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## CHEMISTRY 225 SEMESTER 04-2016 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 single step reaction, labelling the axes, and marking reactants, products, $\Delta \mathrm{E}$, the activation energy $\left(\mathrm{E}_{\mathrm{a}}\right)$ and the transition state/activated complex, 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 $\mathrm{T}_{1}, \mathrm{~T}_{2}$, and $\mathrm{T}_{3}$ as shown below:

a) Mark the activation energy, $E_{a}$, for a reaction on the graph and use it to explain why the rates of chemical reactions are highly temperature dependent.

The proportion of molecules with at least $\mathrm{E}_{\mathrm{a}}$, is given by the area under the curve to the right of the red line. At $T_{1}$ it is virtually zero and almost no reaction occurs. At (higher) $T_{2}$, this proportion is given by the yellow area on the graph. These molecules have sufficient energy to react. At the (highest) $T_{3}$, the proportion is given by the sum of the yellow and green areas, and is much greater so far more molecules can react.

What do we call substances which bring about a reduction in $\mathrm{E}_{\mathrm{a}}$ for a particular reaction?
Catalysts
3) In the reaction

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

the initial rate of reaction with respect to $\mathrm{Fe}^{2+}, \mathrm{R}_{\mathrm{i}}\left(\mathrm{Fe}^{2+}\right)$, is $0 \cdot 30 \mathrm{Ms}^{-1}$. Calculate:
a) the initial rate of reaction with respect to $\mathrm{H}_{2} \mathrm{O}, \mathrm{R}_{\mathrm{i}}\left(\mathrm{H}_{2} \mathrm{O}\right)$.

From the equation, $\mathrm{R}_{\mathrm{i}}\left(\mathrm{H}_{2} \mathrm{O}\right)=(8 / 5) \times \mathrm{R}_{\mathrm{i}}\left(\mathrm{Fe}^{2+}\right)=(8 / 5) \times 0.30 \mathrm{Ms}^{-1}$
$\therefore \mathrm{R}_{\mathrm{i}}\left(\mathrm{H}_{2} \mathrm{O}\right)=0.48 \mathrm{Ms}^{-1}$
4) The reaction
$3 \mathrm{~A}+2 \mathrm{~B}+\mathrm{C} \rightarrow \mathrm{D}+3 \mathrm{E}$
has the following initial rates at a given temperature.

| Experiment | $[\mathbf{A}]$ <br> $/ \mathbf{M}$ | $[\mathbf{B}]$ <br> $\mathbf{M}$ | $[\mathbf{C}]$ <br> $/ \mathbf{M}$ | Initial Rate of <br> disappearance $\mathbf{~ o f ~}$ <br> $\mathbf{B} / \mathbf{M s}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0.630 | 0.122 | 0.152 | $\mathrm{R}_{1}=0.306$ |
| 2 | 0.210 | 0.122 | 0.152 | $\mathrm{R}_{2}=0.0340$ |
| 3 | 0.210 | 0.244 | 0.152 | $\mathrm{R}_{3}=0.0680$ |
| 4 | 0.105 | 0.488 | 0.152 | $\mathrm{R}_{4}=?$ |
| 5 | 0.630 | 0.122 | 0.304 | $\mathrm{R}_{5}=0.306$ |

a) Determine the order of the reaction with respect to $\mathrm{A}, \mathrm{B}$ and C .
(Note that this table format is a very convenient way of answering the question.)

| $[\mathrm{B}] \&[\mathrm{C}]$ constant | [A] \& [C] constant |  | $[\mathrm{A}] \&[\mathrm{~B}]$ constant |  |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{R}_{1} / \mathrm{R}_{2}=$ $[\mathrm{A}]_{1} /[\mathrm{A}]_{2}=$ <br> $0.306 / 0.03$ $0.630 / 0.21$ <br> $40=9$ $0=3$ | $\mathrm{R}_{3} / \mathrm{R}_{2}=$ $0.0680 / 0.0$ $340=2$ | $[\mathrm{B}]_{3} /[\mathrm{B}]_{2}=$ $0.244 / 0.12$ $2=2$ | $\begin{gathered} \mathrm{R}_{5} / \mathrm{R}_{1}= \\ 0.306 / 0.30 \\ 6=1 \end{gathered}$ | $\begin{gathered} {[\mathrm{C}]_{5} /[\mathrm{C}]_{1}=} \\ 0.304 / 0.15 \\ 2=2 \end{gathered}$ |
| Since $9=3^{2}$, order w.r.t. A is 2 | Since $2=2^{1}$ | w.r.t. B is 1 | Since $1=$ | $r$ w.r.t. to C is |

b) Write down the rate equation for the reaction

Rate $=\mathrm{k}[\mathrm{A}]^{2}[\mathrm{~B}][\mathrm{C}]^{0}\left(\right.$ or Rate $\left.=\mathrm{k}[\mathrm{A}]^{2}[\mathrm{~B}]\right)$
c) Calculate the rate constant for the reaction.

From the rate equation, $\mathrm{k}=$ Rate $/\left([\mathrm{A}]^{2}[\mathrm{~B}]\right)$
Using the data from run 1 , we have $\mathrm{k}=0.306 /\left(0.630^{2} \times 0.122\right)=6.3194 \ldots=6.32 \mathrm{M}^{-2} \mathrm{~s}^{-1}$ to 3 s.f.
d) For experiment (4), calculate the initial rate of disappearance of $B, R_{4}$.
$\mathrm{R}_{4}=\mathrm{k}[\mathrm{A}]^{2}[B]=6.3194 \times 0.105^{2} \times 0.488=0.340 \mathrm{Ms}^{-1}$ to 3 s.f.
(Note that an unrounded value for k is used in the calculation.)
e) Could the equation $3 \mathrm{~A}+2 \mathrm{~B}+\mathrm{C} \rightarrow \mathrm{D}+3 \mathrm{E}$ represent an elementary step? Explain your answer.

This equation could not represent an elementary step, since if it did, it would represent the simultaneous collision of $3+2+1=6$ molecules. This is extremely improbable - even 3 body collisions are rare.

