Indian Olympiad Qualifier in Chemistry (IOQC) 2020-2021

conducted jointly by

Homi Bhabha Centre for Science Education (HBCSE-TIFR)

and

Indian Association of Physics Teachers (IAPT)

Part II: Indian National Chemistry Olympiad (INChO)

Homi Bhabha Centre for Science Education (HBCSE-TIFR)

Any alternative method of solution to any question that is scientifically and mathematically correct, and leads to the same answer will be accepted with full credit. Partially correct answers will gain partial credit.

For questions requiring calculations, full credit is given only if necessary steps of the calculations are written.
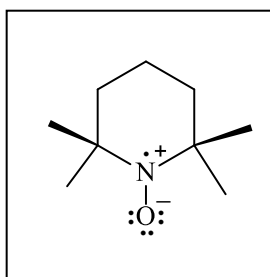
In problems having related sub-parts, consistency of answers of the related sub-parts is also checked in evaluation.

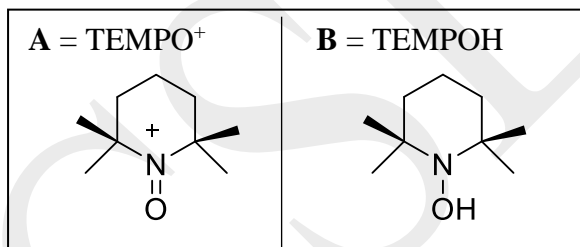## Problem 1   18 marks
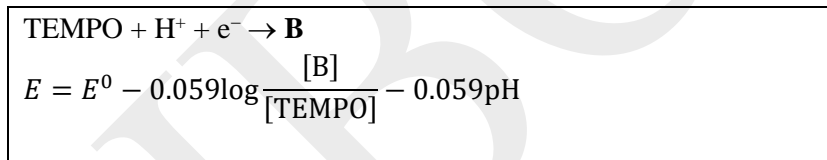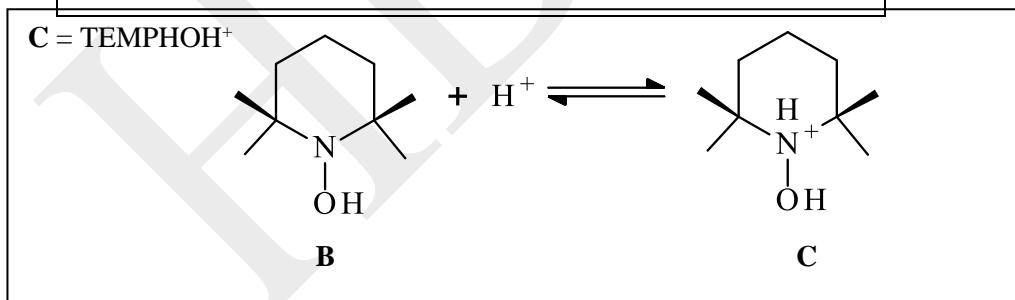
Persistent radical – TEMPO

1.1

(0.5 mark)

1.2

A = TEMPO$^+$	**B** = TEMPOH

(1 mark)

1.3

$$\text{TEMPO} + \text{H}^+ + \text{e}^- \rightarrow \textbf{B}$$

$$E = E^0 - 0.059\log\frac{[\text{B}]}{[\text{TEMPO}]} - 0.059\text{pH}$$

(1.5 marks)

1.4

C = TEMPHOH$^+$

(1 mark)

1.5

Transformation at line 3 can be represented as

$$\text{TEMPO} + 2\text{H}^+ + \text{e}^- \rightarrow \text{C}$$

$$E = E^0 - 0.059\log\frac{[\text{C}]}{[\text{TEMPO}]} - (0.059 \times 2)\,\text{pH}$$

Hence ratio of the slope of segment 3 to that of segment 2 is **2:1**

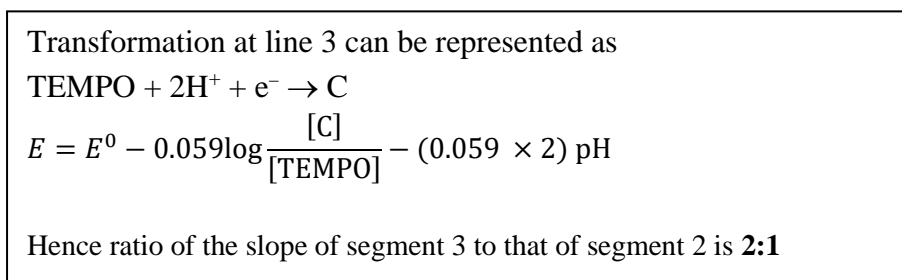**(2 marks)**

1.6

The disproportionation reaction is given by:

$2\text{TEMPO} + 2\text{H}^+ \rightleftharpoons \text{TEMPO}^+ + \text{TEMPHOH}^+$ (1)

$\text{TEMPO} \rightleftharpoons \text{TEMPO}^+ + e^-$ ($E^o = -0.745$ V)   (2)

$\text{TEMPO} + \text{H}^+ + e^- \rightleftharpoons \text{TEMPOH}$ ($E^o = 0.610$ V)   (3)

$\text{TEMPOH} + \text{H}^+ \rightleftharpoons \text{TEMPHOH}^+$ ($pK_a = 7.4$)   (4)

$\Delta G^\circ_{(1)} = \Delta G^\circ_{(2)} + \Delta G^\circ_{(3)} + \Delta G^\circ_{(4)}$

$K = 1.31 \times 10^5$

(4.5 marks)

1.7

$2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$

Working electrode is the anode and counter electrode is the cathode.

(2 marks)

1.8

(1 mark)

1.9 a) i) pH < 7

$\mathbf{B} + \mathbf{A} \rightleftharpoons 2\text{TEMPO} + \text{H}^+$

OR

$\mathbf{B} \rightleftharpoons \mathbf{C} + \text{H}^+$ **and $\mathbf{C} + \mathbf{A} \rightleftharpoons 2\text{TEMPO}$**

(2.5 marks)

ii) pH > 7

$\mathbf{B} \rightleftharpoons \text{TEMPO} + e^-$ and

$\mathbf{B} \rightleftharpoons \mathbf{C} + \text{H}^+$ and $\mathbf{C} + \mathbf{A} \rightleftharpoons 2\text{TEMPO}$

b)

Case ii); conversion of **B** to TEMPO predominantly undergoes electrochemically at the applied potential, without additional consumption of **A**.

1.10

4-carboxy TEMPO

(1 mark)

1.11

4-carboxy TEMPO   <   4-hydoxy TEMPO   <   4-amino TEMPO

(1 mark)

Note that the amino functional group undergoes protonation at pH~7.

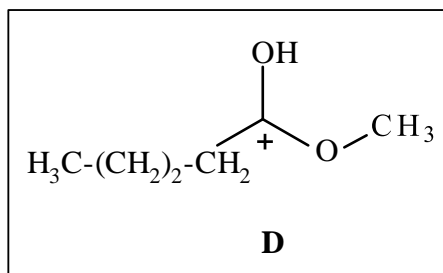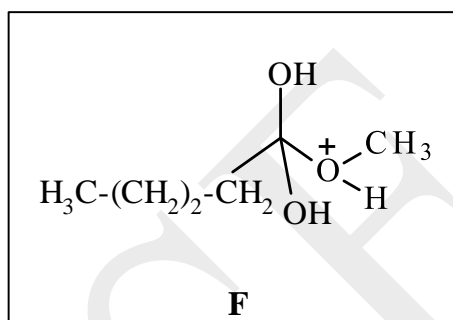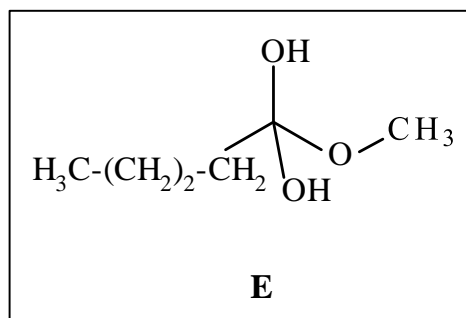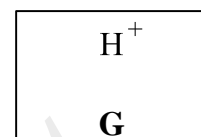## Problem 2   14 marks

Esters

2.1 i)

(1 mark)

Appropriate resonance structure will be accepted

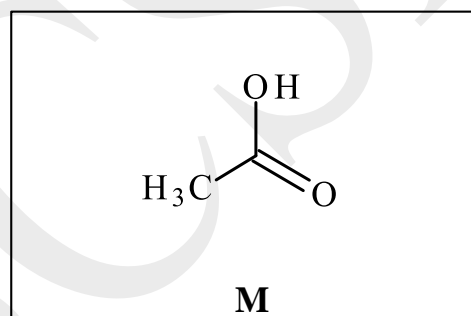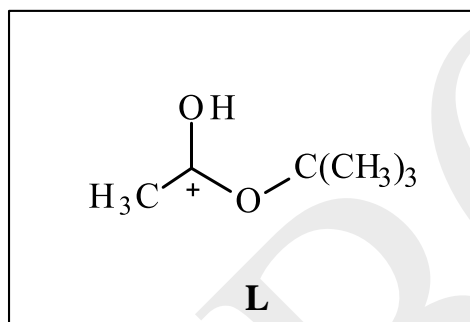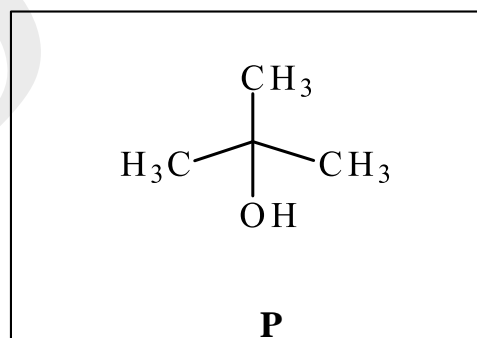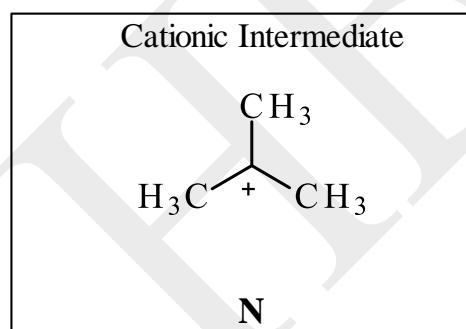**ii)**

(1.5 marks)

2.2 i)

(2 marks)
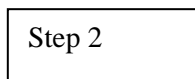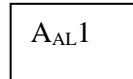
ii) Step 2   **iii)** $A_{AL}1$ **(1.5 marks)**
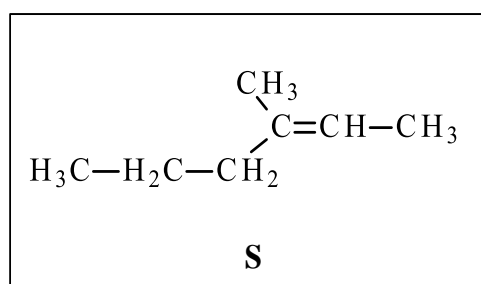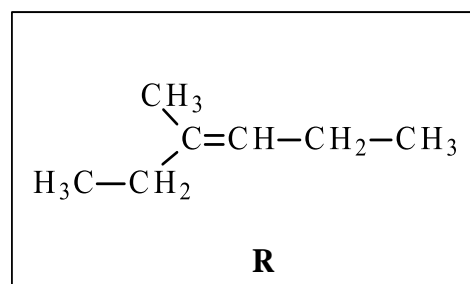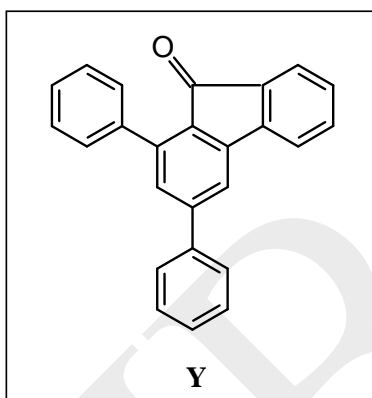
2.3 i)

(1.5 marks)

ii) (1 mark)

T

2.4 (1.5 marks)

V

Cationic intermediate

CH_3OH

W

2.5 (1 mark)

Y

2.6 i) (2.5 marks)

Intermediate

Z₁

$C_2H_5\overset{18}{O}H$

Z₂

Z₃

Z₄
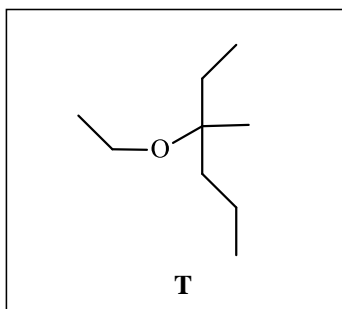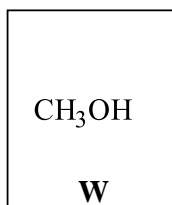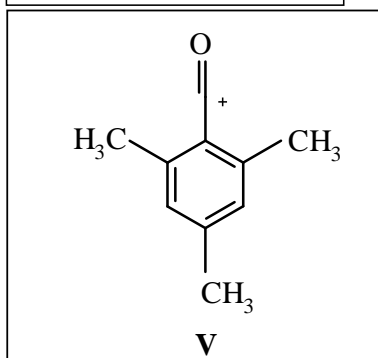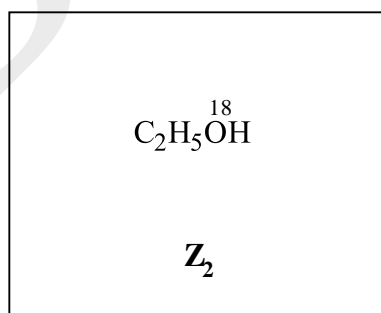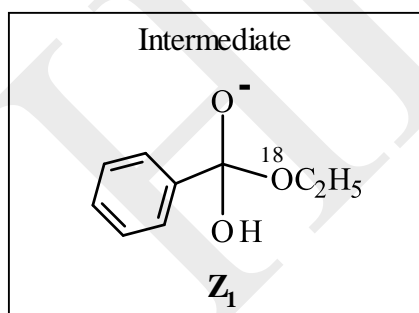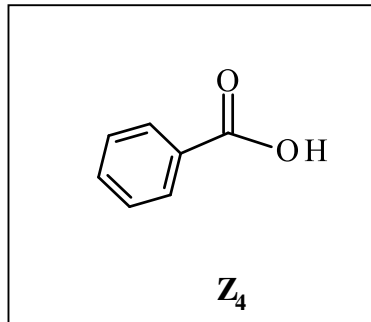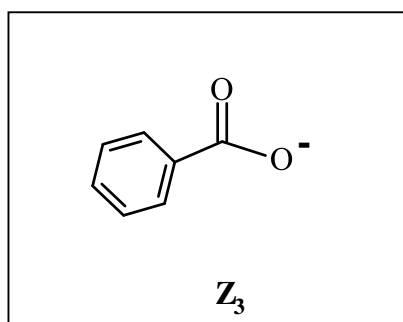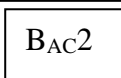
ii) $B_{AC}2$ (0.5 mark)

Problem 3   16 marks

Ozone in Troposphere

3.1

a: CO_2	**b**: $H^\bullet$	**c**: O_2	**d**: NO_2	**e**: $OH^\bullet$

Net reaction from steps i to v: $CO + 2O_2 \xrightarrow{h\nu} CO_2 + O_3$

(3.5 marks)
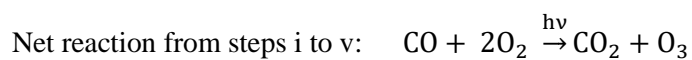
3.2   **(9 marks)**

i) correct.

Statement **S1-S5**	Supporting facts (**R1-R7**)	Supporting Graph(s) (**G1-G9**)
S2	**R1**	**G6, G9 / G4, G7**
S5	**R6**	**G1, G4, G7 / G3, G6, G9**

ii) incorrect.

Statement **S1-S5**	Supporting facts (**R1-R7**)	Supporting Graph(s) (**G1-G9**)
S1	**R4**	**G5, G8**
S3	**R2, R7**	**G1, G3**
S4	**R7, R1**	**G7, G9**

3.3

$O_3 + 2H^+ + 2I^- \rightarrow I_2 + O_2 + H_2O$,
$$I_2 + I^- \rightarrow I_3^-$$
1 mol O_3 = 1 mol I_3^-
Moles of I_3^- produced = 2.6×10^{-8} mol
Concentration of ozone by mass = **211 ppb**

(3.5 marks)
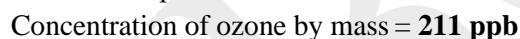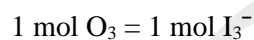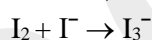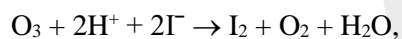
Problem 4   22 marks

Chlorhexidine

4.1   **(1 mark)**

4.2 (1 mark)
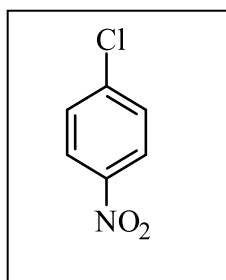
4.3 a. $\boxed{X}$ (1 mark)
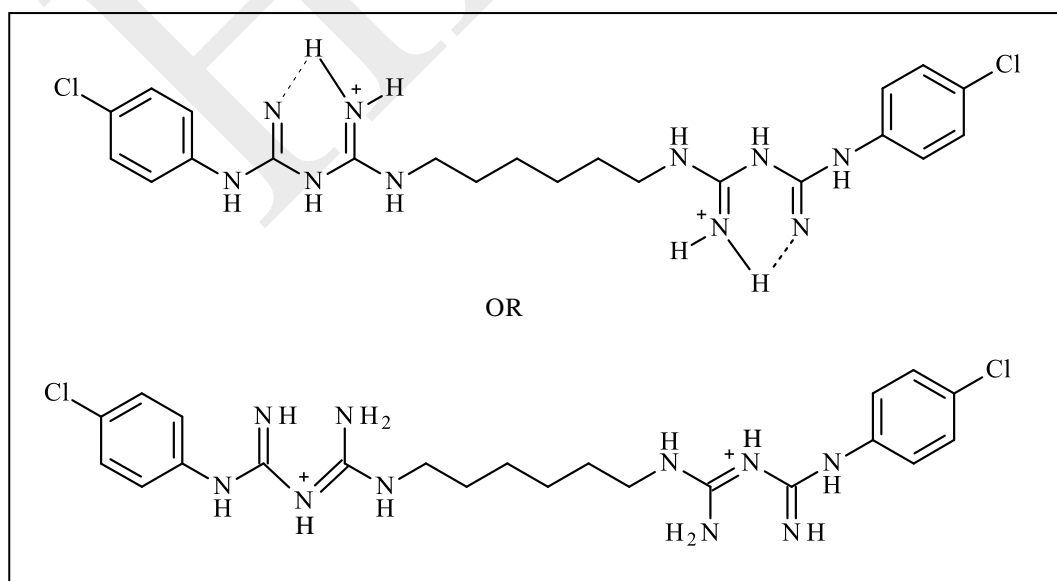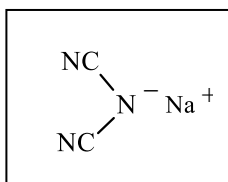
b. $\boxed{}$

c. $\boxed{}$

d. $\boxed{}$

4.4 (1 mark)

4.5 (3.5 marks)

For acetate salt: $ChH_2A_2 \rightleftharpoons [ChH_2{}^{2+}] + 2A^-$

$K_{sp} = [ChH_2{}^{2+}][A^-]^2$,

From dissociation constant, the solubility of ChH_2A_2, s = 0.037 mol/L

$A^- + H^+ \rightleftharpoons HA$

$(0.074 - x)(10^{-7} - x)/x = 1.75 \times 10^{-5}$

$x \ll 0.074$

Hence, change in solubility due to hydrolysis is negligible

Solubility of ChH_2A_2, s = 0.037 mol/L

4.6 (2.5 marks)

Typical aggregate size at this concentration is 2500/898 ~ **3 units**

4.7 (5.5 marks)

(i) 1% solution of NaCl = 10.0/58.44 = 0.17 M.

$K_{sp} = [ChH_2{}^{2+}][Cl^-]^2$

Since concentration of ChH_2G_2, s $\ll$ 0.17

$2.1 \times 10^{-9} = [s][2.89 \times 10^{-2}]$

Thus chloride salt will precipitate and effective concentration of ChH_2G_2 in NaCl solution, s = 0.72×10^{-7} mol/L.

Effectiveness will decrease.

(ii) 0.1% solution of ChH_2G_2 = 1/898 = 0.0011 M

Concentration of acetate ions, x in 0.9 M Acetic acid solution is given by

$x^2/(0.9 - x) = 1.76 \times 10^{-5}$

Ionic product $[ChH_2{}^{2+}][A^-]^2 = 0.0011 \times 0.0039 \times 0.0039 = 1.67 \times 10^{-8}$ which is much less than solubility product of Ch acetate.

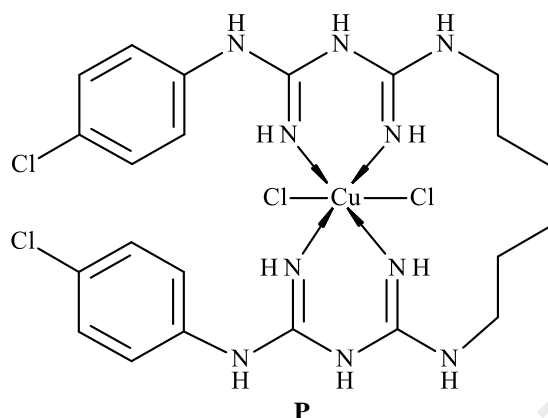**Effectiveness will not decrease.**
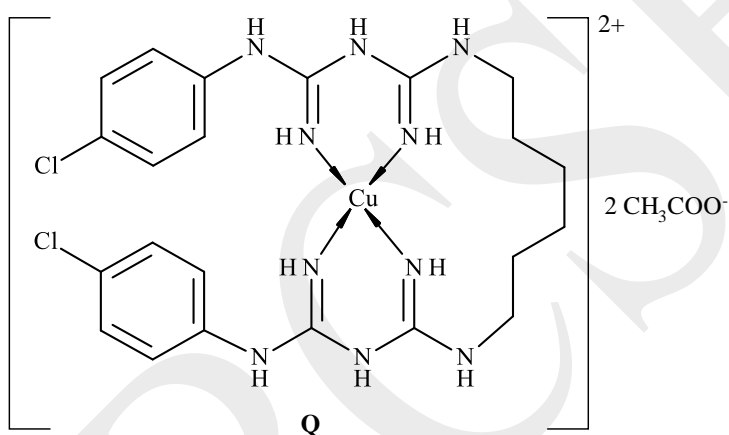
4.8 | b & d,   a & e | **(2 marks)**   **4.9** | NH_2COOH | **(1 mark)**

4.10 (2 marks)

P

Q

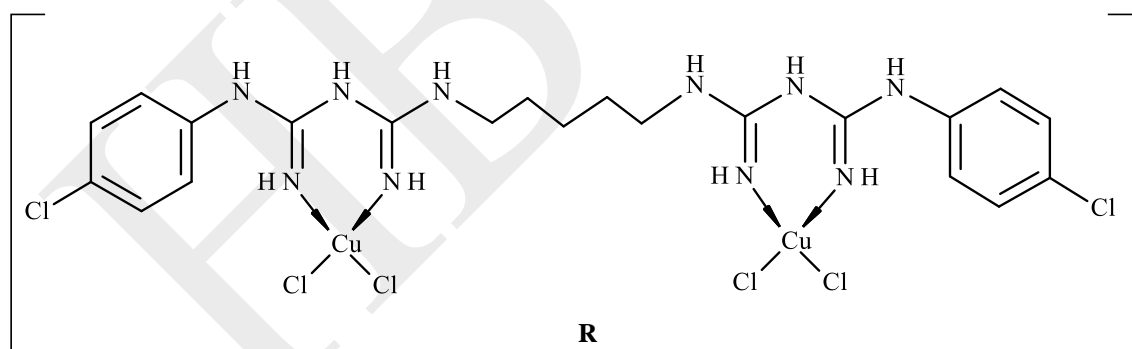**4.11**

R

(1.5 marks)

Problem 5   9 marks

Helium in Rocks

5.1 | Since mass number changes only in α-particle emission,

helium nuclei produced = 8. | **(1 mark)**

5.2 (4 marks)

The decay schemes are as follows-
1. $^{238}U \rightarrow 8\,^4He + {}^{206}Pb$
2. $^{235}U \rightarrow 7\,^4He + {}^{207}Pb$
3. $^{232}Th \rightarrow 6\,^4He + {}^{208}Pb$

The relative production rates $^{238}U : {}^{232}Th : {}^{235}U$

$8 \times [{}^{238}U] \times k_{238}: 6 \times [{}^{232}Th] \times k_{232}: 7 \times [{}^{235}U] \times k_{235}$

$= 1691.2: 418.0: 68.9 = \mathbf{24.5: 6.1: 1}$

5.3 (4 marks)

At STP, He production rate from 1 g $^{238}U = 11.59 \times 10^{-8}\,cm^3\,yr^{-1}$
Similarly, He production rate from 1g $^{232}Th = 2.91 \times 10^{-8}\,cm^3\,yr^{-1}$
Similarly, He production rate from 1g $^{235}U = 0.48 \times 10^{-8}\,cm^3\,yr^{-1}$

Assuming He production rate is constant over the entire residence time,
Residence time of water = Amount of He found per g of rock/ Production rate of He per g of rock

$= \mathbf{1,016,449\ years}$