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 fro ullustrative diagrams, chemical or mathematical equations where necessary

Information: R = 8.314Jmol^{-1} K^{-1} = 0.08205 L-atm mol^{-1}K^{-1}, k (Boltzmann constant) = 1.38 x $^{10-23}$ JK^{-1}

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

   $A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$

   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

   $$\text{Ln}\left(\frac{x_e}{x_e - x}\right) = \frac{K_1 at}{x_e}$$ **8 mks**

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

   $C_2H_4 + H_2 \longrightarrow C_2H_6$

   Given that $H_2 = 2.016 \times 10^{-27}$ kg, $C_2H_4 = 28.05 \times 10^{-27}$ kg and $\sigma_{H_2} = 0.27$nm and $\sigma_{C_2H_4} = 0.64$nm, estimate

   a. The pre-exponential factor
   b. The rate and rate constant
   c. The sterric 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 x 10^{13} Lmol^{-1}s^{-1} and its activation energy is 30.0 kJmol^{-1}. Calculate the
   a. Entropy of activation
   b. Enthalpy of activation
   c. The Gibb's free energy of activation **9 mks**
5. Enzymes catalyse a number of reactions
   a. Give a simple enzyme – substrate reaction mechanism **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 acetalydehyde,
   $CH_3CHO \longrightarrow CH_4 + CO$
   the following mechanism was proposed

$$CH_3CHO \longrightarrow CH_3\cdot + CHO\cdot$$

$$CH_3\cdot + CH_3CHO \longrightarrow CH_4 + CH_3CO\cdot$$

$$CH_3CO\cdot \longrightarrow CH_3\cdot + CO$$

$$CHO\cdot \longrightarrow H\cdot + CO$$

$$H\cdot + CH_3CHO \longrightarrow H_2 + CH_3CHO\cdot$$

$$2CH_3\cdot \longrightarrow C_2H_6$$

   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
   $\frac{-d[CH_3CHO]}{dt} = K[CH_3CHO]$ **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 ^{0}C with 313 nm radiation for 23000 seconds, only 5.23 x 10 ^{19} molecules were decomposed. If 8.52 x 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
   Rate = $K[M]^x[I]^y$

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