



THE OPEN UNIVERSITY OF SRI LANKA  
B.Sc Degree Programme / Stand Alone Course- Level 5  
Assignment - III (Test) (Kinetics-----) - 2006/2007  
CHU 3124/ CHE 5124 Physical Chemistry  
(1 1/2 hours)

21<sup>st</sup> February 2007

3.30 p.m - 5.00 p.m

Gas constant (R)	= 8.314 J K <sup>-1</sup> mol <sup>-1</sup>
Avogadro constant (N <sub>A</sub> )	= 6.023 × 10 <sup>23</sup> mol <sup>-1</sup>
Faraday constant (F)	= 96,500 C mol <sup>-1</sup>
Planks constant (h)	= 6.63 × 10 <sup>-34</sup> J s
Velocity of light (c)	= 3.0 × 10 <sup>8</sup> m s <sup>-1</sup>
Standard Atmospheric pressure (π)	= 10 <sup>5</sup> Pa (N m <sup>-2</sup> )
log <sub>e</sub> (X)	= 2.303 log <sub>10</sub> (X)

- The **total marks** awarded for this paper is **115**; any one scoring 100 or more would be deemed to have scored 100%; the % marks for the rest would correspond to the total obtained for this paper.
- This paper consists of **4 (four)** MCQ type questions and **3 (three)** structured questions; answers to be written only in the space provided.

Choose the correct answer/s to each of the following questions (1-4) and mark your answer/s with a cross ["X"] in the relevant box provided. No **part marks** will be awarded for any of these four questions.

Consider the following reversible first order reaction to answer **Q 1 and 2**

A  $\longleftrightarrow$  B; k<sub>1</sub> and k<sub>2</sub> are the rate constants for the forward and the backward reactions respectively.

1. The rate of the reaction can be written as

- $-\frac{d[A]}{dt} = k_1[A] + k_2[B]$
- $-\frac{d[A]}{dt} = k_1[B] - k_2[A]$
- $-\frac{d[A]}{dt} = k_1[A] - k_2[B]$
- $-\frac{d[A]}{dt} = k_1[B] + k_2[A]$
- $\frac{d[A]}{dt} = (k_1 + k_2)([A] + [B])$

(05 Marks)

2. The rate of the reaction at equilibrium is expected to be

- equal to the rate of formation of B
- equal to the rate of disappearance of A
- equal to the difference between the rate of formation of B and the rate of disappearance of A.
- zero
- None of the above

(05 Marks)

3. Suppose the rate law for the reaction  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$  is given by  $\text{rate} = k [\text{N}_2\text{O}_2][\text{O}_2]$ .

Which of the following mechanism is most likely to be consistent with this rate law?

- $2\text{NO} \rightarrow \text{N}_2\text{O}_2$  fast ;  $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2$  slow;
- $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
- $\text{N}_2\text{O}_2 + \text{O}_2 + \text{O} \rightarrow \text{N}_2\text{O}_5$
- $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$  fast ;  $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$  slow;
- None of the above

(05 Marks)

4 The following statements refer to an elementary reaction  $2\text{A} + \text{B} \rightarrow \text{P}$ . One or more of these statement/s is/are correct. Choose the correct answer/s and mark with a cross [X] in the relevant box/es

- The rate of the reaction is proportional to  $[\text{A}]^2[\text{B}]$
- The rate of the reaction is proportional to  $[\text{A}][\text{B}]^2$
- The molecularity of the reaction is 2.
- The overall order of the reaction is 3.

(05 Marks)

5. The reaction  $\text{P} \rightarrow \text{Q}$  is a first order reaction (first order with respect to P). The initial concentration of P is  $b$  and the concentration of P is reduced to half its initial value in 5000 seconds at  $27^\circ\text{C}$  and in 1000 seconds at  $37^\circ\text{C}$ . (The Arrhenius constant and the activation energy remains unchanged in the temperature range,  $27^\circ\text{C}$  to  $37^\circ\text{C}$ )

(a) Write down the Arrhenius Equation that relates rate constant to the activation energy and absolute temperature.

**(05 Marks)**

(b) Write down the general rate equation (differential form) using the standard symbols and hence, derive the expression for half-life ( $t_{1/2}$ ) in terms of the rate constant.

**(05 Marks)**

(c) Calculate

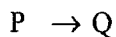
(i) the two rate constants of the reaction (in  $\text{s}^{-1}$ ) at  $27^\circ\text{C}$  and  $37^\circ\text{C}$

(ii) the time (in minutes) required for the concentration to be reduced to one eighth the initial value at  $37^\circ\text{C}$

- (iii) the activation energy (in  $\text{kJ mol}^{-1}$ ) for this reaction in the given temperature range.

(20 Marks)

6.. A kinetic experiment was carried out to study the effect of temperature on the rate constant for a hypothetical first order reaction of the form



The following data are reported.

Temp. / $^{\circ}\text{C}$	22	32	42	52	62
$k \times 10^3/\text{min}^{-1}$	5.00	7.37	10.46	15.00	20.61

Assuming that this data satisfies/fits the relationship given below (exactly)

$$\ln k = -m \left( \frac{1}{T} \right) + c$$

where  $k$  = rate constant,  $T$  = absolute temperature and  $m$  and  $c$  are constants,

- (i) carry out an **appropriate tabulation** of data required to plot a graph.



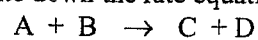
- (ii) Based on the tabulated data, calculate the **gradient and intercept**.

(25 Marks)

7. (a) The balanced equation  $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  represents the decomposition of  $\text{N}_2\text{O}_5(\text{g})$  into  $\text{NO}_2(\text{g})$  and  $\text{O}_2(\text{g})$ . If the rate of decomposition of  $\text{N}_2\text{O}_5(\text{g})$  is  $4.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ , what is the expected rate of appearance of  $\text{NO}_2(\text{g})$  and the rate of appearance of  $\text{O}_2(\text{g})$ ?

(15 Marks)

(b) (i) Write down the rate equation for the following elementary reaction



(ii) Obtain the integrated form of the differential equation you have written down in b(i) above. Assume that the initial concentrations of both A and B are equal to  $p$ .

(iii) If  $p = 0.1 \text{ mol dm}^{-3}$  and the rate constant =  $5.0 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , calculate the concentration of A at the instant reaction has proceeded for 10 minutes.

(25 marks)