

# **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.

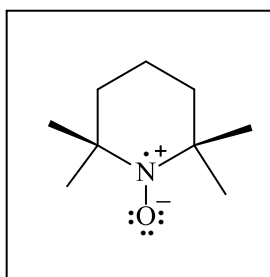
In problems having related sub-parts, consistency of answers of the related sub-parts is also checked in evaluation.

**Problem 1**

**18 marks**

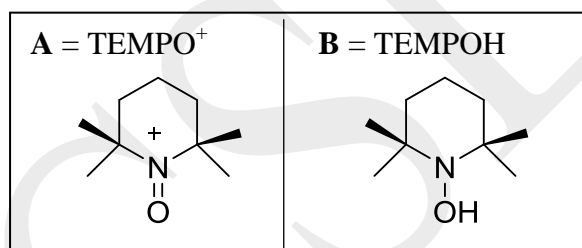
**Persistent radical – TEMPO**

1.1



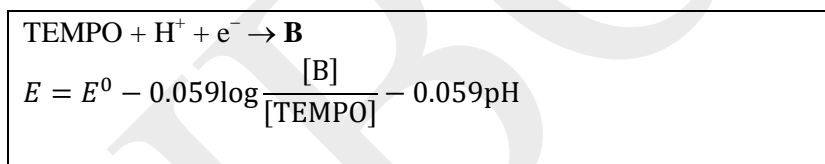
(0.5 mark)

1.2



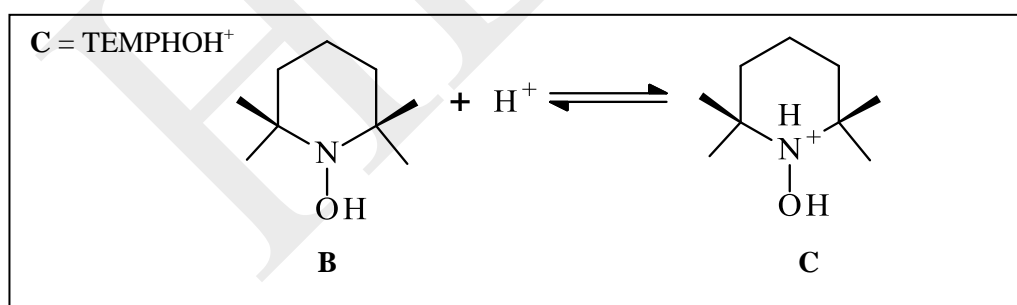
(1 mark)

1.3



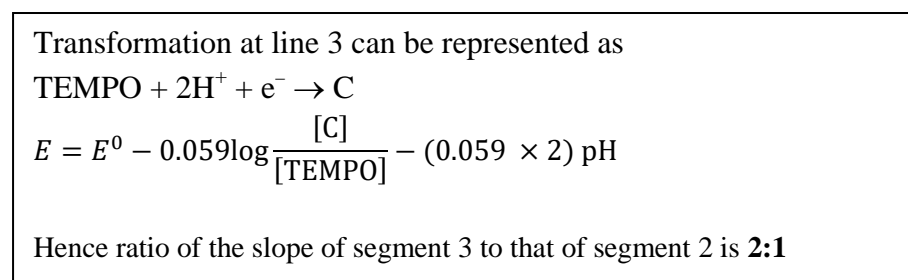
(1.5 marks)

1.4



(1 mark)

1.5



(2 marks)

1.6 The disproportionation reaction is given by:

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

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

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

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

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

**K = 1.31 × 10<sup>5</sup>**

**(4.5 marks)**

1.7  $2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$

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

**(2 marks)**

1.8 

**(1 mark)**

1.9 a) i) pH < 7

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

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

**(2.5 marks)**

ii) pH > 7

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

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

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-hydroxy TEMPO < 4-amino TEMPO

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

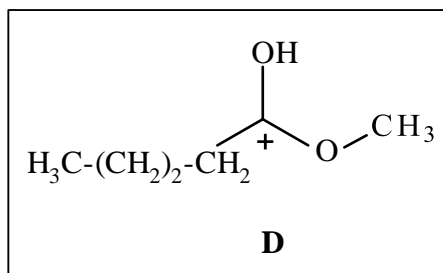
**(1 mark)**

## Problem 2

14 marks

## Esters

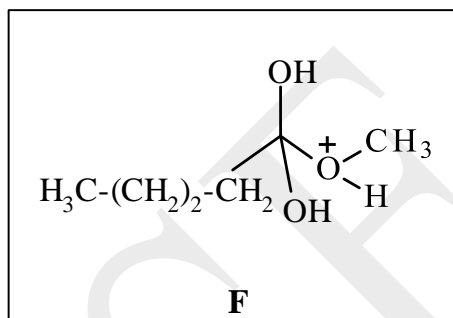
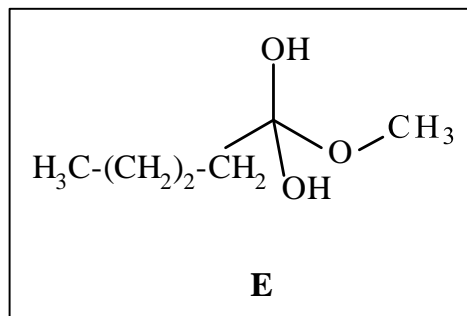
2.1 i)



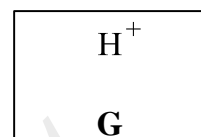
(1 mark)

Appropriate resonance structure will be accepted

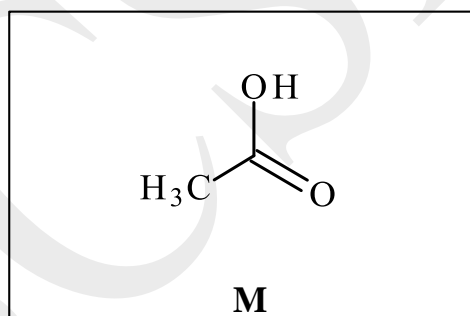
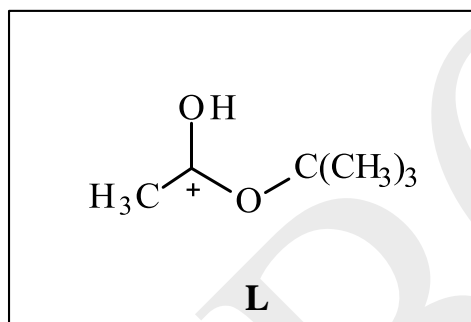
ii)



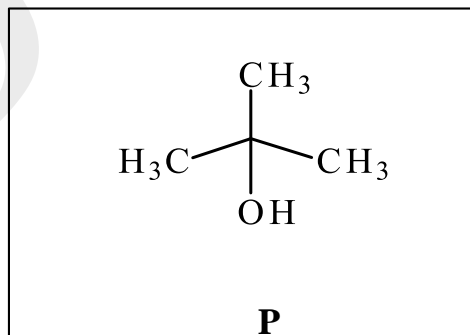
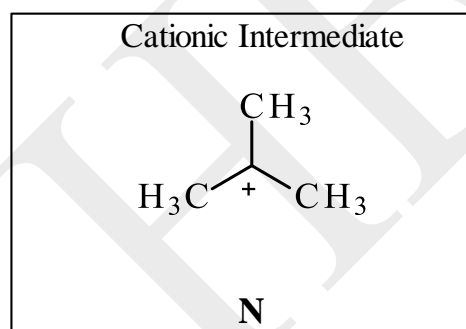
(1.5 marks)



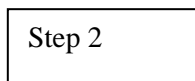
2.2 i)



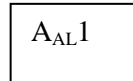
(2 marks)



ii)

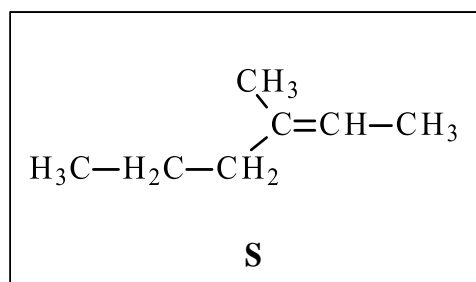
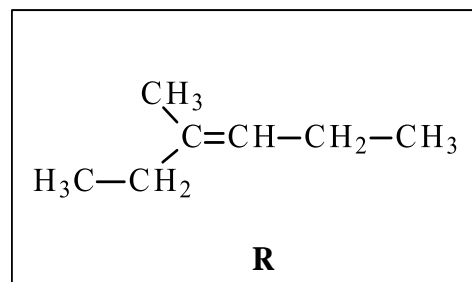


iii)



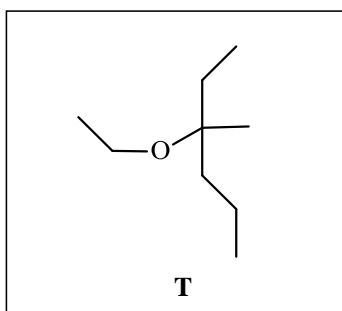
(1.5 marks)

2.3 i)



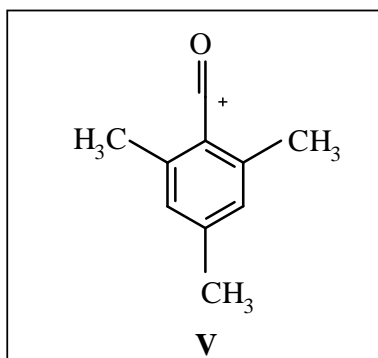
(1.5 marks)

ii)

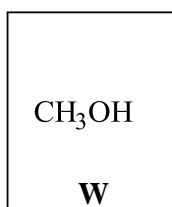


(1 mark)

2.4

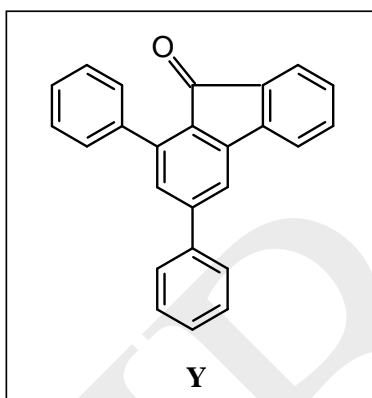


Cationic intermediate



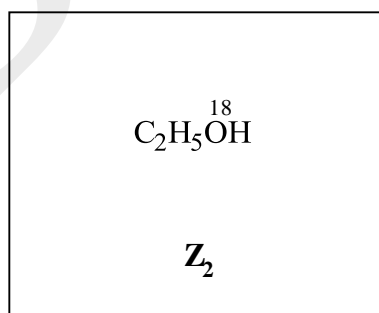
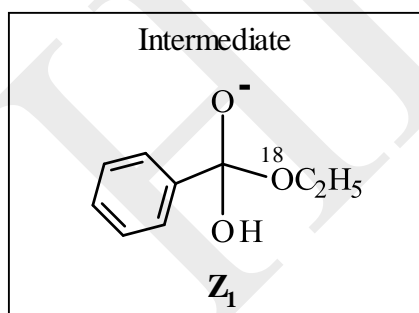
(1.5 marks)

2.5

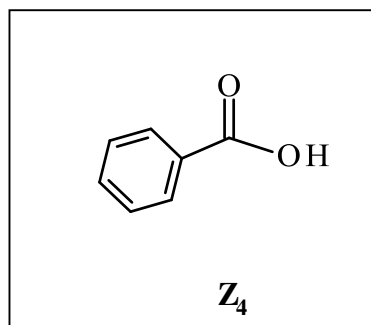
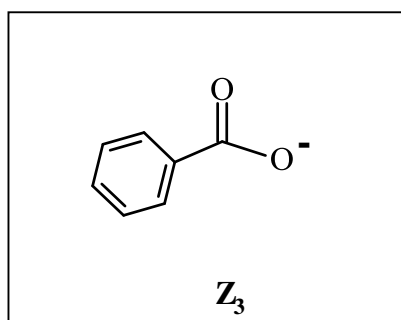


(1 mark)

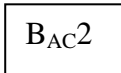
2.6 i)



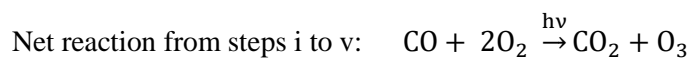
(2.5 marks)



ii)



(0.5 mark)

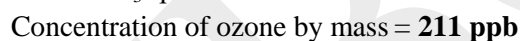
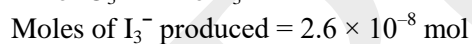
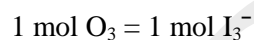
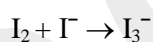
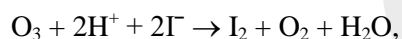
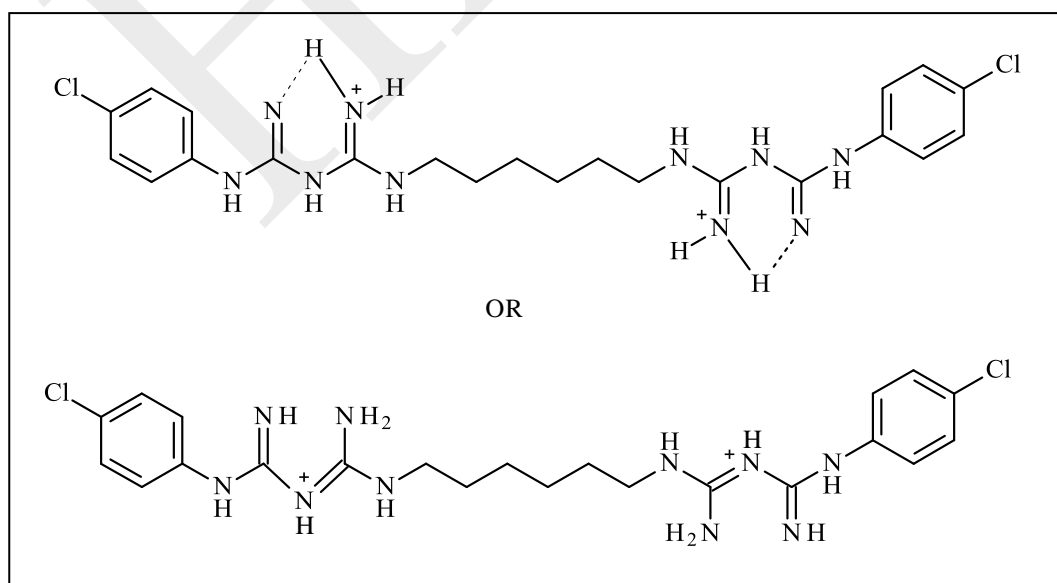
**Problem 3**
**16 marks**
**Ozone in Troposphere**
**3.1** a: CO<sub>2</sub>      b: H<sup>•</sup>      c: O<sub>2</sub>      d: NO<sub>2</sub>      e: OH<sup>•</sup> (3.5 marks)

**3.2** (9 marks)

i) correct.

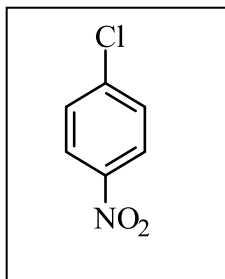
Statement S1-S5	Supporting facts (R1-R7)	Supporting Graph(s) (G1-G9)
S2	R1	G6, G9 / G4, G7
S5	R6	G1, G4, G7 / G3, G6, G9

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** (3.5 marks)

**Problem 4**
**22 marks**
**Chlorhexidine**
**4.1** (1 mark)


4.2



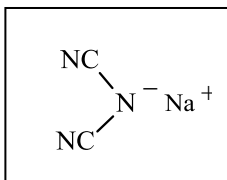
(1 mark)

4.3

- a.
- b.
- c.
- d.

(1 mark)

4.4



(1 mark)

4.5

For acetate salt:  $\text{ChH}_2\text{A}_2 \rightleftharpoons [\text{ChH}_2^{2+}] + 2\text{A}^-$

$$K_{\text{sp}} = [\text{ChH}_2^{2+}][\text{A}^-]^2,$$

From dissociation constant, the solubility of  $\text{ChH}_2\text{A}_2$ ,  $s = 0.037 \text{ mol/L}$



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

$$x \ll 0.074$$

Hence, change in solubility due to hydrolysis is negligible

**Solubility of  $\text{ChH}_2\text{A}_2$ ,  $s = 0.037 \text{ mol/L}$**

(3.5 marks)

4.6

Typical aggregate size at this concentration is  $2500/898 \sim 3 \text{ units}$

(2.5 marks)

4.7

(i) 1% solution of  $\text{NaCl} = 10.0/58.44 = 0.17 \text{ M}$ .

$$K_{\text{sp}} = [\text{ChH}_2^{2+}][\text{Cl}^-]^2$$

Since concentration of  $\text{ChH}_2\text{G}_2$ ,  $s \ll 0.17$

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

Thus chloride salt will precipitate and effective concentration of  $\text{ChH}_2\text{G}_2$  in  $\text{NaCl}$  solution,  $s = 0.72 \times 10^{-7} \text{ mol/L}$ .

**Effectiveness will decrease.**

(ii) 0.1% solution of  $\text{ChH}_2\text{G}_2 = 1/898 = 0.0011 \text{ M}$

Concentration of acetate ions,  $x$  in  $0.9 \text{ M}$  Acetic acid solution is given by

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

Ionic product  $[\text{ChH}_2^{2+}][\text{A}^-]^2 = 0.0011 \times 0.0039 \times 0.0039 = 1.67 \times 10^{-8}$  which is much less than solubility product of  $\text{Ch}$  acetate.

**Effectiveness will not decrease.**

(5.5 marks)

4.8

b & d,

a & e

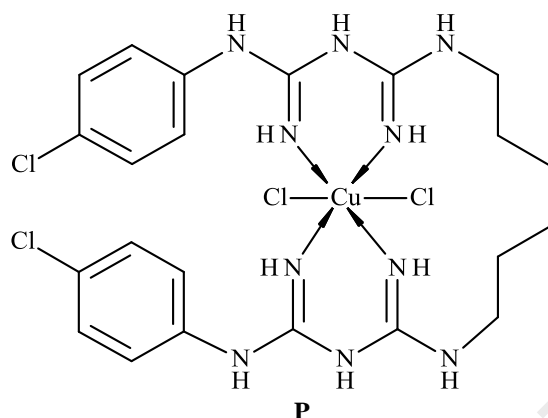
(2 marks)

4.9

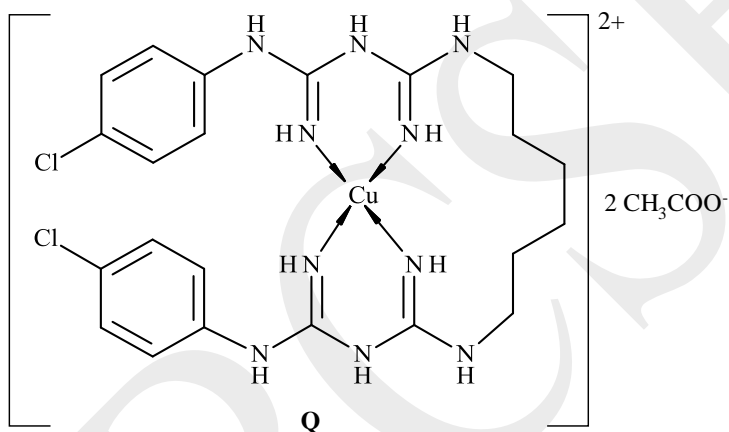
$\text{NH}_2\text{COOH}$

(1 mark)

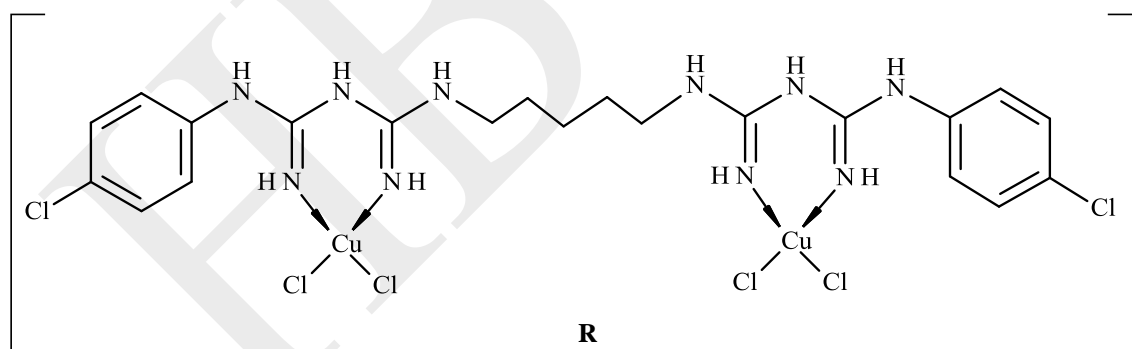
4.10



(2 marks)



4.11



(1.5 marks)

### Problem 5

9 marks

#### Helium in Rocks

5.1

Since mass number changes only in  $\alpha$ -particle emission,  
helium nuclei produced = 8.

(1 mark)



5.2

The decay schemes are as follows-

1.  $^{238}\text{U} \rightarrow 8\ ^4\text{He} + ^{206}\text{Pb}$
2.  $^{235}\text{U} \rightarrow 7\ ^4\text{He} + ^{207}\text{Pb}$
3.  $^{232}\text{Th} \rightarrow 6\ ^4\text{He} + ^{208}\text{Pb}$

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

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

$$= 24.8 : 5.99 : 1 = \mathbf{25 : 6 : 1}$$

(4 marks)

5.3

At STP, He production rate from 1 g  $^{238}\text{U} = 12.72 \times 10^{-8} \text{ cm}^3 \text{ yr}^{-1}$

Similarly, He production rate from 1g  $^{232}\text{Th} = 3.15 \times 10^{-8} \text{ cm}^3 \text{ yr}^{-1}$

Similarly, He production rate from 1g  $^{235}\text{U} = 0.52 \times 10^{-8} \text{ cm}^3 \text{ yr}^{-1}$

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

$$= \mathbf{953314 \text{ years}}$$

(4 marks)