

Kinetics

The study of reaction rates:

Stoichiometry

Reaction Rate

Rate of Change

Kinetics: Stoichiometry



Stoichiometry

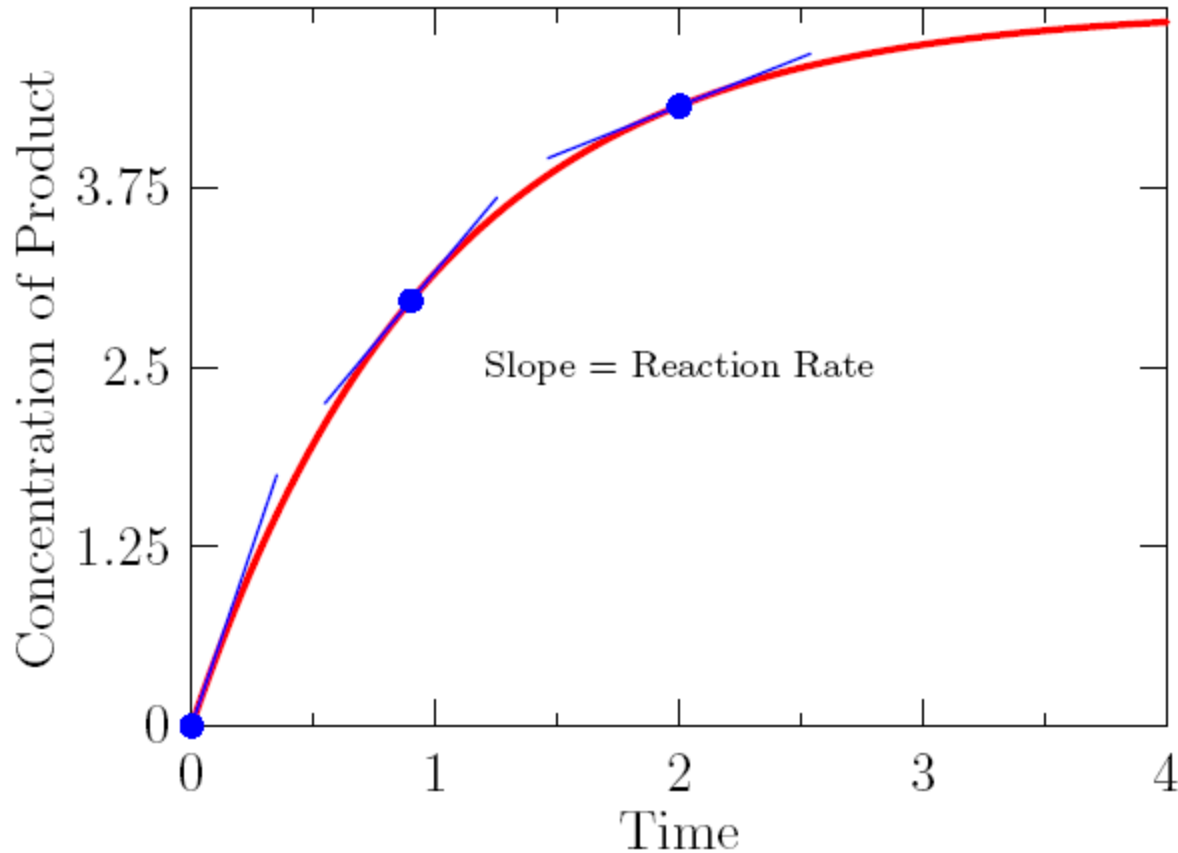
Stoichiometry related to the proportion of reactants and products that take part in a reaction. By convention, the stoichiometries for reactants are **negative** and those for products **positive**.

ADP: -2

ATP: +1

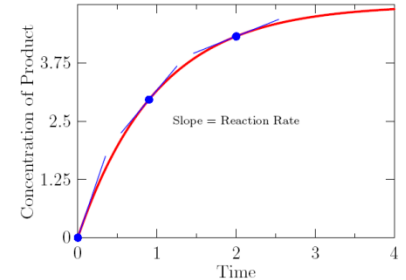
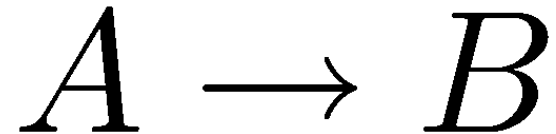
AMP: +1

Kinetics: Rate of Reaction



Ideally, the rate of reaction should be independent of the species being measured.

Kinetics: Rate of Reaction



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Kinetics: Rate of Reaction



$$\text{Rate} = v \equiv \frac{1}{n_1} \frac{d\text{ADP}}{dt}$$

The **rate of reaction** is the rate of change of a designated reactant or product, normalized by its stoichiometry.

This definition means that the rate is independent of the species being measured.

Kinetics: Rate of Change



$$\text{Rate} = v \equiv \frac{1}{n_1} \frac{d\text{ADP}}{dt}$$

$$\frac{dA}{dt} = n_1 v$$

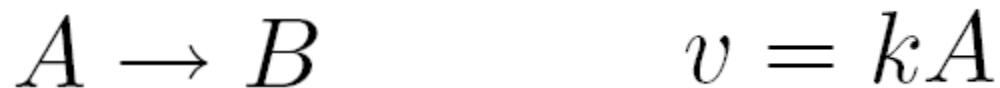
The **rate of change** of a molecular species is not necessarily the same as the **reaction rate**.

Kinetics: Mass-action Kinetics

$$\frac{dA}{dt} = n_1 v$$

What does v look like?

The **law of mass action** states that the rate of a chemical reaction is proportional to the product of the reactant concentrations raised to a given power.



v Has units: moles $L^{-1}t^{-1}$

The units for k are t^{-1} concentration of A , moles L^{-1}

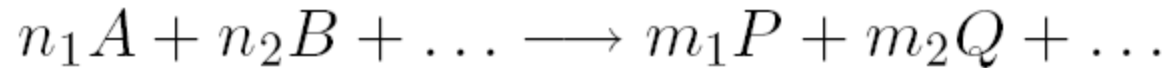
Kinetics: Mass-action Kinetics

The proportionality constant, k , is called the rate constant.



Kinetics: Generalized Mass-action Kinetics

For a general reaction such as:



empirical observations suggest the following general mass-action rate law:

$$v = kA^{n_1}B^{n_2} \dots$$

Kinetics: Reaction Order

Reaction Order:

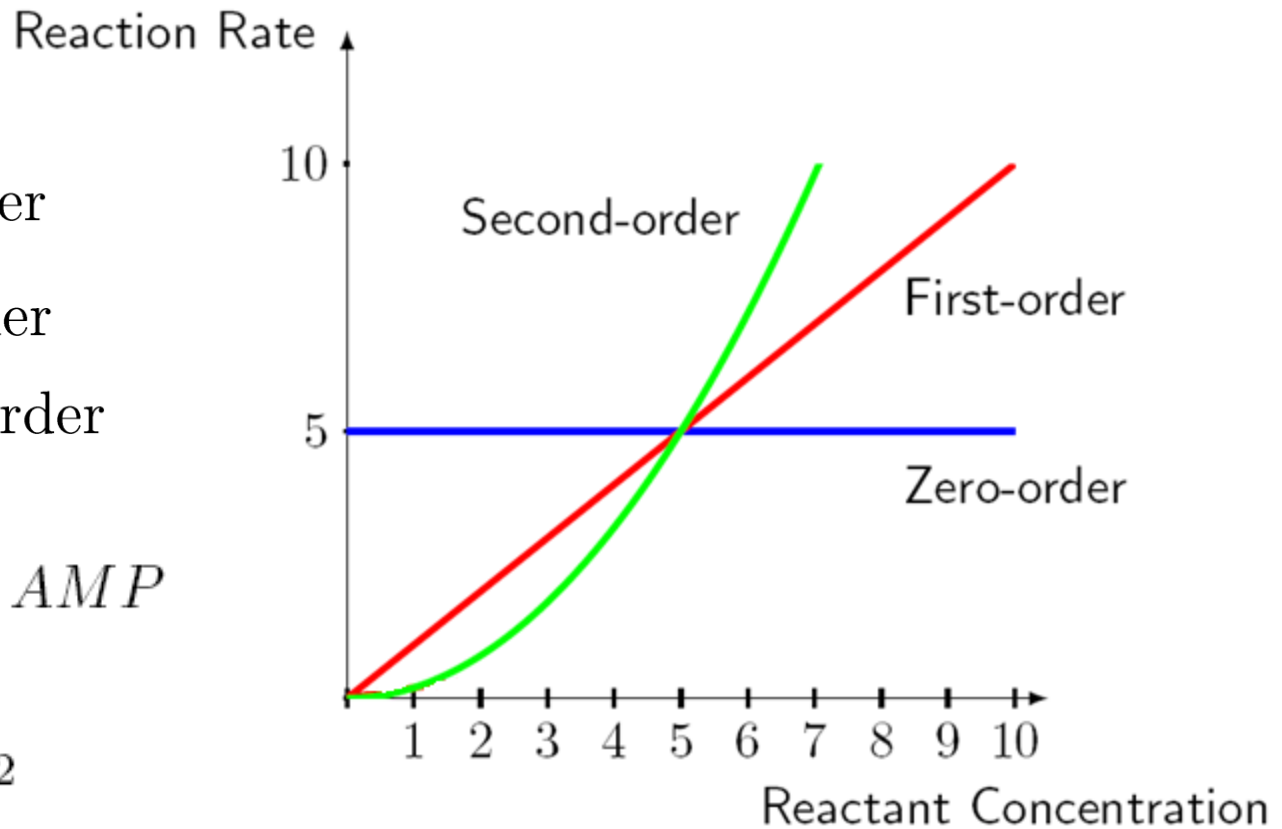
$$v = kA^0 \quad \text{Zero-Order}$$

$$v = kA^1 \quad \text{First-Order}$$

$$v = kA^2 \quad \text{Second-Order}$$



$$v = k ADP^2$$



Kinetics: Reversible Mass-action Kinetics

Reversible Mass-action kinetics:

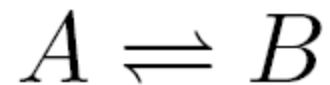


$$v = k_1 A^{n_1} B^{n_2} \dots - k_2 P^{m_1} Q^{m_2} \dots$$

$$v = k_1 ADP^2 - k_2 ATP AMP$$

Kinetics: Equilibrium Constant

All reactions are in principle reversible.



$$v_f = k_1 A$$

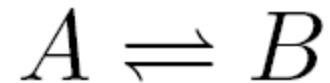
$$v_r = k_2 B$$

$$v = v_f - v_r$$

$$v_f - v_r = 0$$

Kinetics: Equilibrium Constant

All reactions are in principle reversible.



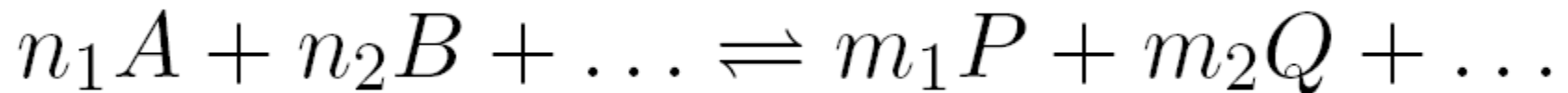
$$v_f - v_r = 0$$

$$k_1 A - k_2 B = 0$$

$$\frac{k_1}{k_2} = \frac{B}{A} = K_{eq}$$

Kinetics: Equilibrium Constant

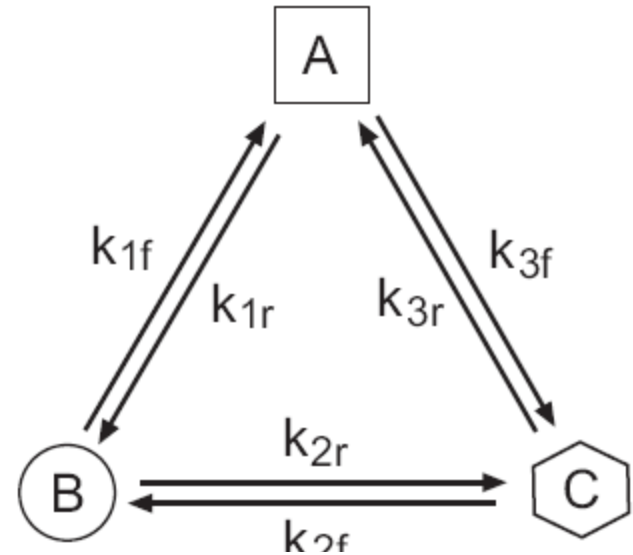
All reactions are in principle reversible.



$$K_{eq} = \frac{P^{m_1} Q^{m_2} \dots}{A^{n_1} B^{n_2} \dots}$$

Principle of Detailed Balance or why you can't get something for nothing

$$\frac{A}{B} \frac{B}{C} \frac{C}{A} = K_{eq1} K_{eq2} K_{eq3} = 1$$



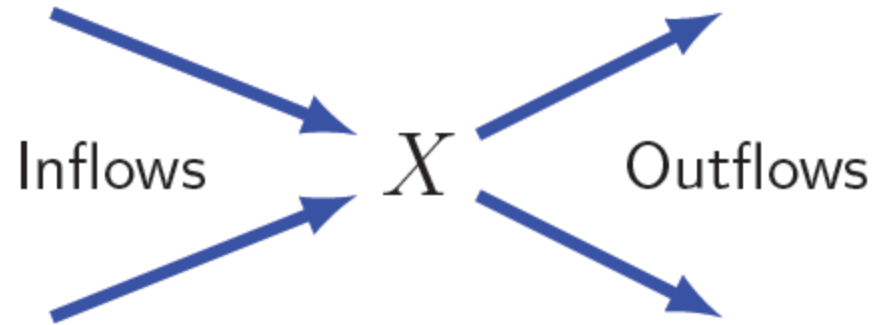
At equilibrium the following must be true:

$$\frac{k_{1f}}{k_{1r}} = \frac{A}{B}, \quad \frac{k_{2f}}{k_{2r}} = \frac{B}{C} \quad \text{and} \quad \frac{k_{3f}}{k_{3r}} = \frac{C}{A}.$$

Combining the three equations and eliminating A , B , and C yields the following relation among the rate constants:

$$k_{1f} k_{2f} k_{3f} = k_{1r} k_{2r} k_{3r}$$

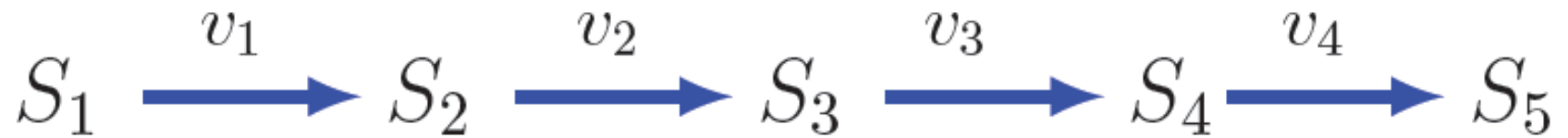
Mass Balance Equations



$$\frac{dS_i}{dt} = \sum \text{Inflows} - \sum \text{Outflows}$$

$$\frac{dS_i}{dt} = \sum_j c_{ij} v_j$$

Mass Balance Equations



$$\frac{dS_1}{dt} = -v_1$$

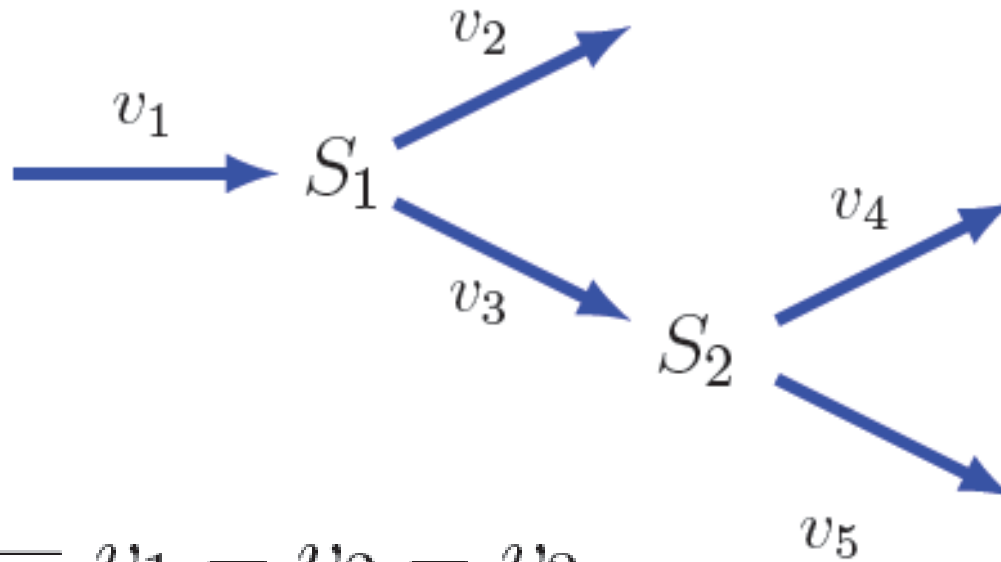
$$\frac{dS_2}{dt} = v_1 - v_2$$

$$\frac{dS_3}{dt} = v_2 - v_3$$

$$\frac{dS_4}{dt} = v_3 - v_4$$

$$\frac{dS_5}{dt} = v_4$$

Mass Balance Equations



$$\frac{dS_1}{dt} = v_1 - v_2 - v_3$$

$$\frac{dS_2}{dt} = v_3 - v_4 - v_5$$

Mass Balance Equations



$$\frac{dX}{dt} = -v_1 + 2v_1 - v_2$$

Mass Balance Equations



$$\frac{dA}{dt} = -v_1$$

$$\frac{dX}{dt} = v_1 - v_2$$

$$\frac{dB}{dt} = v_3$$

$$\frac{dY}{dt} = v_3 - v_2$$

$$\frac{dZ}{dt} = v_2 - v_3$$

Stoichiometry Matrix



$$N = \begin{array}{cccc|l} & v_1 & v_2 & v_3 & v_4 & \\ \left[\begin{array}{cccc} -1 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 \end{array} \right] & S_1 \\ & S_2 \\ & S_3 \\ & S_4 \\ & S_5 \end{array}$$

System Equation



$$\frac{dS}{dt} = Nv$$

$$\frac{dS}{dt} = Nv = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \end{bmatrix}$$

Kinetics: Temperature Dependence

The rates of most chemical reactions increase as the temperature is raised.

As a rule of thumb, a typical reaction rate will double for every ten degree Celsius (50 Fahrenheit) increase in temperature. If something doubles at fixed intervals then the change is exponential.

