# AP CHEMISTRY

## TOPIC 8: KINETICS, REVIEW,

Day 105:

- Reactant Order
- Rates Laws
- First-Order Reactions
- Half-Life
- Second-Order Reactions
- Reaction Mechanisms
- Rate-Determining Step
- Arrhenius Equation
- Catalysts

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1. The reaction

$$A + B \rightarrow C + D$$

using the data below, determine the orders for all three reactants, the rate law, and the value of the rate constant.

| Experiment | [ A ] | [ B ] | Initial Rate ( $M$ sec$^{-1}$ ) |
|---|---|---|---|
| 1 | 0.10 | 0.15 | 2.5 |
| 2 | 0.20 | 0.15 | 5.0 |
| 3 | 0.092 | 0.386 | 15.23 |

a) What is the rate law?

$$\text{Rate} = k\,[\text{ A }]^{\text{m}}\,[\text{ B }]^{\text{n}}$$

$$\frac{Rate_{Exp\ 2}}{Rate_{Exp\ 1}} = \frac{5.0}{2.5} = 2$$

$$\frac{Rate_{Exp\ 2}}{Rate_{Exp\ 1}} = \frac{k\left[\ 0.20\ M\ \right]^m\left[\ 0.15\ M\ \right]^n}{k\left[\ 0.10\ M\ \right]^m\left[\ 0.15\ M\ \right]^n} = 2 \quad ; \quad \frac{\left[\ 0.20\ M\ \right]^m}{\left[\ 0.10\ M\ \right]^m} = 2 \quad ; \quad 2.0^{\text{m}} = 2$$

$$\boldsymbol{m = 1}$$

$$\frac{Rate_{Exp\ 3}}{Rate_{Exp\ 1}} = \frac{15.23}{2.5} = 6.092 \quad ; \quad \frac{Rate_{Exp\ 3}}{Rate_{Exp\ 1}} = \frac{k\left[\ 0.092\ M\ \right]^1\left[\ 0.386\ M\ \right]^n}{k\left[\ 0.10\ M\ \right]^1\left[\ 0.15\ M\ \right]^n} = 6.092$$

$$6.092 = \left(\ 0.92\ \right)\frac{\left[\ 0.386\ M\ \right]^n}{\left[\ 0.15\ M\ \right]^n} \quad ; \quad \frac{6.092}{0.92} = 6.622 = \frac{\left[\ 0.386\ M\ \right]^n}{\left[\ 0.15\ M\ \right]^n} \quad ; 2.573^{\text{n}} = 6.622$$

$$\boldsymbol{n = 2}$$

$$\text{Rate} = k\,[\text{ A }]\,[\text{ B }]^2$$

b) What is the value of the rate constant?

$$\text{Rate} = k\,[\text{ A }]\,[\text{ B }]^2$$

$$k = \frac{Rate}{\left[\ A\ \right]\left[\ B\ \right]^2} = \frac{15.23\ M}{\left(\ 0.092\ M\right)\left(\text{sec}\right)\left(\ 0.386\ M\right)^2} = 1.1\times10^3\ M^{-2}\ \text{sec}^{-1}$$

2. A certain first-order reaction is 31.6 % complete in 31.6 seconds. What are the rate constant and the half-life for this process?

*[ A ] = 68.4% of [ A ]$_0$ or [ A ] = 0.684 [ A ]$_0$*

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt\,, \quad \ln\left(\frac{0.684}{1.00}\right) = -k\ (\ 31.6\ \ \text{sec}\ )$$

$$k = \frac{-0.380}{-31.6\ \ \text{sec}} = 1.20\times 10^{-2}\ \ \text{sec}^{-1}$$

$$Half-life \qquad t_{1/2} = \frac{0.693(\text{sec})}{1.20\times 10^{-2}} = 57.7\ \ \text{sec}$$

4. A first-order reaction is 72.3% complete in 12 seconds.

a) Calculate the rate constant.
b) What is the value at the half-life.
c) How long did it take for the reaction to go to 20 % completion.

***a)***

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt\,, \quad \ln\left(\frac{0.277}{1.00}\right) = -k\ (\ 12\ \ \text{sec}\ )$$

$$k = \frac{\ln(0.277)}{-12\ \ \text{sec}} = 0.107\ \ \text{sec}^{-1}$$

***b)*** 

$$\textbf{\textit{Half – life}} \qquad t_{1/2} = \frac{0.693(\text{sec})}{0.107} = 6.48\ \ \text{sec}$$

***c) 25% consumed, 20% remains, how much time is required for this reaction:***

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt\,, \quad \ln\left(\frac{0.80}{1.00}\right) = -(\ 0.107\ \ \text{sec}^{-1}\ )\ t$$

$$t = \frac{\ln(0.80)(\text{sec})}{-0.107} = 2.09\ \ \text{sec}$$

5. (Past AP Question) An environmental concern is the depletion of $O_3$ in Earth's upper atmosphere, where $O_3$ is normally in equilibrium with $O_2$ and O. A proposed mechanism for the depletion of $O_3$ in the upper atmosphere is shown below:

| | |
|---|---|
| Step I | $O_3 + Cl \rightarrow O_2 + ClO$ |
| Step II | $ClO + O \rightarrow Cl + O_2$ |

a) Write a balanced equation for the overall reaction represented by Step I and Step II above.

$$\boldsymbol{O_3 + O \rightarrow 2\,O_2}$$

b) Clearly identify the catalyst in the mechanism above. Justify your answer.

***Cl is the catalyst in the reaction. It is a reactant in Step I and reappears as a product in Step II (the last step). Again, a catalyst MUST "return" to its original status.***

c) Clearly identify the intermediate in the mechanism above. Justify your answer.

***ClO is the intermediate in the reaction. It is a product in Step I and reappears as a reactant in Step II***

d) If the rate law for the overall reaction is found to be, Rate = $k$ [ $O_3$ ] [ Cl ], determine the following.

i) The overall order of the reaction.

***Overall order is 1 + 1 = 2***

ii) Appropriate units for the rate constant, $k$

$$k = \frac{Rate}{\left[\, O_3 \,\right]\left[\, Cl \,\right]} = \frac{M\ time^{-1}}{M \times M} = M^{-1}\ time^{-1}$$

iii) The rate-determining step of the reaction, along with justification for your answer.

***The reaction rate is affected by the concentrations of [ $O_3$ ] and [ Cl ], both appearing only in step I. Also, if the rate-determining step was the second step, oxygen [ O ] would appear in the rate law.***