 5.00 mol dm^{-3},

When 0.03 mol dm^{-3} vanillin drops to 0.015 mol dm^{-3}, the time taken is 0.095 min

When 0.015 mol dm^{-3} vanillin drops to 0.0075 mol dm^{-3}, the time taken is

0.19 – 0.095 = 0.095 min

The 2 half-lives need to be shown on the graph.

Since the 2 half-lives is constant at 0.095 min, the reaction is 1st order with respect to [vanillin].

Criteria of Success of Drawing Half-Life:

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

(c) Rate = k $[HCN]^x$ [vanillin]

Since HCN is in large excess, rate = k' [vanillin]

$t_{½} = \frac{In\ 2}{k'} = \frac{In\ 2}{k[HCN]^x}$

$t_{½} \propto \frac{1}{[HCN]^x}$

When the concentration of HCN increased 50 times (from 0.1 mol dm^{-3} to 5.00 mol dm^{-3}), half-life decreased 50 times (from 4.75 min to 0.095 min). Therefore, the reaction is 1st order with respect to [HCN].

Topic 8: Chemical Equilibria

1(a) Number of moles of I^- ions = (50/1000) x 0.1 = 0.005 mol

(b) $AgNO_3 + I^- \rightarrow AgI + NO_3^-$

Number of moles of $AgNO_3$ = (30/1000) x 0.1 = 0.003 mol

Number of moles of I^- ions at equilibrium = 0.003 mol

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

Initial/mol		0.005		0
Change/mol		-0.002		+0.001
Eqm/mol		0.003		0.001

Amt of I^- at eqm = <u>0.003 mol</u>

Amt of SO_4^{2-} at eqm = <u>0.001 mol</u>

(c) $K_C = \dfrac{[SO_4^{2-}]}{[I^-]^2}$

$= \dfrac{(0.001)/(50/1000)}{(0.003/(50/1000))^2}$

$= \mathbf{\underline{5.56}}$

2(a) When temperature is low, system will react to increase temperature, favouring the forward exothermic reaction. Position of equilibrium shifts to the right to increase the yield.

However, too low a temperature will result in a slow reaction rate. A moderate temperature of 450°C is used with the presence of catalyst which aids to increase the reaction rate by lowering the activation energy of the reaction.

A high pressure is preferred since system will react to decrease pressure by favouring the formation of fewer gaseous molecules. Position of equilibrium shifts to the right to increase the yield. However, high pressure increase the cost of maintenance of equipment. An optimum pressure of 5 atm is used.

(b) $K_p = \dfrac{P_{SO_3}}{P_{SO_2} P_{O_2}^{1/2}}$

	SO_2 (g) +	½O_2 (g) ⇌	SO_3 (g)
Initial/mol	2	1	0
Change/mol	(95/100) x 2 = −1.9	−0.95	+1.9
Eqm/mol	0.1	0.05	1.9

Total number of moles = 0.1 + 0.05 + 1.9 = 2.05 mol

$p(SO_2)$ = 0.1 / 2.05 x 5 = 0.244

$p(O_2)$ = 0.05 / 2.05 x 5 = 0.122

$p(SO_3)$ = 1.9 / 2.05 x 5 = 4.634

$$K_p = \frac{4.634}{(0.244)(0.122)^{1/2}} = 54.4 \text{ atm}^{-1/2}$$

3(a)

	X_2 (g)	+ $3Y_2$ (g)	$\rightleftharpoons$	$2XY_3$ (g)
Initial/mol	4.0	12.0		0.0
Change/mol	-2.0	- 6.0		+4.0
Eqm/mol	2.0	6.0		4.0

Total no. of moles at equilibrium = 12.0

$p(XY_3)$ = 4.0/12.0 x 1 = 1/3

$p(Y_2)$ = 6.0/12.0 x 1 = ½

$p(X_2)$ = 2.0/12.0 x 1 = 1/6

(b) $K_p = \frac{(1/3)^2}{(1/6)(1/2)^3}$ = 5.33 atm^{-2}

(c)

	X_2 (g)	+ $3Y_2$ (g)	$\rightleftharpoons$	$2XY_3$ (g)
Initial/mol	2.0	6.0		4.0
Change/mol	+1.0	+3.0		-2.0
Eqm/mol	3.0	9.0		2.0

Total no. of moles of gas at equilibrium = 14.0

Let P_T be the new equilibrium pressure

$$K_p = \frac{(2.0/14.0 \text{ x } P_T)^2}{(3.0/14.0 \text{ x } P_T)(9.0/14.0 \text{ x } P_T)^3} = 5.33$$

P_T = 0.259 atm

(d) No effect on the value of K_p. A catalyst speeds up both the forward and backward reaction to the same extent.

4 (a) $K_c = \frac{[\mathbf{Z}]^2}{[\mathbf{X}][\mathbf{Y}])}$

$= \frac{(1.2/3)^2}{(0.4/3)^2}$

= **9**

(b)

	X (g)	+ **Y** (g)	$\rightleftharpoons$	2**Z** (g)
Initial/mol	1.4	1.4		1.2
Change	-x	-x		+2x
Eqm/mol	1.4 – x	1.4 – x		1.2 + 2x

$K_c = \frac{[\mathbf{Z}]^2}{[\mathbf{X}][\mathbf{Y}])}$

$$9 = \frac{[(1.2 + 2x)/3]^2}{[(1.4 - x)/3]^2}$$

x = 0.6

New equilibrium concentration of **Z** = $\frac{1.2 + 2(0.6)}{3}$ = 0.8 mol dm^{-3}

(c) When the volume is reduced, the pressure will increase. The system will react to decrease pressure by favouring the side with fewer gaseous molecules. Since the number of moles of gaseous molecules is the same on both sides of the equilibrium, there is no change in the position of equilibrium.

(d) $K_c = \frac{k_f}{k_b}$

K_c increases with temperature. This implies that the forward rate (or rate constant of forward reaction) increases faster than the backward rate (or rate constant of backward reaction), hence position of equilibrium is shifted to the right. When temperature increases, the system will react to decrease temperature by favouring endothermic reaction. Thus, forward reaction is endothermic.

Things to note:

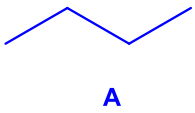
- K_c should be expressed in terms of equilibrium concentrations of reactants and products. Working should show division by volume for 1(c) and 4(a) and not merely substitution in terms of moles.
- K_p should be expressed in terms of partial pressure of reactants and products at equilibrium. Working 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. decrease the pressure by favouring the side with less number of gaseous molecules)
  - State how the position of equilibrium would shift (e.g. right/left/no change)

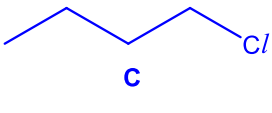
- K_c only changes with temperature because rate constant of forward and rate of backward reaction increase/decrease to different extent. When K_c increase with increasing temperature, it implies that rate constant of forward reaction increases to greater extent than rate constant of backward reaction. 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



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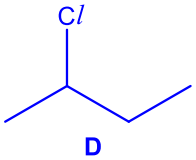

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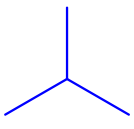

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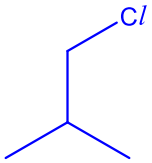

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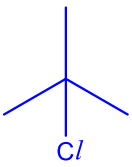


E

Things to note:

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

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

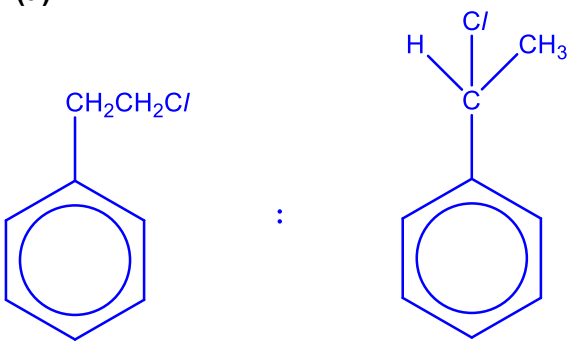
- a **chiral centre** and
- **no plane of symmetry**

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

Free Radical Substitution 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 **hydrogens** that can be substituted in F.R.S. The actual proportion of the isomers depends on the **probability** of forming the intermediates and the **stability** of the intermediates.

2(a)



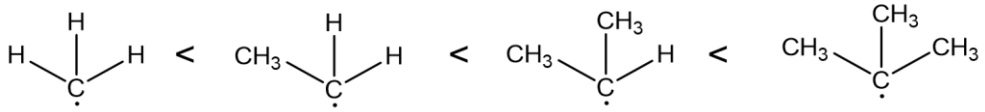
= 3 : 2

(b) The secondary alkyl radical has more electron donating alkyl groups which reduces the electron deficiency on the radical to a greater extent and is more stable than the primary alkyl radical ($C_6H_5CH_2CH_2$.) which produces $C_6H_5CH_2CH_2Cl$.

Things to note:

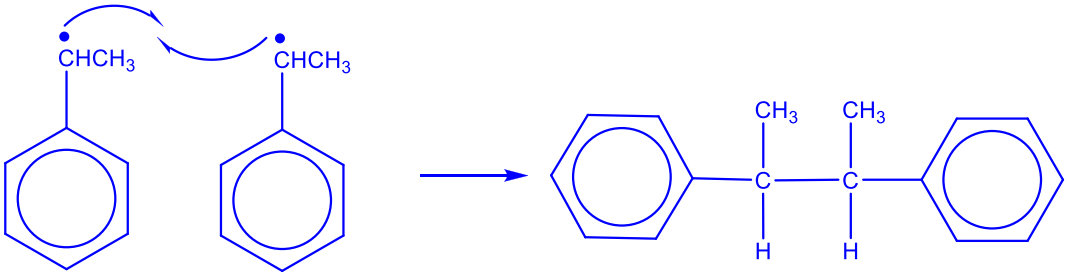
Stability of Radicals

Radicals have different levels of stability based on the **number of alkyl groups** attached to the carbon that has an unpaired electron. Alkyl groups are **electron donating** and **reduce the electron deficiency on the carbon radical** they are attached to, hence **stabilising** the carbon radical. Therefore, the **more alkyl groups** attached to the carbon radical will **increase the stability of the carbon radical**.

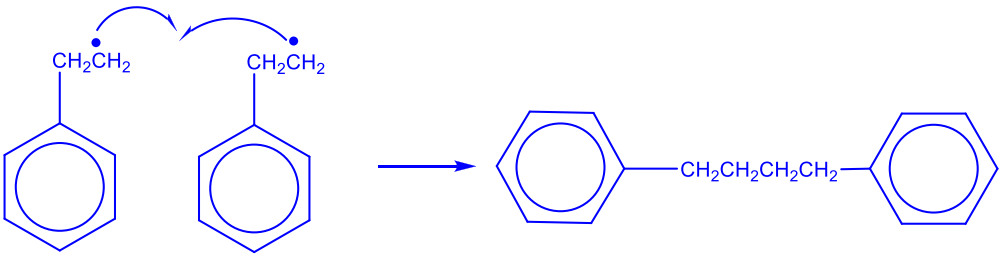


Methyl radical **Least stable** | primary radical | secondary radical | tertiary radical **Most stable**

(c)

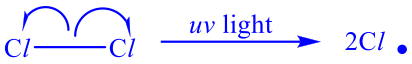


Or

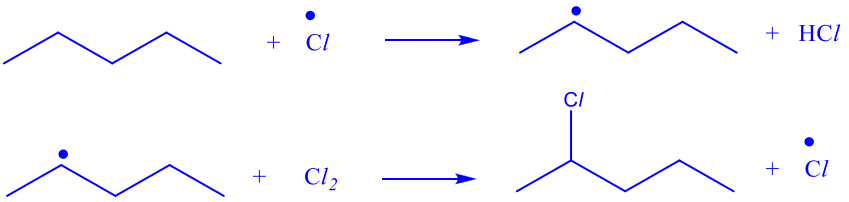


3(a) Free radical substitution

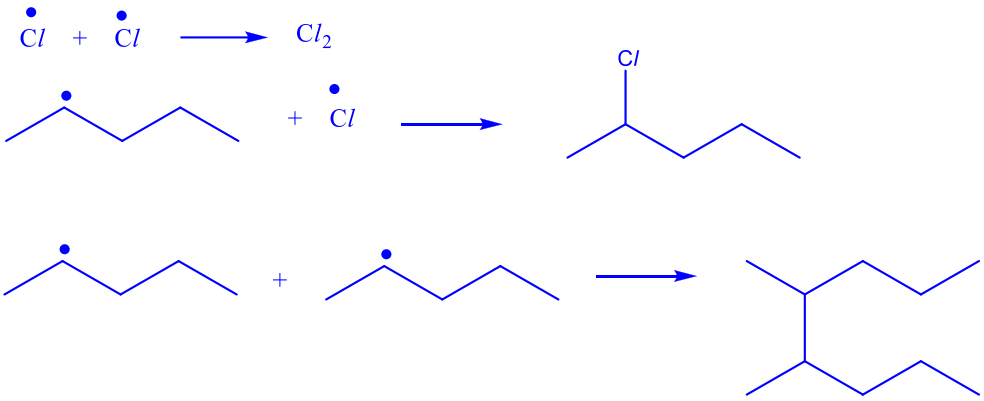
Initiation



Propagation:



Termination



Criteria of Success:

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

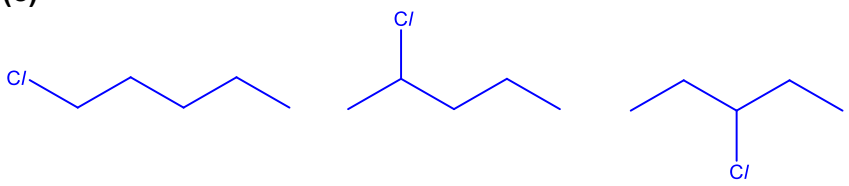
- **Name of the mechanism** (Free Radical Substitution)
- **Steps** in sequential order (Initiation, Propagation, Termination)
- **Half arrows** (representing the flow of one electron)
- **Labels** (radical species with single dot representing one electron on the **correct** carbon)
- Do not use condensed 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)

NO contains a single electron on the nitrogen atom (radical) which can react readily with Cl_2 gas or Cl• to form NOCl. This decreases the concentration of Cl_2 or Cl• for free radical substitution reaction. Hence, the rate of reaction will slow down.

(c)



3 : 2 : 1

(d) During the first propagation step, the C – H bond is broken and the H – X bond is formed.

Bond energy (H – C*l*) = 431 kJ mol^{-1} < Bond energy (H – Br) = 366 kJ mol^{-1}

Since less heat is released when forming H – Br bond than H – C*l* bond, bromination take place less readily / less favourably.

4(a) Na reacts exothermically / explosively with H_2O to form NaOH(aq).

(b) **P**: Propane

Q: Ethane

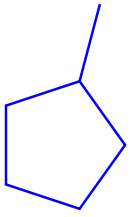
P (propane) : **Q** (ethane) = 2 : 1

Things to note:
The propane is formed from the combination of two different alkyl portions (mixture of **2** C alkyl and **1** C alkyl parts.) Hence, there will be **double** the chance of forming it as compared to ethane which is formed from combining the same type of alkyl parts.

(c) No of moles of CO_2 = 1.44/24 = 0.06 mol

Mole ratio of **K** : CO_2 = 0.01 : 0.06 = 1: 6

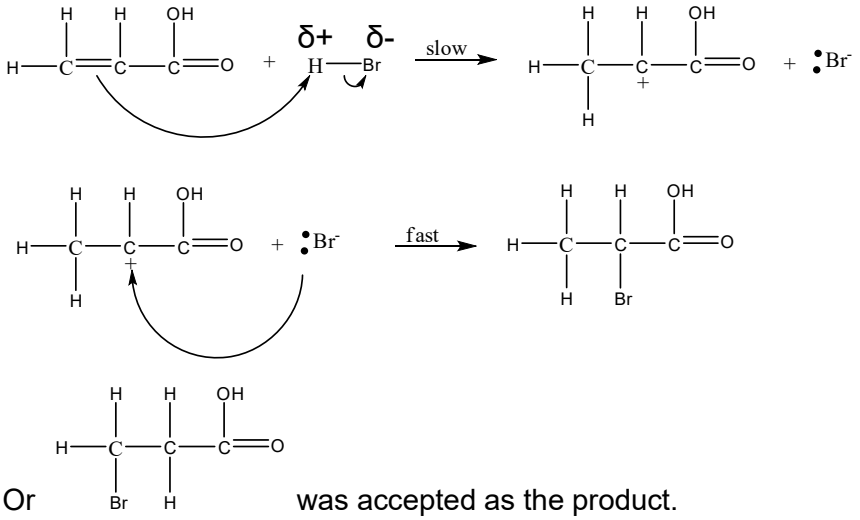
Hence **K** contains 6 C atoms.



K is methylcyclopentane

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 a) Electrophilic Addition



Or was accepted as the product.

Criteria of Success:

In describing the electrophilic addition mechanism, you should include:

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

b) Lactic acid contains a chiral carbon: $CH_3C^*H(OH)COOH$.

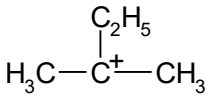
Only **one enantiomer** of lactic acid is found naturally in muscle tissues which rotates plane-polarised light and is optically active. When lactic acid is chemically synthesised, **a racemic mixture** is obtained due to equal probability of OH^- attacking the carbocation on either side of the plane in the fast step.

Things to note:

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

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.

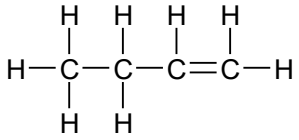
6 (a) (i)



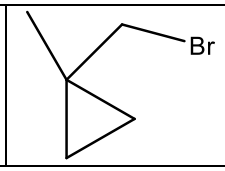
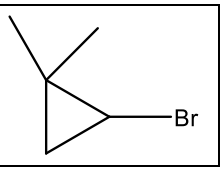
(ii) 2,2-dimethylbutanoic acid

(iii) number of electrons: 6

(iv)



(b)

structural formula		

Ratio = 6 : 4
= 3 : 2

Things to note:

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

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

7(i)

Hexane molecules have greater surface area than 2-methylpentane molecules. Stronger instantaneous dipole-induced dipole (id-id) interactions between hexane molecules than those between 2-methylpentane molecules, resulting in more energy required to overcome the id-id interactions between hexane molecules. Hence, hexane has a higher boiling point.

(ii) The main intermolecular interaction between pentan-2-ol molecules is hydrogen bonding, while that between 2-methylpentane molecules is instantaneous dipole-induced dipole interactions (id-id).

Since hydrogen bonding is stronger than induced dipole – induced dipole attraction, more energy is required to break the stronger hydrogen bonding between pentan-2-ol molecules, resulting in a higher boiling point.