MARKING SCHEME

CHEMISTRY 02

QUESTION NO:01

(a) In order to measure reactions which can take place slowly and some which take place quickly. Since this type of insight about measurement of reaction rate is potential in making new drugs and ways of making other important chemicals more efficiently. By understang the fast and slow reaction either spontaneous or non-spontaneous enables to monitor or control such reactions by focusing on the factor(s) which affects the rate of reactions.

(03marks)

(b) Solution;

As the;

$$\text{rate} \propto k, \quad \frac{\text{rate}_1}{\text{rate}_2} = \frac{k_1}{k_2} = \frac{1}{3} \Big\} \text{(01mark)}$$

$$\text{At } 250K, \quad \log k_1 = \log A - \frac{Ea}{2.303R} \times \frac{1}{250K} \quad \text{and}$$

$$\text{At } 300K, \quad \log k_2 = \log A - \frac{Ea}{2.303R} \times \frac{1}{300K} \Big\} \text{(01mark)}$$

On rearrangement;

$$\log k_2 - \log k_1 = \frac{Ea}{2.303R} \times \left(\frac{1}{250} - \frac{1}{300}\right) \times \frac{1}{k}$$

$$\frac{1}{250} - \frac{1}{300} = \frac{300 - 250}{250 \times 300} = \frac{50}{250 \times 300} \Big\} \text{(01mark)}$$

Question no: 01

1 (b) and $\log k_2 - k_1 = \log \frac{k_2}{k_1}$

$$\therefore E_a = 2.303R \frac{250 \times 300}{50} K \times \frac{\log k_2}{\log k_1}$$ (01 mark)

$$E_a = \frac{2.303 \times 8.3 \text{ kJ mol}^{-1} K^{-1} \times 300 \times 250 \text{ K}}{50} \log 3$$

$$\underline{E_a = 13679 \text{ J.mol} = 13.679 \text{ kJ mol}^{-1}}$$ (02 marks)

(c)(i) In the experiment 2 and 3 the ozone concentration doubles or tripler as compared to experiment 1, while the NO concentration is kept constant. Since the reaction rate also doubles or triples in the respective experiments the rate is proportional to the concentr-ation of ozone:

$$\frac{-d[O_3]}{dt} \propto [O_3] \quad \text{------ (1)}$$

(01 mark)

- In the experiment 4 and 5, the concentration of NO doubles or tripler as compared to exp 3, while the concentration of ozone is kept constant. Again, the rate doubles or tripler respectively. Hence, the rate is also proportional to the concentration of NO.

$$-d[O_3]/dt \propto [NO] \quad \text{------ (2)}$$

- Hence, combining 1 and 2 we obtain the rate law:

(01 mark)

Question no: 01

(c)(i) $$\frac{d[O_3]}{dt} = k[NO][O_3] \quad \text{......} \ ③$$

- Thus, the reaction is of first order in respect of NO as well as O_3 and it is of second overall order.

(01 marks)

(ii) Using the rate law, we obtain for experiment 1:

$$k = \frac{-d[O_3]}{dt} \Big/ [NO][O_3]$$

(01 mark)

$$= \frac{+1.6\times10^{-5}\,mol\,dm^{-3}s^{-1}}{2.1\times10^{-6}\times2.1\times10^{-6}\,mol^{2}dm^{-6}}$$

$$k = 3.6\times10^{6}\,mol^{-1}\,dm^{3}\,s^{-1}$$

(01 Mark)

(iii) $$-\frac{d[O_3]}{dt} = k[NO][O_3]$$

(01 mark)

$$= 3.6\times10^{6}\,mol^{-1}dm^{3}s^{-1}\times 9.0\times10^{-6}\,mol\,dm^{-3}\times10^{-6}\,mol\,dm^{-3}$$

$$\therefore \frac{-d[O_3]}{dt} = 32.4\times10^{-6}\,mol\,dm^{-3}s^{-1}$$

$$\simeq 32\times10^{-6}\,dm^{-3}\,mol\,s^{-1}$$

(01 mark)

Question NO: 01

(d) (i) In acidic conditions

$E^\ominus_{cell} = E^\ominus_{MnO_4^-/Mn^{2+}} - E^\ominus_{I_2/I^-} = +1.51V - 0.54V = +0.97V$

(01 mark)

The reaction is

$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$

(01 marks)

(ii) In alkaline conditions

$E^\ominus_{cell} = E^\ominus_{MnO_4^-/MnO_2} - E^\ominus_{I_2/I^-} = +1.59V - 0.54V = +1.04V$

(01 mark)

The reaction is

$2MnO_4^-(aq) + 6I^-(aq) + 8H^+(aq) \rightarrow 2MnO_2(aq) + 3I_2(s) + 4H_2O(l)$

(01 mark)

Question no: 02

(a) Distribution law is applied in both laboratories and industries for removing (reducing) some dissolved impurities in a given solvents. The extend at which impurity can be removed depend on solubility of that impurity in a given pure of immiscible liquids. The Kd value will also depend on the number of extraction.

(01mark)

(b) Solution;

Mass of Iodine, 5g (original mass) $= M_o$

Volume contained solute (water) $= 400 cm^3 = V_1$

Volume of extractant $= 200 cm^3 = V_2$

From;

$$M_r = M_o \left(\frac{V_1}{K_D V_2 + V_1} \right)^n$$

- Using 200 cm³ of ether at once;

$$M_r = 5g \left(\frac{400 cm^3}{0.8 \times 200 + 400} \right)^1 = 3.57g$$

(02marks)

- Using 100 cm³ of ether;

$$M_r = 5g \left(\frac{400 cm^3}{0.8 \times 100 cm^3 + 400} \right)^2 = 3.47g$$

(02marks)

- Using 50cm³, fourth;

$$M_r = 5g \left(\frac{400 cm^3}{0.8 \times 50 cm^3 + 400 cm^3} \right)^4 = 3.42g$$

(02marks)

- The result above shows that extracting several time in small portions increases the amount of the organic substance extracted therefore the third alternative Mariam has to adopt though the difference is small btn the three results.

(02marks)

Question NO: 02

(c) ~~Solution~~

Positive deviation - the intermolecular forces of attraction between particles in the solution are less than those in the pure components. Therefore due to this the solution has higher tendency of forming the the vapour than and of individual components. Therefore vapour pressure above the solution is higher than expected from Raoult's law. And the viceversa is true for negative deviation. (02marks)

- Examples of the liquids which shews positive deviation are solution of acetone and ethanol, acetone and carbon disulphide (CS_2) water(H_2O) and methanol etc.

- Examples of the liquids which shows negative deviation include; acetone and chloroform, nitric acid (HNO_3) and water (H_2O) etc. (02 marks)

solution;

(d) Vapour pressure of nitrobenzene, $P_n = 760\,mmHg - 733\,mmHg$
$= 27\,mmHg$

Molecular mass of nitrobenzene, $M_n = 123\,g\,mol^{-1}$
Vapour pressure of water, $P_w = 733\,mmHg$
Mass of nitrobenzene = unknown
Mass of water = unknown (02marks)

From;

$$\frac{M_{organic\ liquid}}{M_{water}} = \frac{P_{organic\ liquid} \times M_{organic\ liquid}}{P_{water} \times 18\,g\,mol^{-1}}$$ (02marks)

$$= \frac{27\,mmHg \times 123\,g\,mol^{-1}}{18\,g\,mol^{-1} \times 733\,mmHg} = 0.25$$ (02marks)

Therefore, the proportion of water and nitrobenzene in distillate is 4:1 (01mark)

Question NO: 03

(a)(i) It is possible that he was correct because we might expect a weak acid to give a pH in this region. However, it is possible that the bottle contained a very dilute solution of a strong acid like sulphuric acid. The pH alone does not tell us whether a solution contains a strong or weak acid, pH depends on concentration.

(04marks)

(ii) Solution;

1 mole of sodium ethanoate, $CH_3COONa = 82g$

$3.28g$ sodium ethanoate $= \frac{3.28}{82} = 0.04$ mole

$[H^+] = Ka \times \frac{[acid]}{[salt]}$

$= 1.84 \times 10^{-5} \times \frac{0.01}{0.04}$

$= 4.6 \times 10^{-6} moldm^{-3}$

(02marks)

$pH = -\log [H^+]$

$= -\log (4.6 \times 10^{-6})$

$= -(6.6628) = +6 - 0.6628$

$= 5.34$

$\therefore pH = 5.34 \approx 5.3$

(02marks)

(b) (i) The ether has two lone pairs on the oxygen, like water.

(01mark)

Question NO: 03

(b) (ii) The reaction makes a product very much like that between ammonia and boron trifluoride. The ether donates of its lone pairs to the empty p-orbital on the boron atom. Thus the ether is a Lewis base and the boron trifluoride a Lewis acid. You might also notice that boron trifluoride cannot be regarded as a Brønsted acid (it has no protons to donate). However, as we know, it can be a Lewis acid (electron pair acceptor) Lewis theory is more powerful than Brønsted theory b'se Lewis theory encompasses a greater variety of possibilities.

(03marks)

(C) The values of the solubility products show that $BaSO_4$ is less soluble than $BaCO_3$. (The smaller the solubility product, the less ~~the~~ soluble is the solid.) Therefore in;

(i) there will be no change; but in (ii) over a period of time the free barium ions in the solution will be converted into solid barium carbonate, ie the overall change will be;

$$BaSO_4(s) + CO_3^{2-}(aq) \rightarrow BaCO_3(s) + SO_4^{2-}(aq)$$

04 marks ⓐ

Question NO: 04

(a) (i) The outer electrons are increasingly well shielded from the nucleus by the inner shells of electrons.

(ii) Because they are intencely poisonous. One way in which they poison is by blocking the ~~reaction~~ reactivity of enzymes and other biologically aitive systems, e.g by taking the place of magnesium ion.

(iii) It is due to surface oxidation.

(IV) It is due to the presence of highly mobile electrons of the metallic lattice.

(V) The high MP of Boron is due to the fact that it exicts as giant covalent polymer in both solid and liquid state.

(02marks ⓐ)

(b)(i) Paramagnetism; All simple ions of TE other than d0 (Sc^{3+}, Ti^{++}) or d10 Zn^{2+}, Cu^{2+}) contains unpaired electrons in the d-sub-shells. For this reasons are paramagnetic (Paramagnetic substances are the ones which are attracted in magnetic field).

(ii) Colour formation; Ionic and covalent compounds of TE are coloured compared to s and p block elements which are usually white. The colour is associated with the ability to promote electrons from one energy level to another.

-The d-orbitals are not all identical in energy so that for TE that have partially filled d-sub shell. It is possible to promote electrons from one d-level to another d-level. This correspond to a very small energy difference.

(iii) Melting and Boiling points;
- Transition elements (TE) are extremely small in size, hard, high MP and BP with exception of Zn, Cd and Hg because d-orbitals are completely filled.

(iv) Nature of Bonds and Complex Formation
- TE are ionic in lower oxidation state and covalent in higher oxidation state. Unstable oxidation state are often stabilized by complex formation with suitable groups or molecules (ligands). The complex formation is favoured by presence of vacant d-orbitals which can accept one electron or more electron pair from ligands, high charge density due to small size and availability of several oxidation states.

(v) Low atomic volume and high density.
- Comparing to neighbouring groups, atomic volume of TE are low because as the inner orbital are filled, the increased nuclear charge pulls the electrons in causing volume decrease and hence increase of density.

(01mark @)

Question 4

ⓒ Hall's method is used for purifying bauxite ore which contains iron oxide as the majority impurity. In this process, the bauxite ore is fused with sodium carbonate to form sodium metal-aluminate.

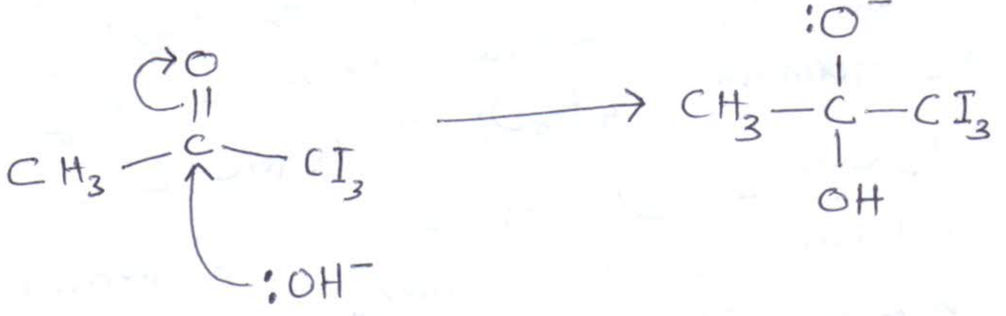
$$Al_2O_3 \cdot 2H_2O_{(s)} + Na_2CO_{3(s)} \xrightarrow{heat} 2NaAlO_{2(s)} + 2H_2O_{(g)} + CO_{2(g)}$$

As for the Bayer's process, the soluble sodium metal-aluminate is extracted with water and iron oxide (impurity) remains behind the residue. The water extract of sodium metal-aluminate is heated to about 50°C in the presence of carbon dioxide and the precipitated aluminium hydroxide is filtered, dried, and ignited to get pure alumina.

Question no. 03

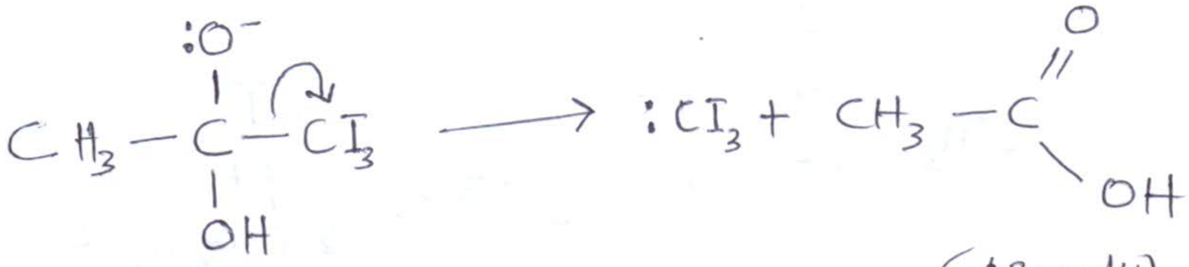
a) The mechanism for the formation of triiodomethane from propanone in the triiodomethane test is as follows;

- Base carries out nucleophilic attack on the carbonyl carbon atom.



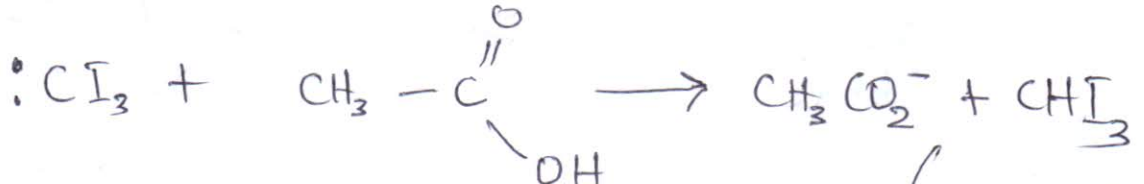
(02 marks)

- The $C-CI_3$ bond breaks to form ethanoic acid and the CI_3^- ion, the three electronegative iodine atoms helping to stabilize the negative charge.



(02 marks)

- Ethanoic acid transfers a proton to the CI_3^- ion to form triiodomethane and the ethanoate ion.



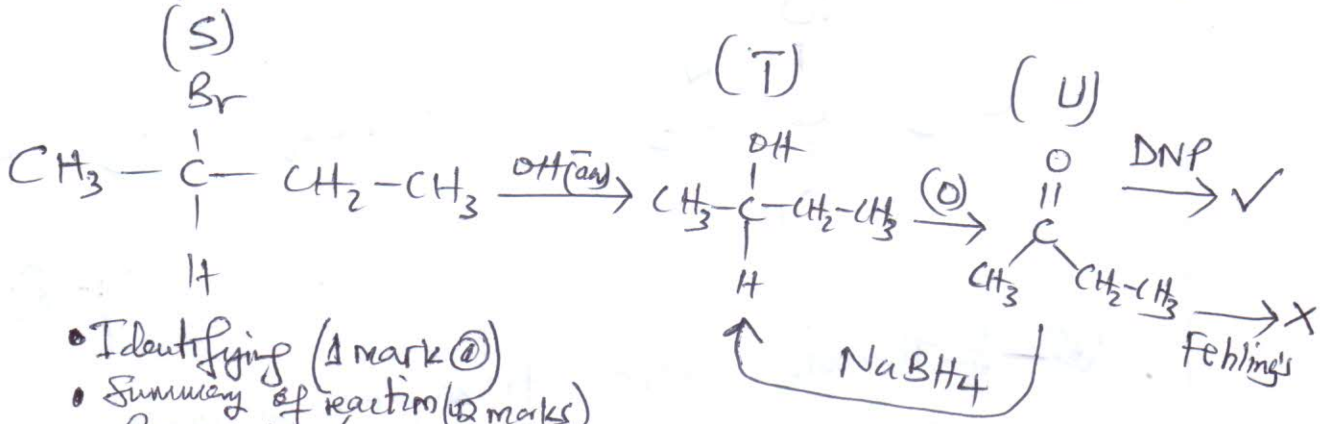
(02 marks)

Question NO: 05

(b) - It is often better to start with the last substance in the sequence, rather than initially concentrating on the first step.

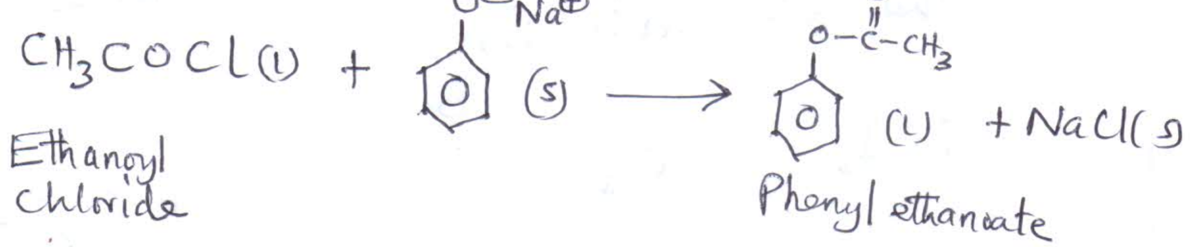
- Because it reacted to form a DNP derivatives, U is a carbonyl compound. A carbonyl compound that does not react with Fehling's solution must be a ketone. There is only one ketone of formula C_4H_8O: therefore U is butanone $CH_3COCH_2CH_3$. A ketone is formed by oxidation of a secondary alcohol.

- Therefore T is butan-2-ol $CH_3CH(OH)CH_2CH_3$. S must be the secondary halogenalkane, $CH_3CHBrCH_2CH_3$. A suitable reagent to convert butanone (U) to butan-2-ol (T) is $NaBH_4$.



- Identifying (1 mark ⓐ)
- Summary of reaction (2 marks)
- Reagent (1 mark)

(c) (i)



Ethanoyl chloride

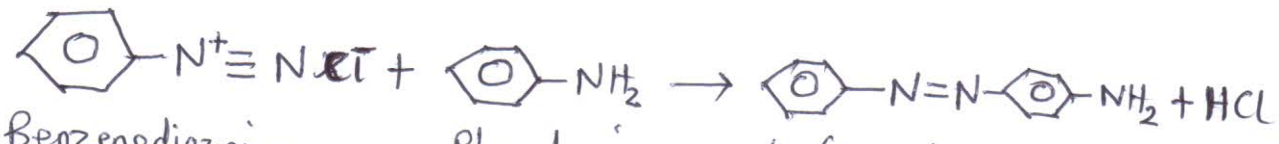
Phenyl ethanoate

(ii) $CH_3COCl\,(l) + C_2H_5OH(l) \xrightarrow{\text{Pyridine}} CH_3CO_2C_2H_5(l) + HCl$

Ethanoyl chloride — Ethanol — Ethyl ethanoate

Question NO:5

(c) (iii)



Benzenediazonium chloride

Phenylamine

4-(Phenylazo)phenylamine

(iv) $C_6H_5COCl + H_2O \longrightarrow C_6H_5COOH + HCl$

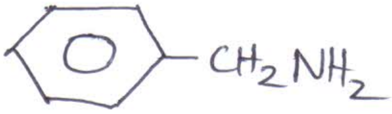
Benzoyl Chloride

Benzoic acid

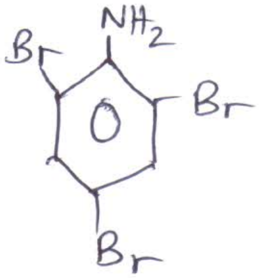
(01 mark ⓐ)

(d)

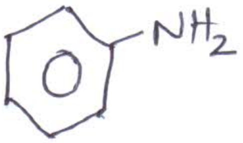
(i)



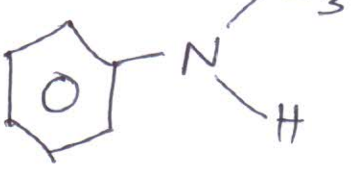
(ii)



(iii)



(iv)



(01 mark ⓐ)

Question No: 06

6 (a) A solution of phenol is acidic, Loss of a proton is possible in phenol because The negative charge in the phenoxide ion is delocalized around The benzene ring;

$$C_6H_5OH + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$$

- Also; $C_6H_5OH + NaOH \rightarrow Na^+C_6H_5O^- + H_2O$

— Also, alcohols do not show This behaviour in solution or with aqueous bases because the negative charge remains localized on the oxygen atom.

(05marks)

(b)(i) The lower alcohols – methanol, ethanol and propanol – are mainly used as solvents. Ethanol is the major component in methylated spirits.

(ii) Large quantities of methanol produced by Catalytic oxidation of methane are oxidized to methanal HCHO, which is used as a chemical feedstock to make so-called "formaldehyde" resins such as melamine.

(iii) Methanol is used as petrol additive to improve combustion. It was also the fuel in the motor racing IndyCar series in the US until the introduction of fuel-grade ethanol in 2007.

(iv) Ethanol has a wide range of applications, including the extraction of essences from fruits and spices, as a dispersant for dyes in lacquers, and as a solvent for fragrances in perfumes and after-shave lotions.

Question NO: 06

(V) Ethanol is the active constituent of alcoholic drinks. In humans it suppresses inhibitions and thereby brings more enjoyment, and misery, to the world than all other drugs put together.

(Vi) Propan-2-ol is the solvent in ink-jet printer ink, many cosmetics and certain food flavouring. It is also present in a wide range of cleaning fluids for items such as compact discs and the record/playback head in tape machines.
(Five(5) points @ 1 mark)

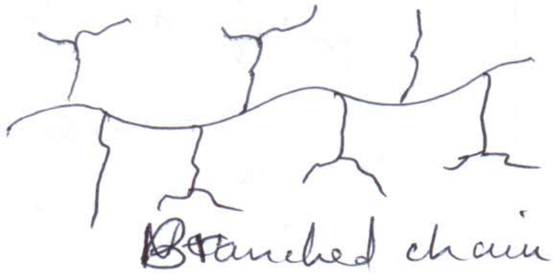
(c) (i) Linear polymers: are well packed and thus have high densities, high tensile strength and high melting points. High-density polythene is an example.

(ii) Branched chain polymers
- are irregularly packed and thus have lower tensile strength and melting points than linear polymers. Low-density polythene is an example.

(iii) Network polymers are hard, rigid and brittle. Bakelite is an example.

crosslinked polymer

~~Branched chain polymers~~



Branched chain

Question No: 6

(iv) Copolymer are made from two or more monomers. The polymer are made of two different monomers, The polyester, Terylene and polyamide nylon - 6, 6 described earlier are examples of copolymers as are many other condensation polymers.

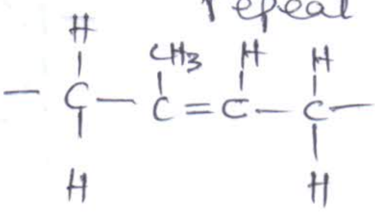
(V) Elastomers – An elastomer is a material that can rapidly recover its original shape after being deformed. The most important example is Vulcanized rubber.

(01 mark ⓐ)

(d) (i) Polymer

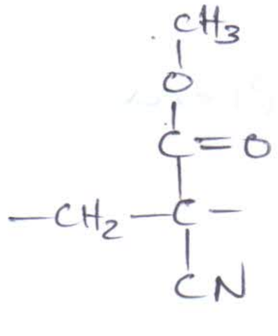
repeat unit

Natural rubber



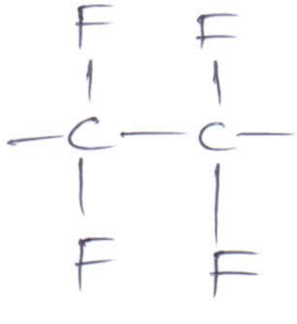
$$-\overset{H}{\underset{H}{C}}-\overset{CH_3}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-$$

(ii) Perspex



$$-CH_2-\overset{\overset{\overset{CH_3}{|}}{O}}{\underset{CN}{C}}-$$

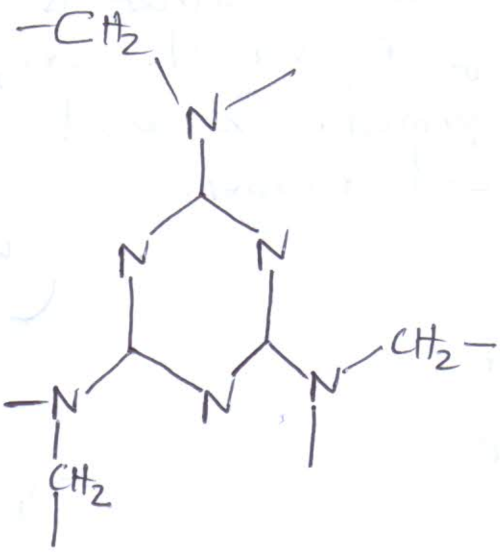
(iii) Teflon



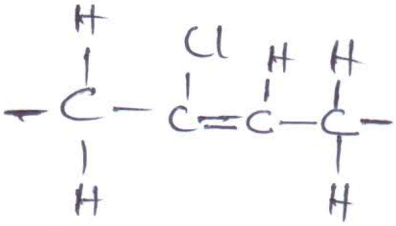
$$-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$$

Question NO: 6

(d) (iv)
Poly (melamine–formaldehyde)



(v) Neoprene



$$-\overset{H}{\underset{H}{C}}-\overset{Cl}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-$$

(01 mark @)