Physical Chemistry

Lecture 4

Introduction to chemical kinetics

Thermodynamics and kinetics

- Thermodynamics
  - Observe relative stability of states
  - Energy differences
  - Static comparisons of states
- Kinetics
  - Observe changes of state over time
  - Several different topics
    - Empirical description of the rate of reaction
    - Determination of experimental parameters
    - Microscopic theories

Rates

- A chemical reaction is described by an equation of the type

$$H_2\,(gas) + \frac{1}{2}O_2\,(gas) \rightarrow H_2O\,(liquid)$$

- Rates:
  - Rate of change of $[H_2O]$: $d[H_2O]/dt$
  - Rate of change of $[H_2]$: $d[H_2]/dt$
  - Rate of change of $[O_2]$: $d[O_2]/dt$
- Rates related by the overall equation
  - 1 oxygen molecule disappears for every 2 hydrogen molecules in the above reaction

Reaction velocity

- The rates of appearance of products and disappearance of reactants are related by stoichiometry of the reaction
- Define the reaction velocity, v, in terms of "normalized" rates of appearance of products and disappearance of reactants

$$v = \frac{1}{\nu_i}\frac{d[i]}{dt}$$

- Example of the production of water:

$$v = -\frac{d[H_2]}{dt} = -2\frac{d[O_2]}{dt} = \frac{d[H_2O]}{dt}$$

Rate laws

- Describe of how reaction velocity depends on parameters such as concentrations, temperature, pressure, etc.

$$v = f([A_{react}],[B_{prod}],T,P)$$

- May be simple or complex
- Gives insight into the manner in which the reaction occurs
  - Reactions do not necessarily occur in the manner indicated by the overall reaction equation

Order

- In many situations, one may write the functional form of the reaction velocity approximately as

$$v = k[A]^a[B]^b[C]^c\cdots$$

- a, b, c are the orders of reaction under the conditions examined
- Many reaction velocities are more complicated functions than the simple one above
  - Example: Production of HBr over a wide range

$$v_{HBr} = k\frac{[H_2][Br_2]^{1/2}}{1+k'\frac{[HBr]}{[Br_2]}}$$

- Orders are often determined over a limited range
  - Initial order of reaction

Determining initial order

- Measure initial velocity as a function of the amount of reactants in the mixture
- Example: $OCl^- + I^- \rightarrow OI^- + Cl^-$

$[OCl^-]$	$[I^-]$	$[OH^-]$	Initial velocity
0.0017	0.0017	1.00	1.75×10^{-4}
0.0034	0.0017	1.00	3.50×10^{-4}
0.0017	0.0034	1.00	3.50×10^{-4}
0.0017	0.0017	0.50	3.50×10^{-4}

Concentrations are in mol dm^{-3}. Rate is mol dm^{-3} sec^{-1}.

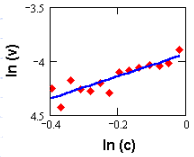
- By comparison, one finds the initial rate equation

$$v_{initial} = k[OCl^-][I^-][OH^-]^{-1}$$

Differential method of determining order

- Calculate approximate derivatives as ratios of differences for specific concentrations
- Plot approximate derivatives versus concentration

$$\ln(v) = k + n\ln(C)$$



- Example: Decomposition of di-tert-butyl peroxide
  - Line slope = 1.04
  - Order with respect to DTBP is close to 1 under these conditions (and probably is 1)

Integrated rate laws - first order in a reactant

- For simple chemical reactions, integrate the rate laws to determine how the reactant concentration changes with time
- First-order rate law
  - Exponential in time
  - Linear form is the logarithm

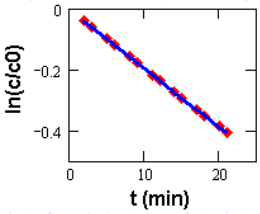
$$v = -\frac{d[A]}{dt} = k_1[A]$$

$$[A(t)] = [A(0)]\exp(-k_1 t)$$

$$\ln([A(t)]) = \ln([A(0)]) - k_1 t$$

First-order rate law

- Example: decomposition of di-tert-butyl peroxide
- slope ≡ - k_1
- Rate constant for this reaction is determined to be $k_1 = 0.0193\ min^{-1}$ from the slope of the line



Reactant or Product?

- What if one can only measure a product concentration with time?
- Sometimes one can derive an equation for the product concentration with time
- Example: First-order reaction

$$A \rightarrow B$$

- Then

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

- Can solve for the concentration of B exactly

First-order Product

- Rely on conservation of matter

$$[B(t)] = [A(0)] - [A(t)]$$
$$= [A(0)] - [A(0)]e^{-kt}$$
$$= [A(0)](1 - e^{-kt})$$

- Rearrange to find the linear form

$$\ln\left(\frac{[A(0)] - [B(t)]}{[A(0)]}\right) = -kt$$

Integrated rate law – second order in reactant (Case I)

- Second-order rate law may be integrated
- Linear plot of 1/[A(t)] versus t
- Often see reported rate constant for disappearance of A
  - $k_{eff} = 2\,k_2$
  - Exercise caution in assessing reported rate constants

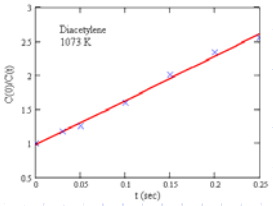
$$v = -\frac{1}{2}\frac{d[A]}{dt} = k_2[A]^2$$

$$\frac{1}{[A(t)]} = \frac{1}{[A(0)]} + 2k_2 t$$

$$= \frac{1}{[A(0)]} + k_{eff}\, t$$

Second-order rate law

- Example:
  - Collision-induced decomposition of diacetylene, DA
  - Hou and Palmer, 1965
- Linear plot of $[DA]^{-1}$ versus t
- k_{eff} = 6.79 x10^7 cm^3/mol-sec



Integrated rate laws for other reactant orders

- Integration gives a general form for all orders (except 1)
- The power of the function of concentration linear in time is related to order of reaction for the conditions under which the system is observed

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

$$\frac{1}{[A(t)]^{n-1}} = \frac{1}{[A(0)]^{n-1}} + (n-1)kt$$

Second-order rate law (Case II)

- Previously considered
  - Homomolecular reaction (A + A)
  - If other species affected reaction, they were held constant
- Consider second-order heteromolecular
  - Second order overall
  - First order in each reactant

A + B ⟶ Products

$$v = k_2[A][B]$$

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

$$[A(t)] = [A]_0 - x \qquad [B(t)] = [B]_0 - x$$

$$\frac{dx}{dt} = k_2([A]_0 - x)([B]_0 - x)$$

$$\ln\left(\frac{[A(t)]}{[B(t)]}\right) = \ln\left(\frac{[A]_0}{[B]_0}\right) - ([B]_0 - [A]_0)k_2 t$$

- Does not work for $[A]_0 = [B]_0$

Half life

- Can describe time dependence in several different ways
  - Rate constant, k
  - Half life, $t_{1/2}$, time for one half of reactant to disappear
  - Other times that describe the amount left

First order

$$t_{1/2} = \frac{\ln 2}{k}$$

Second order

$$t_{1/2} = \frac{1}{k_{eff}[A(0)]}$$

Determining kinetic parameters

- Two conceptual steps
  - Find parameter proportional to concentration
  - Find appropriate function of time to allow evaluation of time course

Phase	Parameter often measured	Parameter needed
Gas	P, total pressure	P_0, partial pressure of reactant
Solution	Total optical absorption	Absorption of a single component
	Total conductance	Conductance of a single component
	Total volume	Volume change of a single component
	Titration	Concentration of a single component

Summary

- Chemical change quantified by the mathematics of chemical kinetics
- Rate constant and order characterize a reaction
- Determining rates and velocities
  - Differential method
  - Integrated-rate-law method
- Results often limited to a particular time scale or situation
  - Initial reaction
  - With some materials in excess