

Chemical Kinetics: Rates of Reaction

STUDY LIST From Paul Groves

I can...

Reaction Rates

- give the correct units to describe the rate of a reaction.

$$\text{Rate} = \frac{\Delta[\text{chemical}]}{\Delta\text{time}} \quad \text{Units} = \frac{M}{s}, \text{ or } \text{molL}^{-1}\text{s}^{-1}$$

- discuss the rate as the rate of **disappearance** of reactant or the rate of **appearance** of product.

- Watch your signs because $-\Delta[\text{Reactants}] = \Delta[\text{Products}]$

- use **coefficients** to change one rate to another (“rate in terms of..”)

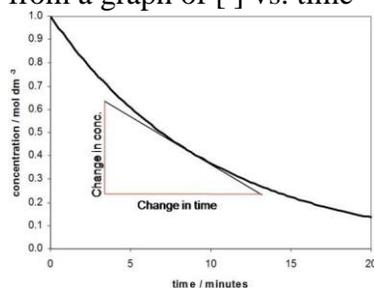


$$-\frac{1}{2} \frac{\Delta[A]}{\Delta t} = -\frac{1}{3} \frac{\Delta[B]}{\Delta t} = \frac{1}{4} \frac{\Delta[C]}{\Delta t}$$

- list ways to speed up a reaction

- Increase **concentration** of reactants
- Increase **temperature** of the rxn
- Increase **surface area**
- Add a **catalyst**

- determine the **average rate** of a reaction as well as the **instantaneous rate** of a reaction from a graph of [] vs. time



Example – to find the rate at 8min, find the slope of the tangent line at 8min.

- describe a catalyst as a substance that speeds up a reaction without getting used up, and describe how a catalyst works.

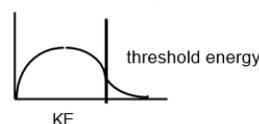
- Provides an alternate pathway with a lower activation energy.
- Helps orient the molecules for proper collisions.

- determine the order of the reaction by graphical methods. Use the graph to find the value of k.

- Look for the straight line plots to determine order if needed
 - $C \rightarrow []$ vs $t = 0^{\text{th}}$ order, slope = $-k$
 - $N \rightarrow \ln []$ vs $t = 1^{\text{st}}$ order, slope = $-k$
 - $R \rightarrow 1/[]$ vs $t = 2^{\text{nd}}$ order, slope = k

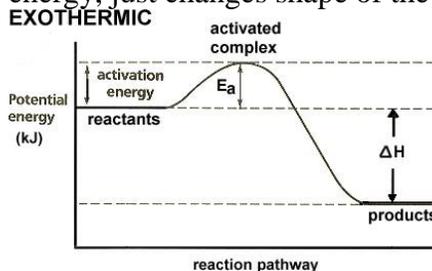
KE & PE Diagrams

- draw a kinetic energy distribution



- sketch the change in the KE distribution if the reactants are warmed or cooled.

- state that the only thing that moves the threshold energy is adding a catalyst. Temperature does not shift the threshold energy, just changes shape of the curve.



- Explain that a catalyst lowers the E_a by changing the way the reaction occurs.

Half Life

- determine the half-life of a chemical from graphical data, or in a word problem.

- use the integrated rate law to solve half-life problems involving in-between times.

- $\ln \frac{[A]_0}{[A]_t} = kt$
- Special case of half life
 - $\ln(2) = 0.693 = k_{t/2}$

Rate Laws:

- write the rough rate law to show how the rate of a reaction depends on concentration.
Ex: $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
Rate = $k [\text{N}_2]^x [\text{H}_2]^y$
- determine the order of reaction with respect to a chemical using the method of initial rates by inspection.
- determine orders of reactions using the mathematical method of initial rates.
- solve for the specific rate constant, k , and determine the correct units.

Reaction Mechanisms:

- explain that a reaction often occurs in several “elementary steps” that often involve only two particles at a time.
- combine the elementary steps in a mechanism to identify the overall reaction, the intermediates, and a catalyst.
- state that the slowest step in a mechanism is called the “rate determining step” and is linked to the rate law.
- give an example of a chain reaction mechanism for $\text{H}_2 + \text{Cl}_2$ or for the destruction of ozone (O_3) by stratospheric chlorine atoms.
- label steps in a chain reaction mechanism as initiation, propagation, and termination steps.

Reaction Order--Graphical Method:

- identify the integrated rate laws for zero, first, and second order reactions.
- explain that the integrated rate laws can be set into the form “ $y = mx + b$ ” which means that a graph indicate the order of reaction and the value of the rate constant, k .

- state the straight-line graph that is identified with each reaction order.
- use the slope of the straight-line graph to determine the value of k .

Arrhenius Equation:

- use the Arrhenius equation to calculate the rate constant, k , using $R = 8.31 \text{ J/mol K}$.
- graphically or algebraically determine the activation energy, E_a , from rate or k data at different temperatures.
- explain that a rate increase with temperature means that the rate constant, k , has increased proportionately.
- explain that the slope of a graph of $\ln k$ vs. $1/T = -E_a/R$.

Chain Reaction Mechanisms:

- cite two examples of chain reaction mechanisms and label the elementary steps as initiation, propagation, and termination steps.

From the AP Exam:

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\ln k = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

$$\begin{aligned} \text{Gas constant, } R &= 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \\ &= 62.4 \text{ L torr mol}^{-1} \text{ K}^{-1} \\ &= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1} \end{aligned}$$