2011 NYJC Prelim H2 Chemistry 9647/03 Answers

1 (a) (i) I.

$\frac{1}{2}(CN)_2 + H^+ + e \rightleftharpoons HCN$ $E^\phi = +0.37$ V

$Cl_2 + 2e \rightleftharpoons 2Cl^-$ $E^\phi = +1.36$V

$E^\phi_{cell} = +1.36 - (+0.37) = +0.99$V

Overall Equation: $Cl_2 + 2HCN \rightarrow (CN)_2 + 2H^+ + 2Cl^-$

II.

$\frac{1}{2}(CN)_2 + H^+ + e \rightleftharpoons HCN$ $E^\phi = +0.37$ V

$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$ $E^\phi = +0.09$ V

$E^\phi_{cell} = +0.37 - (+0.09) = +0.28$ V

Overall Equation: $(CN)_2 + 2H^+ + S_2O_3^{2-} \rightarrow 2\ HCN + S_4O_6^{2-}$

III.

$\frac{1}{2}(CN)_2 + H^+ + e \rightleftharpoons HCN$ $E^\phi = +0.37$ V

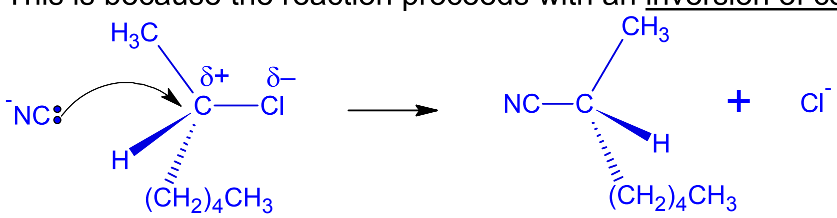
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\phi = +1.33$ V

Both are oxidising agents. Hence reaction cannot proceed.

(ii)

linear

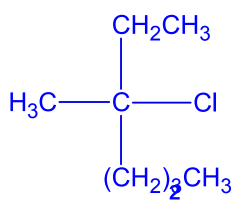
(b) (i) This is because the reaction proceeds with an inversion of configuration.



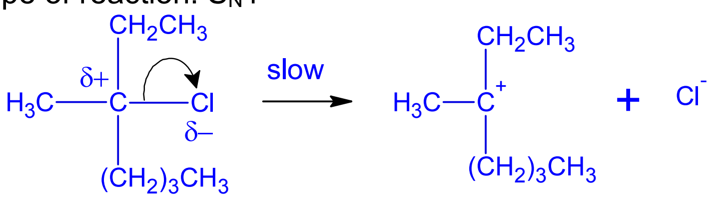
To illustrate the inversion in structural formula (3D wedge diagram)

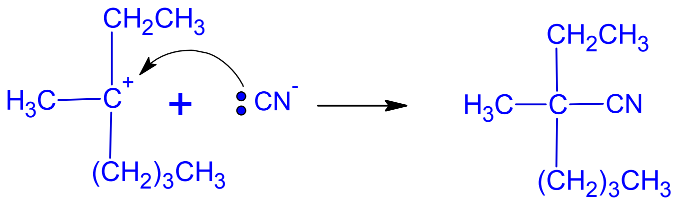
(ii)

Isomer A:



Type of reaction: S_N1

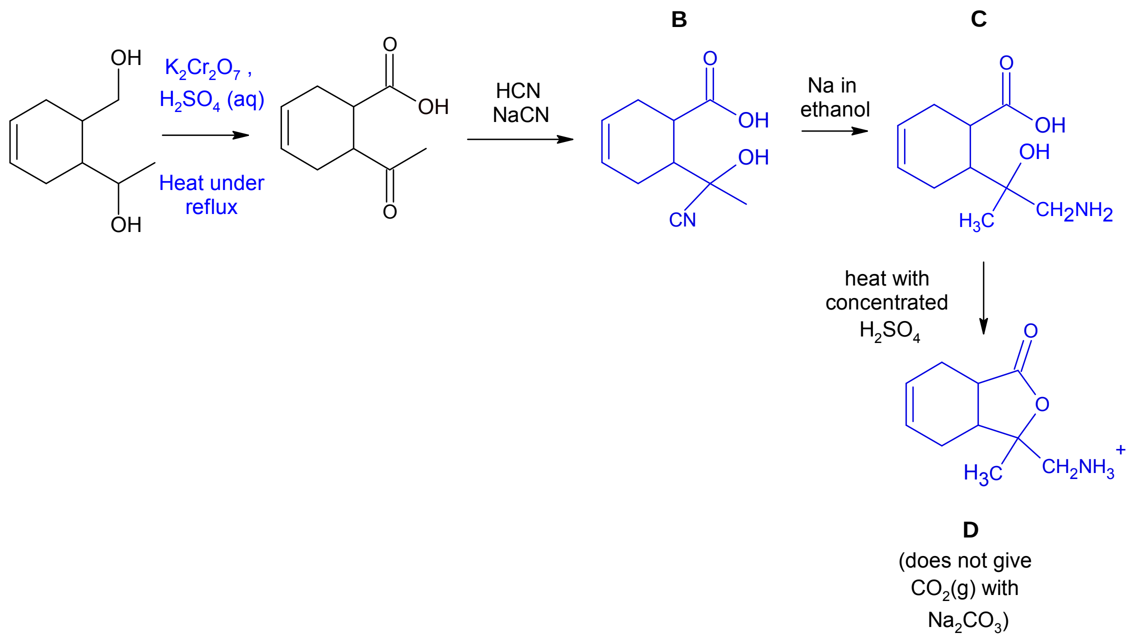




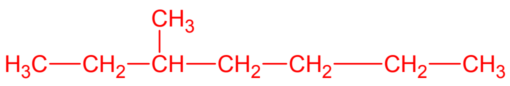
(iii)

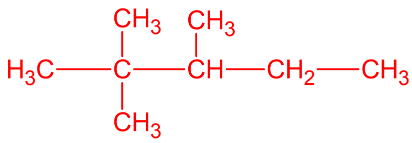
- Reaction b(i) OR S_N2 mechanism is faster.
- The rate determining step in b(i) involves NaCN.
  OR rate = k[NaCN][RX]

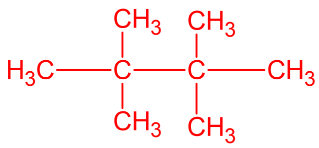
(c)



2(a)(i) (There is a plane of symmetry in the molecule or both chiral centres contain the same groups attached to it), the two chiral centres **rotate the plane of polarised light** to the same extent but in the opposite direction hence cancelling out the optical activity.

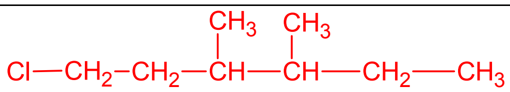
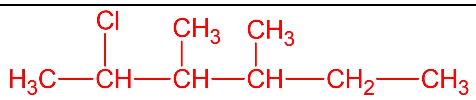
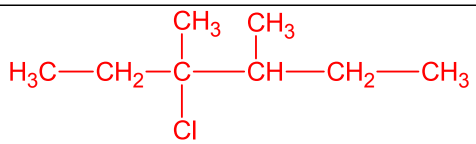
(ii) Compound A: 

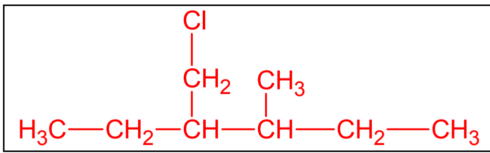
Compound C: 

Compound D: 

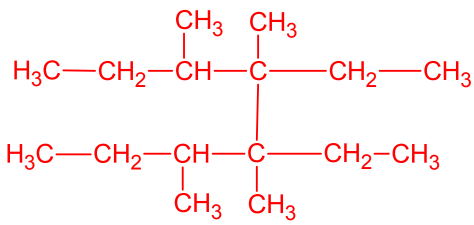
(iii) Isomers A to D are simple molecular compounds with weak van der Waals forces between molecules. However, as we move down the table from A to D, the molecules become increasingly branched, hence they have less surface area of contact with their neighbouring molecules resulting in weaker vdw forces between molecules. Hence less energy is required to break the vdw bonds, resulting in lower b.p. down the table.

(iv) 4 molecules + ratio

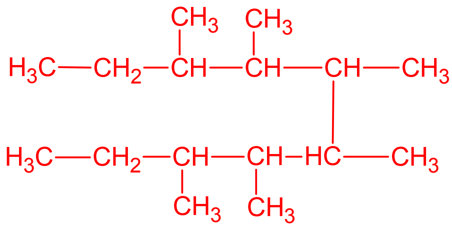
Structural formula	**mole ratio**	
	6	3
	4	2
	2	1

	6	3

(v)

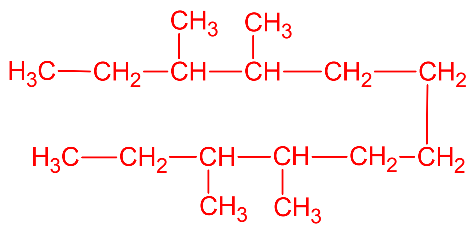


OR



[1st one preferred, because more branched.]

(but not



or any other combination that produces less than 6 branches.)

(b) pH = 7.4;
pOH = 14-7.4 = 6.6;
$[OH^-] = 10^{-6.6} = 2.512 \times 10^{-7}$ $moldm^{-3}$

K_{sp} of $Pb(OH)_2 = [Pb^{2+}(aq)][OH^-(aq)]^2 = 1.43 \times 10^{-20}$;
$[Pb^{2+}(aq)]_{total} = (1.43 \times 10^{-20}) / (2.512 \times 10^{-7})^2 = 2.26 \text{ x } 10^{-7}$ $moldm^{-3}$

K_{sp} of $PbSO_4 = [Pb^{2+}(aq)][SO_4^{2-}(aq)] = 2.53 \times 10^{-8}$;
$[SO_4^{2-}(aq)]_{total} = 2.53 \times 10^{-8} / 2.26 \text{ x } 10^{-7} = 0.1116$ $moldm^{-3}$

K_{sp} of $BaSO_4 = [Ba^{2+}(aq)][SO_4^{2-}(aq)] = 1.08 \times 10^{-10}$;
$[Ba^{2+}(aq)]_{total} = 1.08 \times 10^{-10}/0.1116 = 9.67 \times 10^{-10}$ $moldm^{-3}$

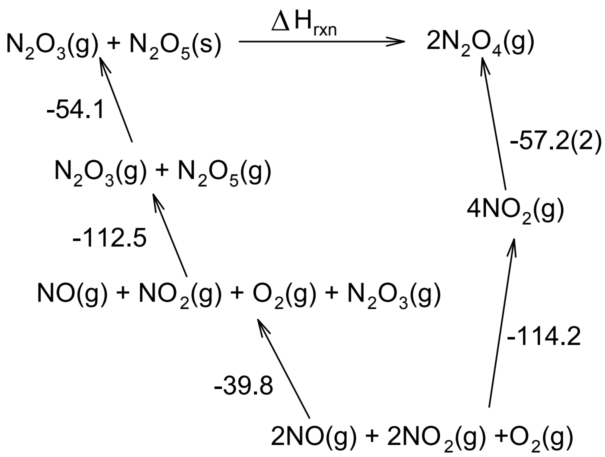
Therefore the barium ion concentration is within safety limits since $[Ba^{2+}]$ is $< 1.45 \times 10^{-5}$ $moldm^{-3}$

(c)(i) Down the group, the Increase in screening effect and atomic radius outweigh the increase in nuclear charge. Hence, net attraction of outermost electron decreases. Less energy required to remove the valence electron.

(ii) Lithium and sodium metals have high boiling points due to their stronger metallic bonding hence can be obtained via electrolysis and (isolated) even in a high temperature environment. [1] Potassium, rubidium and caesium having larger atomic radius, have weaker metallic bonding and vaporises in the high temperature environment.

(iii) Lithium ion behaves like Mg^{2+}. (diagonal relationship). It has a high charge density and is able to polarise the oxygen molecule breaking the O=O double bond[1]. As we come down the group, the other group one ions have larger ionic radii and hence have a lower charge density is unable to polarise the molecule completely, hence giving O_2^{2-} and O_2^- ions.

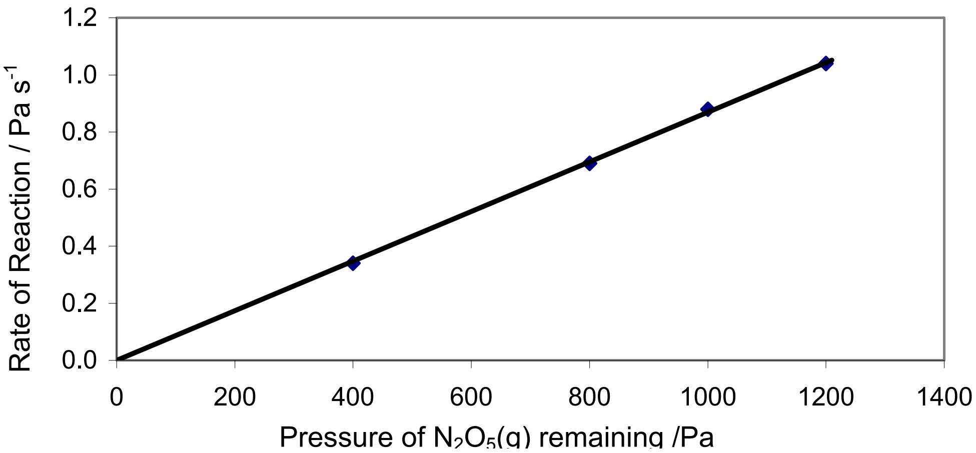
3(a)



$\Delta H_{rxn} = -(-39.8) - (-54.1) + 2x(-57.2) - (-112.5) + (-114.2)$

$= -22.2$ kJ

(b)(i) graph is a straight line (passing through zero)



explanation ; since rate is directly proportional to pressure/concentration of $N_2O_5(g)$, the reaction is first order wrt $N_2O_5(g)$

(ii) rate constant = gradient = (any working) = 9×10^{-4} sec $^{-1}$

(iii) for slow step involving only 1 $N_2O_5(g)$
for sum of all steps adding to $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
e.g. I $N_2O_5(g) \rightarrow NO_2(g) + NO(g) + O_2(g)$ slow
II $N_2O_5(g) + NO(g) \rightarrow 3NO_2(g)$ fast

(c) LiF

CsS

ZnF

$SrBr_2$

(d) (i) **B** CO_2
C $CaCO_3$
D $Ca(HCO_3)_2$

(ii) $MO + H_2O \rightarrow M(OH)_2$

$M(OH)_2 + 2\,HCl \rightarrow MCl_2 + 2H_2O$

n_{HCl} for 25.0 cm^3 aliquots = $0.0985 \times 20.30/1000 = 0.0020$ mol

n_{HCl} reacting with **E** = $0.0020 \times 250/25 = 0.020$ mol

$n_{MO} = n_{M(OH)2} = \frac{1}{2} \times 0.020 = 0.010$ mol

M_A = 1.9735 / 0.010 = 197.35 ≈ **<u>197.4</u>**

(iii) **A** is likely to be a carbonate (since CO_2 is evolved on heating)

Hence formula will be **MCO_3**

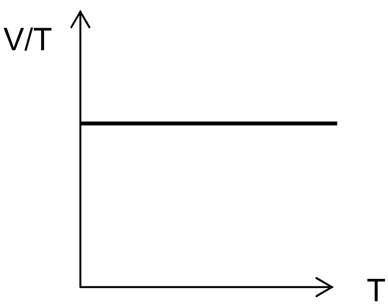
Hence *Ar* of **M** will be 197.35 – 12.0 – 3(16.0) = <u>137.35</u>

M is likely to be <u>Barium</u>.

4(a) Down the group, thermal stability of HX <u>decreases</u> as the <u>H-X bond length increases</u> and it becomes <u>easier to break</u> the H-X bond.

(b) The <u>Si-F bond formed is very strong</u> hence the reaction is very exothermic/very stable products are formed.

(c)(i)



(ii) Gas **X** is HF while Gas **Y** is HCl

Work out V/T values.

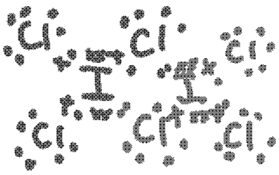
Experiment No.	T / K	Gas X		Gas Y	
		V / dm^3	V /T dm^3K^{-1}	V / dm^3	V /T dm^3K^{-1}
1	200	20 000	100	16 500	82.5
2	300	22 500	75	20 000	66.7
3	600	24 000	40	23 500	39.1

The <u>V/T values</u> of Gas **X** <u>deviates more from a constant value</u> than Gas **Y**.

Hence Gas **X** behaves less like an ideal gas than Gas **Y**.

Gas **X** is HF which has stronger hydrogen bonds between molecules while HCl has weaker permanent dipole-permanent dipole interactions.

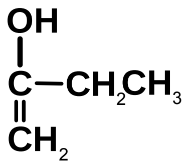
(d)(i) ICl prefers to form stronger permanent dipole-permanent dipole interactions between its polar molecules rather than weak Van der Waal's forces with non-polar solvent molecules.

(ii) 

[NB: Since dimer is planar, iodine should have 4bp and 2lp - square planar]

(iii) $2\ BrF_3 \rightarrow [BrF_2]^+ + [BrF_4]^-$ or $BrF_3 \rightarrow [BrF_2]^+ + F^-$
BrF_3 ionizes/forms ions. The mobile ions (in molten state) are able to act as charge carriers.

(e)(i)

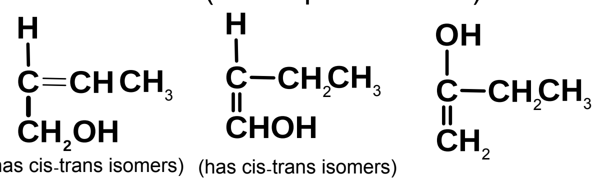


Intermediate **X**

Step I: HCN, trace amount of NaOH/NaCN, 10-20°C
Step III: $LiAlH_4$ in dry ether

(ii) Step IV.
There are 5 isomeric products in all.

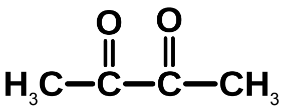
For reference (not required in ans)

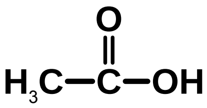


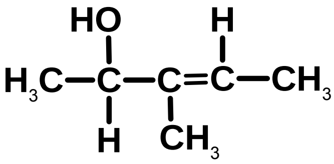
(has cis-trans isomers) (has cis-trans isomers)

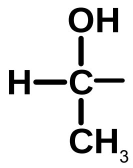
(iii) $(CH_3)_2CHMgBr$

(iv)

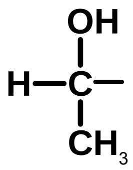
Z 

Y 

X 

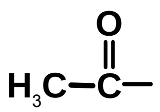
Reaction of CH_3MgBr with Aldehdye: Product **X** contains  (deduce from Grignard reaction)

Reaction with Na: **X** contains 1 alcohol group (do not accept phenol or carboxylic acid as these are not possible in $C_6H_{12}O$)

Reaction with alkaline aq I_2: **X** contains  (do not accept methyl carbonyl)

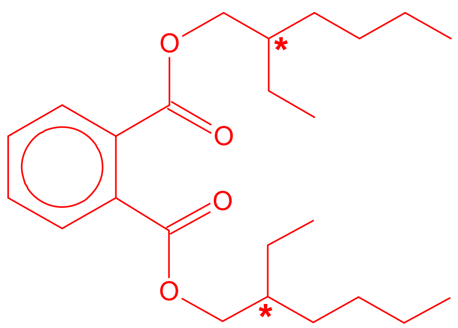
Reaction with concentrated acidified $KMnO_4$: **X** contains an alkene that underwent oxidative cleavage to form 2 products.

Reaction with Na: **Y** contains 1 carboxylic acid group (do not accept phenol or alcohol as **Y** is an oxidised product unless student stated tertiary alcohol)

Reaction with alkaline aq I_2: **Z** contains 2  (do not accept methyl alcohol as **Z** is an oxidised product)

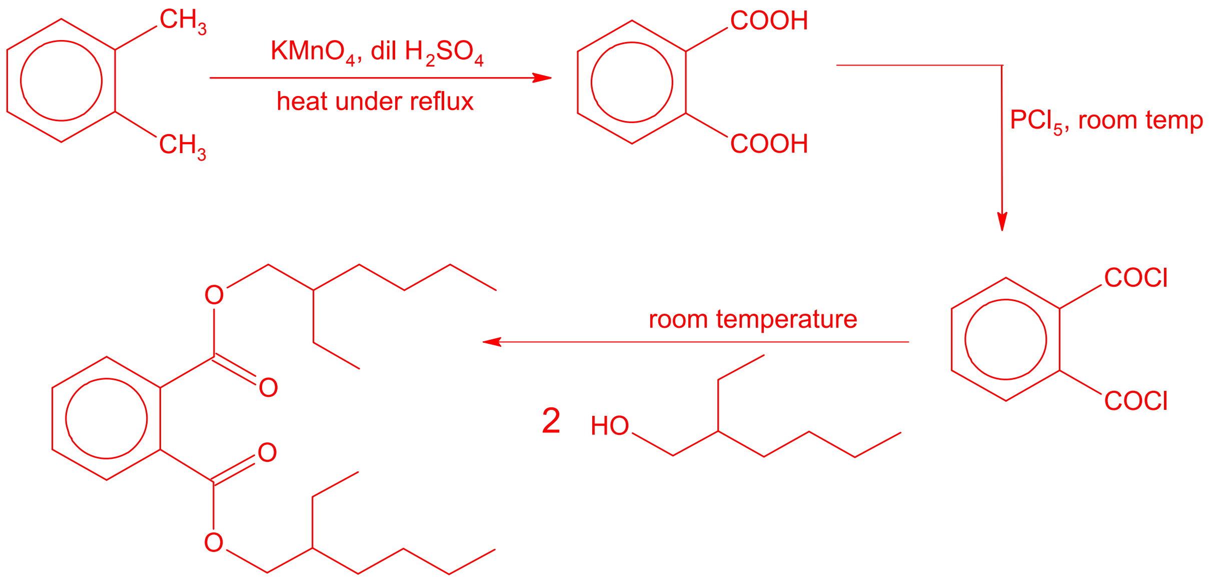
5(a)(i) Ester

(ii)



10 π electrons

(iii)



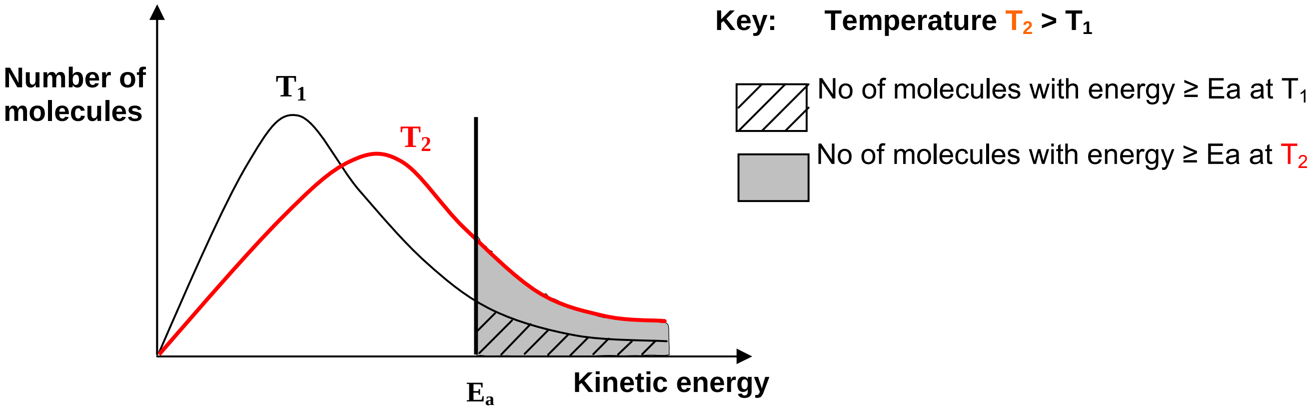
(iv) Test: $KMnO_4$, dilute H_2SO_4, heat

Observation with DEHP: Purple $KMnO_4$ decolorised

Observation with Compound A: Purple $KMnO_4$ remains unchanged

(b)

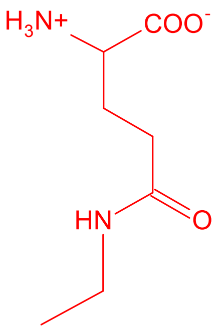
Boltzmann Distribution Curve:



Both curves sketched correctly, including labeled axes and key

As temperature increases, molecules possess <u>greater kinetic energy</u>. Hence, the <u>number of molecules with energy greater or equal to activation energy is larger</u> as <u>shown by the two shaded areas</u> in the diagram above. This results in <u>higher frequency of effective collisions</u> and hence higher rate of reaction.

(c)(i)

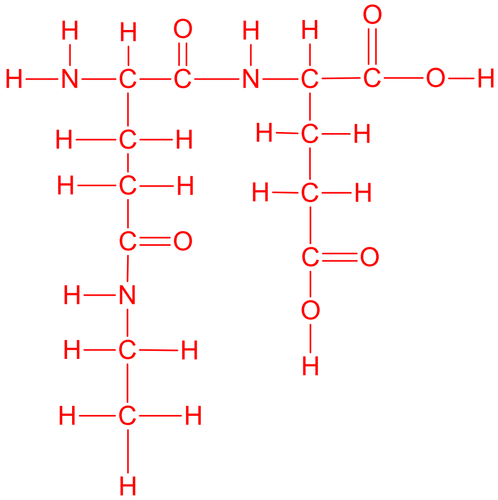


strong ionic bonds between zwitterions
a lot of energy required to overcome the strong bonds

(ii)
NH_2-CH(CH_2CH_2COOH)-COOH + $H^+ \rightarrow {}^+NH_3$-CH(CH_2CH_2COOH)-COOH

NH_2-CH(CH_2CH_2COOH)-COOH + $OH^- \rightarrow NH_2$-CH(CH_2CH_2COOH)-COO^- + H_2O

(iii)



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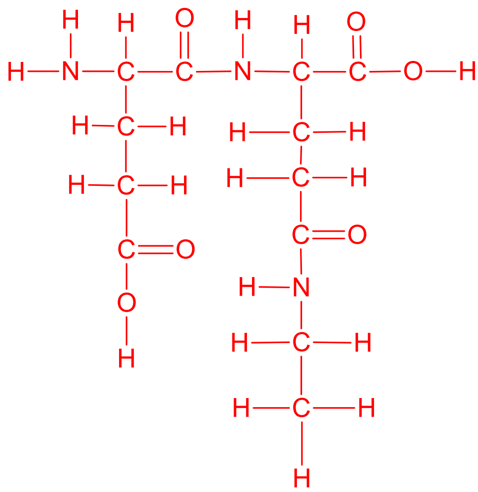

M_r of dipeptide = 303

(iv)
It refers to the three dimensional conformation of a protein results from further folding, cross-linkings and coiling of the amino acid chains caused by interactions between the R-groups of the amino acids.

Illustrate any of the following
Hydrogen bonding between R-groups of glutamine
van der Waals' forces between R-groups of theanine
van der Waals' forces between R-groups of theanine and glutamine