Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
TOTAL	

General Certificate of Education
Advanced Level Examination
June 2011

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 15 June 2011 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

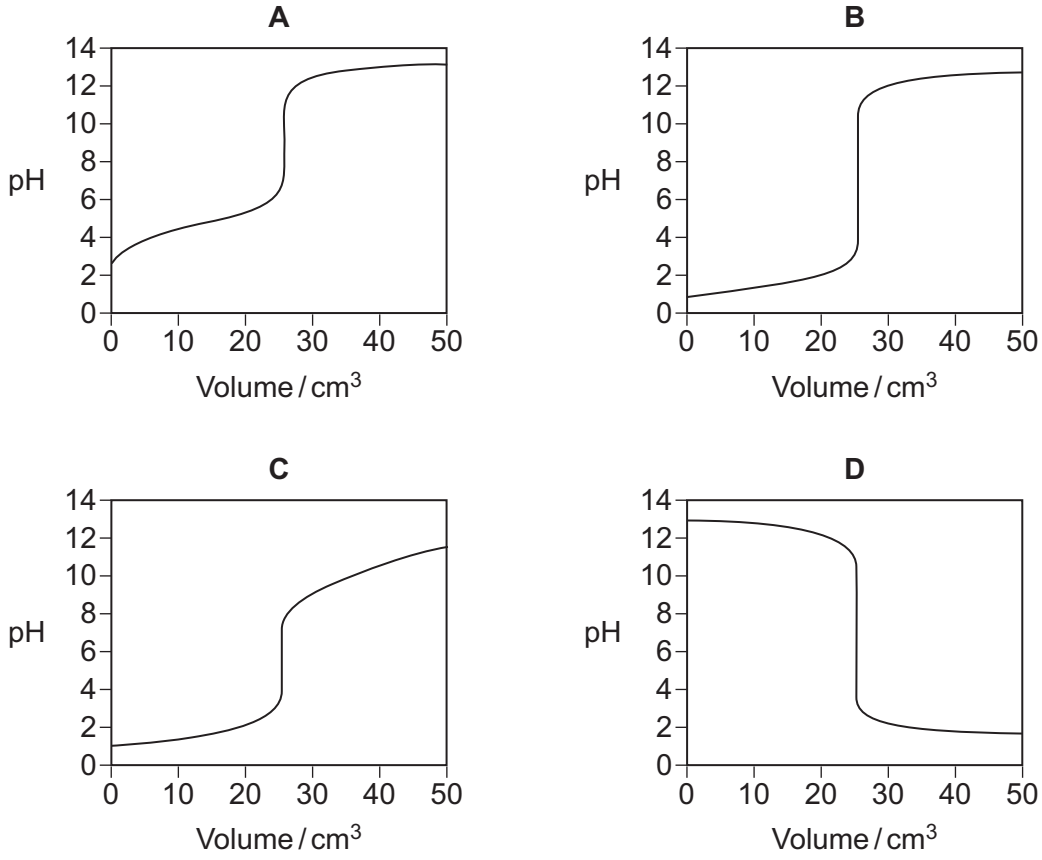
Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

Section A

Answer **all** questions in the spaces provided.

1 Titration curves labelled **A**, **B**, **C** and **D** for combinations of different aqueous solutions of acids and bases are shown below.
All solutions have a concentration of 0.1 mol dm^{-3}.



1 (a) In this part of the question write the appropriate letter in each box.

From the curves **A**, **B**, **C** and **D**, choose the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid ☐

sodium hydroxide to 25 cm^3 of ethanoic acid ☐

nitric acid to 25 cm^3 of potassium hydroxide ☐

(3 marks)

1 (b) A table of acid–base indicators is shown below.
The pH ranges over which the indicators change colour and their colours in acid and alkali are also shown.

Indicator	pH range	Colour in acid	Colour in alkali
Trapaeolin	1.3 – 3.0	red	yellow
Bromocresol green	3.8 – 5.4	yellow	blue
Cresol purple	7.6 – 9.2	yellow	purple
Alizarin yellow	10.1 – 12.0	yellow	orange

1 (b) (i) Select from the table an indicator that could be used in the titration that produces curve **B** but **not** in the titration that produces curve **A**.

.....

(1 mark)

1 (b) (ii) Give the colour change at the end point of the titration that produces curve **D** when cresol purple is used as the indicator.

.....

(1 mark)

5

Turn over for the next question

2 This question is about the pH of some solutions containing potassium hydroxide and ethanoic acid.

Give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for pH.

.....

(1 mark)

2 (a) (ii) Write an expression for the ionic product of water, K_w

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(1 mark)

2 (a) (iii) At 10 °C, a 0.154 mol dm^{-3} solution of potassium hydroxide has a pH of 13.72
Calculate the value of K_w at 10 °C.

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(2 marks)

(Extra space) .....

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2 (b) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

2 (b) (i) Write an expression for K_a for ethanoic acid.

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(1 mark)

2 (b) (ii) Calculate the pH of a 0.154 mol dm^{-3} solution of ethanoic acid at 25 °C.

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(3 marks)

(Extra space) .....

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Question 2 continues on the next page

2 (c) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

2 (c) (i) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

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(4 marks)

(Extra space) .....

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2 (c) (ii) Calculate the pH of the solution formed when 40.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}.

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(4 marks)

(Extra space) .....

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16

Turn over for the next question

3 The following dynamic equilibrium was established at temperature T in a closed container.

$$P(g) + 2Q(g) \rightleftharpoons 2R(g) \qquad \Delta H^{\ominus} = -50\ \text{kJ mol}^{-1}$$

The value of K_c for the reaction was 68.0 $\text{mol}^{-1}\ \text{dm}^3$ when the equilibrium mixture contained 3.82 mol of **P** and 5.24 mol of **R**.

3 (a) Give the meaning of the term *dynamic equilibrium*.

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(2 marks)

(Extra space) .....

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3 (b) Write an expression for K_c for this reaction.

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(1 mark)

3 (c) The volume of the container was 10.0 dm^3.

Calculate the concentration, in mol dm^{-3}, of **Q** in the equilibrium mixture.

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(4 marks)

(Extra space) .....

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3 (d) State the effect, if any, on the equilibrium amount of **P** of increasing the temperature. All other factors are unchanged.

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(1 mark)

3 (e) State the effect, if any, on the equilibrium amount of **P** of using a container of larger volume. All other factors are unchanged.

.....

(1 mark)

3 (f) State the effect, if any, on the value of K_c of increasing the temperature. All other factors are unchanged.

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(1 mark)

3 (g) State the effect, if any, on the value of K_c of using a container of larger volume. All other factors are unchanged.

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(1 mark)

3 (h) Deduce the value of the equilibrium constant, at temperature *T*, for the reaction

$$2R(g) \rightleftharpoons P(g) + 2Q(g)$$

.....

.....

(1 mark)

12

Turn over for the next question

4 The amide or peptide link is found in synthetic polyamides and also in naturally-occurring proteins.

4 (a) (i) Draw the repeating unit of the polyamide formed by the reaction of propanedioic acid with hexane-1,6-diamine.

(2 marks)

4 (a) (ii) In terms of the intermolecular forces between the polymer chains, explain why polyamides can be made into fibres suitable for use in sewing and weaving, whereas polyalkenes usually produce fibres that are too weak for this purpose.

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(3 marks)

(Extra space) .....

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4 (b) (i) Name and outline a mechanism for the reaction of CH_3CH_2COCl with CH_3NH_2

Name of mechanism.....

Mechanism

(5 marks)

4 (b) (ii) Give the name of the product containing an amide linkage that is formed in the reaction in part **4 (b) (i)**.

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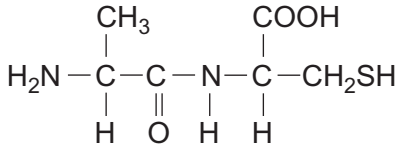
(1 mark)

4 (c) The dipeptide shown below is formed from two different amino acids.

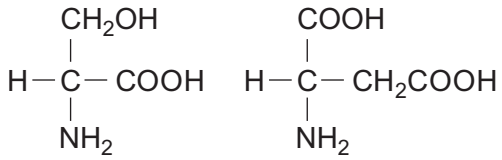


Draw the structure of the alternative dipeptide that could be formed by these two amino acids.

(1 mark)

Question 4 continues on the next page

4 (d) The amino acids serine and aspartic acid are shown below.



serine aspartic acid

4 (d) (i) Give the IUPAC name of serine.

.....

(1 mark)

4 (d) (ii) Draw the structure of the species formed when aspartic acid reacts with aqueous sodium hydroxide.

(1 mark)

4 (d) (iii) Draw the structure of the species formed when serine reacts with dilute hydrochloric acid.

(1 mark)

4 (d) (iv) Draw the structure of the species formed when serine reacts with an excess of bromomethane.

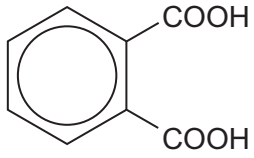
(1 mark)

16

5 Items softened with plasticisers have become an essential part of our modern society.

Compound **S**, shown below, is commonly known as phthalic acid.

Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).



S

5 (a) Give the IUPAC name for phthalic acid.

.....

(1 mark)

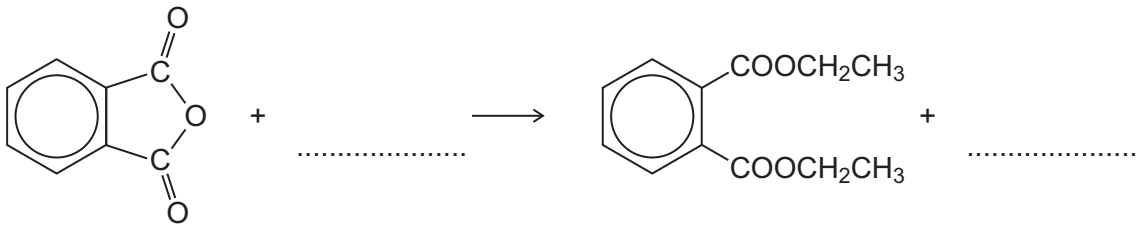
5 (b) Draw the displayed formula of the repeating unit of poly(chloroethene).

(1 mark)

Question 5 continues on the next page

5 (c) The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

5 (c) (i) Complete the following equation showing the formation of DEP from phthalic anhydride.



DEP

(2 marks)

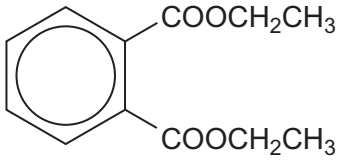
5 (c) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of DEP.

.....

(1 mark)

5 (c) (iii) One of the peaks in the ^{13}C n.m.r. spectrum of DEP is at δ = 62 ppm.
Table 3 on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.



(1 mark)

5 (d) The mass spectrum of DEP includes major peaks at *m*/*z* = 222 (the molecular ion) and at *m*/*z* = 177

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at *m*/*z* = 177

.....

(2 marks)

5 (e) Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

The European Council for Plasticisers and Intermediates is an organisation that represents the manufacturers of plasticisers.

The text below is taken from a document written by the organisation.

'Research demonstrates that phthalates, at current and foreseeable exposure levels, do not pose a risk to human health or to the environment. Experimental evidence shows that phthalates are readily biodegradable and do not persist for long in the environment.'

5 (e) (i) Hydrolysis of DEP in an excess of water was found to follow first order kinetics.

Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

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(1 mark)

5 (e) (ii) Suggest what needs to be done so that the public could feel confident that the research quoted above is reliable.

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(2 marks)

(Extra space) .....

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11

6 (a) In the presence of the catalyst rhodium, the reaction between NO and H_2 occurs according to the following equation.

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

The kinetics of the reaction were investigated and the rate equation was found to be

$$\text{rate} = k[NO]^2[H_2]$$

The initial rate of reaction was 6.2×10^{-6} mol dm^{-3} s^{-1} when the initial concentration of NO was 2.9×10^{-2} mol dm^{-3} and the initial concentration of H_2 was 2.3×10^{-2} mol dm^{-3}.

6 (a) (i) Calculate the value of the rate constant under these conditions and give its units.

Calculation .....

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Units .....

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(3 marks)

6 (a) (ii) Calculate the initial rate of reaction if the experiment is repeated under the same conditions but with the concentrations of NO and of H_2 both doubled from their original values.

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(1 mark)

6 (b) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.

Step **1** $NO + NO \longrightarrow X$

Step **2** $X + H_2 \longrightarrow Y$

Step **3** $Y + H_2 \longrightarrow N_2 + 2H_2O$

Suggest which **one** of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step.....

Explanation .....

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(2 marks)

(Extra space) .....

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6

Turn over for the next question

Section B

Answer **all** questions in the spaces provided.

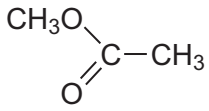
7 Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

7 (a) The following compounds can be distinguished by observing what happens in test-tube reactions.

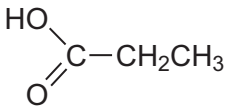
For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

7 (a) (i)



E



F

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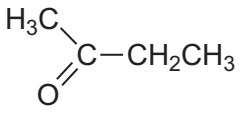
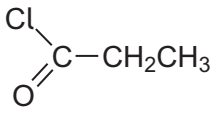
(3 marks)

7 (a) (ii)



G



H

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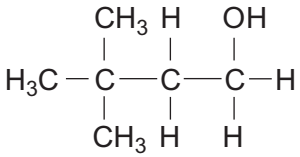
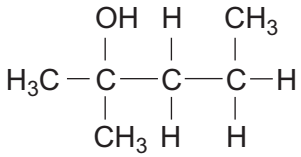
(3 marks)

7 (a) (iii)



J



K

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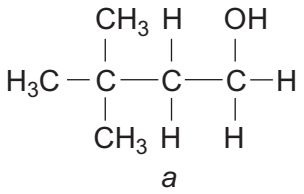
(3 marks)

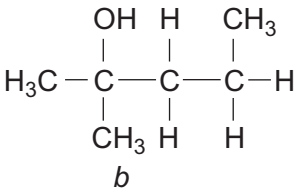
Question 7 continues on the next page

7 (b) Compounds **J** and **K** can also be distinguished using spectroscopic techniques such as ^{1}H n.m.r.



a

J



b

K

7 (b) (i) Name compound **J**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **J**.

State the splitting pattern, if any, of the peak for the protons labelled *a*.

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(3 marks)

7 (b) (ii) Name compound **K**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **K**.

State the splitting pattern, if any, of the peak for the protons labelled *b*.

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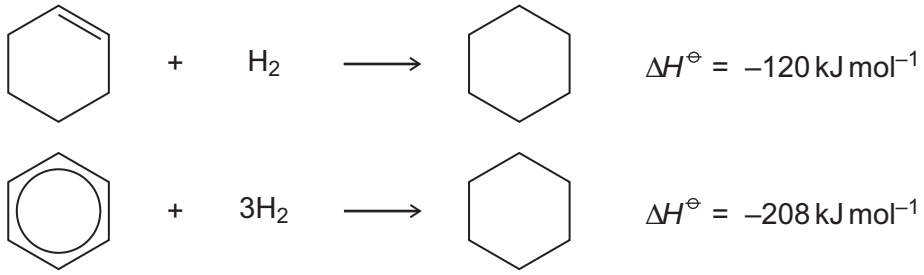
(3 marks)

15

8 The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

8 (a) The molecule cyclohexatriene does not exist and is described as hypothetical. Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



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(4 marks)

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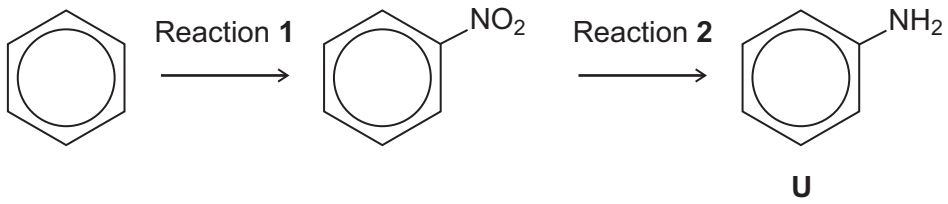
Question 8 continues on the next page

8 (b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



U

The mechanism of Reaction **1** involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction **1**.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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(6 marks)

(Extra space) .....

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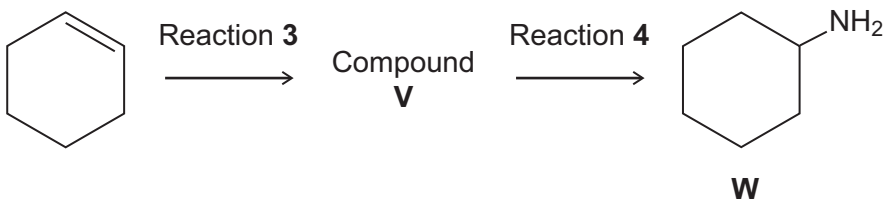
8 (c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



W

Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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(6 marks)

(Extra space) .....

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Question 8 continues on the next page

8 (d) Explain why amine **U** is a weaker base than amine **W**.

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(3 marks)

(Extra space) .....

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19

END OF QUESTIONS