CHEM 116
Reaction Mechanisms and Intro to Nuclear Chemistry

Lecture 14
Prof. Sevian

Today we will begin with the end of Lecture 13 notes that we didn't finish last Thursday, about reaction mechanisms. If you have already printed Lecture 13, then bring it to lecture with you, and you can avoid re-printing those pages by printing all <u>except</u> pages 3 to 8 of these Lecture 14 notes. In other words, print only pages 1-2, and pages 9-13.

Today's agenda

Kinetics: the study of the rates of chemical reactions

- Modeling kinetics at the particle level (finish ch. 14)
  - Reaction mechanisms
- Nuclear chemistry (the only parts we will cover in ch. 21)
  - Types of radiation
  - Nuclear decay equations

---- End of material that is covered on Exam 2 ---

- Introduce the concept of equilibrium (ch. 15, this material will be on Exam 3)

Clicker question on rate laws

For the following reaction

$$2\ CO\ (g) + O_2\ (g) \rightarrow 2\ CO_2\ (g)$$

[CO] (mol/L)	$[O_2]$ (mol/L)	Initial rate $\left(\frac{\text{mol}}{\text{L} \cdot \text{min}}\right)$
0.20	0.20	1.84×10^{-4}
0.20	0.40	3.68×10^{-4}
0.60	0.20	1.66×10^{-3}

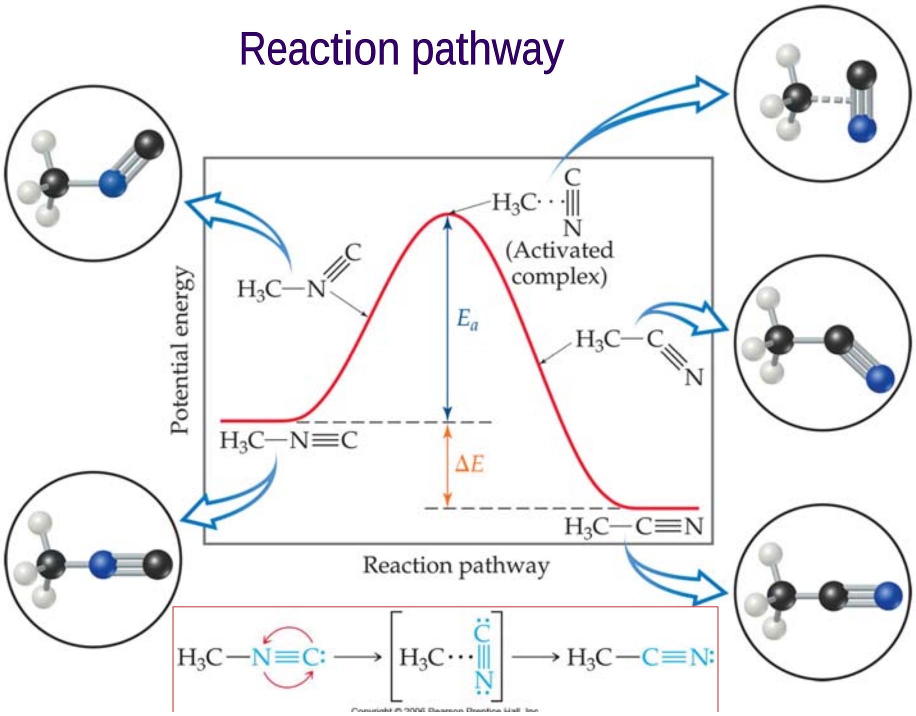
the data above were obtained in laboratory experiments. What is the form of the rate law for this reaction?

(A) Rate = k [CO] $[O_2]$
(B) Rate = k [CO] $[O_2]^2$
(C) Rate = k $[CO]^2$ $[O_2]$
(D) Rate = k $[CO]^2$ $[O_2]^2$

Key points about kinetics so far

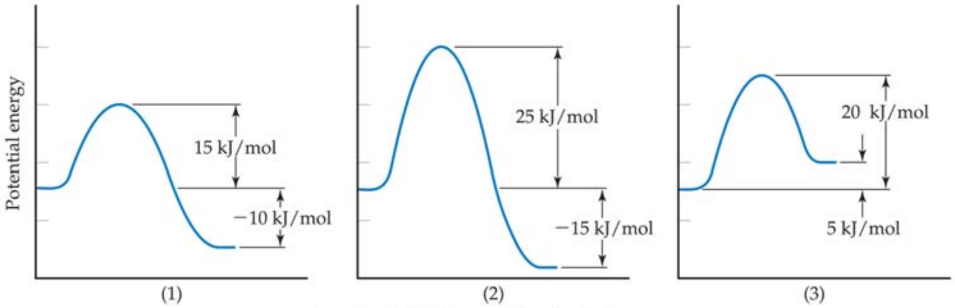
- There are two ways to determine a rate law experimentally
  1. Data needed: concentration vs. time as a single experiment progresses
     Process: graph versions of [A] vs. *t* to determine value of *n* in $d[A]/dt = -k[A]^n$
  2. Data needed: multiple experiments varying initial concentration, measure 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. Value of k is slope of (ln *k*) vs. (*1/T*) line. *T* must be in Kelvin.

Reaction pathway



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



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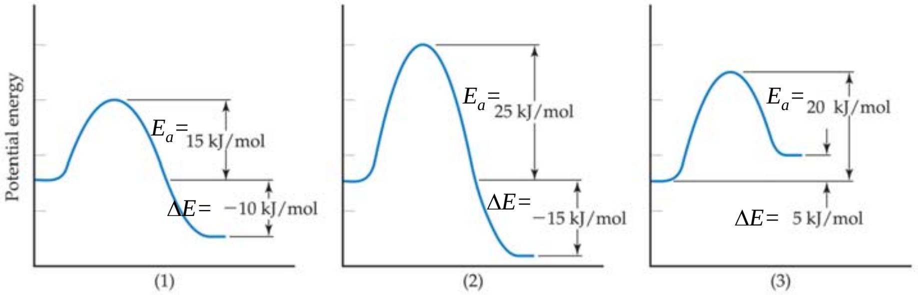
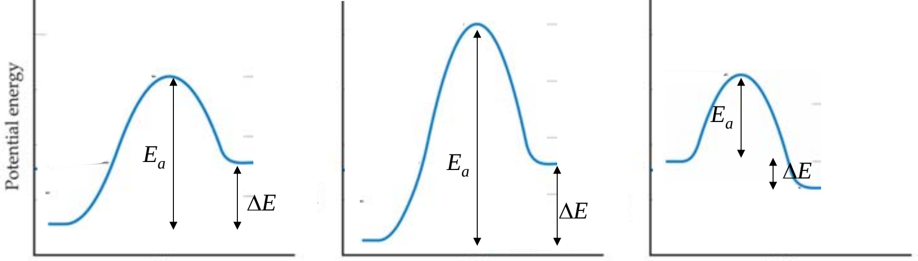
What would the energy profiles look like if you were talking about the reverse reactions?

Reversing an energy profile

Forward reactions

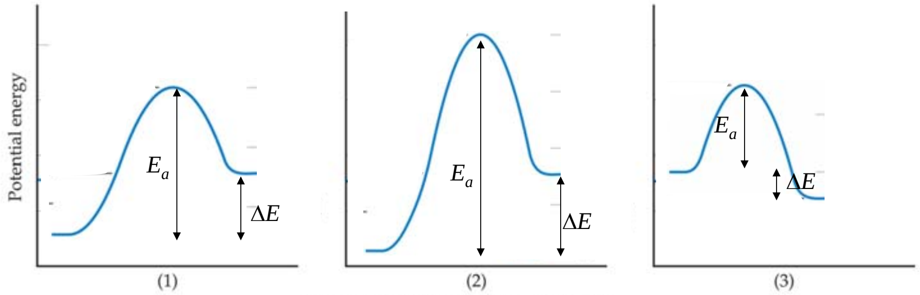


Reverse reactions



Clicker question:
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, $k = Ae^{-Ea/RT}$).



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Clicker choices:

(A) Rxn (1) is the fastest

(B) Rxn (2) is the fastest

(C) Rxn (3) is the fastest

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:

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

Rate-determining step

Proposed reaction mechanism (is this plausible?)

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) $\text{Rate} = ?$

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

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

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

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

✓ 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

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

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: $NO_2Cl \leftrightharpoons NO_2 + Cl$ (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?

Key points about rxn mechanisms

- A rxn mechanism is plausible if it satisfies two conditions
    1. The elementary steps must sum to the overall rxn
    2. The rate of the slowest elementary step has the same form as the experimentally determined rate law (may involve mathematical manipulation)
- You cannot write down a rate law by inspection of an overall reaction
- You CAN write down a rate law by inspection of an elementary step, because it contains information about the molecularity of the step
- Fast equilibrium/fast reversible reaction means forward rate equals reverse rate
- The chemicals that cancel out when you sum elementary steps are the intermediates in a rxn mechanism

A little bit about nuclear chemistry

- This is chapter 21
- Chemical bonding and chemical reactions are about what electrons do when one atom is near another atom – balance between energy changes and entropy changes
- Nuclear chemistry is about energy changes that occur when nuclear particles interact
- Practical uses of learning this
  - Medical applications (radiation therapy, diagnostic tools)
  - Archaeological dating
  - Nuclear power accounts for 20% of electricity generated in US
  - Nuclear weapons pose threats, are used in political bargaining…

Nuclear particles and processes

- Recall that protons determine identity and that different isotopes of an element result from differing quantities of neutrons
- Different isotopes of an element have different natural abundances
- Some isotopes are radioactive (unstable) and decay by specific processes to form more stable isotopes
- If a decay process results in a product with a different number of protons, then the identity of the product element is different than the original reactant
- Although conservation of mass does not apply (because mass and energy are inter-convertible), some conservation laws still apply in nuclear decays:
  - Conservation of mass number
  - Conservation of atomic number

Where does the mass go?

- Examples of nuclear processes
  - Alpha decay

$${}^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\mathrm{He}$$

$${}^{222}_{86}\mathrm{Ra} \rightarrow {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{He}$$

This is an alpha (α) particle, sometimes represented as ${}^{4}_{2}\alpha$

  - Beta decay

$${}^{131}_{53}\mathrm{I} \rightarrow {}^{131}_{54}\mathrm{Xe} + {}^{0}_{-1}\mathrm{e}$$

$${}^{231}_{90}\mathrm{Th} \rightarrow {}^{231}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e}$$

This is a beta (β) particle, which is a high-speed/energy electron that is ejected from the nucleus when a neutron changes into a proton and an electron. It is sometimes represented as ${}^{0}_{-1}\beta$

  - Positron is a positive electron (antielectron)

$${}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\mathrm{e}$$

More nuclear processes

- Gamma decay
  - Symbol is ${}^{0}_{0}\gamma$
  - Since no nuclear transmutations, no need to write equation
- Electrons and positrons can be captured

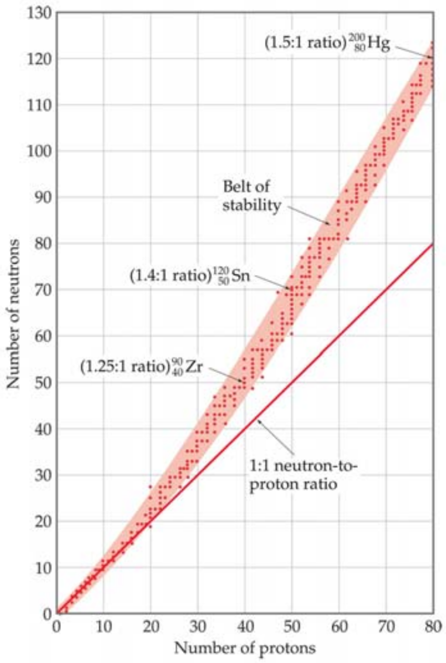
$${}^{81}_{37}\mathrm{Rb} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{81}_{36}\mathrm{Kr}$$

- Larger nuclei can split (fission) into smaller nuclei (often by neutron bombardment)

$${}^{1}_{0}\mathrm{n} + {}^{239}_{94}\mathrm{Pu} \rightarrow {}^{95}_{40}\mathrm{Zr} + {}^{142}_{54}\mathrm{Xe} + 2\,{}^{1}_{0}\mathrm{n}$$

- Smaller nuclei can fuse into larger nuclei

$${}^{1}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He}$$



Why are some nuclei stable and others are not?

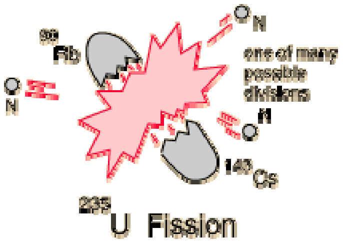
- Neutron to proton ratio
- If n/p is above belt of stability, need to make n smaller and/or p larger. How?

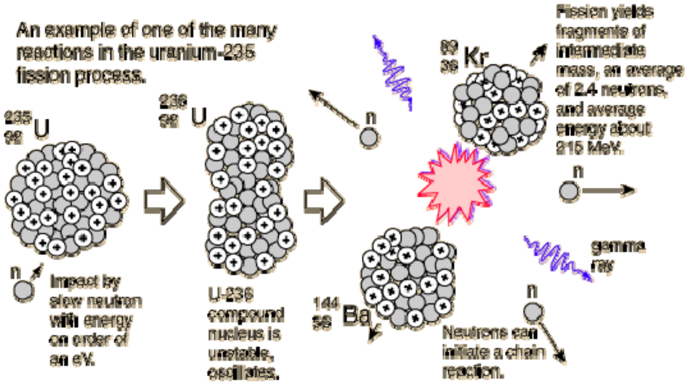
- Vice versa. How?

Where does nuclear energy come from?

- E = mc^2
- Example

$$^{1}_{0}\mathrm{n} + {}^{235}_{92}\mathrm{U} \rightarrow {}^{90}_{37}\mathrm{Rb} + {}^{143}_{55}\mathrm{Cs} + 3\ {}^{1}_{0}\mathrm{n}$$





Images from http://hyperphysics.phy-astr.gsu.edu/Hbase/nucene/fission.html

Key points about nuclear chemistry

- To write a nuclear equation, balance the protons (bottom number) and mass number (top number).
- There are many different kinds of nuclear processes.
- Most isotopes that exist are stable, some are unstable. Stability has to do with the n/p ratio.
- Protons and neutrons are held together in the nucleus by forces that are stronger than the + to + electrical repulsions. When the composition of the nucleus is changed, energy is released or must be absorbed.
- Energy and mass are related by $E=mc^2$.

What is equilibrium?

$$2\ NO_2 \leftrightarrows N_2O_4$$

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/no2n2o4equilV8.html

In this animation of the system at the particle level, what indication is there that the system is at equilibrium?

- Concentration of each chemical remains constant in time
- Both the forward and reverse reactions are occurring
- The rate of the forward reaction is EQUAL to the rate of the reverse reaction

At the macroscopic observable level:

When a system is at equilibrium, it looks like nothing is happening!

Mathematically, what is equilibrium?

$$2\ NO_2 \leftrightarrows N_2O_4$$

Remember from mechanisms that “$\leftrightarrows$” is shorthand for saying:

Forward reaction: $2\ NO_2 \rightarrow N_2O_4$

happens simultaneously with

Reverse reaction: $N_2O_4 \rightarrow 2\ NO_2$

Remember that:

$\text{Rate}_{\text{forward}} = k_{\text{forward}}\,[NO_2]^2$

and

$\text{Rate}_{\text{reverse}} = k_{\text{reverse}}\,[N_2O_4]$

Remember that at (dynamic) equilibrium, the forward and reverse rates reach the point of being equal

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

Therefore,

$k_{\text{forward}}\,[NO_2]^2 = k_{\text{reverse}}\,[N_2O_4]$

$$Q \equiv \frac{k_{forward}}{k_{reverse}} = \frac{[N_2O_4]}{[NO_2]^2}$$

This equation can be rearranged to define a new variable called *Q* (the reaction quotient) which is a function of reaction progress (think “time”) and can be measured at any time during the progress toward equilibrium, and which reaches (asymptote) a constant value *K* when the reaction reaches equilibrium:

$$\boxed{Q\,(t) \text{ approaches } K \text{ as } t \text{ approaches equilibrium}}$$