9746 2007 H2 Paper 3
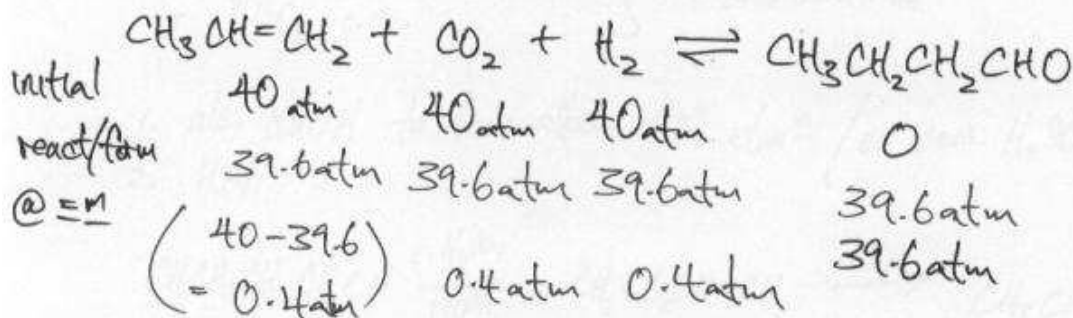
(ca) $K_p = \dfrac{P_{CH_3CH_2CH_2CHO}}{(P_{CH_3CH=CH_2})(P_{CO_2})(P_{H_2})}$ atm$^{-2}$ #

(b)(i) $PV = nRT$

as volume & Temp is unchanged, $P \propto n$

$$CH_3CH=CH_2 + CO_2 + H_2 \rightleftharpoons CH_3CH_2CH_2CHO$$

| | $CH_3CH=CH_2$ | $CO_2$ | $H_2$ | $CH_3CH_2CH_2CHO$ |
|---|---|---|---|---|
| initial | 40 atm | 40 atm | 40 atm | 0 |
| react/form | 39.6 atm | 39.6 atm | 39.6 atm | 39.6 atm |
| @ $\equiv^m$ | $\left(\begin{array}{c}40-39.6\\=0.4\text{ atm}\end{array}\right)$ | 0.4 atm | 0.4 atm | 39.6 atm |

Partial Pressure $C_3H_6$, CO & $H_2$ = 0.4 atm each #

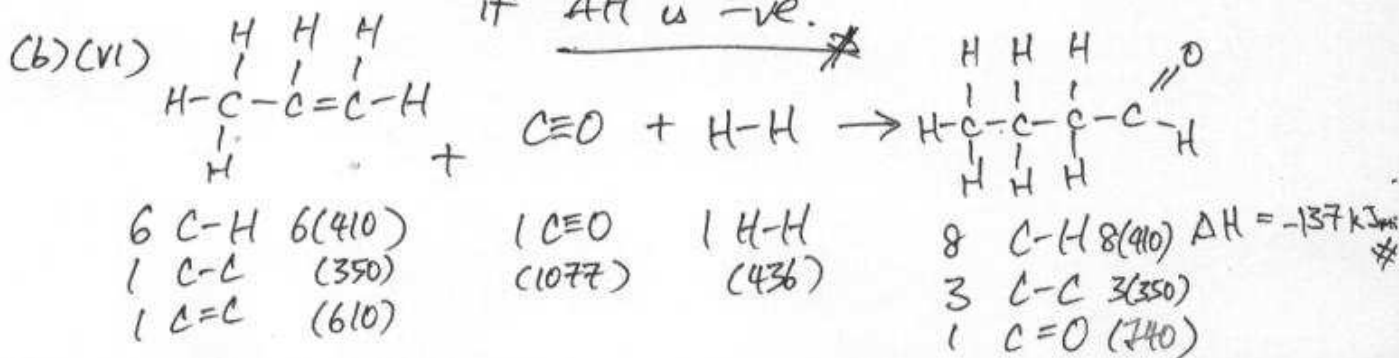(b)(ii) $K_p = \dfrac{39.6}{(0.4)^3} = 618.8$ atm$^{-2}$ #

(b)(iii) By Le Chatelier's Principle, for sym in $\equiv^m$, when P is ↑ the $\equiv^m$ would shift to side that contains fewer moles of gas particles to remove the excess P. Hence forward react$^n$ which produces fewer moles of gas (butanal) is favoured @ high P. #

(b)(iv) $\Delta S$ is negative as there is a ↓ in disorder with fewer moles of gas (& hence fewer ways of arranging particles) formed as compared to reactants.

(b)(v) $\Delta G = \Delta H - T\Delta S$

As $\Delta S$ is -ve ⟹ $-T\Delta S$ is +ve
⟹ $\Delta G$ can only be -ve if $\Delta H$ is -ve. #

(b)(vi)



H–C–C=C–H (with H's) + C≡O + H–H → H–C–C–C–C(=O)–H

| | |
|---|---|
| 6 C–H 6(410) | 8 C–H 8(410)  $\Delta H = -137$ kJ mol$^{-1}$ # |
| 1 C–C (350) | 3 C–C 3(350) |
| 1 C=C (610) | 1 C=O (740) |
| 1 C≡O (1077) | |
| 1 H–H (436) | |

(ci) Rex$^n$ II : acidified KMnO$_4$ reflux

Rex$^n$ III : LiAlH$_4$ in dry ether r.t.

(cc) cii) c. H$_2$SO$_4$ + NaBr heat  } 1-bromobutane
or PBr$_3$ r.t.

1. alc. NaOH to form alkene thr$^u$ elm$^n$ / or conc. H$_2$SO$_4$ 170°C  } 2-bromobutane
2. HBr

$$CH_3CH_2CH_2CH_2OH \xrightarrow[170°C]{c.H_2SO_4} CH_3CH_2CH=CH_2 \xrightarrow{HBr} CH_3CH\overset{H}{\underset{Br}{C}}-CH_3$$
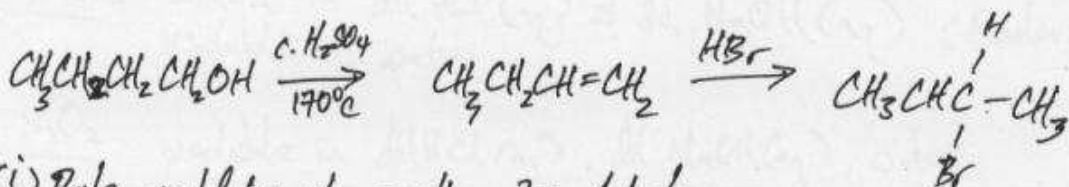
(d) ci) Rate would be slower than 2-iodobutane

∴ C-Br bond is shorter, stronger, higher BE c.f C-I.

(d) cii) $\xrightarrow[NaCN]{alc}$ $CH_3CH_2\overset{H}{\underset{CN}{C}}-CH_3$ $\xrightarrow{LiAlH_4}$ $CH_3CH_2\overset{}{\underset{CH_2NH_2}{CH}}-CH_3$

$\xrightarrow[NaOH]{ethanol}$ $CH_3CH=CHCH_3$ $\xrightarrow[KMnO_4]{cold}$ $CH_3\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-CH_3$

(e)
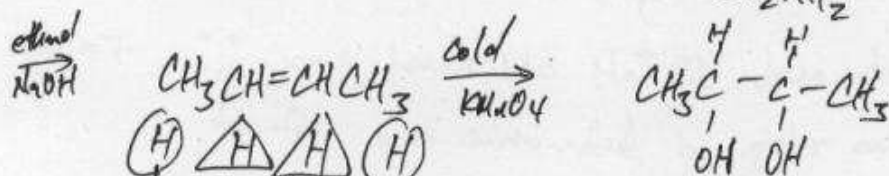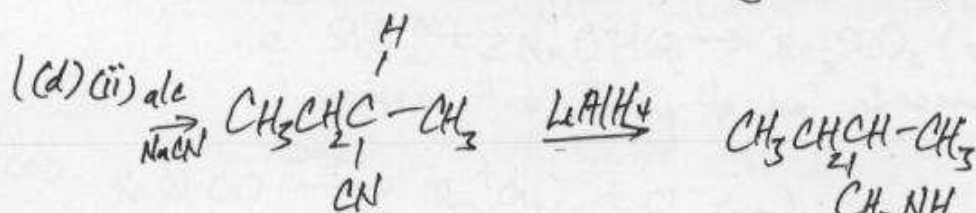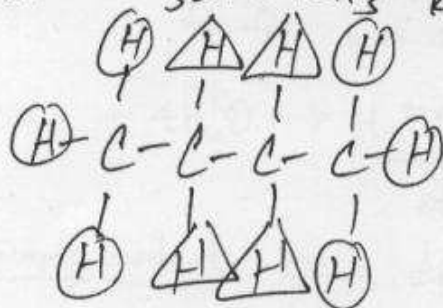
1-bromo 2-bromo
6 : 4
= 3 : 2

$\rightarrow$ Refer Pg5 Chem. Periodicity Notes.

Note: Mg & Al    anomalous trend.

P & S

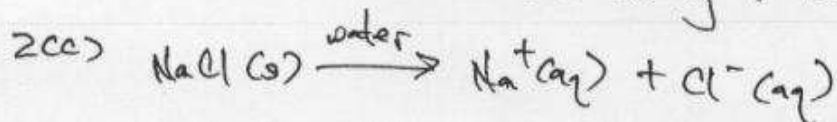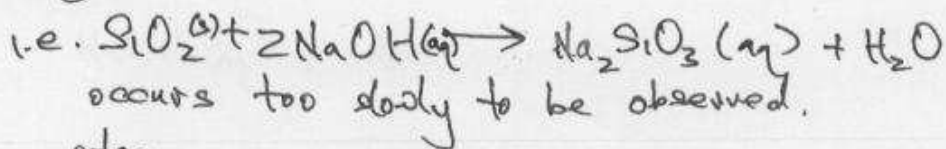* Include Ar

26)

$\underline{MgO}$ soluble in dil HCl (aq) (dissolves)
insoluble in water & alkali.

$\underline{Al_2O_3}$ soluble in dil HCl (aq) & dil NaOH (aq) (dissolves)
insoluble in water

$\underline{SiO_2}$  insoluble in dil HCl (aq), dil NaOH (aq), water.

* Rex^n btw $SiO_2$ & NaOH takes place too slowly to observe any changes.

i.e. $SiO_2 (s) + 2NaOH (aq) \rightarrow Na_2SiO_3 (aq) + H_2O$
occurs too slowly to be observed.

2(c)) $NaCl (s) \xrightarrow{water} Na^+ (aq) + Cl^- (aq)$

pH = 7  $\because$ ionic bonds btw $Na^+ Cl^-$ dissociate in water
to form ions surrounded by polar water molecules.

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

$\underbrace{\phantom{xxxxxx}}$
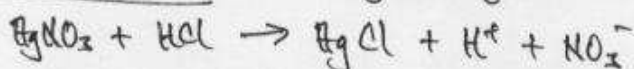strong acids $\rightarrow$ pH = 1
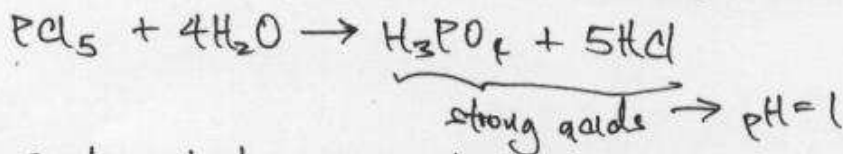
$\underline{Simple\ covalent}$ $PCl_5$ dissolves vigorously in water to give acidic
solutions with evolution HCl (g).

2(d)(i) Use of fume cupboard when carrying out expt as $SO_2$ is poisonous
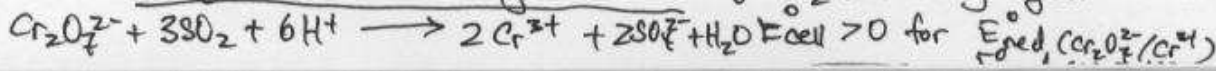& HCl is acidic.
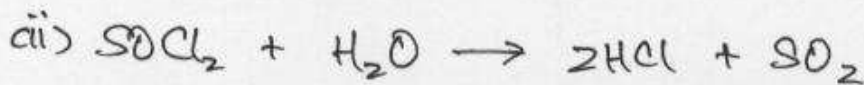
(ii) $SOCl_2 + H_2O \rightarrow 2HCl + SO_2$
use eq^n given: $ROH + SOCl_2 \rightarrow RCl + HCl + SO_2$ to deduce eq^n w̄ $H_2O$.

(iii) white ppt $\underline{AgCl}$ when $AgNO_3 (aq)$ added
$AgNO_3 + HCl \rightarrow AgCl + H^+ + NO_3^-$

Orange $K_2Cr_2O_7$ turn green $Cr^{3+}$ $\because$ $SO_2$ is reducing agent.

$Cr_2O_7^{2-} + 3SO_2 + 6H^+ \rightarrow 2Cr^{3+} + 2SO_4^{2-} + H_2O$ E°cell > 0 for E°_red, $(Cr_2O_7^{2-}/Cr^{3+})$

e)ci)



A $C_8H_6O_4$ $\xrightarrow{SOCl_2}$ B $C_8H_4O_2Cl_2$ $\xrightarrow{NH_3}$ C + 2HCl
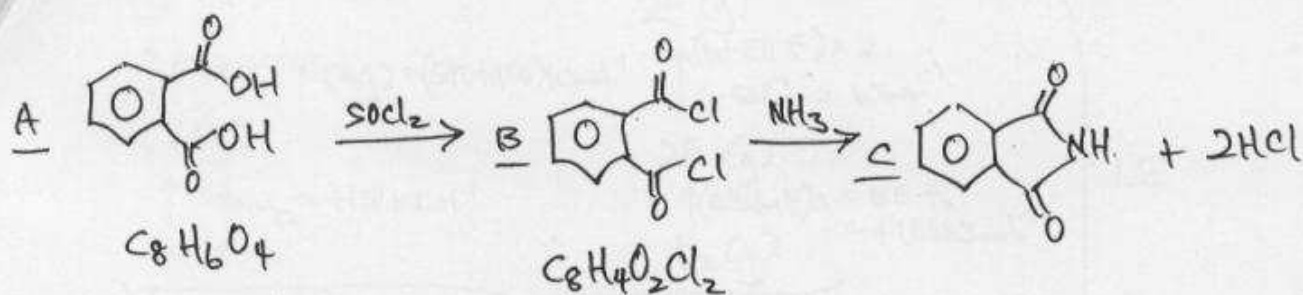
cii) Rex$^n$ I : Neutralisation / acid-base rex$^n$.

Rex$^n$ II : Nucleophilic substitution.

Rex$^n$ III : Hydrolysis (Amide)

ciii) Dilute $H_2SO_4$ (aq), reflux   or

$NaOH$ (aq), reflux.

a) ci)

$Ca^{2+}(g)$         $2F^-(g)$

$\uparrow$ 1st & 2nd IE $(Ca(g)) = (590+1150)\,kJmol^{-1}$    $\uparrow$ (1st EA E) $\times 2$
                                               $(-328) \times 2\ kJmol^{-1}$

$Ca(g)$                      $2F(g)$           LE

$\uparrow \Delta H_{atom}\ Ca = +178\ kJmol^{-1}$    $\uparrow (\Delta H_{atom}\ E)2 = BE\ F_2$
                                        $= +158\,kJmol^{-1}$

$Ca(s)$                    $F_2(g)$

$\downarrow \Delta H_f\ CaF_2(s) = -1220\,kJmol^{-1} \downarrow$

                                                   $CaF_2(s)$
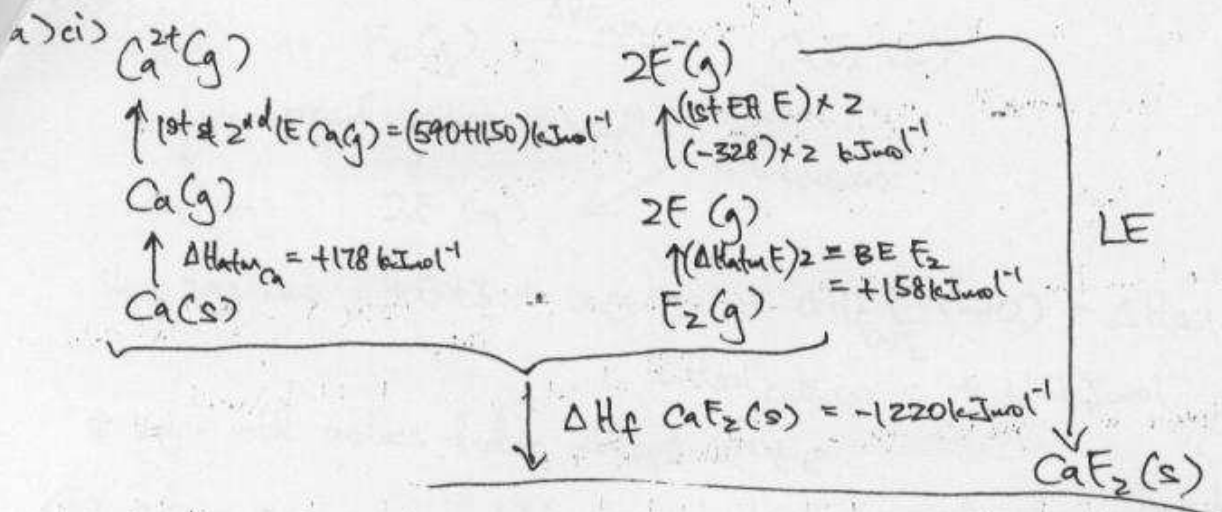
By Hess' Law   $+178 + 590 + 1150 + 158 + 2(-328) + LE = -1220$

                                  $LE = -2640\ kJmol^{-1}$ #

cii) $\left| LE \right| \alpha \left| \dfrac{q_1 q_2}{r_1 + r_2} \right|$    $q_1$ = charge cation   $q_2$ = charge anion
                                  $r_1$ = cation radius   $r_2$ = anion radius

$\rightarrow$ ionic radii of $F^- <$ ionic radii of $Cl^-$
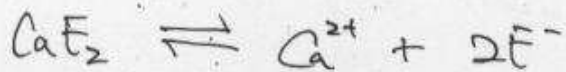
    $\therefore$ magnitude of LE $CaF_2 > CaCl_2$

$\rightarrow$ charge on oxygen anion $\equiv -2$, charge on fluorine anion $\equiv -1$

despite $O^{2-}$ ionic radius $> F^-$ ionic radius, charge of
oxygen anion is double that of fluorine anion.

    $\therefore$ magnitude of LE $CaF_2 \lesssim CaO$

3(b) ci)   $K_{sp} = [Ca^{2+}][F^-]^2\ mol^3\,dm^{-9}$ #

         $CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

At saturation, $[CaF_2]_{original} \equiv [Ca^{2+}]_{formed}$     $\Big\}$ 1 mole $CaF_2$
      similarly          $[F^-]_{formed} \equiv 2[CaF_2]_{original}$     forms 1 mole $Ca^{2+}$ &
                                                    2 moles $F^-$
                                                    & volume constant

        $\therefore K_{sp} = (2.3 \times 10^{-4})(2 \times 2.3 \times 10^{-4})^2$

              $= 4.87 \times 10^{-11}\ mol^3\,dm^{-9}$ #

) cii)

$$Ca(s) + F_2(g) \xrightarrow{\Delta H f_{CaF_2(s)}} CaF_2(s)$$

$\Delta Hf = -543 \text{kJmol}^{-1}$    $2 \times \Delta Hf = 2(-333) \text{kJmol}^{-1}$    $\Delta H_{sol} CaF_2(s)$

$$Ca^{2+}(aq) \qquad 2F^-(aq)$$
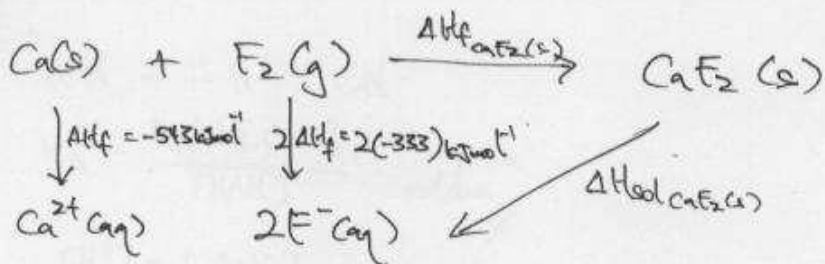
Using Hess's Law, $+543 + 2(+333) + \Delta H f_{CaF_2}(-1220) = \Delta H_{sol} CaF_2(s)$

$\Delta H_{sol} CaF_2(s) = +11 \text{ kJmol}^{-1}$ #

* longer mtd involves finding $\Delta H_{hyd}$ $Ca^{2+}$ & $F^-$

ciii) $CaF_2$ will be more soluble in hotwater as according to Le Chatelier's Principle, Higher T favours the (forward) endothermic rex$^n$ which results in more $CaF_2(s)$ dissolving into sol$^n$.
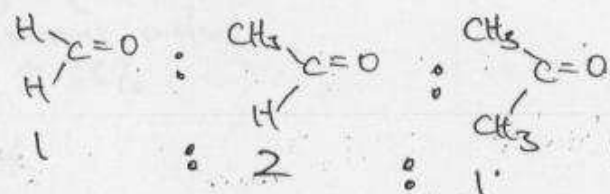
$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \quad \Delta H^{\oplus} > 0.$$
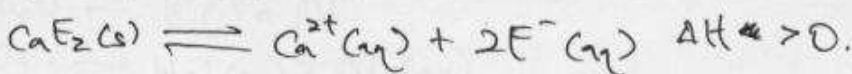
3(c) ci) Be$(NO_3)_2$ with its low m.pt. is a simple molecular covalent compound with weak intermolecular forces b/w Be$(NO_3)_2$ molecules.

Ca$(NO_3)_2$ with its relatively higher m.pt. is a giant ionic compound with strong ionic bonds b/w $Ca^{2+}$ & $NO_3^-$ ions.

cii) $MgNO_3)_2(s) \longrightarrow MgO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$ #
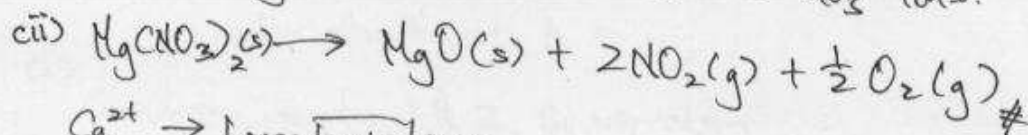
$Ca^{2+} \rightarrow$ larger [ionic] size
$\rightarrow$ lower charge density / weaker polarising power
$\rightarrow$ $NO_3^-$ anion polarised less
$\rightarrow$ lesser degree covalency
$\rightarrow$ stronger ionic bond, higher m.pt. #

3(d) Three Carbonyl cpds:

$$H \underset{H}{\overset{}{\rangle}} C = O \quad ; \quad CH_3 \underset{H}{\overset{}{\rangle}} C = O \quad ; \quad CH_3 \underset{CH_3}{\overset{}{\rangle}} C = O$$

| | ratio | 1 : | 2 : | 1 |
|---|---|---|---|---|

| Test | obsv$^n$ | obsv$^n$ | obsv$^n$ # |
|---|---|---|---|
| Fehling's sol$^n$ | orange ppt | orange ppt. | no orange ppt. |
| Triodomethane sol$^n$. | no yellow ppt | yellow ppt | yellow ppt. |

#

(a)(i)    $HCN \rightleftharpoons H^+ + CN^-$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \quad moldm^{-3} \quad \#$$

(ii)    $[H^+] = [CN^-]$

$\therefore \quad 4.9 \times 10^{-10} = \frac{[H^+]^2}{0.100}$

$[H^+] = 7.0 \times 10^{-6} \; moldm^{-3} \; \#$

% HCN molecules ionised $= \frac{7.0 \times 10^{-6}}{0.100} \times 100\%$

$= 0.007\% \; \#$

(iii) NaCN acts a source of $CN^-$ nucleophile as HCN being a weak acid is a poor source of $CN^-$.

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

4(b)(i)    $$NaCN(aq) \longrightarrow Na^+(aq) + CN^-(aq).$$
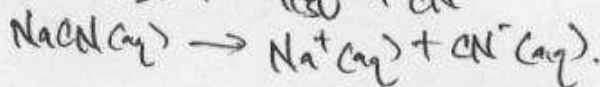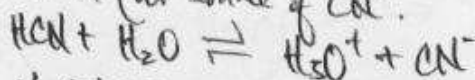
The order of rex^n with respect to a reactant is the power to which that concentration is raised in the rate equation.

i.e.    rate $= k[A]^m$

order of rex^n w.r.t A $= m$ $\#$

(ii)
Considering expts 1 & 2, By inspection
when [HCN] & [NaCN] remains constant,
when $[(CH_3)_2CO] \uparrow 25\%$ rate $\uparrow 25\%$
$\Rightarrow$ order w.r.t. $(CH_3)_2CO = 1$ $\#$

Considering expts 3 & 1, By inspection
when $[(CH_2)_2CO]$ & [HCN] remains constant,
when $[NaCN] \uparrow 33\%$, rate $\uparrow 33\%$
$\Rightarrow$ order w.r.t. NaCN $= 1$ $\#$

By considering expts 3 & 4

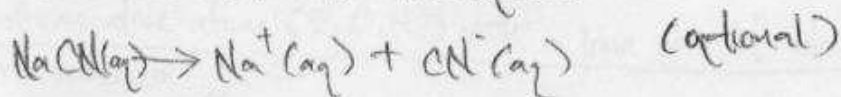$$\frac{rate_3}{rate_4} = \frac{0.75}{0.94} = \frac{k(0.04)^1(0.04)^m(0.006)^1}{k(0.05)^1(0.05)^m(0.006)^1}$$
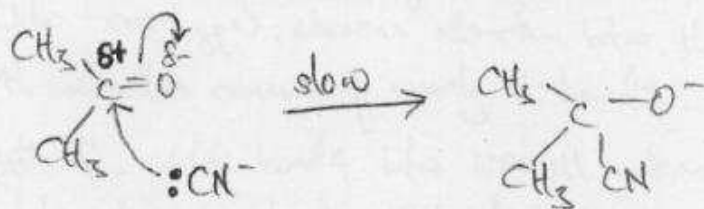
$m \approx 0$
$\Rightarrow$ order w.r.t HCN $= 0$ $\#$

rate $= k[NaCN][(CH_3)_2CO]$ $\#$

(b)(iii) Step 1: Generation of $CN^-$ nucleophile.

$$NaCN_{(aq)} \rightarrow Na^+(aq) + CN^-(aq) \qquad \text{(optional)}$$

Step 2: Attack $CN^-$ nucleophile on $(CH_3)_2CO$



Step 3:



(iv)



propanal          propanone
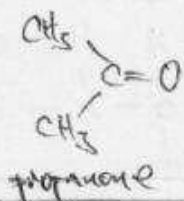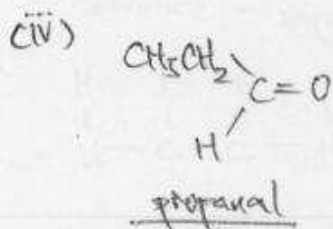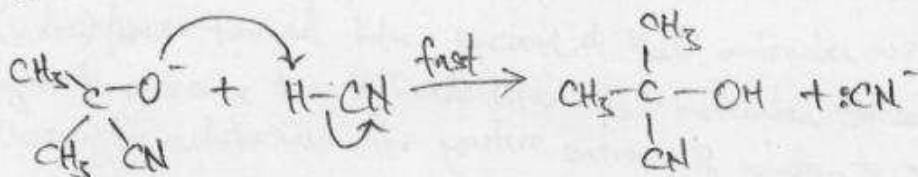
Propanal reacts at faster rate ∵ (1) 2 alkyl groups reduce partial +ve charge on carbonyl C making propanone less susceptible to nucleophilic attack. (2) presence of 2 alkyl groups in propanone provides steric hindrance in nucleophile approaching the δ+ carbonyl C.
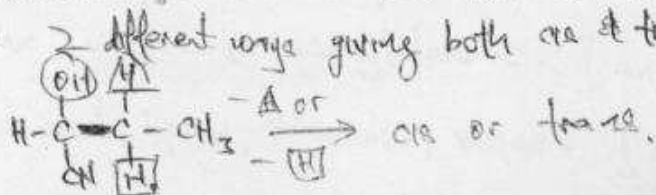
(v) NaCN is catalyst providing $CN^-$ nucleophile especially @ initial stage reaction. HCN is Bronsted acid by ɛ donating proton to intermediate.

4(c) optical isomerism.
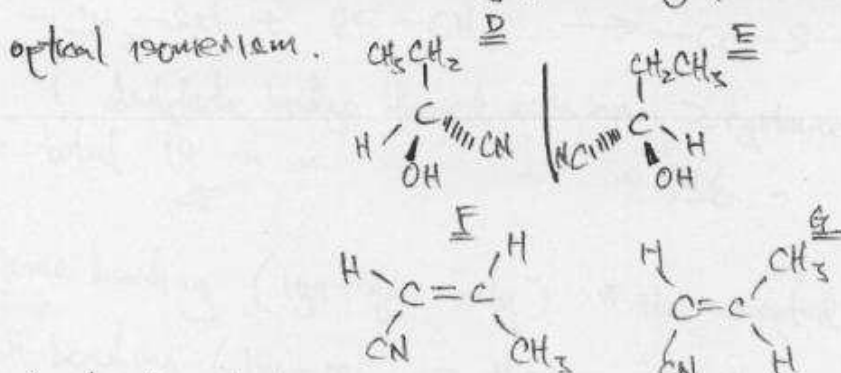


Reaction with optical isomers D & E with non chiral agents are identical.

OR Both isomers D & E can each lose a H & OH from adjacent C atoms in 2 different ways giving both cis & trans isomers F & G.
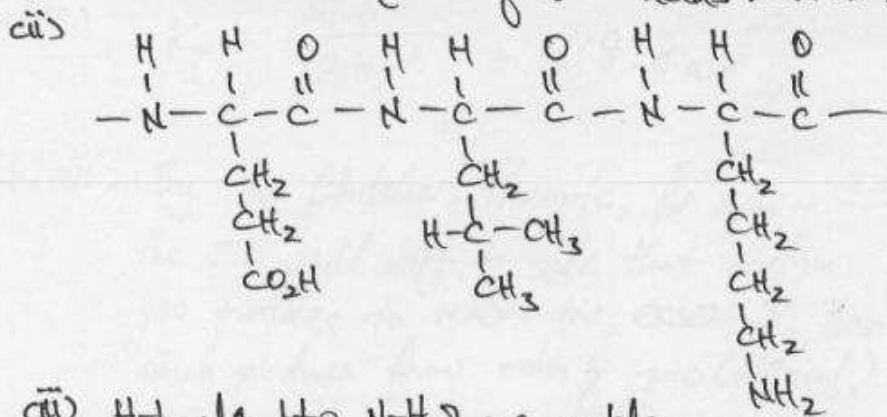
(ci) a H atom joined to an electronegative atom (F, O, N) in one molecule, and an electronegative atom (F, O, N) with a lone pair of electrons in the other molecule. #

(cii) Attraction btw RCOOH molecules consist of both van der Waals' forces (btw R-chains) & H-bonds (btw -COOH gps), whereas attraction btw $H_2O$ molecules & btw $H_2O$ & RCOOH molecules consist of mainly H-bonds.
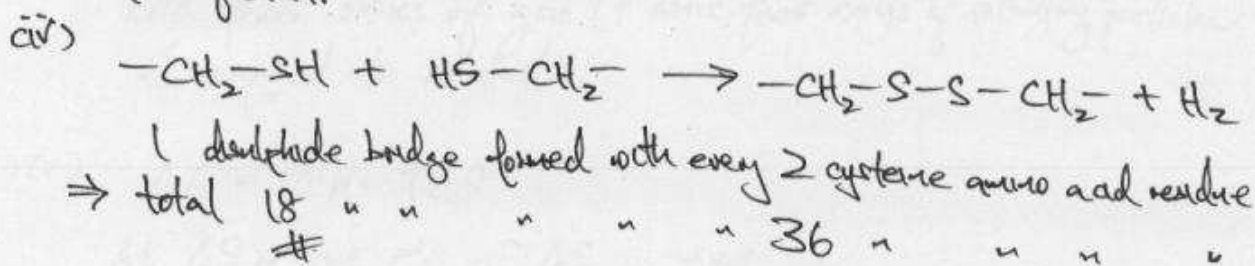
As chain length ↑, vdw bonds btw RCOOH molecules become predominant & long hydrophobic chains interfere H-bonds btw $H_2O$ & RCOOH molecules. Thus the (vdw) forces formed btw R-COOH & $H_2O$ molecules are not strong enough to overcome the H-bonds btw $H_2O$ molecules for solvation to occur. (Process too endothermic for positive entropy of solution to counter).

5(b)(c)(i) 1° structure — sequence of amino acids residues in protein chain.

(cii)

```
    H   H   O       H   H   O       H   H   O
    |   |   ||      |   |   ||      |   |   ||
  — N — C — C  —  N — C —  C  —  N — C — C —
        |               |               |
        CH₂             CH₂             CH₂
        |               |               |
        CH₂         H — C — CH₃         CH₂
        |               |               |
        CO₂H            CH₃             CH₂
                                        |
                                        CH₂
                                        |
                                        CH₂
                                        |
                                        NH₂
```

(ciii) H-bonds btw N-H of one peptide & C=O of another peptide in another (sketch α-helix diagram) part of chain.

(civ)
$$—CH_2—SH + HS—CH_2— \rightarrow —CH_2—S—S—CH_2— + H_2$$

1 disulphide bridge formed with every 2 cysteine amino acid residue
⇒ total 18 "  "    "     "    " 36 "   "    "    "    "

(cv) Ionic bonding (lys-glu only)  # Not accepted for H-bonds.
    H-bonding (lys-ser or thr-ser or thr-glu)
    vdw      (val-phe)   (leu-val) (leu-phe)
                       #

(cvi) leucine, valine or phenylalanine. } any 2. #

(cvii) glutamic acid, lysine, threonine, serine. } any 3.
                                                    #