NJC SH2 Preliminary Examinations Paper 3 Solutions

1(a) Pressure is approximately zero at **A**
Volume occupied by gas particles is small compared to the volume of the container
\NH_3 is almost an ideal gas.

Low pressure at **B**, intermolecular attractions are dominant, thus NH_3 molecules are pulled closer together. This reduces the impact on wall collisions and makes them softer. $P_{NH3} < P_{ideal}$, hence the negative deviation. Volume occupied by gas particles is still relatively small compared to container.

High pressure at **D** , mainly repulsion between particles. The volume of the molecules becomes a significant fraction of the volume of the container, and thus is no longer negligible. $V_{NH3} > V_{ideal}$, hence the positive deviation.

At **C**, NH_3 appears to follow the ideal gas equation, because the two deviations balance out.

1(b)(i) A relatively low temperature of 400 $_{o}$C is used to increase the yield of the exothermic reaction. Iron catalyst is used to compensate for any reduction in rate due to the low temperature used.
A high pressure of 200 atm caters to the forward reaction, which is accompanied by a reduction in volume. Pressure exceeding 200 atm would increase the cost of production.

1(b)(iii) P_{NH3} = 0.363 x 200 = 72.6 atm
P_{H2} = 0.47775 x 200 = 95.55 atm
P_{N2} = 0.15925 x 200 = 31.85 atm

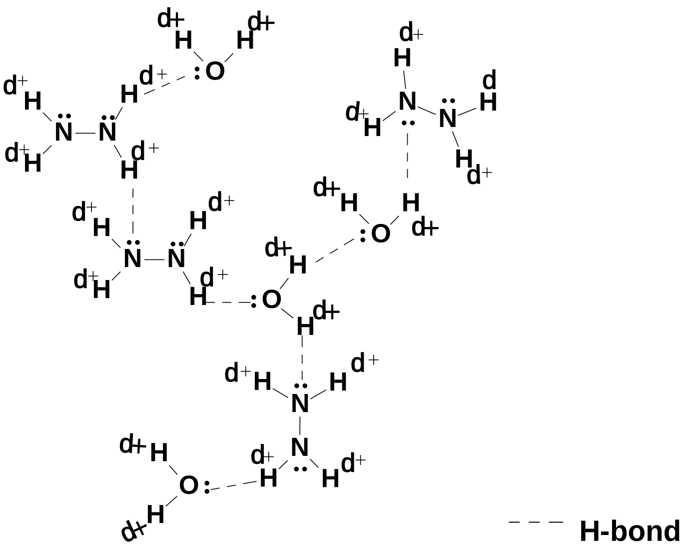
K_p = = 1.90 x 10^{-4} atm^{-2}

1(c) The - NH_2 in hydrazine has a stronger electron-withdrawing effect than the – H in ammonia
\the lone pair of electrons in ammonia is more available for donation to a proton

\ the stronger base & the bigger K_b value

1(d)(i) Hydrazine and water form a miscible mixture

Free intermingling of the molecules of hydrazine & water through mutual H-bonding
\ Exists as a homogeneous phase

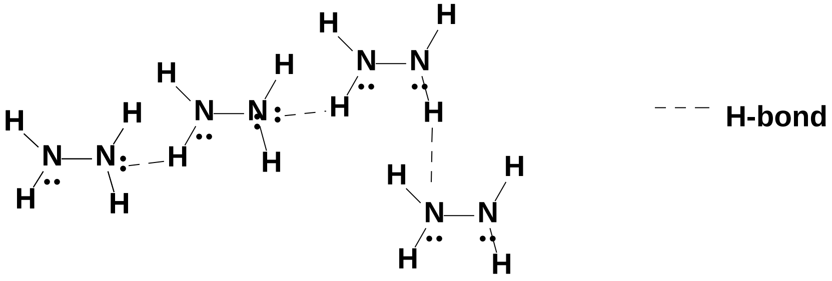


Hydrazine and trichloromethane are immiscible

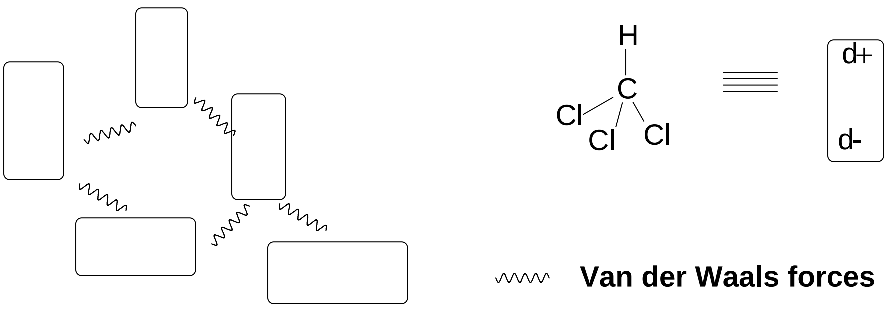
Segregation between the molecules of hydrazine & trichloromethane into 2 distinct layers

- NH_2NH_2 have strong H-bond with one another
- $CHCl_3$ have van der Waals attraction for one another

Each cannot establish any significant attraction for the other and will be squeezed out from one another's layer

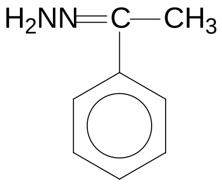


Phase boundary



1(d)(ii) -2 oxidation state in N of hydrazine is oxidized to 0 in N_2

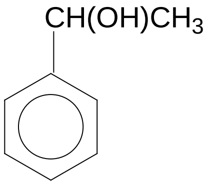
1(e)(i)



Compound E

CHI_3

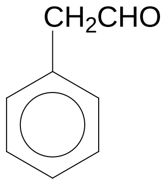
Compound F



Compound G

1(e)(ii) Reagent X is I_2(aq) with NaOH(aq); and the reaction mixture is warmed.

1(f)

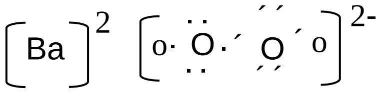


Compound H

2 a (i) Distillation and collect the distillate that boils over at 150 ^{O}C.

(ii) Solid $BaSO_4$ will be formed and it can be removed by filtration.

(iii)



b (i) Ba + $2H_2O$ ® $Ba(OH)_2$ + H_2

(ii) Reaction in b(i) involves the reduction of water by the group II metals. Reaction is more vigorous with barium as barium is a stronger reducing agent than magnesium as evidenced by the following data:

Mg ® Mg^{2+} + 2e E^{o}_{oxid} = +2.38V
Ba ® Ba^{2+} + 2e E^{o}_{oxid} = +2.90V

c (i) Standard enthalpy of formation of barium chloride is the <u>heat change</u> or enthalpy change when <u>1 mole of solid barium chloride</u> is formed from its elements in their standard states (25^{o}C and 1 atmosphere) i,e, formed from <u>barium solid</u> and <u>chlorine gas</u>.

(ii) $BaCl_2(s) + aq \rightarrow Ba^{2+}(aq) + 2Cl^-(aq)$ $\Delta H = -13.2$ kJ mol^{-1}

(iii)

$$\begin{tikzcd}
\mathbf{Ba(s) + Cl_2(g)} + O_2(g) + 2H_2(g) \arrow[r, "\Delta H_f"] \arrow[d, "+\text{aq}\ (-1002"] & \mathbf{BaCl_2(s)} + O_2(g) + 2H_2(g) \arrow[d, "2\ (-285.9)"] \\
Ba(OH)_2(aq) + Cl_2(g) + H_2(g) \arrow[d, "2\ (-92.3)"] & BaCl_2(s) + 2H_2O(l) \arrow[dd, "+aq\ (-13.2)"] \\
Ba(OH)_2(aq) + \mathbf{2}HCl(g) \arrow[d, "+\text{aq}\ 2\ (-71.9)"] & \\
Ba(OH)_2(aq) + \mathbf{2}HCl(aq) \arrow[r, "(-114.4)"] & BaCl_2(aq) + 2H_2O(l)
\end{tikzcd}$$

Using Hess' Law,

$\Delta H_f + 2(-285.9) + (-13.2) = (-1002) + 2(-92.3) + 2(-71.9) + (-114.4)$

$\Delta H_f = -859.8$ kJ mol^{-1}

$= -$ **860 kJ mol^{-1}**

(iii) $BaCl_2(s) \rightarrow Ba(s) + Cl_2(g)$

Using $\Delta S = \Sigma S_{products} - S_{reactants}$

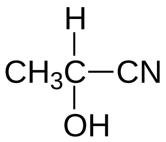
$= (63 + 223) - (124) = +162$ JK^{-1} mol^{-1}

For the reaction to be feasible, $\Delta G = \Delta H - T\Delta S$ must be less than zero.

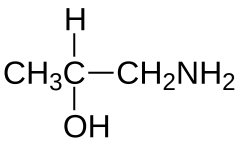
$$T = \frac{\Delta H}{\Delta S} = \frac{+859.8}{+162 \times 10^{-3}} = 5307K$$

Lowest temp for the reaction to be feasible is 5307K.

d **D**: CH_3COCl **E**: CH_3CHO

F: 

$\mathrm{CH_3}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CN}$

G: 

$\mathrm{CH_3}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2NH_2}$

Reagents and conditions for step (i):
$LiAlH_4$ in dry ether or H_2 with Pt as catalyst ‘

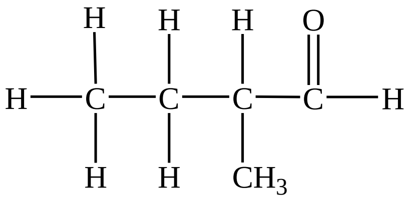
3 **(a)**
- **W** contains chiral carbon.
- **W** is an aldehyde.

No of moles of $CO_2 = \dfrac{33.6}{22.4} = 1.50$ mol

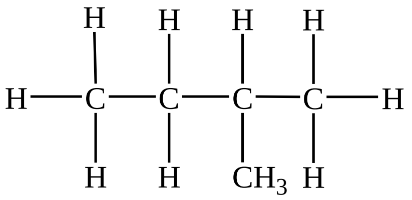
n**Y** : n CO_2
0.3 : 1.50
1:5

- **Y** contains 5 carbon atoms.

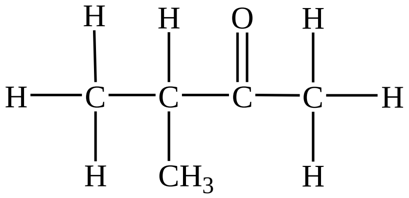
Structure of **W**:



Structure of **Y**:



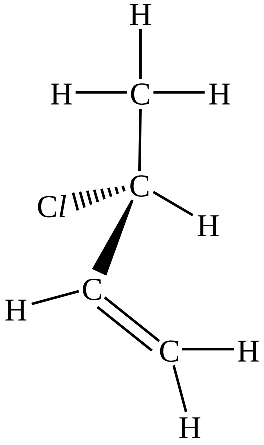
Structure of **X**:



(b)

Observations	**Deductions**
J has molecular formula of C_4H_7Cl.	**J** is a halogenoalkane.
J reacts with acidified potassium manganate(VII), giving effervescence of a colourless gas.	**J** undergoes oxidative cleavage. **J** contains terminal alkene.
J reacts with ethanolic potassium cyanide to produce compound **K** with molecular formula C_5H_7N.	**J** undergoes nucleophilic substitution of C*l* with CN.
J rotates plane-polarised light.	**J** contains a chiral carbon.

Displayed formula of **J**:



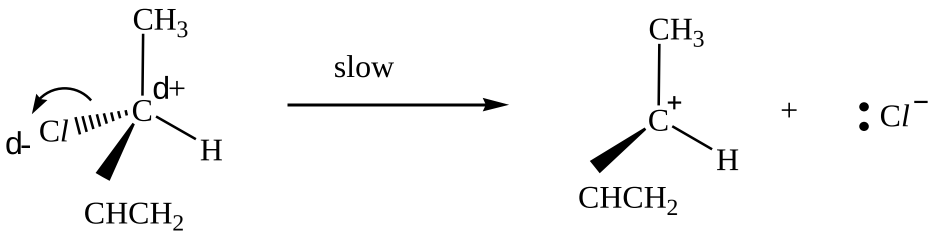
(c) **(i)** Comparing Expt **1** & **2**, when [**J**] triples while [KCN] is kept constant, initial rate of formation of product triples. Hence, reaction is first order wrt **J**.

Comparing Expt **1** & **3**, when [**J**] doubles and [KCN] doubles, initial rate of formation of product only doubles. Hence, reaction is zero order wrt KCN.

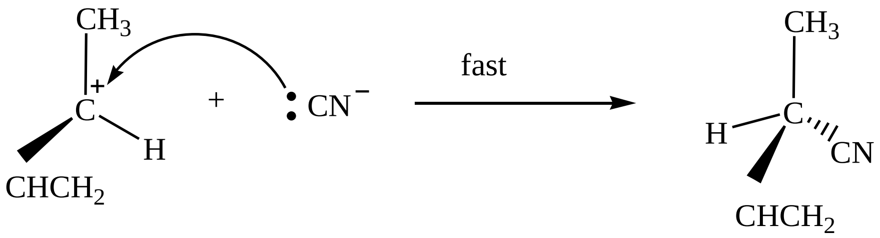
Rate = k[**J**]

Mechanism:
<u>Nucleophilic Substitution (SN1)</u>

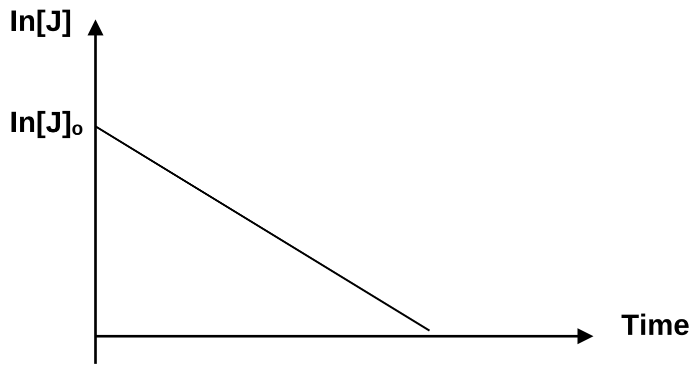
Step 1:



Step 2:



(ii)



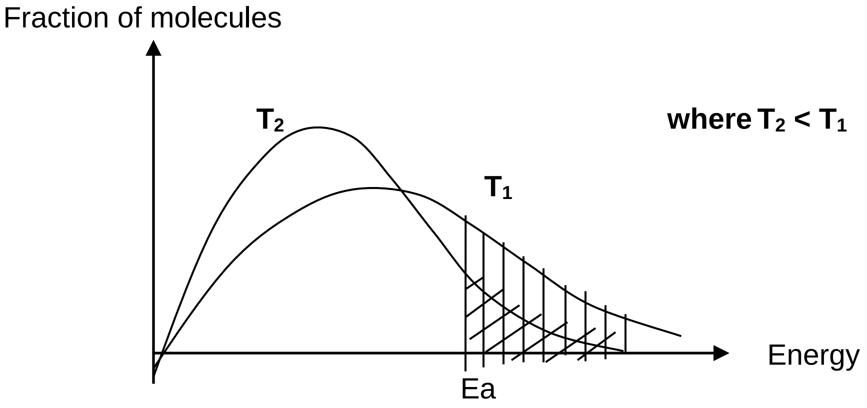
$\text{In}[J] = \text{In}[J]_o - kt$
$\text{In}[J] = -kt + \text{In}[J]_o$ [y = mx + c]

Hence, rate constant = – gradient

(d) **(i)** overall order = **2**

(ii) Ethanol is **more polar** than propanone, **stabilizes carbocation to a greater extent** through formation of **stronger ion-dipole interactions**. Hence SN1 mechanism is favoured when ethanol is used as the solvent.

(e)



Legend: ▥ fraction of molecules having energy ≥ Ea at T_1

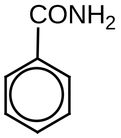
▨ fraction of molecules having energy ≥ Ea at T_2

At a lower temperature T_2, the fraction of molecules having energy greater than or equal to Ea decreases**,** from ▥ to ▨

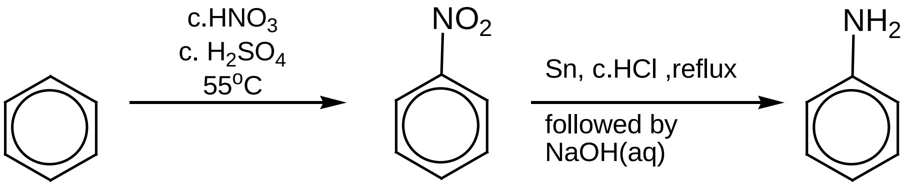
Hence, the number of effective collisions decreases and rate of reaction decreases**.**

4 **(i)** NH_3 in ethanol, in sealed tube

P:



(ii)



(iii) Add neutral aqueous iron(III) chloride to both.

An intense violet complex will be observed for phenol.
No violet complex for phenylamine.

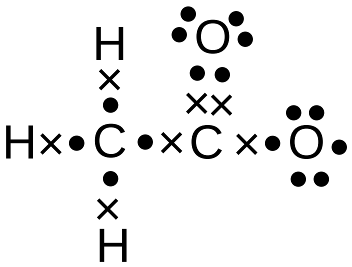
Or Add sodium metal to both.

Effervescence will be observed for phenol. Gas evolved extinguished burning splinter with a “pop” sound.
No gas evolved for phenylamine.

(b)

(i) a “radical” contains a lone/unpaired electron or odd number of electrons.

(ii)



OCO bond angle = 120°

(iii) $2\ H_2O + 2e \rightarrow H_2 + 2OH^-$

(b) (iv) (I) Mr of CH_3COOK = 98.1

Amt of CH_3COOK in 2.43g = 0.02477 mol

1 mol of CH_3COOK gives rise to 1 mol of CH_3 radical.
2 mol of CH_3 gives rise to 1 mol of CH_3CH_3 molecule.

Step 1	$CH_3COO^- \rightarrow CH_3COO + e$	…….	Anode reaction
Step 2	$CH_3COO \rightarrow CH_3 + CO_2$	…….	Decarboxylation
Step 3	$2\ CH_3 \rightarrow CH_3CH_3$	…….	Dimerization

Theoretical amt of CH_3CH_3 to be produced = $\dfrac{0.02477}{2}$ = 0.01238 mol

Theoretical volume of CH_3CH_3 to be produced :

$$pV = nRT$$
$$(101000)V = (0.01238)(8.31)(28 + 273)$$
$$V = 3.065 \times 10^{-4}\ m^3$$

Percentage yield of CH_3CH_3 = $\dfrac{200 \times 10^{-6}}{3.065 \times 10^{-3}} \times 100\%$ = 65.2%

OR

$$pV = nRT$$
$$(101000)(200 \times 10^{-6}) = n\ (8.31)(28 + 273)$$
$$n = 8.075 \times 10^{-3}$$

8.075×10^{-3} mol of CH_3CH_3 produced.

Percentage yield of CH_3CH_3 = $\frac{8.075 \times 10^{-3}}{0.01238} \times 100\% = 65.2\%$

(II) electron : CH_3COO^-

1 : 1

Amt of electrons required = 0.02477 mol

$Q = It$

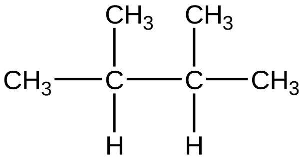
$(0.02477)(96500) = 0.5\,\mathbf{t}$

$t = 4778s$

$= 79.6min$

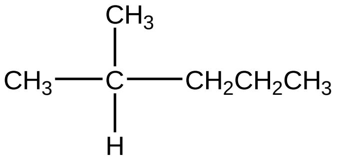
(c) (i)

P :



$CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_3$

or



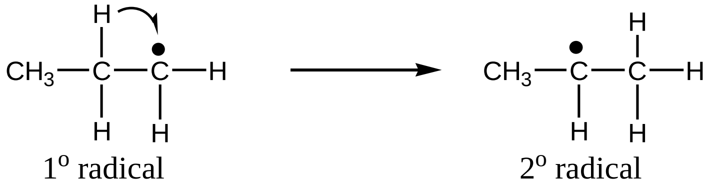
$CH_3-\overset{CH_3}{\underset{H}{C}}-CH_2CH_2CH_3$

Step 1 $CH_3CH_2CH_2COO^- \rightarrow CH_3CH_2CH_2COO\bullet + e$

Step 2 $CH_3CH_2CH_2COO\bullet \rightarrow CH_3CH_2\overset{\bullet}{C}H_2 + CO_2$

Step 3 $2\ CH_3CH_2\overset{\bullet}{C}H_2 \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3$

In step 2, once the primary radical is formed. It immediately forms a **more stable secondary radical** by **rearrangement of radical/ h**ydride shift.



Collision of 2 secondary radicals give rise to **P**.

(ii)

Hexane has a higher boiling point than **P** as hexane is straight-chain with a higher surface area of contact between its molecules compared to **P** which is branched.

More energy is required to overcome the stronger temporary dipole induced dipole between hexane molecules.

(d)

	Radical	Product
Potassium ethanoate CH_3COOK	**•CH_3**	CH_3CH_3
Potassium methanoate HCOOK	•H	H_2
Mixture of CH_3COOK + HCOOK	•H , **•CH_3**	CH_3CH_3 [½] CH_4 [½]

Potassium methanoate :

Step 1 $HCOO^- \rightarrow HCOO\bullet + e$

Step 2 $HCOO\bullet \rightarrow H\bullet + CO_2$

Step 3 $H\bullet \rightarrow H_2$

5 **(a)** **(i)** SnO_2
PbO

(ii) $PbO(s) + 2NaOH(aq) + H_2O(l) \rightarrow Na_2Pb(OH)_4(aq)$

(b)

(i) Amount of $PbSO_4$ dissolved in 100 cm^3= $\dfrac{0.00425}{207 + 32.1 + 4(16.0)}$

$= 1.402 \times 10^{-5}$ mol

Solubility = 1.402×10^{-5} mol x $\dfrac{1000}{100}$ = 1.402×10^{-4} mol dm^{-3}

(ii) $K_{sp} = [Pb^{2+}][SO_4^{2-}] = (1.402 \times 10^{-4})^2$

$= 1.97 \times 10^{-8}$ $mol^2 dm^{-6}$

(iii) $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

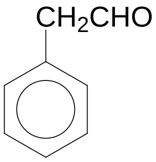
The solubility will be lower due to common ion effect. By LCP, equilibrium above shifts to LHS due to a higher concentration of SO_4^{2-} ion.

(c) **(i)** CO_2 has a simple covalent structure whereas SiO_2 has a giant covalent structure. A greater amount of energy is required to break the strong covalent bonds between Si and O atoms as compared to the weak van der Waals forces between CO_2 molecules.

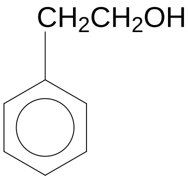
(ii) SiO_2 has a giant covalent structure and PbO has a giant ionic structure. Both covalent and ionic bonds are strong. The covalent bonds between Si and O atom is stronger than the ionic bonds between the Pb^{2+} and O^{2-} ions in this case. Hence a greater amount of energy is required to break the covalent bonds in SiO_2.

(d) **(i)** Step **I**: excess conc.H_2SO_4, 170°C
Step **II**: conc.H_2SO_4, conc.HNO_3, 55°C

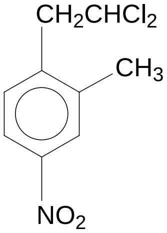
S:



T:

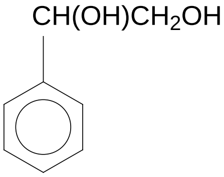


(ii) U:



The $–CH_2CHCl_2$ group is 2,4-directing whereas the $–NO_2$ group is 3-directing. Hence the next substitution will occur on position 2 relative to the $–CH_2CHCl_2$ group or the 3rd position relative to the $–NO_2$ group. Both are essentially the same position.

(iii) Mild oxidation occurs. $KMnO_4$ decolourised with the formation of brown MnO_2 ppt.



(iv)