CHEM 116
Collision Theory and Reaction Mechanisms

October 17, 2006
Prof. Sevian

Agenda

Kinetics: the study of the rates of chemical reactions
- Kinetics at the particle level
  - Collision theory
  - Arrhenius equation
- Reaction mechanisms

Group problem

(please sit with your groups from the start of class today, so we can minimize disruption and maximize your work time on the group problem)

General equation for half-life

If the reaction is first-order, meaning

$$\begin{cases} \text{Rate} = \dfrac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}] & \textbf{differential rate law} \\ \ln[\mathrm{A}]_t = \ln[\mathrm{A}]_0 - k\,t & \textbf{integrated rate law} \end{cases}$$

and if you know the value of the rate law constant k, then you can determine the half-life algebraically

Looking for value of t when $[\mathrm{A}]_t = \frac{1}{2}[\mathrm{A}]_0$, or $\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = 2$

$$\ln[\mathrm{A}]_t = \ln[\mathrm{A}]_0 - k\,t$$

Rearranging,

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}\right) = k\,t$$

So at the time where half the reactant is gone:

$$\ln(2) = k\,t_{half-life}$$

$$t_{half-life} = \frac{\ln(2)}{k}$$

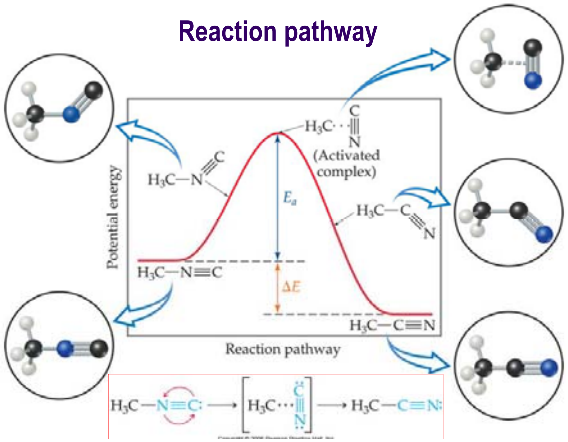
Note: 2nd equation was backwards in last week's notes. This one is correct.

$$\boxed{t_{half-life} = \frac{0.693}{k} \quad \text{or} \quad k = \frac{0.693}{t_{half-life}}}$$

Key points about kinetics so far

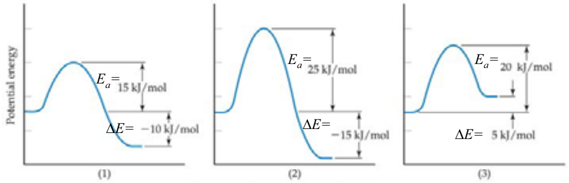
- There are two ways to determine a rate law experimentally
  1. Data needed: concentration vs. time as a single experiment progresses
     Process: graph versions of [A] vs. versions of t to determine value of *n* in $d[A]/dt = -k[A]^n$
  2. Data needed: multiple experiments varying initial concentration, measure initial rate for a chemical in the rxn
     Process: compare experiments to determine values of *n* (and *m*) for each reactant in rate $= k[A]^n[B]^m$
- In a first-order reaction, it is often easier to work with half-life to predict amount of reactant remaining
- Rate law constant, k, depends on temperature and activation energy, E_a, as well as other factors (e.g., % of collisions that are properly oriented). Value of E_a can be determined by measuring k vs. T and using Arrhenius equation to interpret results.

Reaction pathway

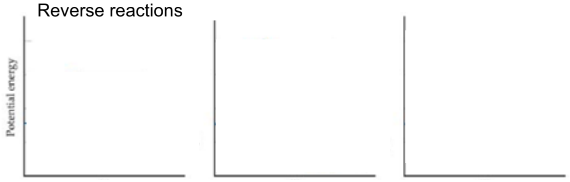


Reversing an energy profile

Forward reactions

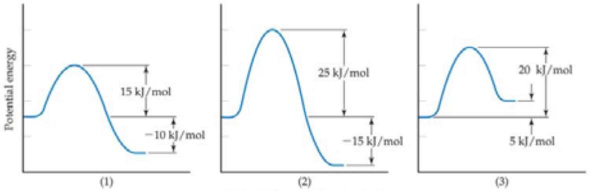


Reverse reactions



Relating energy profiles, activation energies, and speeds of reaction

Rank these three reactions from slowest to fastest, assuming they have the same value for A (in Arrhenius equation, $k = Ae^{-Ea/RT}$).



Copyright © 2006 Pearson Prentice Hall, Inc.

What would the energy profiles look like if you were talking about the reverse reactions?

Relating energy profiles, activation energies, and speeds of reaction

Rank the reverse reactions from slowest to fastest, assuming they have the same value for A (in Arrhenius equation, $k = Ae^{-Ea/RT}$).

What is a reaction mechanism?

- A proposed sequence of ELEMENTARY STEPS by which the reaction *could* proceed, in such a way that the EXPERIMENTALLY DETERMINED RATE LAW can be derived from the combination of the elementary steps.
    1. The steps must sum to the overall reaction
    2. The mathematical combination of the rates of the elementary steps must result in the experimentally determined rate law
- There is often more than one possible reaction mechanism that would result in the same experimentally determined rate law.
- Very important to remember: the only way to find out the form of the actual rate law is to determine it experimentally. The actual rate law cannot be predicted from the overall reaction.

Elementary reactions

- An elementary reaction is one of the steps in a reaction mechanism
- Elementary reactions are (we propose) the actual steps that chemicals go through as they progress from initial reactants to final products
- Because elementary reactions are the actual steps, they contain information about the molecularity of the collisions that must happen in order for an elementary step to occur
- Since the molecularity information is in the elementary reaction, you can write down a rate law based on that molecularity
- Examples of rate laws for some elementary reactions

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

- Be careful: you cannot write down the rate law for an overall reaction by inspection of the reaction, because most overall reactions are not elementary (i.e., most reactions have complicated mechanisms)

Example of a reaction mechanism

Talk about molecularity

Overall reaction

$$2\,I^- + 2\,H^+ + H_2O_2 \rightarrow I_2 + 2\,H_2O$$

✓ Condition 2 is satisfied

Has experimentally observed rate law:

$$\text{Rate} = k\,[I^-]\,[H_2O_2]$$

Proposed reaction mechanism (is this plausible?)

Rate-determining step (RDS)

Step 1: $I^- + H_2O_2 \rightarrow HOI + OH^-$ (slow step) $\text{Rate} = k_1\,[I^-]\,[H_2O_2]$

Step 2: $HOI + I^- \rightarrow OH^- + I_2$ (fast step) $\text{Rate} = k_2\,[HOI]\,[I^-]$

\+ Step 3: $[H^+ + OH^- \rightarrow H_2O] \times 2$ (fast step) $\text{Rate} = k_3\,[H^+]\,[OH^-]$

$$I^- + H_2O_2 + \cancel{HOI} + I^- + 2\,H^+ + \cancel{2\,OH^-} \rightarrow \cancel{HOI} + \cancel{OH^-} + \cancel{OH^-} + I_2 + 2\,H_2O$$

Intermediates

$$\boxed{2\,I^- + 2\,H^+ + H_2O_2 \rightarrow I_2 + 2\,H_2O}$$

✓ Condition 1 is satisfied

Another example of a reaction mechanism

Overall reaction

$$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$$

Has experimentally observed rate law:

$$\text{Rate} = k\,[N_2O_5]$$

Proposed reaction mechanism (is this plausible?)

Step 1: $[N_2O_5 \leftrightarrows NO_2 + NO_3] \times 2$ (fast reversible) $\text{Rate} = ?$

RDS

Step 2: $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ (slow step) $\text{Rate} = k_2\,[NO_2]\,[NO_3]$

\+ Step 3: $NO_3 + NO \rightarrow 2\,NO_2$ (fast step) $\text{Rate} = k_3\,[NO_3]\,[NO]$

$$2\,N_2O_5 + \cancel{NO_2} + \cancel{NO_3} + \cancel{NO_3} + \cancel{NO} \rightarrow 2\,NO_2 + 2\,\cancel{NO_3} + \cancel{NO} + \cancel{NO_2} + O_2 + 2\,NO_2$$

$$\boxed{2\,N_2O_5 \rightarrow 4\,NO_2 + O_2}$$

✓ Condition 1 is satisfied

What is a "fast reversible" reaction?

- Reversible means reaction proceeds in both directions
- Equilibrium means forward rate = reverse rate (a state of dynamic equilibrium)
- Sometimes "fast reversible" is written "fast equilibrium" these are equivalent terms

$$N_2O_5 \leftrightarrows NO_2 + NO_3$$

is shorthand for saying

$$\left.\begin{array}{l} N_2O_5 \rightarrow NO_2 + NO_3 \\ \text{happens simultaneously with} \\ NO_2 + NO_3 \rightarrow N_2O_5 \end{array}\right\} \begin{array}{l} \text{Rate}_{\text{forward}} = k_{\text{forward}}\,[N_2O_5] \\ \text{and} \\ \text{Rate}_{\text{reverse}} = k_{\text{reverse}}\,[NO_2]\,[NO_3] \end{array}$$

but since forward rate and reverse rate are equal,

$$k_{\text{forward}}\,[N_2O_5] = k_{\text{reverse}}\,[NO_2]\,[NO_3]$$

How do we combine a fast reversible rate with a rate-determining step?

Goal: to find out if the rate law predicted by the mechanism has the same mathematical for as the experimentally determined rate law

So far we have:

Experimentally determined rate law: $\text{Rate} = k\,[N_2O_5]$

Proposed mechanism's RDS: $\text{Rate} = k_2\,\boxed{[NO_2]\,[NO_3]}$

Proposed mechanism's fast reversible: $k_{\text{forward}}\,[N_2O_5] = k_{\text{reverse}}\,\boxed{[NO_2]\,[NO_3]}$

Solve the second equation for $([NO_2][NO_3])$ and substitute into RDS

$$Rate = k_2\left(\frac{k_{forward}}{k_{reverse}}\right)[N_2O_5]$$

$$= k_{combination}[N_2O_5]$$

✓ Condition 2 is satisfied

Another example

(similar to Sample Exercise 14.15, p. 606)

Overall reaction

$$2\,NO_2Cl \rightarrow 2\,NO_2 + Cl_2$$

Has experimentally observed rate law:

$$Rate = k\frac{[NO_2Cl]^2}{[NO_2]}$$

Is the following proposed reaction mechanism plausible?

Step 1: $NO_2Cl \leftrightarrows NO_2 + Cl$ (fast reversible)

Step 2: $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$ (slow step)

- Identify intermediates
- What effect does increasing the concentration of the product NO_2 have on the reaction rate?