



KENYATTA UNIVERSITY
UNIVERSITY EXAMINATIONS 2011/2012
SECOND SEMESTER EXAMINATION FOR THE DEGREE OF MASTER OF
SCIENCE

SCH 542: ADVANCED CHEMICAL KINETICS

DATE: Friday, 30th March, 2012

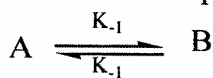
TIME: 9.00 a.m. – 12.00 p.m.

INSTRUCTIONS:

Answer all Questions: Marks may be awarded for illustrative diagrams, chemical or mathematical equations where necessary

Information: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08205 \text{ L-atm mol}^{-1} \text{ K}^{-1}$, k (Boltzmann constant) = $1.38 \times 10^{-23} \text{ J K}^{-1}$

1. Define the following terms
2. Consider two opposing first order reactions

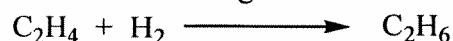


with k_1 and k_{-1} being the rate constants for forward and reverse reactions respectively. Taking x to be the amount of A that reacts at a particular time t and x_e to be the amount of reacted A at equilibrium, show that

$$\ln \left(\frac{x_e}{x_e - x} \right) = \frac{k_1 t}{x_e}$$

8 mks

3. Consider the following reaction at 628 K and 1 atmosphere



Given that $\text{H}_2 = 2.016 \times 10^{-27} \text{ kg}$, $\text{C}_2\text{H}_4 = 28.05 \times 10^{-27} \text{ kg}$ and $\sigma_{\text{H}_2} = 0.27 \text{ nm}$ and $\sigma_{\text{C}_2\text{H}_4} = 0.64 \text{ nm}$, estimate

- a. The pre-exponential factor
- b. The rate and rate constant
- c. The steric factor for the reaction

20 mks

4. The pre-exponential factor for the gas phase decomposition of ozone at 298 K and low pressures is $2.3 \times 10^{13} \text{ L mol}^{-1} \text{ s}^{-1}$ and its activation energy is 30.0 kJ mol^{-1} . Calculate the
 - a. Entropy of activation
 - b. Enthalpy of activation
 - c. The Gibbs free energy of activation
5. Enzymes catalyse a number of reactions
 - a. Give a simple enzyme – substrate reaction mechanism

9 mks

4 mks

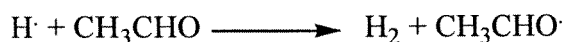
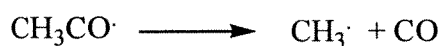
b. Show that $\frac{1}{v} = \frac{K}{v_{\max} [S]} + \frac{1}{v_{\max}}$ where symbols used have their usual meaning

10 mks

6. For the decomposition of acetaldehyde,



the following mechanism was proposed



a. Using the various factors of a mechanism, show that the mechanism is plausible
6 mks

b. Show that the mechanism supports the rate reaction

$$\frac{-d[\text{CH}_3\text{CHO}]}{dt} = K[\text{CH}_3\text{CHO}]$$

10 mks

c. Identify the intermediates in the mechanism

4 mks

d. Identify the various steps of a chain reaction with explanations from the mechanism

6 mks

7. When acetone was photolysed at 56°C with 313 nm radiation for 23000 seconds, only 5.23×10^{19} molecules were decomposed. If 8.52×10^{-3} joules of radiation were absorbed per second, calculate the quantum yield
6 mks

8. The solution polymerization of methyl methacrylate using benzoyl peroxide as initiator and benzene as solvent follows the rate equation of the form
 $\text{Rate} = K[\text{M}]^x[\text{I}]^y$

where M and I refer to monomer and initiator respectively. From the following set of data, determine x and y. Outline a kinetic scheme which would explain these results. Identify the various aspects of the kinetic scheme given

[I]	Rate	[M]	Rate
0.04	0.95	0.02	0.40
0.1	1.60	0.03	0.66
0.15	2.00	0.04	0.88
0.2	2.23	0.05	1.06
0.3	2.90	0.06	1.30
0.4	3.21	0.07	1.52
		0.08	1.72

20 mks