CEM01A3/CEM3A10 JUNE/JULY 2022 EXAMINATION B

EXAMINER:	**PROF K. MALLICK**
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DATE:	**JUNE/JULY 2022**
TIME:	**3 HOURS**
MARKS:	**100**

INSTRUCTIONS:

1. This paper consists of 6 pages.
2. There are **10 QUESTIONS** in this examination paper.
3. Calculators are allowed

QUESTION 1:

[10]

For a unimolecular surface reaction, consider a single reactant (A) chemisorbed on surface atom (S) of the solid and subsequently breaks up into products. Prove and calculate the following statements:

(i) Rate of the reaction is proportional to the partial pressure of A and the reaction is first order with respect to A
(ii) At low pressure, the reaction is the first order with respect to A and rate is proportional to the partial pressure of A
(iii) At high pressure, the reaction rate is independent of pressure and the reaction is zero order with respect to 'A'.

QUESTION 2: **[10]**

Show the rate of adsorption follows the first order reaction kinetics with respect to the partial pressure of the gas molecule on the substrate.

QUESTION 3: **10 [3+3+2+2]**

[a] The optical rotations of sucrose in 0.5 M HCl at 35 °C at various time intervals are given below. Show that the reaction is of first order:

Time (minutes)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	-11.1

[b] In an enzyme solution, sucrose undergoes fermentation. If 0.10 M solution of sucrose is reduced to 0.05 M in 10 hours and to 0.025 M in 20 hours, what is the order of the reaction and what is the rate constant?

[c] The half-life of the following homogenous gaseous reaction obeys first order kinetics, is 8 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$

[d] Show that for a first order reaction, the time required for 99.9% completion of the reaction is 10 times that required for 50% completion.

QUESTION 4: **10 [3+4+3]**

[a] Write the three fundamental differences regarding the assumptions of Langmuir and Brunauer, Emmett and Teller (BET) adsorption isotherm.

[d] Graphically test the applicability of Langmuir isotherm the following data referring the adsorption of gas on charcoal.

P	100	200	500	900
x/m	1.56	1.97	2.29	2.41

From the graph, calculate the value of K and k_1

Langmuir imperial equation:

$$\frac{P}{\frac{x}{m}} = \frac{1}{k_1 K} + \frac{P}{k_1}$$

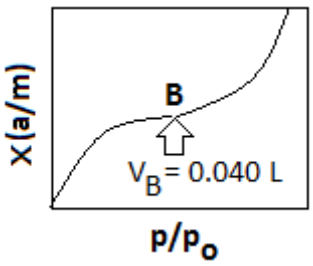
$$K = Adsorption\ coefficient$$

$$k_1 = Proportionality\ constant$$

[c] The following data have been obtained for the adsorption of nitrogen on silica at 77 K. P_o is the vapour pressure of liquid nitrogen at this temperature.

p/p_0	0.05	0.15	0.25	0.40	0.60	0.80
ml. adsorbed /gram of silica	30	38	42.5	48	55	108

Calculate the surface area of silica in terms $m^2.g^{-1}$ by Brunauer, Emmett and Teller (BET) method at the point B (see the figure below, assume the area of N_2 molecule as 16.2 $Å^2$).



QUESTION 5:

10 [3+3+4]

[a] Use the following data and show that the following reaction is second order:

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

$Initial\ concentration\ of\ CH_3COOC_2H_5 = NaOH = 10\ moles/litre$

Time (min.) [t]	0	15	25	35	55
(a-x) [a = initial concentration and x = concentration after time (t)]	10	4.9	3.6	2.9	2.1

[b] Decomposition of a certain gas follows the second order reaction. Suppose the initial concentration of the gas is 5×10^{-4} moles/litre and 40% of it decomposed in 50 mim. What is the value of velocity constant of the decomposition reaction?

[c] For the following second order reaction:

$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$

Calculate the time required for the hydrolysis of 90% ester

if the initial concentration of the reaction in the reaction mixture are:

(1) 0.05 M ester+0.1 M of base

(2) 0.1 M ester+0.1 M of base

QUESTION 6:

10 [4+3+3]

(a) Using the Arrhenius equation, calculate activation energy and pre-exponential factor for a reaction in which rate constants at 500K and 700K are 0.02 sec^{-1} and 0.07 sec^{-1} respectively.

(b) The rate constant of a second order reaction is 5.70 x 10^{-5} $dm^3\ mol^{-1}\ sec^{-1}$ at 25 °C and 1.64 x 10^{-4} $dm^3\ mol^{-1}\ sec^{-1}$ at 40°C. Calculate the activation energy and pre-exponential factor.

(c) Calculate the activation energy of a reaction whose rate constant is tripled by a 10°C rise in temperature in the vicinity of 27°C

QUESTION 7:

10 [6+4]

(a) Using the Lambert-Beer law show the absorbance is directly proportional to the molar absorption coefficient and the path-length of the solution.

(b) The molar extinction coefficient of phenanthroline complex of iron (II) is 12.0 $dm^3\ mol^{-1}\ cm^{-1}$ and the minimum detectable absorbance is 0.01. Calculate the minimum concentration of the complex that can be detected in a Lambert-Beer law cell of path length 1.0 cm.

QUESTION 8:

10 [2+3+3+2]

(a) Calculate the energy associated with (a) one photon; (b) one Einstein of radiation of wavelength 8000 Å.
h = 6.62 x 10^{-27} erg-sec; c = 3x 10^{10} cm sec^{-1}.

(b) When a substance A was exposed to light, 2×10^{-3} mole of it reacted in 20 minutes and 4 seconds. In the same time A absorbed 2.0 x 10^6 photons of light per second. Calculate the quantum yield of the reaction. (Avogadro number N= 6.02 x 10^{23})

(c) When irradiated with light of 5000 Å wavelength, 1 x 10^{-4} mole of a substance is decomposed. How many photons are absorbed during the reaction if its quantum yield is 10?

(d) A monochromatic radiation is incident on a solution of 0.05 molar concentration of an absorbing substance. The intensity of the radiation is reduced to one-fourth of the initial value after passing through 10 cm length of the solution. Calculate the molar extinction coefficient of the substance.

QUESTION 9:

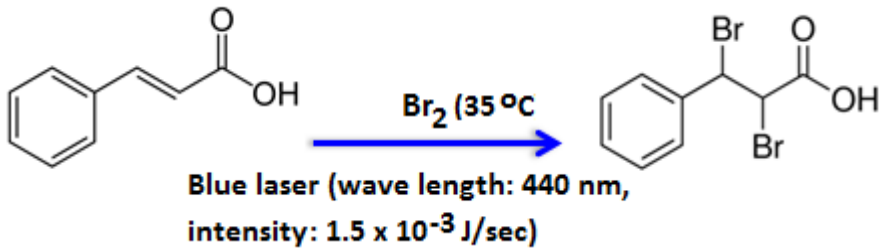
[10]

Based on the Jablonski diagram, explain the various photo-physical process, such as, non-radiative transition and radiative transitions (fluorescence and phosphorescence).

QUESTION 10:

10 [5+5]

(a) In the following reaction an exposure of blue laser for the duration of 20 minutes causes a decrease of 0.075 millimole of bromine concentration. The solution absorbed 80% of the light passing through it. Calculate the quantum yield of the reaction.



(b) Give the reasons: The quantum yield value deviate from unity in most of the photochemical reactions.