**Chapter 13 Chemical Kinetics**

- Some reaction are faster than others!

**Three factors** (in addition to the nature of the reacting chemicals themselves…)
1. Concentrations of the reactants
2. Temperature
3. "Catalysts"

13.1 Reaction Rates

Rate: Change in something (x) per time interval

$\Delta$ = "change in" $\frac{\Delta x}{\Delta t}$

Any average rate can be determined between measurements at 2 points in time.

Car Example: What is the average speed of a car that between 1:00 ($t_1$) and 1:30 ($t_2$) travels from point O ($x_1$) to 30 miles away ($x_2$) ?

Chemical Reaction Example: **A → B**

Chemical rates are defined by change in concentration (M) per time interval.

rate = $\frac{\Delta [B]}{\Delta t} = \frac{-\Delta [A]}{\Delta t}$ Units = $\frac{M}{S}$

Notes

1. Rates can be written based on products or reactants, which are linked by stoichiometry.
   - [B] increases as [A] decreases

2. Rate of changes decrease with time
   - declines as starting reactant is depleted
   - especially for reactions involving two or more chemicals that need to collide
   - the lower the concentration, the less probable a collision

3. Rate can be found from:
   a. 2 time points
   b. Known rate of change for another chemical (factor in coefficients)
   c. Graphical analysis (not tested)
      - tangent slope, or calculus! $rate_t = \frac{d[B]}{dt}$

4. Extra emphasis: The Relative Rate of Change for reactants/products has a stoichiometric relationship:

Calculating the rates of change for one chemical given the rate of change for some other chemical

- Seeing the relationship between stoichiometry, rate of change, and directions of change.

Reaction: **2A + B → 1C + 2D**

1. For the above reaction, if the concentration of B is dropping by 0.5 M/min, what is the rate of change for the following?

[A]: [C]: [D]:

2. If [A] is dropping by 0.8 M/min, what is the rate of change for:

[B]: [C]: [D]:

3. Write the rate law, relative to each reactant or product, beginning with [B]. (Put +/- signs to reflect whether the concentration is dropping or increasing.):

4. Reaction: **2A → B** If $\Delta[A]/\Delta t = -0.10$ M/s, what is $\Delta[B]/\Delta t$?

Two-Point Calculation: Calculating the average rate of change based on measurements at two points in time

5. Reaction: **A → B**
   a. Calculate the average rate (per second) from 0 → 10 sec if [A] goes from 0.100M → 0.080M?

   b. If [B] = 0 M at 0 sec, what is [B] after 5 sec?

13.2,3 Rate Laws and the Effect of Concentrations on Rates.

- since reactants must collide to react, rates depend on concentrations

A. General Form for a "Rate Law"

Rate = $k[A]^x [B]^y [C]^z$…… A, B, C reactants (or catalyst)

1. Describes dependence of rate on concentration of each reactant
   - Concentrations in molarity, mole/liter

   Rate $\propto [A]^x$ Rate $\propto [B]^y$ Rate $\propto [C]^z$

| If: | Effect of Doubling [A] | Effect of Tripling [A] | Effect of Multipying [A] by Ten-fold |
|---|---|---|---|
| x = 1 | | | |
| x = 2 | | | |
| x = 0 | | | |

2. k is "rate constant":
   - the rate changes with time and concentration, k doesn't
   - k is a fixed constant for a given reaction at a given temperature
   - if the temperature changes, then k changes too….

3. Each reaction has it's own rate law and rate constant (not like ideal gas law)
   - **both must be determined experimentally**

Problem 1: Given rate law, actual concentration, and actual rate, solve for k

Example: What is the rate constant for a reaction given the following info:

- rate law: rate = $k[A]^2$
- [A] = 0.20 M
- rate = $3.6 \times 10^{-3}$ M/s $^{-1}$

Problem 2: Given rate law, actual concentration, and actual k, solve for actual rate

Example: What is the rate constant for a reaction given the following info:

- rate law: rate = $k[A]^2$
- [A] = 0.60 M
- k = 0.090 $M^{-1}s^{-1}$

4. Rate laws can't be predicted from balanced equation.

5. Reactant "Order" Terminology
   a. For a given reactant

      rate $\propto [A]^x$ x = 0 zero order
      = 1 first order
      = 2 second order

   b. Overall reaction order = sum of individual orders (x+y+z…..)

6. Units for k: Whatever it takes to balance units!
rate = M/s = k $M^{x+y+z....}$

| | | |
|---|---|---|
| First Order | M/s = k M | k = 1/s = $s^{-1}$ |
| Second Order | M/s = k $M^2$ | k = $M^{-1}s^{-1}$ |
| Third Order | M/s = k $M^3$ | k = $M^{-2}s^{-1}$ |

| Examples of Rate Laws | Overall Reaction Order | Order of A | Effect on rate of Doubling [A] | Rate Constant Units |
|---|---|---|---|---|
| r = k[A] | | | | |
| r = k[A][B] | | | | |
| r = $k[A]^2$ | | | | |
| r = $k[A]^{½}$ [B] | | | | |
| r = $k[A]^2$[B] | | | | |
| r = $k[A]^3$[B] | | | | |

B. Determination of Rate Laws

**Need Either:**
1. Known mechanism (see later, section 13.7) OR,
2. Systematic variation of each reactant, with experimental measurement of rate

- each reactant, one at a time!
- Only one reactant should vary

General determination of reactant "order", when numbers aren't simple:

- Set the ratio of 2 rates = the ratio of the 2 concentrations to the "x" power.
- "x" gives you the actual "order" for the reactant

Ratio of the two actual rates → $\frac{r_2}{r_1} = \left[\frac{[A]_2}{[A]_1}\right]^x$ ← Ratio of the two concentrations to the "x" power

Routinely the concentration ratio is set at some nice easy ratio: 2:1, or 3:1, or 10:1, or 1:2, or something like that.

Example Problem: Figure out the order of A if the concentration of [A] is Doubled, with the effect onrate shown:

| Rate | Order of [A] | Means |
|---|---|---|
| doubles | | |
| x 4 | | |
| x 8 | | |
| unchanged (1) | | |
| x 1.4 | | |

Problems: Determining Rate Laws from Actual Rate Measurements Using Different Concentrations

1. A + B → C + D

| | [A] | [B] | rate |
|---|---|---|---|
| 1) | 0.20 | 0.20 | 0.0078 |
| 2) | 0.40 | 0.20 | 0.0156 |
| 3) | 0.20 | 0.40 | 0.0078 |

Order of A:
Order of B:
Rate law:
k (number + units):
What is rate when [A]= 0.80, [B]= 0.80

2. A + B → C + D

| [A] | [B] | rate |
|---|---|---|
| 0.20 | 0.20 | 0.15 |
| 0.40 | 0.20 | 0.30 |
| 0.20 | 0.40 | 0.30 |
| 0.40 | 0.40 | 0.60 |
| 0.80 | 0.40 | |
| 0.80 | 0.80 | |

Rate law:

Number for k:

3. A + B + C→ D + 2E

| [A] | [B] | [C] | rate |
|---|---|---|---|
| 0.20 | 0.20 | 0.20 | 0.15 |
| 0.40 | 0.20 | 0.20 | 0.60 |
| 0.20 | 0.40 | 0.20 | 0.30 |
| 0.20 | 0.20 | 0.40 | 0.15 |

4. A + B → C

| [A] | [B] | Rate |
|---|---|---|
| 0.1 | 0.1 | 1 |
| 0.2 | 0.1 | 4 |
| 0.1 | 0.2 | 1 |

5. A + B → C

| [A] | [B] | Rate |
|---|---|---|
| .1 | .1 | 3 |
| .2 | .1 | 6 |
| .1 | .2 | 24 |

6. The effect of Solvent on Concentrations and Rates. Shown below are three scenarios using the same amount of reactants but differing volumes of solvent. Calculate the relative rates, assuming r= k[A][B]

| Moles A | [A] | Moles B | [B] | Liters of Solvent | Relative Rate |
|---|---|---|---|---|---|
| 0.5 | | 0.5 | | 1 | 1 |
| 0.5 | | 0.5 | | 2 | |
| 0.5 | | 0.5 | | 0.5 | |

7. Which is true for: A + 2B → C + D r= k[A[B]?
   a) doubling [A] will not affect rate
   b) doubling both [A] and [B] will make rate 4 times faster
   c) doubling both [A] and [B] will multiply rate by 8
   d) doubling [B] will double rate

15.7 Some Specific Calculations Available for First Order Reactions

rate = k[A] = -Δ[A]/Δt use calculus, integrate: $\boxed{\ln [A]_t = -kt + \ln[A]_o}$

- Equation in the form of a linear plot: y = mx + b form.
  - If actual concentration $[A]_t$ is measured and plotted (y axis) as a function of time (x axis), the slope of the line equals –k.
  - Note: only in the case of a 1st order reaction will this plot as a straight line.

Versions of the equation that are useful for 2-point analyses.

| | | | | | |
|---|---|---|---|---|---|
| $\ln\left(\frac{[A]_o}{[A]_t}\right) = kt$ | Variations: | $\frac{[A]_o}{[A]_t} = (kt)^e$ | $[A]_o = [A]_t(kt)^e$ | $[A]_t = \frac{[A]_o}{(kt)^e}$ | $t = \frac{1}{k}\ln\left(\frac{[A]_o}{[A]_t}\right)$ |

Applications: Solve for
1. $[A]_t$ at any time, given k and t
2. the time "t" for an original $[A]_o$ to decline to $[A]_t$
3. k

Handling "In"

1. Enter $[A]_o/[A]_t$ ratio, then hit LN button
2. "antiln" Find "x", given: $\ln\frac{100}{x} = 1.83$

   a. Solution: enter 1.83, hit $e^x$
   b. Set the resulting number = 100/x
      - In the general case, whatever follows "ln"
   c. Solve from there.

Practice using ln:

a. ln 1.8 =

b. ln (100/18) =

c. ln (18/7.2) =

d. ln x =1.43

e. ln (14/x) =1.86

f. ln (100/x) =1.13

Assume 1st Order Rate Laws for the Following:

$$\boxed{\ln\left(\frac{[A]_o}{[A]_t}\right) = kt}$$

Variations: $\frac{[A]_o}{[A]_t} = (kt)^e$

1. **FIND k**. What is rate constant if [A] goes from 1.0 M → 0.32 M in 46 sec?

2. **FIND t**. If k = 113 $years^{-1}$, how long will it take for 10% of A to react?

Hint: $[A]_o$ =
$[A]_t$ =

3. **FIND $[A]_t$** If k = 0.061 $days^{-1}$, what % of a spilled poison remains after 12 days?

Hint: set $[A]_o$ =
$[A]_t$ =

C. Half-Life $t_{1/2}$: Time for Concentration to Drop by Half (for 1st order reaction)

at $t_{1/2} \Rightarrow [A]_t = {}^1/_2\,[A]_o$

$$kt_{\frac{1}{2}} = \ln\frac{[A]_t}{[A]_0} = \ln 2 = 0.693$$

$$\boxed{\mathbf{kt_{1/2} = 0.693}}$$

Assume 1st Order Rate Laws for the following Problems

1. The half life for A is 30 sec. If you start with 128 A, how many will be left after

| t (sec) | Amount | | t (sec) | Amount |
|---|---|---|---|---|
| 0 | 128 | | 120 | |
| 30 | | | 150 | |
| 60 | | | 180 | |
| 90 | | | 210 | |

2. If k is 0.36 $days^{-1}$, what is $t_{1/2}$ and how long will it take for 75% to decay?

3. $^{14}C$ decomposes with $t_{1/2}$ = 5730 years. What is k for decomposition?

Higher Order Reactions

- -time/concentration/half-life relationships more complex
- -not responsible

13.4, 13.5 Reactions, Energetics, and Temperature

Q: Why are rates influenced by concentration, temp.?

A. Nanoscale Reactions

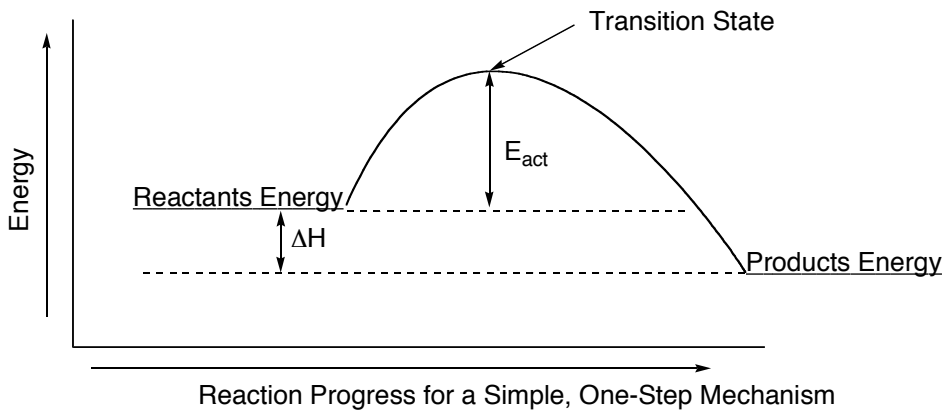
- While an overall reaction may involve many steps (13.7), elementary steps are either unimolecular or bimolecular

1. Unimolecular: A single molecule either rearranges or decomposes
   - Examples:
     a. A → B
     b. A → B + C
   - Energy is required

2. Bimolecular: 2 molecules collide
   a. Orientation, angle must be suitable
      - Most collisions do not succeed
   b. Reactants must collide with enough energy
      - Called "activation energy, $E_a$"

| |
|---|
| Higher concentration → mole collisions → faster rate<br>Higher temperature → higher energy → more of the collisions that do occur succeed |

B. Energy Diagrams, Activation Energy, Transition State




- **Transition State**: the energy maximum on the road to products (worst spot energetically)
- **Activation Energy $E_a$ or $E_{act}$**: the energy gap between reactants and Transition-state
- **ΔH**: The energy gap between reactants and products

1. **the higher the activation barrier, the slower the reaction**
2. the transition-state is higher in energy than either the reactants or the products, but it must be crossed
3. even exothermic reactions have activation barrier
   - because the cost of breaking old bonds precedes the payoff of making new and improved bonds
4. the higher the temperature, the higher the odds that the reactants have enough energy to clear the barrier
   - at a higher temperature, a higher fraction of the molecules are able to clear the barrier
   - note: at higher temperature, the rate law for the reaction will stay basically the same, but the k value will be higher
5. $E_{act}$ is unique for each reaction
6. $E_{act}$ has no correlation with ΔH
7. **Catalysts** change a reaction mechanism in such a way that the transition state is lowered

C. Arrhenius Equation: Not for Test, but **<u>May be Helpful for Lab</u>**

$k = Ae^{-Ea/RT}$ R = constant = 0.00831
A = constant unique to each reaction

| | |
|---|---|
| Qualitative: | 1. Large $E_{act}$ → smaller k (and slower rate)<br>2. higher temperature → larger k (and faster rate) |

<u>Math: take the natural log of both sides, end up with some practical variations:</u>

a. Graphical Format $$\ln k = \frac{-E_{act}}{0.00831}\left(\frac{1}{T}\right) + \ln A$$

- y = mx + b form
- Graph ln k vs 1/T
  - slope solves for $E_{act}$ and intercept solves for A constant

b. Two-Point Format $$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_{act}}{0.00831}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$E_{act}$ in kJ/mol
T in Kelvin

<u>Applications of Two-Point Solution:</u>
1. Given measured k's at 2 temps, can find $E_{act}$
2. Given $E_{act}$ and the k at one temp, can find the k at any other temp
3. Given $E_{act}$ and the k at one temp, can find whatever temperature is required to produce a desired rate constant (for example, if I know a reaction is way too slow, and I want to know what it would take to make it ten times faster…)

13.6,7 Reaction Mechanisms and Rate Laws
A. Examples
1. Elementary steps are uni- or bimolecular
2. Most reactions are multistep (especially catalyzed reactions)
3. "Intermediates": shortlived, forms in one step, destroyed in another
   - observed on both product and reactant sides, cancel out
   - since concentrations normally too low to measure → they do not appear in the final rate law
   - key note for multiple choice questions!
4. **The final rate law should only include reactants (in the balanced reaction) and perhaps catalyst. NOT INTERMEDIATES.**
5. Rate laws of <u>elementary steps</u> depend directly on reactants! Examples:

| | |
|---|---|
| A → B | r = k[A] |
| A + A → B + C | r = k[A]$^2$ |
| A + B → C + D | r = k[A][B] |

Note: this is in complete contrast to balanced reactions

6. **<u>Given a mechanism, you can deduce the rate law</u>**
7. Elementary steps must sum to give the overall balanced equation

For the following, classify the molecularity of the elementary steps, identify intermediates (scratch them out), and write overall rate laws.

Molecularity Intermediates Overall Rate Law

1. $A \rightarrow B$

2. $CH_3Br + {}^{\ominus}OH \rightarrow CH_3OH + Br^{\ominus}$

3. $2A \rightarrow B + C$ slow
   $B + D \rightarrow E$ fast
   Sum:

4. $A + B \rightleftharpoons C$ fast
   $C + D \rightarrow E + F$ slow
   Sum

5. $A + A \rightarrow B$ fast
   $B + C \rightarrow D + E$ slow
   Sum

6. $A \rightarrow B + C$ slow
   $B + C + D \rightarrow E + F$ fast
   Sum

C. Deducing Rate Laws from Multistep Mechanisms: Determined by the Slowest Step = "The Rate Determining Step"
   1. The slowest step is the bottleneck
   2. Any step after the slow step has no impact on the overall rate of conversion
      - Any reactant after the slow step does not appear in the rate law
   3. **Any reactant in or before the slow step does appear in rate law**
      - **If it appears twice in or before the slow step, it will be 2nd order, etc..**
   4. No intermediates should appear in any overall rate law

Some practical skills

Given a mechanism → write the rate law

Given a rate law → distinguish plausible from implausible mechanisms

Distinguishing among possible mechanisms, given a rate law:

1. Which mechanism is plausible for the reaction shown, given the rate law:

$A + 2B \rightarrow C$ rate = k[A]

a. $A + B \rightarrow D$ (slow)
$D + B \rightarrow C$ (fast)

b. $B + B \rightarrow E$ (slow)
$A + E \rightarrow C$ (fast)

c. $A \rightarrow F$ (slow)
$F + B \rightarrow G$ (fast)
$G + B \rightarrow C$ (fast)

d. $B + B \rightarrow H$ (fast)
$A + H \rightarrow C$ (slow)

<u>Identifying a Rate Law, given the Mechanism:</u>

2. Given the mechanism shown, what is a reasonable rate law?

$2A + 2B \rightarrow C$

Mechanism: $A + B \rightarrow D$ (slow)
$D + B \rightarrow E$ (fast)
$A + E \rightarrow C$ (fast)

a. $r = k[A][B]$

b. $r = k[A][E]$

c. $r = k[A]^2[B]^2$

d. $r = k[A]^2[B]^2[D][E]$

<u>Derivation of Rate Law when 1st Step Is Not the Slow Step, and which Proceed Via a Reactive Intermediate (not for test)</u>

Example Mechanism:

Step 1 $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$ fast, but reversible

Step 2 $C + D \xrightarrow{k_2} E + F$ slow

$A + B + D \longrightarrow E + F$

Overall rate law:

- Intermediates (C in this example) don't build up. They reach a steady state (usually a very low concentration), in which the rate of formation equals the rate of destruction

  Rate of formation = Rate of destruction

  $k_1[A][B] = k_{-1}[C] + k_2[C]$
- Since step 2 is slow, it probably makes a small contribution to the rate of destruction and can be dropped.

  Thus, the equality can be simplified to: $k_1[A][B] = k_{-1}[C]$
- Rearrange: $[C] = \frac{k_1}{k_{-1}}[A][B]$
- The overall rate is given by the slow step: $r = k_2[C][D]$
- Substitution in for [C] → $r = k_2(\frac{k_1}{k_{-1}}[A][B])[D]$
- Since $k_2 \frac{k_1}{k_{-1}}$ is itself a constant, the overall rate can be rewritten as: $r = k'[A][B][D]$

15.7 Catalysts

**General Considerations**

1. Increase Rates
2. Tiny quantities of catalysts suffice (because they are continuously recycled)
3. Not used up, the final quantity of catalyst equals the initial quantity
   - They are recycled ("catalytic converter")

**Mechanistic and Energetics Considerations**

4. A catalyst speeds up a reaction by providing a **new mechanism** with a lower transition-state
   - "Tunnel" through energy barrier
5. The new mechanism is always more complex
6. While $E_{act}$ is reduced, the overall $\Delta H$ is unchanged. (metabolism…)
7. Catalysts dramatically reduce temperature/heat requirements for reactions (metabolism…)
   - Industrial Attraction: cost effective, small amounts, lower temperatures, easier engineering, reduces waste disposal, etc..
8. A catalyst reacts early in a mechanism, but is then regenerated later in a mechanism

| | At Beginning | In Between | At End |
|---|---|---|---|
| "Intermediates" | Not present | They form but then react away | Not present |
| "Catalysts" | Present | They react away, but then reform again | Present |

**Recognition:**

9. A catalyst does not appear in balanced equation
10. A catalyst does appear in rate law

**Enzymes (Section 13.9)**

11. Enzymes are Big Proteins that Catalyze Biochemical Reactions (Section 13.9)
    - >100,000 enzymes
    - can increase rates by millions or billions!
    - Remarkable specificity
    - Most diseases involve enzyme malfunction
    - Medicinal research addresses these problems, why enzymes don't turn on or off correctly

# Chapter 13 Kinetics Math Summary

- Handling "ln y = x" on calculator:
  1. When you know "y" but want to solve for "x", enter "y" and hit your "ln" button. (On some calculators, you will instead hit "ln" button first, then enter "y")
  2. When you know "x" but want to solve for "y", enter "x", then hit your $e^x$ button

- Determining the "Order" of a Particular Reactant in a Rate Law

  Use two different concentrations ($[A]_1$ and $[A]_2$), and then measure the rates ($r_1$ and $r_2$). Set the rate ratio ($r_2/r_1$) equal to the concentration ratio ($[A]_2/[A]_1$) to the "x" power. "x" is the "Order" for reactant A. Usually "x" will be a small whole number [0, 1, 2, occasionally 3].

$$\mathbf{r_2/r_1 = ([A]_2/[A]_1)^x}$$

  - In general, for $y = m^x$ , what does the "x" mean? It's the number of times you would have to multiply "m" times "m" to equal "y". Examples: $2 = 2^x$ then x = 1; $4 = 2^x$ then x = 2, since 2 x 2 = 4. For $8 = 2^x$ then x = 3, since 2 x 2 x 2 = 8. And for $16 = 2^x$ then x = 4, since 2 x 2 x 2 x 2= 16.
  - In general for $y = m^x$ then x = (ln y)/(ln m).

- Rate Constants, Quantities and Half-Lives for First-Order Reactions

$$\mathbf{kt_{1/2} = .693}$$

  - Given k, can find $t_{1/2}$
  - Given $t_{1/2}$ can find k.

$$kt = \ln([A]_O/[A]_t)$$

  - $[A]_O$ is the amount of material at time zero
  - $[A]_t$ is the amount of stuff at time "t"
  - when dealing with problems involving "percents", the original percent is 100%

- The Arrhenius Equation (won't be test-responsible)

$$k = Ae^{(-E_a/RT)}$$

  - R = constant = 0.00831
  - T in Kelvin
  - $E_a$ is the activation energy in kJ/mol
  - A is a constant for each reaction

- Solving for $E_a$ (activation energy) given known rate constants at two temperatures (won't be test responsible, but used for laboratory)

$$E_a = [0.00831\ln(k_2/k_1)] / (1/T_1 - 1/T_2) \qquad \text{Answer in kJ/mol}$$