5.111 Lecture Summary #31 **Wednesday, November 26, 2014**

Reading for Today: 14.6, 17.7 in 5th ed and 13.6, 17.7 in 4th ed.
Reading for Lecture #32: 14.7-14.8, 14.10 in 5th ed and 13.7-13.8, 13.10 in 4th ed

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Topic: Kinetics

I. Radioactive Decay
II. Second Order Integrated Rate Laws
III. Relationship Between k and K
IV. Elementary Steps and Molecularity

I. **Radioactive Decay** is an example of a first order process. Current research includes topics ranging from nuclear waste storage to designing new radioactive tracers for use in medicine. MIT Chemistry Professor Alan Davison was a patent holder of Cardiolite™, which uses Technetium-99 for diagnostic organ imaging and bone scans.

The decay of a nucleus is ____________________ of the number of surrounding nuclei that have decayed. We can apply first order integrated rate laws:

$[A] = [A]_0\, e^{-k\,t}$ and $t_{1/2} = \frac{0.6931}{k}$

However, instead of concentration, the first order integrated rate law is expressed in terms of N (number of nuclei)

$N = N_o e^{-k\,t}$ k is the decay constant

t is time

N_0 is the number of nuclei originally present

Chemical kinetics – monitor changes in ______________________ over time

Nuclear kinetics – monitor rate of occurrence of ________________ events with a Geiger counter (radiation detector)

Decay rate is also called Activity (A)

$$\text{Activity} = A = \frac{-dN}{dt} = k\,N$$

because activity is proportional to the number of nuclei (N):

$N = N_o e^{-k\,t}$ can be expressed as $A = A_o e^{-k\,t}$ A is Activity
A_0 is original activity

<u>Units</u>
S.I. unit for Activity is the becquerel (Bq) 1 Bq = 1 radioactive disintegration per second
Older unit is the curie (Ci) 1 Ci = 3.7×10^{10} disintegrations per sec

Types of nuclear radiation
There are numerous types of nuclear radiation. Some types involve a mass change and others do not.

An alpha particle is the equivalent of a helium-4 nucleus (2 protons, 2 neutrons) whereas a beta particle is an electron. Thus, alpha decay involves a mass change whereas beta decay does not.

There is a huge variation in half-life, from milliseconds "ms" to days "d" to years "y" or "a" to Giga years "Ga" (10^9 years)

Some nuclear decay series (e.g. Uranium238) involve more than one type of decay process. (A = atomic mass, Z= atomic number)

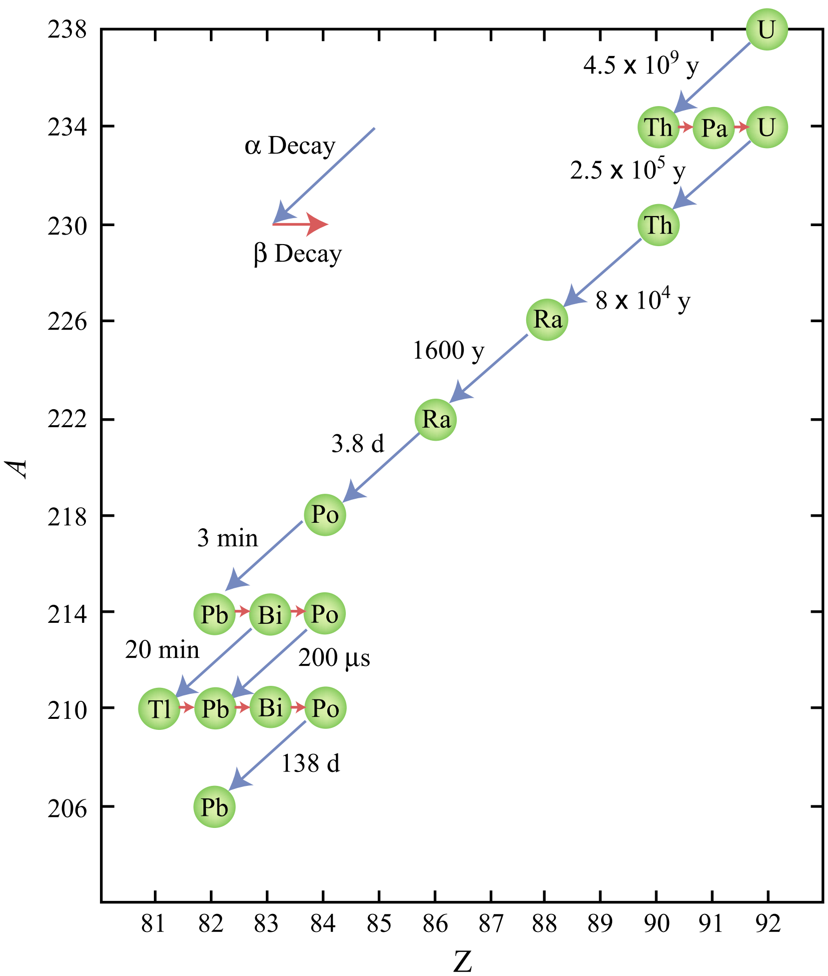


Figure by MIT OpenCourseWare.

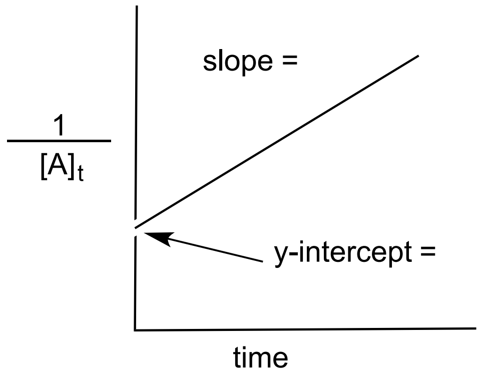
Days of Our Half-Lives
by MIT graduate: Professor Mala Radhakrishnan

Published in Atomic Romances, Molecular Dances (2011)

II. Second Order Integrated Rate Laws

The equation for second order integrated rate law is $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

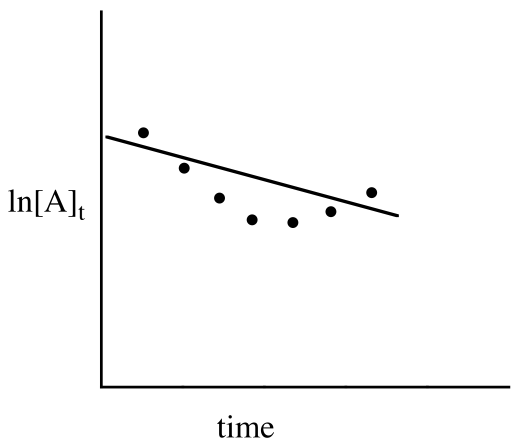
Plotting gives us:



The equation for second order half-life is:

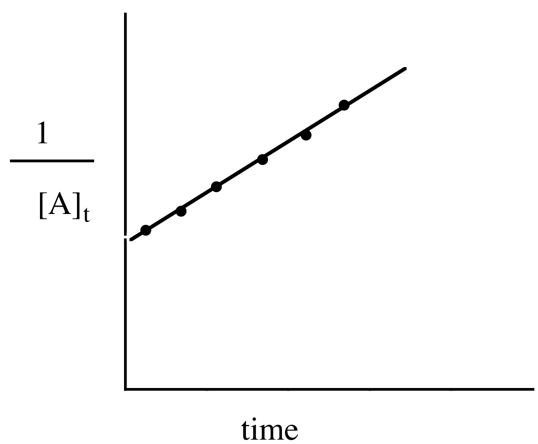
$t_{1/2} = \frac{1}{k[A]_0}$ Second order half-life depends on ______________________________

We can determine if the data are a better fit to a first-order equation or a second-order equation. Here the data fit better to a second-order equation.



first-order plot

$\ln[A]_t = -kt + \ln [A]_o$



second-order plot

$$\frac{1}{[A]_t} = k\,t + \frac{1}{[A]_0}$$

III. Relationship between k and K

At equilibrium, the rates of the forward and reverse reactions are _______________.
The equilibrium constant for a chemical reaction that has form A + B ⇔ C + D is

K =

Suppose experiments show both the forward reaction and reverse reaction are second order, with the following rate laws:

$$A + B \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} C + D$$

forward reaction $rate_f =$

reverse reaction $rate_r =$

At equilibrium, these rates are equal: $k_1 [A][B] = k_{-1} [C][D]$

and $\frac{[C][D]}{[A][B]} = \frac{k_1}{k_{-1}}$

Therefore $K =$

The equilibrium constant for a reaction is equal to the ratio of the rate constants for the forward and reverse elementary reactions that contribute to the overall reaction.

Equilibrium constants in kinetics terms:

$K > 1$ k_1 _____ k_{-1}

$K < 1$ k_1 _____ k_{-1}

IV. Elementary Steps and Molecularity

Reactions do not typically occur in 1 step, but proceed through a series of steps.

Each step is called an elementary reaction.

For an overall reaction, the order and the rate law ________________________ be derived from the stoichiometry of the balanced reaction.

For an elementary reaction, the order and rate law________________________ predicted.

Elementary reactions occur exactly as written.

The number of reactant molecules that come together to form product is the **molecularity**

An unimolecular process involves ____reactant (example(s): _________________________)

A bimolecular process involves _____ reactants (common)

A termolecular process involves _____ reactants (rare)