

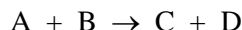
AP CHEMISTRY

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

1. The reaction



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?

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

$$\frac{\text{Rate}_{\text{Exp 2}}}{\text{Rate}_{\text{Exp 1}}} = \frac{5.0}{2.5} = 2$$

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

$$m = 1$$

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

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

$$n = 2$$

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

b) What is the value of the rate constant?

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

$$k = \frac{\text{Rate}}{[A] [B]^2} = \frac{15.23 M}{(0.092 M) (\text{sec}) (0.386 M)^2} = 1.1 \times 10^3 M^{-2} \text{ sec}^{-1}$$

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?

$$[A] = 68.4\% \text{ of } [A]_0 \text{ or } [A] = 0.684 [A]_0$$

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

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

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

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

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

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

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

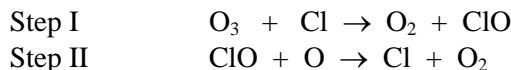
$$b) \quad \text{Half - life} \quad t_{1/2} = \frac{0.693(\text{sec})}{0.107} = 6.48 \text{ sec}$$

- 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:



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



- 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, $\text{Rate} = k [O_3] [Cl]$, determine the following.

- i) The overall order of the reaction.

$$\text{Overall order is } 1 + 1 = 2$$

- ii) Appropriate units for the rate constant, k

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

- 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.