Radioactive Decay Kinetics

I Kinetics of First-Order Processes

A. Mechanism:

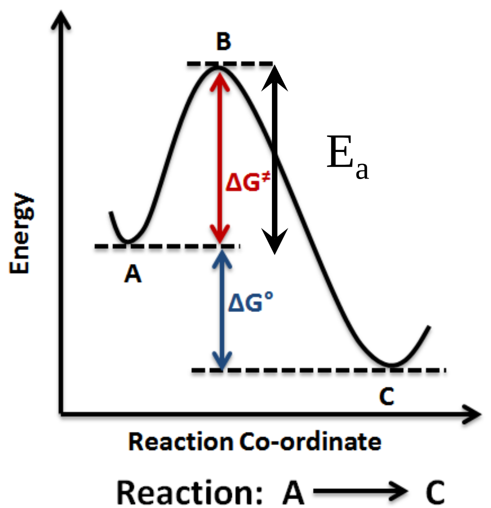
1. Nucleus has Internal Structure

$${}^{A}_{Z}X \rightarrow {}^{A'}_{Z'}Y + B + Q_B \qquad Q_B > 0$$

Decay involves internal rearrangement of the system

RANDOM PROCESS: Identical to Unimolecular Decomposition

2. Chemical Analogy



$$N_2O_4 \rightarrow 2NO_2$$

$$Rate = -\frac{d[N_2O_4]}{dt} = k[N_2O_4]$$

$$k = e^{-\frac{E_a}{RT}} f(J, \pi, \ldots)$$

NOTE: Since atoms and molecules are neutral, if $T > 0$, they will have $(3/2)\ kT$ kinetic energy;

$\therefore$ Collisions may also induce reactions.

$\therefore$ Collisions are <u>SECOND ORDER</u>; $\therefore$ must distinguish order for chemical reactions

For nuclei, $T \approx 0$ and Coulomb barrier prevents collisions;

$\therefore$ ONLY FIRST ORDER DECAY

3. Nuclear System

a. <u>Nomenclature Change</u>

$[\ ]_o \Rightarrow N_o$, the number of nuclei initially (Not Avogadro's number)

$k \Rightarrow \lambda$, the rate constant = $f(Q, I\pi)$

$\therefore$ First-order Rate Law is

$$Rate = -\frac{dN}{dt} = \lambda N$$

Instantaneous decay rate

b. <u>Example</u>

$$^{137}_{55}\mathrm{Cs} \rightarrow \, ^{0}_{-1}\beta^{-} + \, ^{137m}\mathrm{Ba} + \bar{\nu} \quad (t_{1/2} = 30y)$$

$$^{137m}_{56}\mathrm{Ba} \rightarrow \gamma + \, ^{137}\mathrm{Ba} \quad (t_{1/2} = \mathrm{TBA})$$

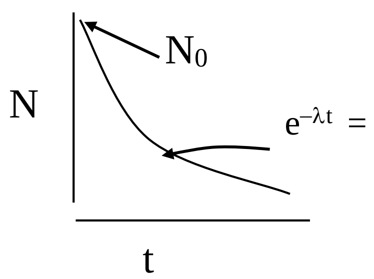
B. Mathematics of First Order Decay

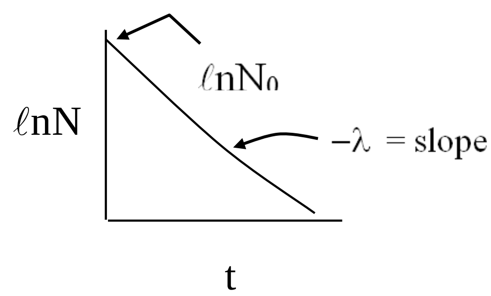
Rate constant $\lambda \Rightarrow$ Probability

1. Solution: $\frac{dN}{dT} = -\lambda N \Rightarrow \int_{N_0}^{N} \frac{dN}{N} = -\lambda \int_0^t dt \Rightarrow \ell n\left(\frac{N}{N_0}\right) = -\lambda t$

   or $N = N_0 e^{-\lambda t}$, where λ is different for every nuclide

2. For a pure sample





$t_{1/2}$: The Half-Life

Expresses probability in terms of a characteristic time
i.e., high probability, short decay time and vice versa

DEFINITION: The half-life ($t_{1/2}$) of a nucleus is the time required for one-half the nuclei in a sample to decay.

i.e., after $t = t_{1/2}$, $N = N_0/2$

$$\frac{N}{N_0} = e^{-\lambda t_{1/2}} = \frac{N_0/2}{N_0} = \frac{1}{2} = e^{-\lambda t_{1/2}}$$

$\ell n\ 2 = \lambda\ t_{1/2} \Rightarrow \quad \therefore \quad t_{1/2} = 1n\ 2/\lambda = \quad 0.693/\lambda = t_{1/2}$

Mathematical Shortcuts (but $N = N_0e^{-\lambda t}$ always works).

a. If $t << t_{1/2}$

$$\frac{N}{N_0} = e^{-\lambda t} \qquad e^{-x} = 1 - x + \ldots$$

$$\frac{N}{N_0} = 1 - \lambda t$$

$$N = N_0(1 - \lambda t) = N_0 - N_0\lambda t$$

$$N_0 - N = N_0\lambda t$$

$$\Delta N = \lambda N_0 \Delta t$$

$$\frac{\Delta N}{\Delta t} = \lambda N_0$$

ALWAYS TRY TO SEE IF THIS WORKS;
RULE: If $t < 0.1\ t_{1/2}$, good to 3 sig. figs.

b. **Problem:** How many ^{238}U nuclei will decay in 1.0 y from a sample that contains 2.38 mg of uranium? remain?
^{238}U abundance = 99.275%, $t_{1/2} = 4.468 \times 10^9$ y

- Test Rule: $1.0 << 4.468 \times 10^9$y, $\therefore$ OK to use $\Delta N = \lambda N_0 \Delta t$

- $N_0 = \left(\frac{2.38 \times 10^{-3} g}{238\ g/mole}\right)(0.99275)\left(6.02 \times 10^{23} \frac{atoms}{mole}\right) = 5.98 \times 10^{18}$ atoms ^{238}U

- $\lambda = 0.693/4.468 \times 10^9 y = 1.55 \times 10^{-10} y^{-1}$

- $\Delta N = (1.55 \times 10^{-10}\ y^{-1})\ (5.98 \times 10^{18}$ atoms$)\ (1.0y) = 9.27 \times 10^9$ atoms decay

- N (remaining) = $N_0 - \Delta N = 5.98 \times 10^{18} - 9.27 \times 10^9 = 5.98 \times 10^{18}$ atoms remain

i.e., no change at 3 sig fig level

c. If $t >> t_{1/2}$, trivial result

$$e^{-\lambda t} = e^{-0.693\ t/(t1/2)} = e^{-\infty} = 0$$

i.e., $N = 0$ and $\Delta N = N_0$; i.e., all (or most of) sample has decayed

RULE: **IF $t >> 10\ t_{1/2}$, $N \cong 0$**

d. Integral half-lives

let $n = t/t_{1/2}$ = integer 0, 1, 2, 3 … etc.

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$

e. <u>Average Lifetime τ</u>

$$\tau = \sum_{i=N_0}^{0} t_i / N = \frac{1}{N_0} \int_{N_0}^{0} t dN$$

$\tau = 1/\lambda = 1.44\ t_{1/2}$

i.e., average is longer because long times skew distribution.

5. Rate of Energy Loss

Importance: Heating of earth's crust (^{40}K, ^{232}Th, $^{235,238}U$)

Miniature power sources (^{238}Pu)

Spurious heating in thermochemistry of radioactive elements

a. Definitions:

$$Rate = -\frac{dE}{dt} = \frac{dE}{dN}\frac{dN}{dt} = Q\lambda N \Rightarrow Q\lambda N_0 e^{-\lambda t} = \frac{\Delta E}{\Delta t}$$

b. **Problem**: Calculate the rate of energy loss for ^{210}Po in kJ/mole-min.

α-decay ; $t_{1/2} = 138.4$ d ; $Q_\alpha = 5.305$ MeV

$\therefore \quad \Delta t << t_{1/2}$

$\therefore \quad \Delta E/\Delta t = Q_\alpha \lambda N$

$Q_\alpha = 5.305$ MeV $(1.602 \times 10^{-16}$ kJ/MeV$) = 8.499 \times 10^{-16}$ kJ/atom

$\lambda = 0.693/(138.4$ d$)(1440$ min/d$) = 3.48 \times 10^{-6}$/min

$N = 1$ mole $= 6.022 \times 10^{23}$ atoms

$\Delta E/\Delta t = (8.499 \times 10^{-16}$ kJ/atom$)(3.48 \times 10^{-6}$/min$)(6.022 \times 10^{23}$ atoms)

$\Delta E/\Delta t = 1870$ kJ/min-mole

Comparable to chemical reactions (ΔH), but at end of day, still have same source.

After 138.4 d $\Delta E/\Delta t = 935$ kJ/min-mole.

II. Activity – Practical Aspects of Radioactivity

Usually measure emitted particles, not N (parent or daughter nuclei).

A. Definition: Activity is the radiation that is measured from a radioactive source. – A = Activity

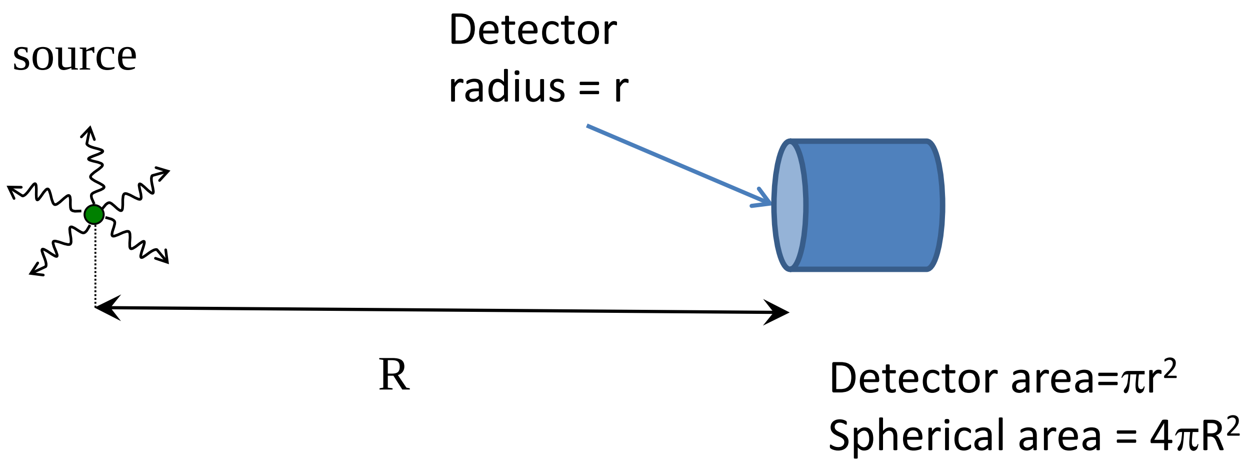
$$A = c\left(-\frac{dN}{dt}\right) = c\lambda N \approx c\frac{\Delta N}{\Delta t}$$

1. $-dN/dt$ = ABSOLUTE DISINTEGRATION RATE (dps, dpm, dph, etc.)

c = detection coefficient = $G\varepsilon$. when

G is a geometry factor and

ε is the detection efficiency



- $G = \pi r^2 / 4\pi R^2 = r^2/4R^2$ ⇐ BASIC PRINCIPLE OF RADIATION SAFETY activity decreases at square of distance R

- $\boldsymbol{\varepsilon}$ = Fraction of particles that strike the detector and give signal
- Accurate determination of **c** is critical to absolute measurements

B. First-Order Decay Law in Terms of Activity

$$N = N_0 e^{-\lambda t}$$

$$c\lambda N = c\lambda N_0 e^{-\lambda t}$$

$$A = A_0 e^{-\lambda t}$$

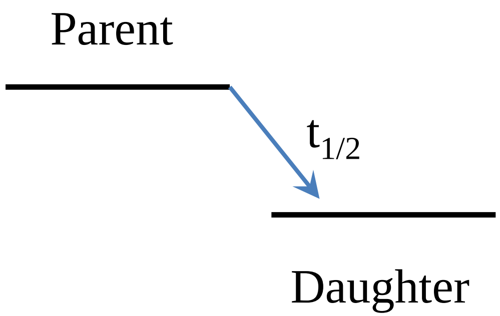
uncertainty is $\pm(\Delta N)^{1/2}$
where ΔN is number of counts
$\Delta N = N_0 - N$ = emitted particles

C. Units of Reactivity

1. Curie: Ci — 1 Ci = 3.70×10^{10} dps
2. Bequerel: Bq — 1 Bq = 1 dps

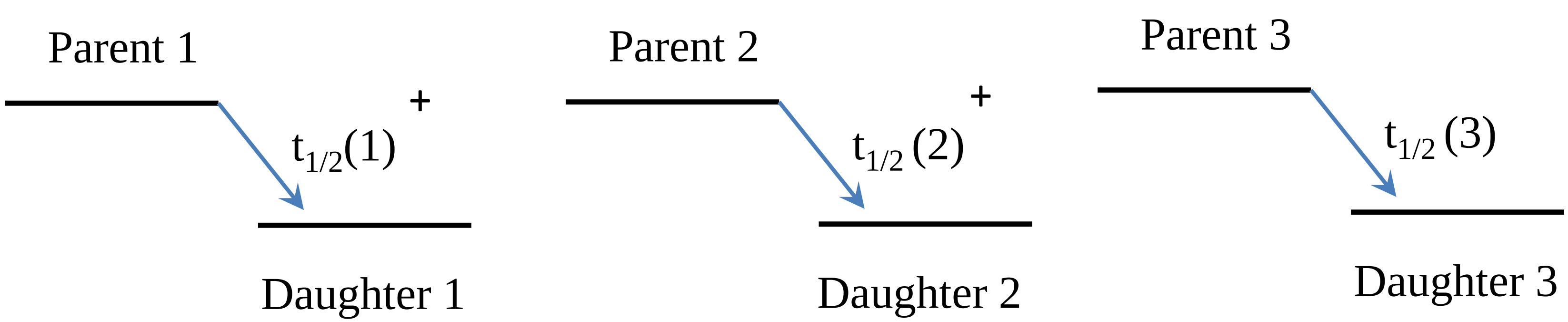
III. Mixture of Independent Activities

Previously we have discussed:



One pure initial radioactive sample which decays to a daughter nuclide that is stable

Now the situation is:



An initial mixture of two or more radioactive parents each of which decays to a daughter nuclide that is stable

Number of components = Number of slope changes + 1

Example Three Components General Case

$$A_{total} - A_{bkg} = A(1) + A(2) + A(3) + \ \dots$$

$$= A_0(1)\ e^{-\lambda t} + A_0(2)\ e^{-\lambda t} + A_0(3)\ e^{-\lambda t} + \dots$$

- RULE: As $t \to \infty$, SHORTEST-LIVED COMPONENTS *DISAPPEAR*
- c_i, λ_i, N_i can all differ

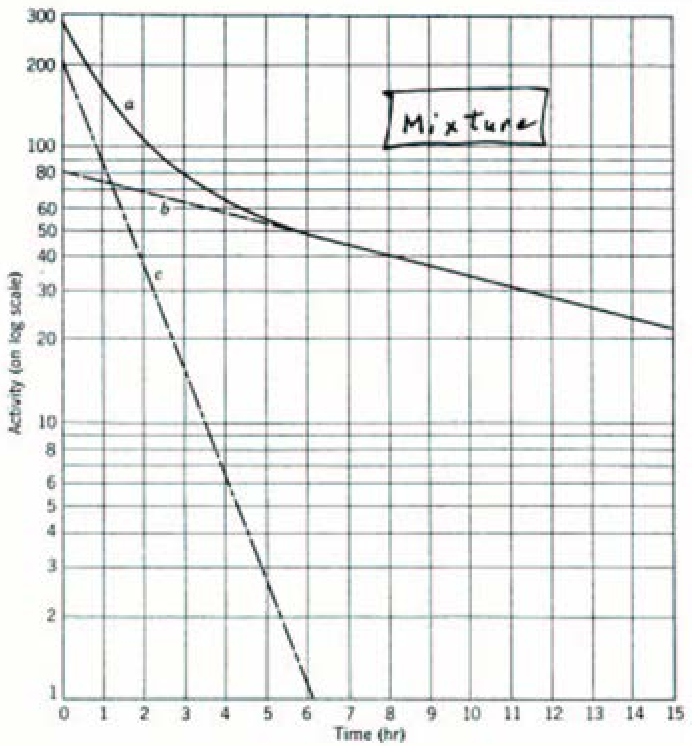


Fig. 3-1 Analysis of composite decay curve:

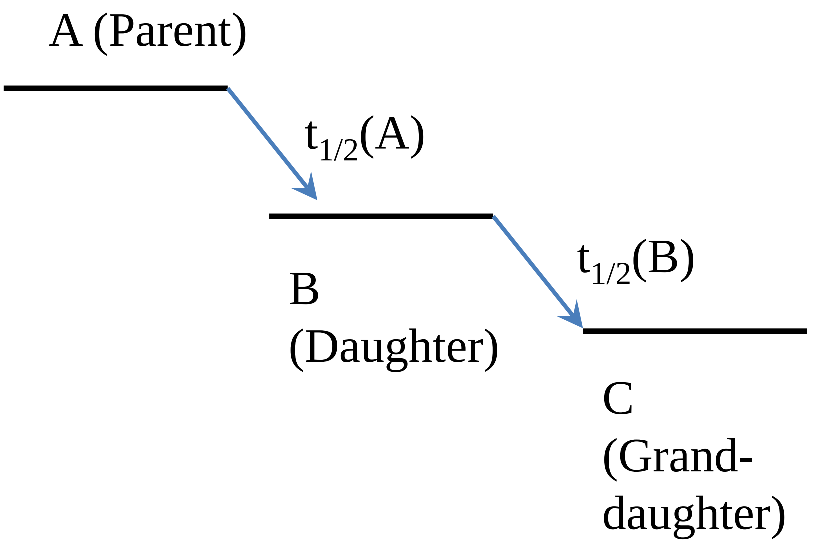
How many radioactive species are there in the initial mixture? How do you know?

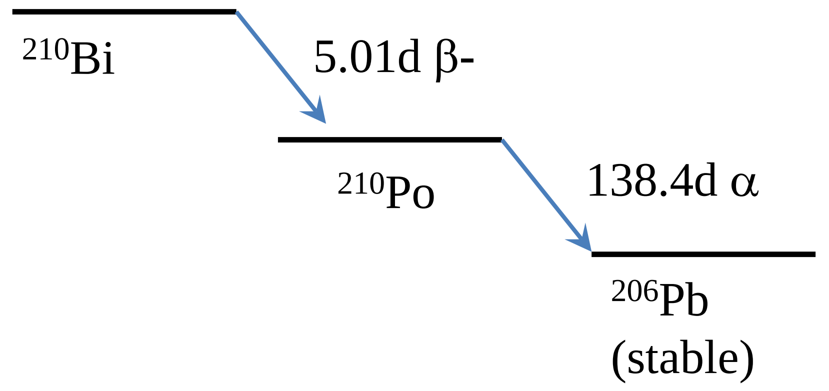
- How would you determine the half-life of the long lived component?
- How would you determine the half-life of the short-lived component?

IV. Parent-Daughter Relationships

Key point: The Rate-Determining Step

A. Case of Radioactive Daughter





Same problem as a stepwise chemical reaction!

B. Mathematics of the Problem

1. Parent: A

Decay: $$-\frac{dN_A}{dt} = \lambda_A N_A \Rightarrow N_A(t) = N_A^0 e^{-\lambda_A t}$$

Nothing new here

2. Daughter: B

Formation: $dN_B/dt = \lambda_A N_A$

Decay: $dN_B/dt = -\lambda_B N_B$

NET: $$\frac{dN_B}{dt} = \lambda_A N_A - \lambda_B N_B = \lambda_A N_A^0 e^{-\lambda_A t} - \lambda_B N_B$$

This is a linear first-order differential equation

3. Solution

$$N_B = \frac{\lambda_A N_A^0}{\lambda_B - \lambda_A}\left(e^{-\lambda_A t} - e^{-\lambda_B t}\right) + N_B^0 e^{-\lambda_B t}$$

If the sample is pure A initially, second term vanishes since $N_B^0 = 0$

4. Daughter: C

$N_A^0 = N_A + N_B + N_C$ Conservation of atoms

5. Special Cases: Long time solutions

classification	time relationship	Rate-determining step
a. No Equilibrium	$t > t_B > t_A$	$B \rightarrow C$
b. Transient Equilibrium	$t > t_A > t_B$	$A \rightarrow B$
c. Secular Equilibrium	$t_A >> t > t_B$	$A \rightarrow B$

(c. is case of U-Th decay series)