Frozen Solutions

Problem 1 **20 Marks**

Sulphate dynamics in Wastewaters

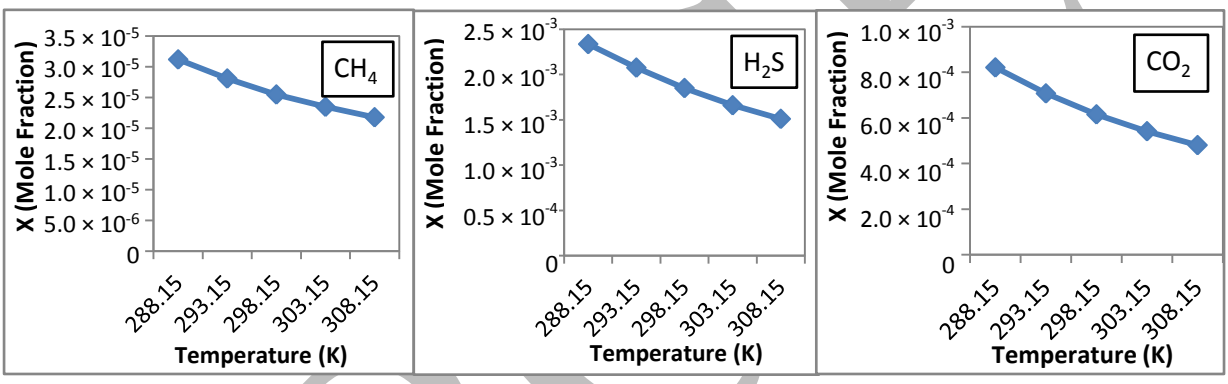
1.1 $\Delta G^\circ = -201$ kJ **(1 mark)**

1.2 $K = [HS^-][CO_2]^2/([SO_4^{2-}][H_3O^+])$ **(1 mark)**

1.3 $K = 10^{34.7}$ **(1 mark)**

1.4 Concentration of H_2S = 0.25 mM **(2 marks)**

1.5 i)



ii) CH_4 **(2 marks)**

1.6 Density of the air = **1.16 kg m^{-3}** **(2 marks)**

1.7 CH_4 A CO_2 C H_2S C **(1.5 marks)**

1.8

$HS^-(aq) + 2O_2 + H_2O \rightleftharpoons SO_4^{2-}(aq) + H_3O^+$

$CaO(s) + H_2SO_4(aq) \rightleftharpoons CaSO_4(s) + H_2O$ **(1.5 marks)**

1.9 $[Cr_2O_7^{2-}]/[Cr^{3+}] = 10^{20}$ **(if p_{O2} is taken in Pascal then 10^{23} is also accepted as correct).** **(4 marks)**

1.10 $[SO_4^{2-}]$ = 1.49 mM $[Cr^{3+}]$ ~0 mM. $[Cr_2O_7^{2-}]$ = **0.68** mM **(1.5 marks)**

1.11

$4Cr_2O_7^{2-}(aq) + 29H_3O^+(aq) + 3HS^-(aq) \rightleftharpoons 8Cr^{3+}(aq) + 45H_2O + 3SO_4^{2-}(aq)$

$E^\circ = 1.58$ V

$SO_4^{2-}(aq) + 2\{CH_2O\}(s) + H_3O^+(aq) \rightleftharpoons HS^-(aq) + 2CO_2(aq) + 3H_2O(l)$

$E^\circ = 0.26$ V **(2.5 marks)**

Problem 2 **24 Marks**

Olefin Chemistry

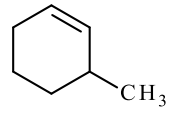
2.1

3-E, 5-Z-3-bromo-5-chloro-4-cyclohexylocta-3, 5-diene-7-ynal

(2 marks)

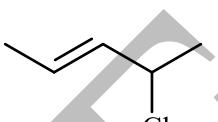
2.2

i)



A

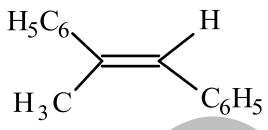
ii)



B

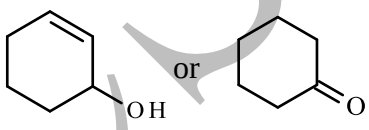
% C = 57.4

iii)



C

iv)



D

% C = 73.5 %H = 10.2

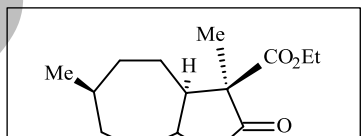
(2.5 marks)

2.3

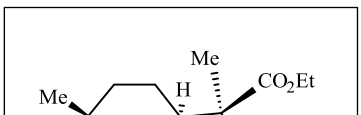
i)

F

ii)



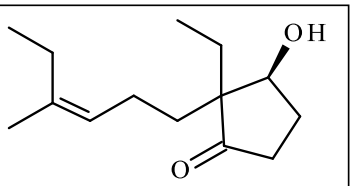
G



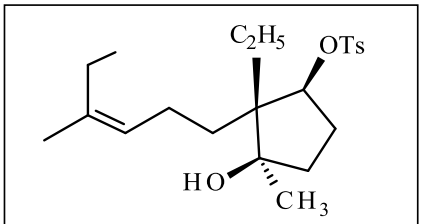
H

(3 marks)

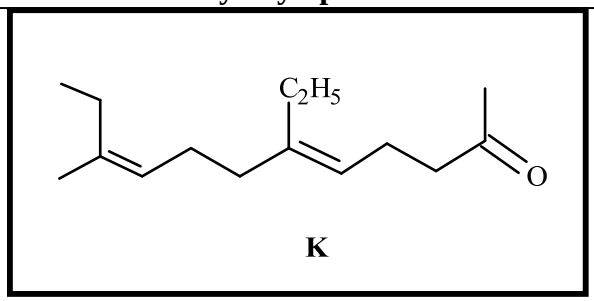
2.4



I



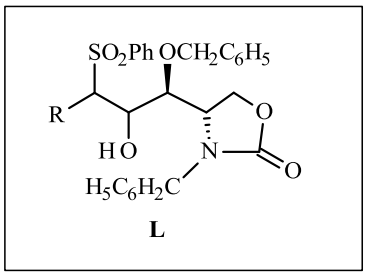
J



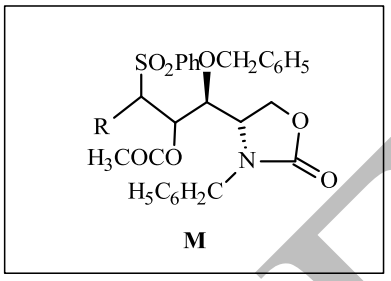
K

(3.5 marks)

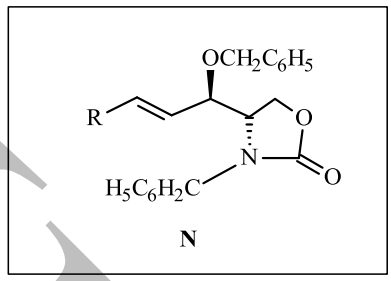
2.5



L



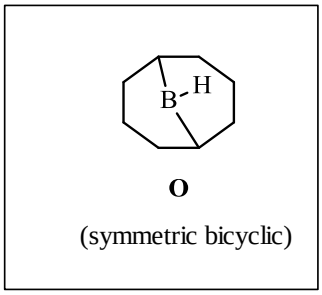
M



N

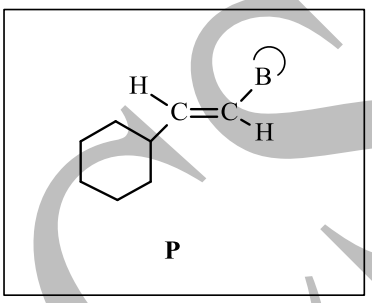
(2.5 marks)

2.6

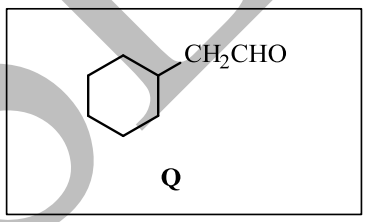


O

(symmetric bicyclic)



P

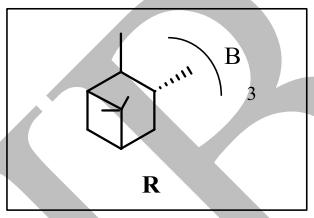


Q

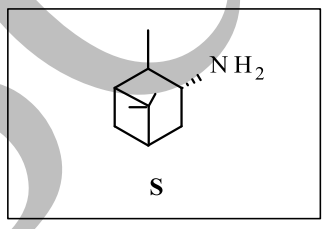
(3 marks)

2.7

i)

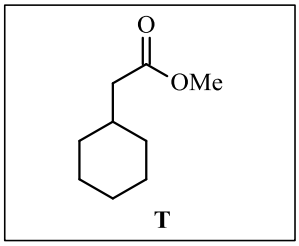


R



S

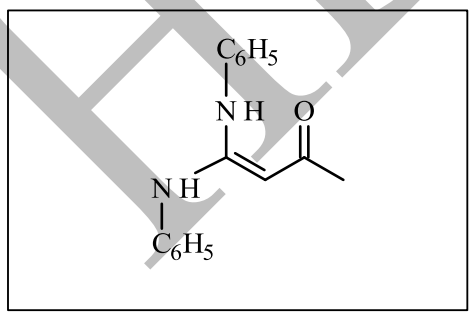
ii)



T

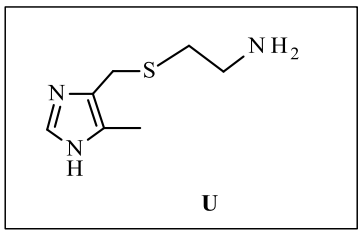
(3 marks)

2.8



(1 mark)

2.9



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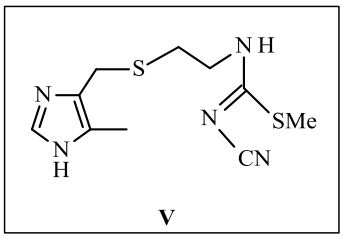
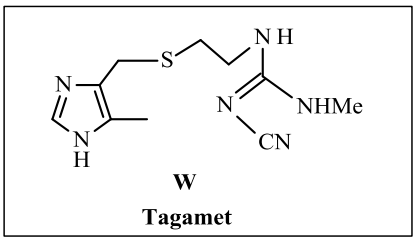


V



W

Tagamet

(3.5 marks)

Problem 3 **17 marks**

Chemical Kinetics and Nuclear Reactions

Part A

3.1 $5\ Br^-(aq) + BrO_3^-(aq) + 6\ H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O$ **(1 mark)**

3.2 Total order = 4 **(1 mark)**

3.3 $r = k_{eff}[BrO_3^-]$, $k_{eff} = k[Br^-][H^+]^2$ **(1 mark)**

3.4

i) ☐

ii) ☐

iii) ☐

iv) X

v) ☐

(2 marks)

3.5 $0.314\ M^{-3}\ sec^{-1}$ **(3 marks)**

3.6

(i) ☐

(ii) ☐

(iii) X

(iv) ☐

(v) X

Answer marked with only (v) is also accepted as correct.

(2 marks)

Part B

3.7 i) $^{238}U_{92} \rightarrow {}^{206}Pb_{82} + 8\ {}^{4}He_2 + 6\beta$ **(1 mark)**

ii) a) 0.16 g **(1 mark)**

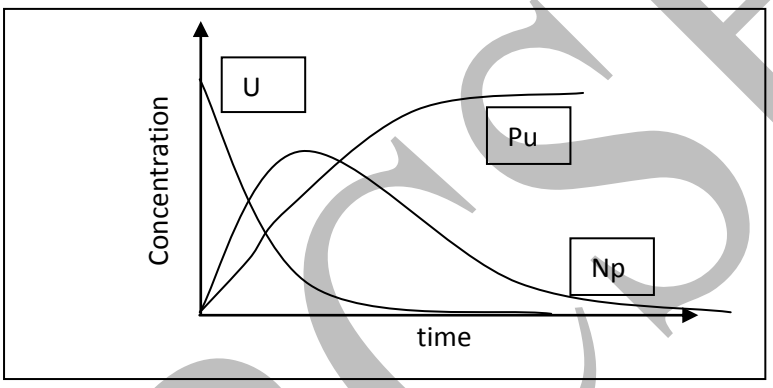
b) 1 billion years. **(1 mark)**

3.8 i) $d[^{239}U_{92}] / dt = -k_1 [^{239}U_{92}]$

$d[^{239}Np_{93}] / dt = k_1 [^{239}U_{92}] - k_2 [^{239}Np_{93}]$ **(1.5 marks)**

ii) $[^{239}Np_{93}] = k_1[^{239}U_{92}]_o / k_1 (e^{-k_2 t}) = [^{239}U_{92}]_o \times e^{-k_2 t}$ **(1mark)**

iii)



(1mark)

iv)

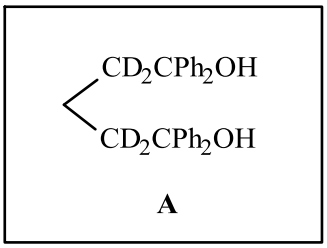
True ☐ False X

(0.5 mark)

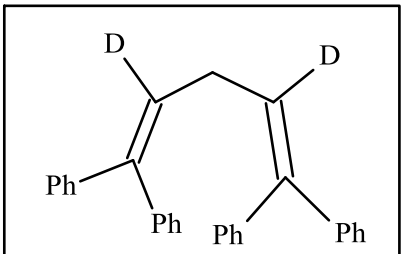
Problem 4 **17 Marks**

Synthesis of Natural Products

4.1



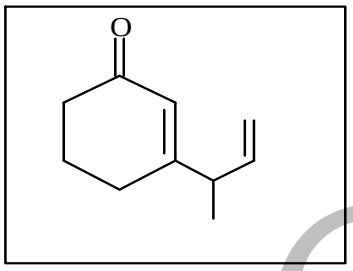
A



B

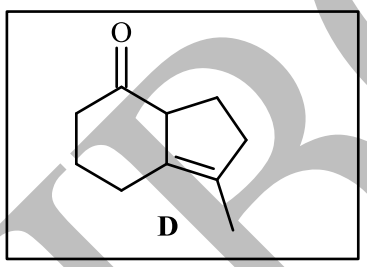
(1.5 marks)

4.2

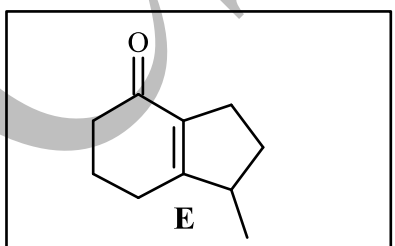


(1 mark)

4.3

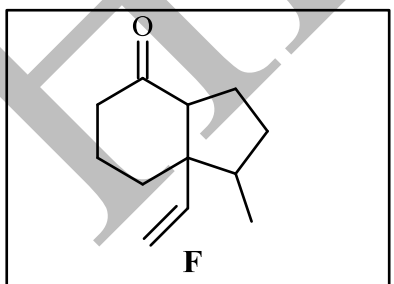


D



E

more stable isomer of **D**

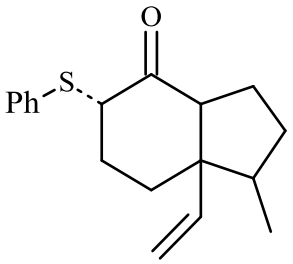
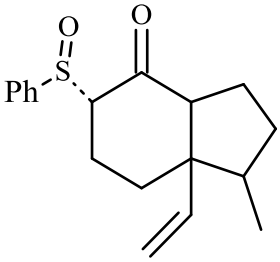
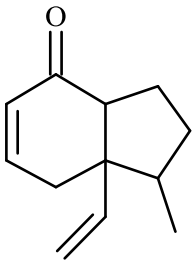


F

gives positive 2, 4 - DNP test

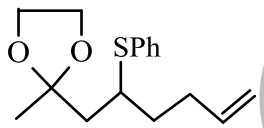
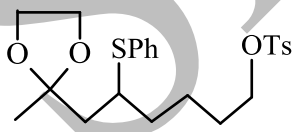
(2.5 Marks)

4.4

		
G	**H**	I
	Intermediate	% C = 81.77 % H = 9.15

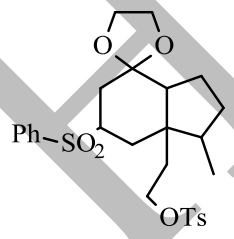
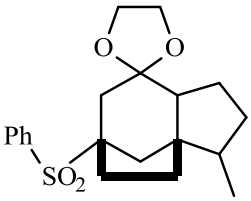
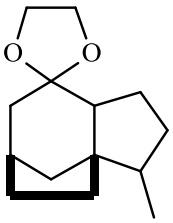
(2 marks)

4.5

	
J	K

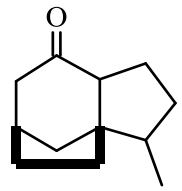
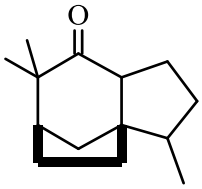
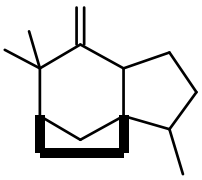
(3 marks)

4.6 Identify **L**, **M** and **N**.

		
L	**M**	**N**
%C = 60.55 %H = 6.41 %O = 20.95		%C= 75.63 %H = 9.97

(3.5 marks)

4.7

		
O	**P**	**Zizaene**

(3 marks)

4.8 4

(0.5 Mark)

Problem 5 **24 Marks**

Nickel and its chemistry

5.1 i)

Step-I: **$2FeS\ (s) + 3O_2\ (g) \rightarrow 2FeO\ (s) + 2SO_2\ (g)\uparrow$** **and**

$FeO\ (s) + SiO_2\ (s) \rightarrow FeSiO_3\ (s)\downarrow$

Or **$2FeS\ (s) + 3O_2\ (g) + 2SiO_2\ (s) \rightarrow 2FeSiO_3\ (s)\downarrow + 2SO_2\ (g)\uparrow$**

Step-II: $Ni_2S_3\ (s) + 4O_2\ (g) \rightarrow 2NiO(s) + 3\ SO_2\ (g)\uparrow$

Step-III: $2NiO(s) + 9CO(g) + H_2(g) \rightarrow 2Ni(CO)_4(g)\uparrow + H_2O(g)\uparrow + CO_2(g)$

Step-IV: $Ni(CO)_4\ (g) + 2O_2\ (g) \rightarrow Ni(s)\downarrow + 4\ CO_2(g)\uparrow$

(2.5 marks)

ii)

a) [X]

b) [X]

c) [ ]

d) [ ]

(1mark)

5.2 i)

Element	Coordination No.		Coordination geometry			
Ni	6	4	Octahedral	Trigonal Prismatic	Square planar	Tetrahedral
	X		X			
As	6	4	Octahedral	Trigonal Prismatic	Square planar	Tetrahedral
	X			X		

(2 marks)

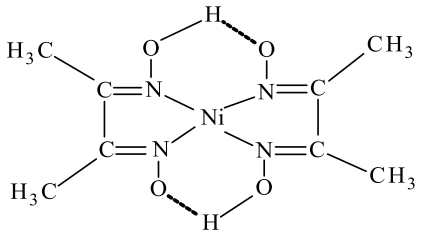
ii)

x = 1 or 6	y = 1 or 6

(0.5 mark)

5.3

i)



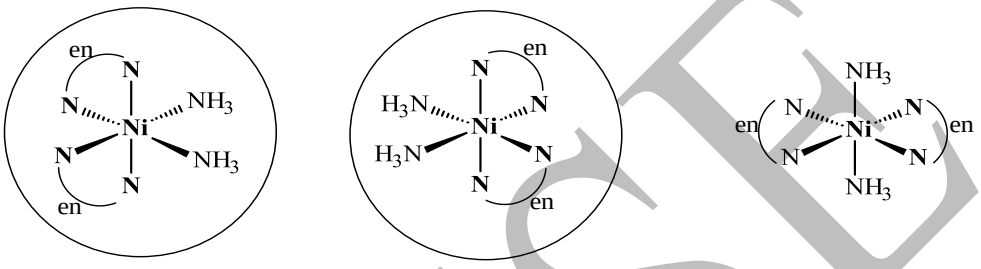
(1 mark)

ii) The % of Ni in stainless steel sample is 7.66% **or 7.72%**

(2 marks)

5.4

i)



(2 marks)

ii) $\Delta S^0 = + 39.79 \ JK^{-1} \ mol^{-1}$

(2 marks)

5.5

$2 \text{ Ni-Al} + 2 \text{ NaOH} + 6 \text{ H}_2\text{O} \rightarrow 2\text{NaAl(OH)}_4 \text{ (s)} + 3 \text{ H}_2 \text{ (g)}\uparrow + 2 \text{ Ni (s)}\downarrow$

or

$2 \text{ Ni-Al} + 2 \text{ NaOH} + 2 \text{ H}_2\text{O} \rightarrow 2\text{NaAlO}_2 \text{ (s)} + 3 \text{ H}_2 \text{ (g)}\uparrow + 2 \text{ Ni (s)}\downarrow$

(1 mark)

5.6

i)

ii)

iii) X

iv) X

(1 mark)

5.7

Case I

i) The CFSE of Co^{3+} in octahedral sites = – 8,304 cm^{-1} **or – 98.81 kJ mol^{-1}**

ii) The CFSE of Co^{3+} in tetrahedral sites = – 5,535.6 cm^{-1} **or – 65.87 kJ mol^{-1}**

Case II

i) The CFSE of Fe^{3+} in octahedral sites = 0

ii) The CFSE of Fe^{3+} in tetrahedral sites = 0

Case III

i) The CFSE of Ni^{2+} in octahedral sites = – 10,200 cm^{-1} **or – 121.38 kJ mol^{-1}**

ii) The CFSE of Ni^{2+} in tetrahedral sites = – 3,024 cm^{-1} **or – 35.98 kJ mol^{-1}**

(2.5 marks)

iii)

Octahedral site preference energy calculations:

Case I – 2,768.4 cm^{-1} **or – 32.94 kJ mol^{-1}**

Case II zero

Case III – 7,176 cm^{-1} **or – 85.4 kJ mol^{-1}**

(1 mark)

iv)

Compound	**Normal**	**Inverse**
$NiFe_2O_4$		X
$NiCo_2O_4$		X

(1 mark)

5.8

i) $2\ NaOH(aq) + Cl_2(g) \rightarrow NaClO(aq) + NaCl(aq) + H_2O$ **(0.5 mark)**

ii) $2Ni(OH)_2 + NaClO(aq) \rightarrow 2NiOOH(s) + NaCl(aq) + H_2O$ **(1 mark)**

5.9

i) $NiOOH(s) + Fe^{2+}(aq) + 3H^+(aq) \rightarrow Ni^{2+}(aq) + Fe^{3+}(aq) + 2H_2O$

ii) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$ **(1 mark)**

iii) 96.5 %

(2 marks)