

## SUPPLEMENTARY / SPECIAL EXAMINATIONS

## FOURTH YEAR EXAMINATION FOR THE AWARD OF BACHELOR DEGREE IN

## CHEM 323: CHEMICAL KINETIC

STREAMS:
TIME: 2 HOURS
DAY/DATE: WEDNESDAY 18/11/2020
8.30 A.M - 10.30 A.M.

## INSTRUCTIONS:

- Answer all questions


## QUESTION ONE (30 MARKS)

1a (i). For the reaction

$$
2 \mathrm{NO}+2 \mathrm{H}_{2} \xrightarrow{\mathrm{~K}} \mathrm{~N}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

Following mechanism has been proposed:
$\mathrm{NO}+\mathrm{NO} \rightleftharpoons \mathrm{N}_{2} \mathrm{O}_{2}$; with $\mathrm{K}_{1}$ as the rate of forward reaction and $\mathrm{K}_{-1}$ as the rate of the reverse reaction

$$
\begin{aligned}
& \mathrm{N}_{2} \mathrm{O}_{2} \xrightarrow{\mathrm{~K}_{2}} \mathrm{~N}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \\
& \mathrm{~N}_{2} \mathrm{O}+\mathrm{H}_{2} \xrightarrow{K_{3}} \mathrm{~N}_{2}+\mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

On the basis of the above mechanism, derive the rate law of $N_{2}$
(ii) Consider the parallel reaction


In an experiment, it was observed that $80 \%$ decomposition of A takes place in 40 minutes and analysis of product showed that $60 \%$ of B and $40 \%$ of C are present. Calculate $\mathrm{K}_{1}$ and $\mathrm{K}_{2}$.
(b) Write short notes on catalytic poisoning
(c). Predict how the total pressure varies during the gas phase decomposition in a constant volume container
(4 marks)
$2 \mathrm{~N}_{2} \mathrm{O}_{5(\mathrm{~g})} \rightarrow 4 \mathrm{NO}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})}$

## QUESTION TWO (20 MARKS)

$2 \mathrm{a}(\mathrm{i})$. An actinometer uses a solution of $\mathrm{K}_{3}\left[\mathrm{Fe}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$ in which $\mathrm{Fe}^{3+}$ is reduced and the oxalate ion is oxidized. Assuming $\emptyset=1.24$ at 310 nm . Calculate the intensity of the incident light which produces $1.3 \times 10^{-5}$ moles of $\mathrm{Fe}^{2+}$ in 36.5 min .
(9 marks)
(ii). The same light source is used to irradiate a sample of $\mathrm{CH}_{2} \mathrm{CO}$ for a period of 15.2 min . If the quantum yield of $\mathrm{C}_{2} \mathrm{H}_{2}$ is 1.0 and that of CO is 2.0 , determine the amount of each gas produced by the photochemical reaction. $\left(\mathrm{h}=6.62608 \times 10^{-34} \mathrm{JS}, \mathrm{NA}=6.02214 \times 10^{23} \mathrm{~mol}^{-1}\right.$, $\mathrm{C}=2.99792558 \times 10^{8} \mathrm{~ms}^{-1}, 1 \mathrm{~nm}=10^{-9} \mathrm{M}$ )
(5 marks)
(b) An aqueous solution of a compound A of concentration $10^{-3}$ moles/litre absorbs $50 \%$ of incident radiation in a cell length 1 cm and another compound B of concentration $2 \times 10^{-3}$ moles/litre absorbs $60 \%$ of the incident radiation at a particular wavelength. Calculate the percentage absorbed in a solution containing $10^{-3}$ moles/litre of A and Beach in the same cell at the wavelength.

QUESTION THREE (20 MARKS)
3a. A undergoes two simultaneous reactions to produce Band C according to $A \xrightarrow{K_{1}} B, A \xrightarrow{K_{2}} C$,
Show that Ea, the observed activation energy for the disappearance of A is given by the equation:
$E a=\frac{K_{1} E_{1}+K_{2} E_{2}}{K_{1}+K_{2}}$
(7 marks)
(b). The decomposition of PH 3 at 950 K is observed and noting the change in total pressure as a function of time. The reaction is;
$4 \mathrm{PH}_{3(\mathrm{~g})} \rightarrow P_{4(\mathrm{~g})}+6 \mathrm{H}_{2(\mathrm{~g})}$
The following measurements were made on the system containing only $\mathrm{PH}_{3}$ initially

| Time (sec) | 0 | 50 | 100 |
| :--- | :--- | :--- | :--- |
| $\mathbf{P}_{\text {(total) }} \mathbf{m m H g}$ | 200 | 299 | 332 |

Show that, it is a first order reaction and also calculate the rate constant
(c) Derive the Michaelis- Menten equation

