Chap. 9. The rates of chemical reactions

Chemical Kinetics - study of reaction rates, enables understanding of reaction mechanism

Reaction rates are sensitive to temperature and pressure in general

Reaction rates can be monitored by spectrophotometry, emission spectroscopy, mass spectroscopy, gas chromatography, NMR, EPR

Experimental techniques to determine rates:

- Real time analysis
- Flow method
- Stopped-flow technique
- Flash photolysis
- Quenching

For a chemical reaction, $\sum_J \nu_J J = 0$ **(Product, positive sign)**

Rate of reaction: $v = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_J}\frac{1}{V}\frac{dn_J}{dt} = \frac{1}{\nu_J}\frac{d}{dt}[J]$

For a chemical reaction involving reactants, A, B, …

Rate law: $v = f([A],[B],\cdots)$

Determination of this function is one of the goals of chemical kinetics

Reaction order: $v = k[A]^a[B]^b\cdots$

Order a with respect to A

Order b with respect to B

Overall order: a+b+…

Method of initial rates

For $$v_0 = k[A]_0^a \ ,$$
$$\log v_0 = \log k + a \log[A]_0$$

Integrated rate laws

For $$\frac{d}{dt}[A] = -k[A], [A] = [A]_0 e^{-kt}$$

Half-life: $$t_{1/2} = \frac{\ln 2}{k}$$

Time constant: $$\tau = \frac{1}{k}$$

Second-order reactions

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

$$\rightarrow \quad \frac{1}{[A]} = \frac{kt[A]_0 + 1}{[A]_0}$$

Plot of 1/[A] against t becomes a straight line.

$$\rightarrow \quad [A] = \frac{[A]_0}{1 + kt[A]_0}$$

Half-time: $t_{1/2} = \dfrac{1}{k[A]_0}$

n-th order reaction (n>1)

$$\frac{d}{dt}[A] = -k[A]^n \quad \rightarrow \quad \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt$$

Half-time: $t_{1/2} = \dfrac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$

For $\quad A + B \rightarrow P,$

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

Let $[A] = [A]_0 - x$, and $[B] = [B]_0 - x$

$$\rightarrow \quad \frac{d}{dt}x = k([A]_0 - x)([B]_0 - x)$$

$$\rightarrow \quad -\ln([A]_0 - x) + \ln([B]_0 - x)\Big|_0^t = k([B]_0 - [A]_0)t$$

$$\ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = ([B]_0 - [A]_0)kt$$

Reactions approaching equilibrium

$$A \underset{k'}{\overset{k}{\leftrightarrow}} B$$

$$\frac{d}{dt}[A] = -k[A] + k'[B] = -(k+k')[A] + k'[A]_0$$

$$\Rightarrow \quad \frac{d}{dt}\left(e^{(k+k')t}[A]\right) = k'[A]_0 e^{(k+k')t}$$

$$\Rightarrow \quad [A] = \frac{k}{k+k'}[A]_0 e^{-(k+k')t} + \frac{k'}{(k+k')}[A]_0$$

In the limit of $t \to \infty$

$$[A]_{eq} = \frac{k'}{k+k'}[A]_0 \quad \textbf{and} \quad [B]_{eq} = \frac{k}{k+k'}[A]_0$$

$$\Rightarrow \quad K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k}{k'}$$

Relaxation - **return to equilibrium** after being perturbed, eg., by temperature or pressure jump

$$k[A]_{eq} = k'[B]_{eq}$$

Let $[A] = [A]_{eq} + x$ **and** $[B] = [B]_{eq} - x$

$$\frac{dx}{dt} = -(k + k')x \quad \Rightarrow \quad x = x_0 e^{-t/\tau}, \ \frac{1}{\tau} = k + k'$$

Combination of relaxation rate and equilibrium constant can be used to determine k and k' .

Temperature dependence

Arrhenius equation: $k = Ae^{-E_a/RT}$

activation energy

$$\ln k = \ln A - \frac{E_a}{RT}$$

pre-exponential factor

High activation energy → Strong dependence of rate on temperature

General expression for activation energy including non-Arrhenius behavior:

$$E_a = RT^2 \left(\frac{d \ln k}{dT} \right)$$

Caused by complex reaction mechanism, quantum tunneling, …

Elementary reactions - **Reactions involving only small number of molecules and ions**

Unimolecular reaction - single molecule goes through reaction, e.g., isomerization reaction

$$A \rightarrow P, \qquad \frac{d[A]}{dt} = -k[A]$$

Bimolecular reaction - a pair of molecules collide or exchange energy

$$A + B \rightarrow P, \qquad \frac{d[A]}{dt} = -k[A][B]$$

Consecutive elementary reactions

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

$$\frac{d}{dt}[A] = -k_a[A]$$

$$\frac{d}{dt}[I] = k_a[A] - k_b[I]$$

$$\frac{d}{dt}[P] = k_b[I]$$

solve for [A] → $[A] = [A]_0 e^{-k_a t}$

$$\frac{d}{dt}[I] + k_b[I] = k_a[A]_0 e^{-k_a t}$$

solve for [I] → $[I] = [I]_0 e^{-k_b t} + \frac{k_a[A]_0}{k_b - k_a}\left(e^{-k_a t} - e^{-k_b t}\right)$

$$[I] = \frac{k_a[A]_0}{k_a - k_b}\left(e^{-k_a t} - e^{-k_b t}\right)$$ **(for $[I]_0$=0)**

$$[P] = [A]_0 - [A] - [I] = [A]_0\left(1 - \frac{k_b e^{-k_a t}}{k_b - k_a} + \frac{k_a e^{-k_b t}}{k_b - k_a}\right)$$

Steady-state approximation

Quasi-steady state approximation: $\frac{d[I]}{dt} \approx 0$

$$\rightarrow \quad k_a[A] - k_b[I] \approx 0 \quad \rightarrow \quad [I] \approx \frac{k_a}{k_b}[A]$$

$$\frac{d}{dt}[P] = k_b[I] \approx [A] = k_a[A]_0 e^{-k_a t}$$

$$\rightarrow \quad [P] \approx [A]_0(1 - e^{-k_a t})$$

This is same as approximating $k_b - k_a \approx k_b$

and neglecting $\frac{k_a}{k_b - k_a}$ **in the exact solution**

Rate limiting step

Slowest step in a mechanism, a gateway controlling the overall rate of reaction

For $A \xrightarrow{k_a} I \xrightarrow{k_b} P$

Formation of [A] depends only on k_a **if** $A \rightarrow I$ **is the rate limiting step**

Pre-equilibria

$$A + B \underset{k'_a}{\overset{k_a}{\leftrightarrow}} I \xrightarrow{k_b} P$$

For $k'_a >> k_b$ **A, B, and I are in equilibrium** $K = \frac{[I]}{[A][B]} = \frac{k_a}{k'_a}$

$$\frac{d}{dt}[P] = k_b[I] = k_b K[A][B] = k[A][B], \; k = \frac{k_a k_b}{k'_a}$$