

Chemical Kinetics -- Chapter 14

1. Factors that Affect Reaction Rate

- (a) Nature of the reactants:
molecular structure, bond polarity, physical state, etc.
- heterogeneous* reaction: reactants in different phases
e.g., solid / gas or solid / liquid
- homogeneous* reaction: all reactants in same phase
e.g., reaction in solution
- (b) Concentrations of the reactants
- (c) Temperature of the System
- (d) Presence of a *Catalyst*
(substance that increases the reaction rate without being consumed itself)

2. Measurement of Reaction Rate

Experimentally

monitor the change in concentration of one or more reactants or products with time as reaction proceeds

$$\text{reaction rate} = \Delta(\text{conc}) / \Delta(\text{time})$$

units: mole L⁻¹ s⁻¹ mole / L sec

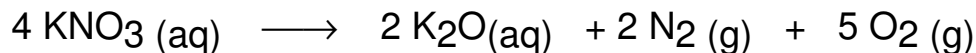
products: conc increases with time, rate is (+)

reactants: conc decreases with time, rate is (-)

The rates expressed for various reactants and products are related by the stoichiometry of the reaction.

Problem:

At a certain temperature, oxygen (O₂) is produced by the following reaction at a rate of 0.30 mole / L sec. What are the rates of formation of the other products and the rate of disappearance of the reactant?



$$\begin{aligned} \text{rate (N}_2) &= (0.30 \text{ mole O}_2 / \text{L s}) \times (2 \text{ mole N}_2 / 5 \text{ mole O}_2) \\ &= 0.12 \text{ mole N}_2 / \text{L s} \end{aligned}$$

likewise, rate (K₂O) = 0.12 mole / L sec

$$\begin{aligned} \text{rate (KNO}_3) &= - (0.30 \text{ mole O}_2 / \text{L s}) \times (4 \text{ mole KNO}_3 / 5 \text{ mole O}_2) \\ &= - 0.24 \text{ mole KNO}_3 / \text{L s} \end{aligned}$$

Change of Rate with Time

For most reactions, the rate depends on concentrations of the reactants. ∴ Reaction rate changes with time.

In a *Concentration vs Time Plot*, the Reaction Rate is equal to the *slope* of the curve at any given time

see Figure 14.2 -- plot of [HI] vs time for the reaction:



rate decreases with time (curve flattens out) because the concentration of the reactant decreases with time

initial rate: rate at time = 0 (easiest to measure)

3. **Rate Law** (concentration and reaction rate)

For a general reaction: $a A + b B \longrightarrow \text{products}$

the "Rate Law" is the following type of relationship between rate and concentrations of reactants.

$$\text{Rate} = k [A]^x [B]^y$$

{ All values of k, x, and y must be determined experimentally ! }

x and y are normally small integers (often 1, 2, or 0)

x = "order of the reaction" with respect to A

e.g., if $x = 2$, the rate depends on the square of [A]

i.e., double [A], then Rate increases by 4 times

triple [A], then Rate increases by 9 times, etc.

y = "order of the reaction" with respect to B

overall "order" of reaction = $x + y$

in general, the exponents x and y are *not* equal to or directly related to the coefficients in the balanced equation

$$\text{Rate} = k [A]^x [B]^y$$

where, k = "rate constant"

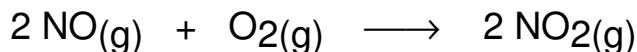
(units depend on x and y, etc.)

Units: [A] and [B] are mole / L,

Rate is mole / L s or mole L⁻¹ s⁻¹

Example -- Determination of a Rate Law from rate vs conc data

In a kinetic study of the reaction,



the following rate data was obtained.

Expt	[NO]	[O ₂]	Rate (mole L ⁻¹ s ⁻¹)
1	0.0010	0.0010	7.10
2	0.0010	0.0040	28.4
3	0.0030	0.0040	256

- (a) Determine the rate law for this reaction.
(b) Determine the rate constant, with its proper units.

Part (a) Rate Law: rate = k[NO]^x[O₂]^y

First: Compare Expts 1 and 2 with constant [NO]
 shows how rate changes with [O₂]

$$\text{rate} \propto [\text{O}_2]^y \quad \text{or} \quad \text{rate}_2 / \text{rate}_1 = \{[\text{O}_2]_2 / [\text{O}_2]_1\}^y$$

$$28.4 / 7.10 = \{0.0040 / 0.0010\}^y$$

$$4 = (4)^y \quad \therefore y = 1 \quad (\text{1st order in O}_2)$$

Second: Compare Expts 2 and 3 with constant [O₂]
 shows how rate changes with [NO]

$$\text{rate} \propto [\text{NO}]^x \quad \text{or} \quad \text{rate}_3 / \text{rate}_2 = \{[\text{NO}]_3 / [\text{NO}]_2\}^x$$

$$256 / 28.4 = \{0.0030 / 0.0010\}^x$$

$$9.0 = (3)^x \quad \therefore x = 2 \quad (\text{2nd order in NO})$$

Overall Rate Law: rate = k [NO]² [O₂]

Part (b) Use data from any single expt to calc k
(all expts should give same value for k)

e.g., From expt 1:

$$\text{rate} = k [\text{NO}]^2 [\text{O}_2]$$

$$7.10 \text{ mole L}^{-1} \text{ s}^{-1} = k (0.0010 \text{ mole L}^{-1})^2 (0.0010 \text{ mole L}^{-1})$$

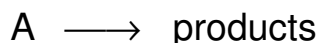
$$\therefore k = 7.10 \times 10^9 \text{ L}^2 \text{ mole}^{-2} \text{ s}^{-1}$$

{ Note: units of k must be determined algebraically }

4. Concentration and Time (Half Lives)

The Rate Law for a reaction shows how the reaction rate changes with concentration of reactants. However, what about changes in actual concentrations with time?

Consider only for a first order reaction (i.e., in Section 14.4):



$$\text{rate} = k[\text{A}] = d[\text{A}] / dt \quad \text{integrating this equation:}$$

$$\ln \{ [\text{A}]_0 / [\text{A}]_t \} = kt \quad \text{and rearranging:}$$

$$\ln [\text{A}]_t = -kt + \ln [\text{A}]_0$$

\therefore plot of $\ln [\text{A}]$ vs t is a straight line with
slope = $-k$ and intercept = $\ln[\text{A}]_0$ (see Fig 14.8)

Half Life ($t_{1/2}$) = time required for one-half of a given reactant to disappear

for first order reaction: $t_{1/2} = (\ln 2) / k$

more often, we're interested in how much of a reactant remains after given time

e.g., [half-life of iodine-131](#) is 8 days, therefore:

# half-lives	0	1	2	3	4	5
# days	0	8	16	24	32	40
% I-131 left	100	50	25	12.5	6.25	3.13

OMIT: Conc vs Time and half-lives for 2nd order reactions

5. **Activation Energy**

(a) Two important kinetic theories:

Collision Theory

Rate of a reaction depends on the frequency of *effective* collisions between the reactant molecules.

To be "effective" collisions must occur with proper *orientation* and *sufficient energy*.

Activation Energy (E_a) = minimum energy required for reaction to occur

Transition State Theory

Uses *reaction coordinate* diagrams to illustrate the energy changes that occur as reactants combine to form products.

E_a = energy difference between reactants and the "activated complex" or "*transition state*"

(b) Measuring the Activation Energy

Arrhenius Equation

Relationship between Temperature and rate constant:

$$k = A e^{-E_a / RT} \quad (A = \text{"frequency factor"})$$

more useful in logarithmic form:

$$\ln k = \ln A - E_a / RT$$

plot of $\ln k$ vs $1/T$ is a straight line with slope = $-E_a/R$

if rate constant is measured at two temps:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

\therefore given two k's and T's, calculate E_a

for example,

Given: $k_1 = 3.20 \text{ L mol}^{-1} \text{ s}^{-1}$ @ $T_1 = 350^\circ\text{C}$ (623 K)

$k_2 = 23.0 \text{ L mol}^{-1} \text{ s}^{-1}$ @ $T_2 = 400^\circ\text{C}$ (673 K)

Find E_a -- plug in k's, T's, and $R = 8.314 \times 10^{-3} \text{ kJ / mole K}$

$E_a = 138 \text{ kJ / mole}$ { watch the units !!! }

6. Reaction Mechanism

A "reaction mechanism" is a proposed sequence of steps, called elementary processes by which the reactants are converted into products.

Rate-Determining Step: slow step in the reaction mechanism determines the overall rate law

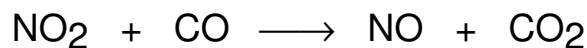
Relationship between mechanism and kinetics:

For a proposed mechanism, it is possible to predict the rate law that is consistent with the mechanism.

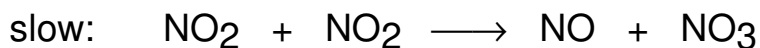
The predicted rate law can then be compared with the *experimentally determined (actual)* rate law. If the predicted and experimental rate laws are the same, then the proposed mechanism is possible.

For an elementary process, the exponents in the rate expression are equal to the coefficients in the balanced equation for that individual process.

e.g., for the overall reaction,



the following mechanism is proposed.



the slow step, predicts: $\text{rate} = k [\text{NO}_2]^2$

the actual, experimental rate law: $\text{rate} = k [\text{NO}_2]^2$

\therefore this is a possible mechanism !

What about an alternate, one-step mechanism?



This would predict: $\text{rate} = k [\text{NO}_2] [\text{CO}]$
which is not observed experimentally.

\therefore this is not a possible mechanism !

7. Effect of Catalysts

A *catalyst* is a substance that increases the rate of a reaction without itself being consumed.

Two types: *homogeneous* or *heterogeneous*

Mode of action

Catalyst alters the reaction mechanism by providing a lower energy (smaller E_a) pathway for the reaction.

Catalysts often activate (weaken) one or more bonds in the reactants and/or help to properly orient the reacting molecules (especially on surface of *heterogeneous* catalysts), thus promoting their reaction.