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5.111 Principles of Chemical Science
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5.111 Lecture 32

Kinetics Topics: Radioactive Decay, Second Order Integrated Rate Laws, Kinetics and Chemical Equilibrium, Introduction to Reaction Mechanisms
Chapter 13 (p 498-501, 507-508) and Chapter 17 (p 660-664)

Radioactive Decay

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

$[A] = [A]_0 e^{-kt}$ 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)

$N = N_o e^{-kt}$ $k \equiv$ decay constant

$t \equiv$ time

$N_0 \equiv$ number of nuclei originally present

Chemical kinetics – monitor changes in concentration over time

Nuclear kinetics – monitor rate of occurrence of decay 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):

$N = N_o e^{-kt}$ can be expressed as $A = A_o e^{-kt}$ $A \equiv$ Activity
$A_0 \equiv$ original activity

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

Table of types of radiation p. 701
- alpha decay – mass change of helium-4 nucleus (2 protons, 2 neutrons)
- beta decay – no mass change (particle = electron)

Table of half-lives p. 713

Uranium238 decay series
p. 706 (A = atomic mass, Z= atomic number)

Days of Our Half-Lives
by Chemistry Poet: Mala Radhakrishnan

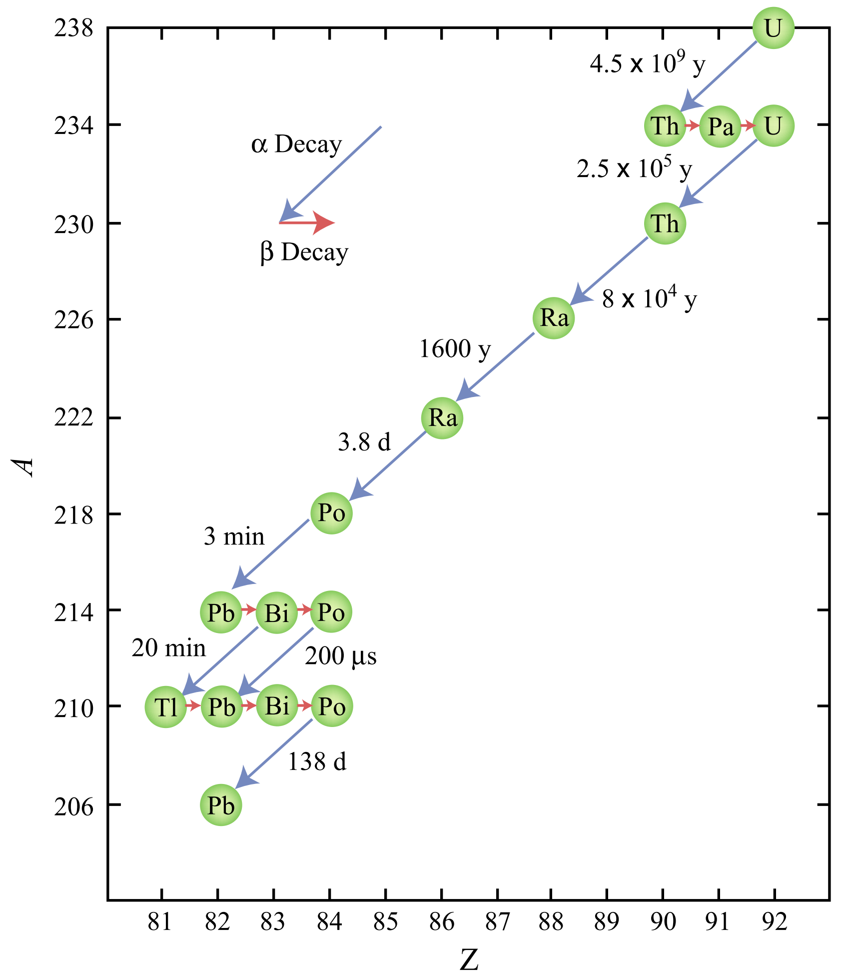


Figure by MIT OpenCourseWare.

<u>Radioactive Decay Example</u>

Find the original activity and the activity after 17 years (5.4×10^8 sec) of 0.50 g of

$^{239}_{94}Pu$ ($t_{1/2}$ = 24,000 years (7.6×10^{11} sec))

Find N_0

Find k

Find A_0

Find A

<u>Medical uses of Radioactive Decay</u>. Example: Technetium-99 is the most widely used radioactive nuclide in medicine. It is used for diagnostic organ imaging and bone scans, with over 7 million uses annually in the US alone. One of the patent holders for technetium, "cardiolite™", is our own, Professor of Chemistry, Alan Davison.

<u>Second Order Integrated Rate Laws (Chapter 13.6)</u>

$2A \rightarrow B$ rate of disappearance of A $= -\frac{d[A]}{dt} = k[A]^2$

Separate concentration and time terms

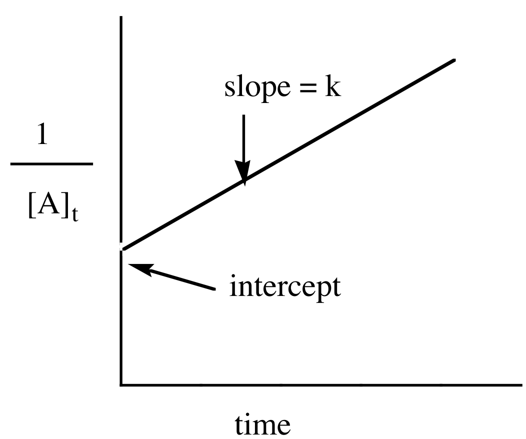
$$\frac{1}{[A]^2}\,d[A] = -k\,dt$$

$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]^2}\,d[A] = -k\int_0^t dt$$

$$-\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) = -kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$



Second order half-life

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{([A]_0/2)} = kt_{1/2} + \frac{1}{[A]_0}$$

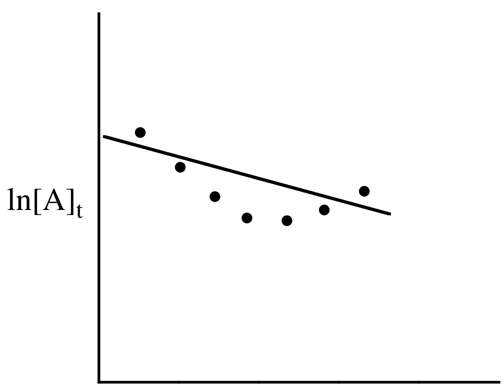
$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = k\, t_{1/2}$$

$$\frac{1}{[A]_0} = k\, t_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

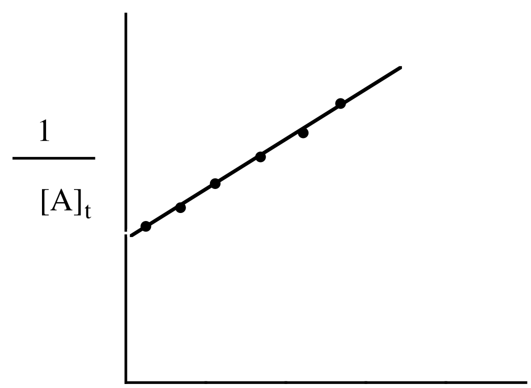
Second order half-life depends on ________________________________

In real life, need to experimentally determine if reaction is first or second order.



first-order plot

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



second-order plot

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

<u>Kinetics and Chemical Equilibrium</u>

At equilibrium, the rates of the forward and reverse reactions are equal.
The equilibrium constant for a chemical reaction that has form $A + B \Leftrightarrow C + D$ 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 $\quad rate_f =$

reverse reaction $\quad rate_r =$

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

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

Therefore $\quad K = \dfrac{k_1}{k_{-1}}$

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:

$K > 1 \qquad k_1 \;?\; k_{-1}$

$K < 1 \qquad k_1 \;?\; k_{-1}$

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

Each step is called an <u>elementary reaction</u>.

For an overall reaction, the order and the rate law cannot be derived from the stoichiometry of the balanced reaction.

For an elementary reaction, the order and rate law can be predicted. Elementary reactions occur exactly as written.

<u>Example: decomposition of ozone</u>

$2O_3\ (g) \quad \rightarrow \quad 3O_2\ (g)$

proposed mechanism has two elementary reaction steps

1st step	$O_3 \rightarrow O + O_2$	unimolecular	rate = k $[O_3]$
2nd step	$O + O_3 \rightarrow O_2 + O_2$	bimolecular	rate =

molecularity ≡ number of reactant molecules that come together to form product.

Unimolecular – 1 reactant ex. Decomposition, radioactive decay

Bimolecular – 2 reactants ex. Two reactants collide to form product

Termolecular – 3 reactants ex. Three reactants collide to form product (rare)

Individual steps (elementary reactions) can be added together to get the overall equation for the reaction.

1st step	$O_3 \rightarrow O + O_2$	"O" is a reaction intermediate
2nd step	$O + O_3 \rightarrow O_2 + O_2$	
Overall	$O_3 + O_3 \rightarrow O_2 + O_2 + O_2$	"O" does not appear in the overall reaction equation

Reaction mechanisms (which are a series of elementary reaction steps) must be tested experimentally. Reaction mechanisms cannot be proven to be correct. At best, data are consistent with a reaction mechanism.