CHEM 116
Reaction Mechanisms, Nuclear Chemistry and Reaction Quotients

October 19, 2006
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Agenda

- Kinetics: Reaction mechanisms
- Nuclear chemistry: a very very brief introduction to some aspects of the field
- Equilibrium
  - Measuring concentrations in the lab
  - Reaction quotient is a measure of the ratio of concentrations of chemicals that are changing in the reaction
  - Reaction quotient approaches a constant value as equilibrium is achieved
  - What is equilibrium?

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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?

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Key points about rxn mechanisms

- A rxn mechanism is plausible if it satisfies two conditions
  - The elementary steps must sum to the overall rxn
  - 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

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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 aspects 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…

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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

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Where does the mass go?

- Examples of nuclear processes
  - Alpha decay

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

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

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

    $^{231}_{90}\mathrm{Th} \rightarrow {}^{231}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e}$
  - Positron is a positive electron (antielectron)

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

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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

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

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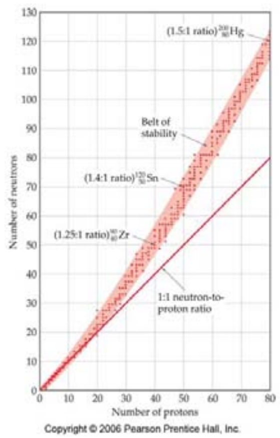

Why are some nuclei stable and others are not?

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

Key points about nuclear chemistry

- To write a nuclear process, 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 $E=mc^2$.

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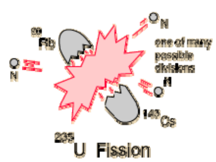
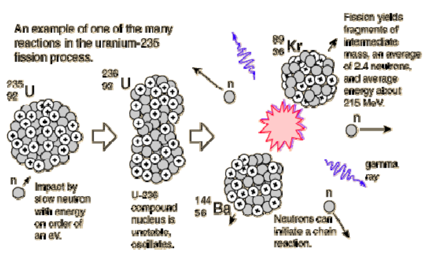
Where does nuclear energy come from?

- $E = mc^2$
- Example

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





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

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!

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Mathematically, what is equilibrium?

$$2\ NO_2 \leftrightarrows N_2O_4$$

Is shorthand for saying:

Forward reaction: $2\ NO_2 \rightarrow N_2O_4$ — $\text{Rate}_{forward} = k_{forward}\,[NO_2]^2$

happens simultaneously with — and

Reverse reaction: $N_2O_4 \rightarrow 2\ NO_2$ — $\text{Rate}_{reverse} = k_{reverse}\,[N_2O_4]$

Remember that at (dynamic) equilibrium, the forward and reverse rates are equal

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

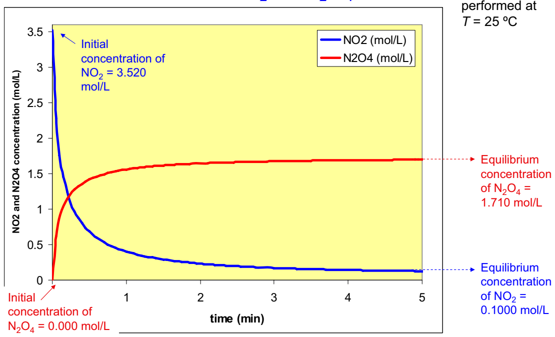
Therefore,

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

Concentrations: what we measure in lab

$$2\ NO_2 \leftrightarrows N_2O_4$$

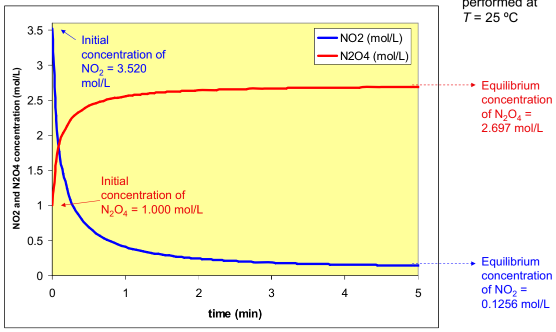
Experiment performed at T = 25 °C



Different initial conditions, same temperature

$$2\ NO_2 \leftrightarrows N_2O_4$$

Experiment performed at T = 25 °C



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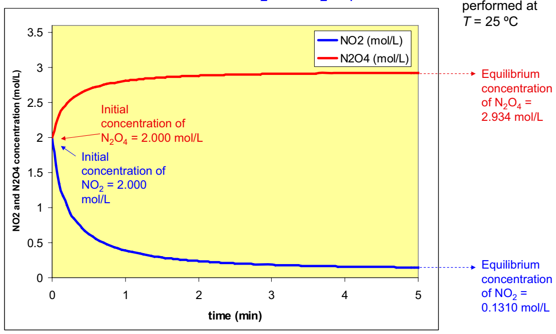

What does it mean?

Remember that at (dynamic) equilibrium

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

Therefore, theoretically

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

Rearranging, at equilibrium: $\dfrac{k_{forward}}{k_{reverse}} = \dfrac{[N_2O_4]}{[NO_2]^2}$

Since the forward and reverse rate constants only depend on temperature, then their ratio also does. In particular, let's define something called the REACTION QUOTIENT, Q, which is what the ratio of $k_{forward}/k_{reverse}$ would be if you set the forward and reverse rates to be equal.

In the case of the NO_2 and N_2O_4 system we are examining,

$$Q = \frac{[N_2O_4]}{[NO_2]^2}$$

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Comparing Q to its value at equilibrium

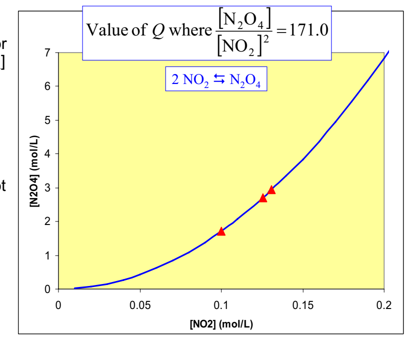
There are many sets of values for $[NO_2]$ and $[N_2O_4]$ where

$$\frac{[N_2O_4]}{[NO_2]^2} = 171.0$$

If a system is not at equilibrium, the value of

$$Q = \frac{[N_2O_4]}{[NO_2]^2}$$

is not 171.0



What does it mean if Q > 171.0? What does it mean if Q < 171.0?

Reaction quotient always approaches the same constant as the reaction approaches equilibrium

- Experimentally, we find that that after enough time, no matter what the starting concentrations, the reaction quotient always approaches a constant that depends only on temperature (and not at all on the initial concentrations)

	Equilibrium value of $[NO_2]$ in mol/L	Equilibrium value of $[N_2O_4]$ in mol/L	Value of Q at equil.
Initial conditions $[NO_2]$ = 3.520 M, $[N_2O_4]$ = 0.000 M	0.1000	1.710	$Q = \frac{1.710}{(0.1000)^2} = 171.0$
Initial conditions $[NO_2]$ = 3.520 M, $[N_2O_4]$ = 1.000 M	0.1256	2.697	$Q = \frac{2.697}{(0.1256)^2} = 171.0$
Initial conditions $[NO_2]$ = 2.000 M, $[N_2O_4]$ = 2.000 M	0.1310	2.934	$Q = \frac{2.934}{(0.1310)^2} = 171.0$

The value that the reaction quotient approaches is called the EQUILIBRIUM CONSTANT

- The reaction quotient is always a ratio of product concentrations over reactant concentrations

$$\textit{General reaction}: \quad a\,A + b\,B \leftrightarrows c\,C + d\,D$$

$$\textit{Reaction quotient}: \quad Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

- There is information contained in the value of the reaction quotient before equilibrium is reached
- The reaction quotient approaches a constant value after enough time has passed and the system is at equilibrium
- The equilibrium constant, K, is the value of Q when all the chemicals in the reaction reach their equilibrium concentrations
- The equilibrium constant depends only on temperature

Reaction Quotient vs. Equilibrium Constant

Reaction Quotient

- Symbol: Q

$$\text{General reaction: } a\,\text{A} + b\,\text{B} \leftrightarrows c\,\text{C} + d\,\text{D}$$
$$\text{Reaction quotient: } Q = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

- Situation: when the system is not at equilibrium
- The concentrations of the chemicals in the reaction continue to change as the reaction progresses toward equilibrium

Equilibrium Constant

- Symbol: K_c

$$\text{General reaction: } a\,\text{A} + b\,\text{B} \leftrightarrows c\,\text{C} + d\,\text{D}$$
$$\text{Equilibrium constant: } K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

- Situation: when the system is at equilibrium
- Once the system has reached equilibrium, the concentrations of chemicals involved in the reaction do not change

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Which chemicals are part of the expression for Q?

- Determine phase (liquid, gas, aqueous) the reaction takes place in
- Only chemicals that are in that phase are part of the reaction quotient, because chemicals in other phases remain in those phases
- In an aqueous reaction, spectator ion concentrations do not change, so spectator ions are not part of the reaction quotient either
- Examples:
  1. $N_2\,(g) + 3\,H_2\,(g) \leftrightarrows 2\,NH_3\,(g)$ $\quad Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$
  2. $2\,S\,(s) + 3\,O_2\,(g) \leftrightarrows 2\,SO_3\,(g)$ $\quad Q = \frac{[SO_3]^2}{[O_2]^3}$
  3. $Cu(NO_3)_2\,(aq) + Zn\,(s) \leftrightarrows Zn(NO_3)_2\,(aq) + Cu\,(s)$
     net ionic reaction: $Cu^{2+}\,(aq) + Zn\,(s) \leftrightarrows Zn^{2+}\,(aq) + Cu\,(s)$ $\quad Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$
  4. $PbCl_2\,(s) \leftrightarrows Pb^{2+}\,(aq) + 2\,Cl^-\,(aq)$ $\quad Q = \frac{[Pb^{2+}][Cl^-]^2}{1} = [Pb^{2+}][Cl^-]^2$

An easy way to remember it: only the highest entropy phases appear in Q