Physical Chemistry 152

Intro

- Runs either fast/slow
- Thermodynamics explain where ES position is
- Kinetics = determines how quickly you get there.
  - Kinetics = work at detailed mechanisms of chemical processes
- Mechanism = sequence of elementary steps - can't be broken into simpler ones.
- Mechanisms = unimolecular, bi, and trimolecular (1, 2, or 3 molecules)
- Most important gas phase elementary steps = bimolecular.

Rate of Reaction

\[ \frac{dy}{dt} = \text{rate} \]

Rate = how quick the [y] reactant/product changes with time.

\[ \text{O}_2 + 2\text{O}_3 \rightarrow 3\text{O}_2 \]

\[
\begin{align*}
[\text{O}_3]_3 & \rightarrow [\text{O}_2]_3 \\
\text{(molecules)} & \text{(molecules)}
\end{align*}
\]

\[ \text{O}_2 \rightarrow \text{SO}_2 \]

\[ -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = +\frac{3}{2} \frac{d[\text{O}_2]}{dt} \]

\[ (\text{+) = product} \]

\[ (\text{-) = reactant} \]

Euler = definition of rate of reaction.
Second Order

When the rate equation = $k[A][B]$, conditions chosen: $[A]=[B]$ throughout the experiment. Rate equation = became same as $k[A]^2$

The Integrated 2^nd Order Rate Equation

$$- \frac{d[A]}{dt} = k[A]^2$$

Proof:

$$- \frac{d[A]}{dt} = -k[A]^2$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$[-[A]^{-1}]_0^{[A]} = [-kt]_0^t$$

Testing for 2^nd order reaction:

$$y = mx + c$$

$$(m = k)$$

Half Life

Half life is $t_{1/2}$ = time taken to use up half of the reactants.

2^nd Order: $t_{1/2} = \frac{CA_0}{2k}$

$e^{-kt}$ as $\frac{1}{2}$ life of

$2^nd$ Order: $t_{1/2} = \frac{1}{k[A]_0}$

1^st Order: $t_{1/2} = \frac{ln2}{k}$

- $t_{1/2}$ does not depend on $[A]_0$
- Half life remains constant.

- Use: Endore (Thyroid cancer) & Carbon (Carbon dating)
Eg: How much of a \( 1 \times 10^{-3} \) mol dm\(^{-3} \) Erdrie sample is left after 4 weeks? (1lye = 8 days)?

\[
8.07d = 697000s, \quad 4w = 2419200s
\]

\( A) \quad k = \frac{6n^2}{t^2} = \frac{6n^2}{697000} = 9.94 \times 10^{-7} \)

\[
[A] = 5x0J e^{-kt}
\]

\[
[A] = 1 \times 10^{-8} \times e^{-9.94 \times 10^{-7} \times 2419200}
\]

\( [A] = 9.03 \times 10^{-10} \) M after 4 weeks.