

# Physical Chemistry

## Lecture 4

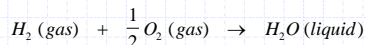
### Introduction to chemical kinetics

## 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



- ◆ 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

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

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

- ◆ 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

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

- ◆  $a, b, c$  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:  $\text{OCl}^- + \text{I}^- \rightarrow \text{OI}^- + \text{Cl}^-$

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

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

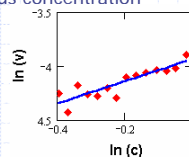
- ◆ By comparison, one finds the initial rate equation

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

## 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

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

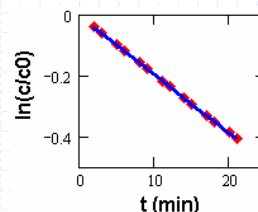
- ◆ First-order rate law
  - Exponential in time
  - Linear form is the logarithm

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

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

## First-order rate law

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



## Integrated rate law – second order in reactant

- ◆ Second-order rate law may be integrated

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

- ◆ Linear plot of  $1/[A(t)]$  versus  $t$
- ◆ Often see reported rate constant for disappearance of A

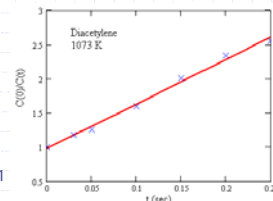
$$\frac{1}{[A(t)]} = \frac{1}{[A(0)]} + 2k_2 t$$

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

- $k_{\text{eff}} = 2k_2$
- Exercise caution in assessing reported rate constants

## Second-order rate law

- ◆ Example:
  - Collision-induced decomposition of diacetylene, DA
  - Hou and Palmer, 1965
- ◆ Linear plot of  $[\text{DA}]^{-1}$  versus  $t$
- ◆  $k_{\text{eff}} = 6.79 \times 10^7 \text{ cm}^3/\text{mol}\cdot\text{sec}$



## Integrated rate laws for other reactant orders

- Integration gives a general form for all orders (except 1)

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

- 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

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

## 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, 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