Chapter 11 − Rates

Michael Brodskiy
Instructor: Mr. Morgan

January 28, 2021

- General Rate = Change in concentration per change in time.
- Rate is dependent on concentration − More collisions, more reactions, faster rate.
- Rate Law Formula = $k[A]^m$, where k is a constant, A is the reactant, and m is the order.
- If there are two reactants, then the rate = $k[A]^m[B]^n$, where B is the other reactant, and n is the order for the second reactant
- Order − Tells how rate changes when concentration changes $(0, 1, 2)$
- Example: Calculate k for $CH_3CHO \longrightarrow CH_4 + CO$

Concentration:	.1	.2	.3	.4
Rate:	.085	.34	.076	1.4

$$\begin{aligned} \frac{Rate_1}{Rate_2} &= \left(\frac{(CH_3CHO)_1}{(CH_3CHO)_2}\right)^m \\ \frac{.085}{.34} &= \left(\frac{.1}{.2}\right)^m \\ m &= 2 \\ .085 &= k(.1)^2 \\ k &= 8.5 \end{aligned} \tag{1}$$

- Example: Calculate k for $2\,NO + Cl_2 \longrightarrow 2\,NOCl$

Experiment	NO	Cl_2	Rate
1	.0125	.0255	$2.27 \cdot 10^{-5}$
2	.0125	.051	$4.55 \cdot 10^{-5}$
3	.025	.0255	$9.08 \cdot 10^{-5}$

$$
\begin{aligned}
\frac{Rate_1}{Rate_3} &= \left(\frac{(\mathrm{NO})_1}{(\mathrm{NO})_3}\right)^m \\
\frac{Rate_1}{Rate_2} &= \left(\frac{(\mathrm{Cl_2})_1}{(\mathrm{Cl_2})_2}\right)^n \\
\frac{2.27}{9.08} &= \left(\frac{.0125}{.025}\right)^m \\
m &= 2 \\
\frac{2.27}{4.5} &= \left(\frac{.0225}{.051}\right)^n \\
n &= 1 \\
2.27 \cdot 10^{-5} &= k[.0125]^2[.0255]^1 \\
k &= 5.7
\end{aligned} \tag{2}
$$

- The temperature dependence of the rate is contained in the rate constant, k
- Concentration and Time
  1. For first order reactions: $\ln\left(\frac{x_0}{x_f}\right) = kt$
  2. For second order reactions: $\frac{1}{x_f} - \frac{1}{x_0} = kt$
  3. Half Life: $t_{1/2} = \frac{.693}{k} = \frac{\ln(2)}{k}$
  4. x_0 is the initial concentration, x_f is the final concentration, k is the rate constant, t is time, and $t_{1/2}$ is the half life.
- If half life is constant over a period of time, the reaction is first order.
- For the AP test, it is written as such: $\ln[A] - \ln[A_0] = -kt$
- To determine order, graph the concentration vs time. Must be a linear fit:

  A vs Time means it is of zeroth order

  1. ln[A] vs Time means it is of first order
  2. $\frac{1}{[\mathrm{A}]}$ vs Time means it is of second order
- Activation Energy − Reactions occur because of collisions. These collisions must have enough energy to break bonds (E_a). Only collisions having sufficient energy to break bonds and proper orientation will lead to products.
- In a graph, the difference between the maximum and react energy is E_a. The difference between the maximum and products is E_a'. $\Delta H = E_a - E_a'$. If $E_a > E_a'$, the reaction is endothermic. IF $E_a' > E_a$, the reaction is exothermic. The maximum is where intermediates are formed, also known as the Activated Complex.

- Catalyst − A substance that lowers the reaction energy without being used up.
- Homogeneous − Two things in the same phase (liquid and liquid)
- Heterogeneous − Two things in different phases (liquid and solid)
- Reaction Mechanisms − A sequence of steps
- $A \rightarrow B$, $B \rightarrow C$, and $A \rightarrow C$. One of the steps is always the slowest. The slowest determines the rate.
- Rate is written off of the slow step.
- Substitutions for rate laws can be done as follows

$$\begin{aligned} \mathrm{I_2} &\longrightarrow 2\,\mathrm{I} \text{ fast} \\ 2\,\mathrm{I} + \mathrm{H_2} &\longrightarrow 2\,\mathrm{HI} \text{ slow} \\ rate &= k[\mathrm{I}]^2[\mathrm{H_2}] \\ [\mathrm{I_2}] &= [\mathrm{I}]^2 \\ rate &= k[\mathrm{I_2}][\mathrm{H_2}] \end{aligned} \tag{3}$$