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## CHEMISTRY 225 SEMESTER 04-2011 SECTION 2 (EVENING) TEST NO. 1: REACTION KINETICS

## For full marks you must show your working in numerical questions and display results to the correct number of significant figures.

1) Using the axes below, sketch an energy profile diagram for a simple one-step reaction, labelling the axes, and marking reactants, products, $\mathrm{E}_{\mathrm{a}}$, and the transition state, on your diagram.

2) The effect of temperature on reaction rate can be calculated using the Arrhenius equation

$$
k=A e^{\frac{-E_{a}}{R T}}
$$

which may be related to a Boltzmann distribution of molecular energies at (increasing) temperatures $\mathrm{T}_{1}$ and $\mathrm{T}_{2}$ as shown below:

a) Mark the activation energy, $\mathrm{E}_{\mathrm{a}}$, for a reaction on the graph above and use it to explain why the rates of chemical reactions are highly temperature dependent.
The red area to the right of $\mathrm{E}_{\mathrm{a}}$ shows the proportion of molecules with kinetic energy greater than or equal to $\mathrm{E}_{\mathrm{a}}$ at $\mathrm{T}_{1}$. It shows the proportion of molecules which can react on collision at $\mathrm{T}_{1}$. The area is much larger at temperature $\mathrm{T}_{2}$ (green and red area together) than at $\mathrm{T}_{1}$ meaning that the rate is much higher at higher temperature.
b) What do we call substances which are used up in one step of the mechanism of a reaction but reformed in a later step?
These are catalysts.
3) In the reaction

$$
\begin{equation*}
5 \mathrm{Fe}^{2+}(9 \mathrm{aq})+\mathrm{MnO}_{4}^{-}(\mathrm{aq})+16 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow 5 \mathrm{Fe}^{3+}(\mathrm{aq})+\mathrm{Mn}^{2+}(\mathrm{aq})+8 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \tag{2}
\end{equation*}
$$

the initial rate of reaction with respect to $\mathrm{Fe}^{2+}$ is $0.30 \mathrm{Ms}^{-1}$. Calculate
a) the initial rate of reaction with respect to $\mathrm{H}_{2} \mathrm{O}$.

The initial rate of reaction with respect to $\mathrm{H}_{2} \mathrm{O}=\frac{8}{5} \times 0.30=\underline{\underline{0.48 M s^{-1}}}$
4) The reaction

$$
3 \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{C}+3 \mathrm{D}
$$

has the following initial rates at a given temperature.

| Experiment | $[\mathbf{A}] /$ <br> $\mathbf{M}$ | $[\mathbf{B}]$ | Initial Rate of <br> $\mathbf{M}$ |
| :---: | :---: | :---: | :---: |
| i | 0.630 | 0.122 | 0.306 |
| ii | 0.210 | 0.122 | 0.0340 |
| iii | 0.210 | 0.244 | 0.0340 |
| iv | 0.105 | 0.488 | $?$ |

a) Determine the order of the reaction with respect to $A$ and $B$, showing your reasoning.

Since $R=k[A]^{m}[B]^{n}$

$$
\begin{aligned}
& \therefore \frac{R_{i i}}{R_{i}}=\frac{k\left([A]_{i i}\right)^{m}\left([B]_{i i}\right)^{n}}{k\left([A]_{i}\right)^{m}\left([B]_{i}\right)^{n}}=\left(\frac{[A]_{i i}}{[A]_{i}}\right)^{m} \text { since other terms cancel. } \\
& \therefore \frac{0.306}{0.0340}=\left(\frac{0.630}{0.210}\right)^{m} \\
& \therefore 9=3^{m} \\
& \therefore m=2
\end{aligned}
$$

Since $R=k[A]^{m}[B]^{n}$
$\therefore \frac{R_{i i i}}{R_{i i}}=\frac{k\left([A]_{i i}\right)^{m}\left([B]_{i i i}\right)^{n}}{k\left([A]_{i i}\right)^{m}\left([B]_{i i}\right)^{n}}=\left(\frac{[B]_{i i i}}{[B]_{i i}}\right)^{n}$ since other term s cancel.
$\therefore \frac{0.0340}{0.0340}=\left(\frac{0.244}{0.122}\right)^{n}$

$$
\therefore 1=2^{n}
$$

$$
\begin{equation*}
\therefore m=0 \tag{1}
\end{equation*}
$$

b) Write down the rate equation for the reaction
$R=k[A]^{2}[B]^{0}$ or $R=k[A]^{2}$
c) Determine the rate constant for the reaction.
$k=\frac{R}{[A]^{2}}=\frac{0.306}{(0.630)^{2}}=0.770975 \approx \underline{\underline{0.771 \mathrm{M}^{-1} s^{-1}}}$ to 3 s.f.
For experiment (iv), calculate the initial rate of disappearance of B.
$R=k[A]^{2}=0.770975 \times(0.105)^{2}=\underline{\underline{0.00850 \mathrm{Ms}^{-1}}}$
d) Could the reaction $3 \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{C}+3 \mathrm{D}$ occur in a single elementary step? Explain your answer.

This reaction could not occur in one elementary step because it would have to involve the collision of 4 particles. Collisions between 4 particles are extremely rare and so cannot be invoked as elementary steps in mechanisms since they would result in unobservably slow reactions.

