

## SECTION A <br> Answer all questions in this section

## QUESTION 1

(a) State any two limitations of classical mechanics which necessitated the birth of quantum mechanics
(b) Explain the following terms i) quantum

> ii) wave particle duality [4 marks]
(c) State first three postulates of quantum mechanics [3 marks]
(d) Write brief notes on
i) unimolecular reactions
ii) bimolecular reactions
iii) rate equation
iv) steady state approximation
v) mechanism of reaction
(e) Describe the instrumentation and applications of the following spectroscopic techniques
i. UV-Vis
ii. FTIR
iii. iii) Raman Spectroscopy

## SECTION B

Answer any three questions in this section

## QUESTION 2

In this question you may want to use the following constants:

$$
1 \mathrm{eV}=1.602 \times 10^{-19} \mathrm{~J}, \mathrm{~h}=6.63 \times 10^{-34} \mathrm{Js} \text {, mass of an electron }=9.11 \times 10 \mathrm{~kg}
$$

a) During a lecture on photoelectric effect, the lecturer gave this statement as part of the introduction; "One of the factors that affect photoelectric emission is the threshold frequency of the metal" Explain the meaning of the terms
i) photoelectric equation
ii) Photoelectric emission
iii) Threshold frequency
[6 marks]
b) Suggest any other factor besides threshold frequency which affect photoelectric emission
c) i) Briefly explain the three laws of photoelectric emission ii) Give any four applications of photoelectric emission
d) The work function of zinc, silver and sodium are $4.31 \mathrm{eV}, 4.73 \mathrm{eV}$ and 2.28 eV respectively. Use the photoelectric equation to calculate
i) Maximum kinetic energy of an electron ejected from silver by a 3.13 $\mathrm{x} 10^{15} \mathrm{hz} \quad$ [3 marks]
ii) Maximum kinetic energy and velocity of the ejected electrons from zinc using 275 nm photon
[3 marks]
iii) The threshold frequency for the emission of photoelectrons from the surface of sodium metal, and hence the maximum wavelength of light that can cause photoemission.
[5 marks]

## QUESTION 3

a) Sketch a graph to show how rate of reaction depends on concentration in a first order reaction.
[3 marks]
b) State the Arrhenius equation and explain each term present in the equation
[4 marks]
c) The rate constants for the reaction $\mathbf{A}_{\mathbf{2}}+\mathbf{B}_{\mathbf{2}}=\mathbf{2} \mathbf{A B}$ were measured at five different temperatures. The results are shown in Table 2

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## Table 2

| Experiment | Rate constant $(\mathrm{k}) / \mathrm{s}^{-1}$ | Temperature $/ \mathrm{K}$ |
| :---: | :---: | :---: |
| 1 | $1.25 \times 10^{-9}$ | 250 |
| 2 | $2.27 \times 10^{-8}$ | 303 |
| 3 | $6.81 \times 10^{-7}$ | 400 |
| 4 | $3.73 \times 10^{-6}$ | 500 |
| 5 | $4.11 \times 10^{-7}$ | 667 |

i) Rewrite Arrhenius equation using natural logarithms
ii) Produce a completed table of $\ln \mathrm{k}$ and $1 / \mathrm{T}$ using the data from the table
iii) Plot a graph of $\ln \mathrm{K}$ against $1 / \mathrm{T}$
iv) Use the graph to deduce the activation energy of the reaction [13 marks]
d) In another experiment the rate constant of the reaction $\mathbf{H}_{\mathbf{2}}+\mathbf{I}_{\mathbf{2}}=\mathbf{2 H I}$ was measured at two different temperatures.
At $\mathbf{6 0 0} \mathrm{K}, \mathrm{k}=2.15 \times 10^{-7} \mathrm{~s}^{-1}$ At $\mathbf{7 0 0} \mathbf{K}, \mathrm{k}=2.39 \times 10^{-6} \mathrm{~s}^{-1}$
Calculate the activation energy of the reaction

## Question 4

a) What do you understand by the term complex reaction? [2 marks]
b) Compare and contrast the Linderman and the RRKM theories
c) Describe
i) Chain reactions
ii) Reaction intermediate
iii) Elementary step of a mechanism
iv) Adiabatic modes of vibration
v) Active modes of vibration
d) Steady state approximation can be used to deduce the rate law from elementary steps. Given that
$A+M=A^{*}+M k_{1}$ Activation of $A$ via collisions

$$
\begin{aligned}
& \mathrm{A}^{*}+\mathrm{M}=\mathrm{A}+\mathrm{M} \mathrm{k}_{-1} \text { Deactivation of } \mathrm{A}^{*} \text { via collisions } \\
& \mathrm{A}^{*}=\mathrm{P}
\end{aligned} \mathrm{k}_{2} \text { Spontaneous decomposition of } \mathrm{A}^{*} .
$$

(where M is any particle which can be an inert particle, a molecule of the product P or another particle of A ), use steady state approximation to deduce that
i) $\quad\left[A^{*}\right]=k_{1}[A][M] / k_{-1}[M]+k_{2}$
ii) $\quad \mathrm{dP} / \mathrm{dt}=\mathrm{k}_{2} \mathrm{k}_{1}[\mathrm{~A}][\mathrm{M}] / \mathrm{k}_{-1}[\mathrm{M}]+\mathrm{k}_{2}$

## QUESTION 5

a) State Beer's law
b) Describe the concept of molecular spectroscopy
c) An aqueous solution of substance X was analysed using UV-VIS at a wavelength of 275 nm at which molar absorptivity is $€=8400 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$. The pathlength was 1 cm . the absorbance ( $\mathrm{A}_{275}$ ) was found to be 70 . What was the concentration of X in the sample? [5 marks]
d) During the analysis of dye concentration in a sample, a set of five standards were analysed at 500 nm to produce a calibration curve before running the sample. The equation of the line of best fit was found to be
$y=1.65 x-0.05$ where $y$ is the absorbance, $x$ is the concentration. If the sample gave an absorbance reading of 0.85 , what will be the concentration of the dye in the sample?
e) Calculate the number of degrees of freedom for the following molecules
i) $\quad \mathrm{CO}_{2}$
ii) $\mathrm{SO}_{2}$
iii) $\mathrm{CH}_{4}$
iv) HCN

## END OF EXAM

