Nuclear Decay kinetics : Transient and Secular Equilibrium

What can we say about the plot to the right?

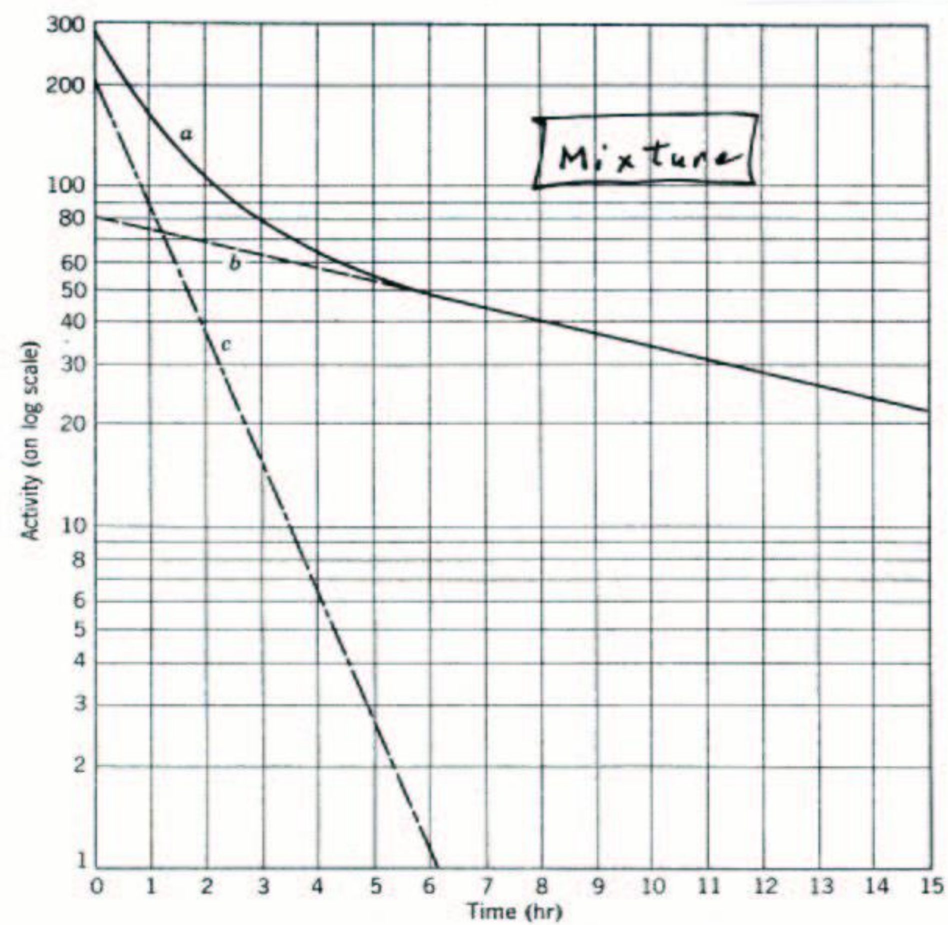
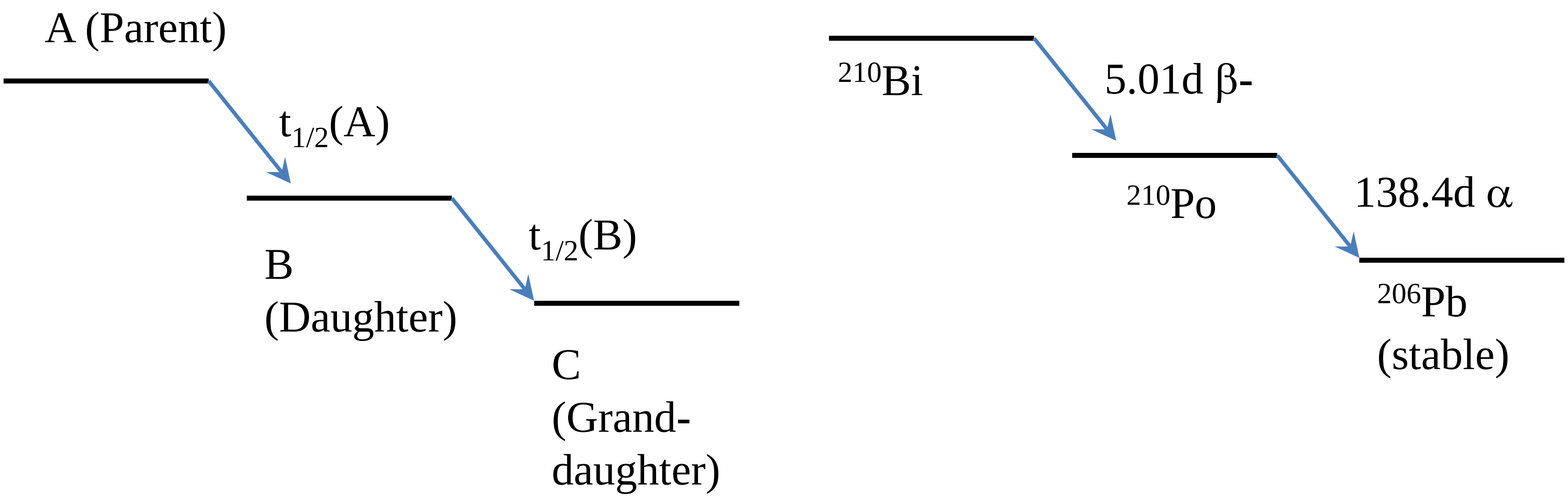


Fig. 3-1 Analysis of composite decay curve:

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

<u>Formation</u>: $dN_B/dt = \lambda_A N_A$

<u>Decay</u>: $dN_B/dt = -\lambda_B N_B$

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

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)

C. No Equilibrium

Daughter is rate-determining step

$t_{1/2}$ (B) > $t_{1/2}$ (A)

1. Figure 3-4 (on right)

a. Curve a: Total activity of initially **PURE** sample of A
NOTE: resembles two-component independent decay curve. <u>**NOT !!!**</u>

$$A(total) = A(A) + A(B)$$

b. Curve b: Parent activity, A(A)

c. Curve d: Daughter activity, A(B) ; note growth curve

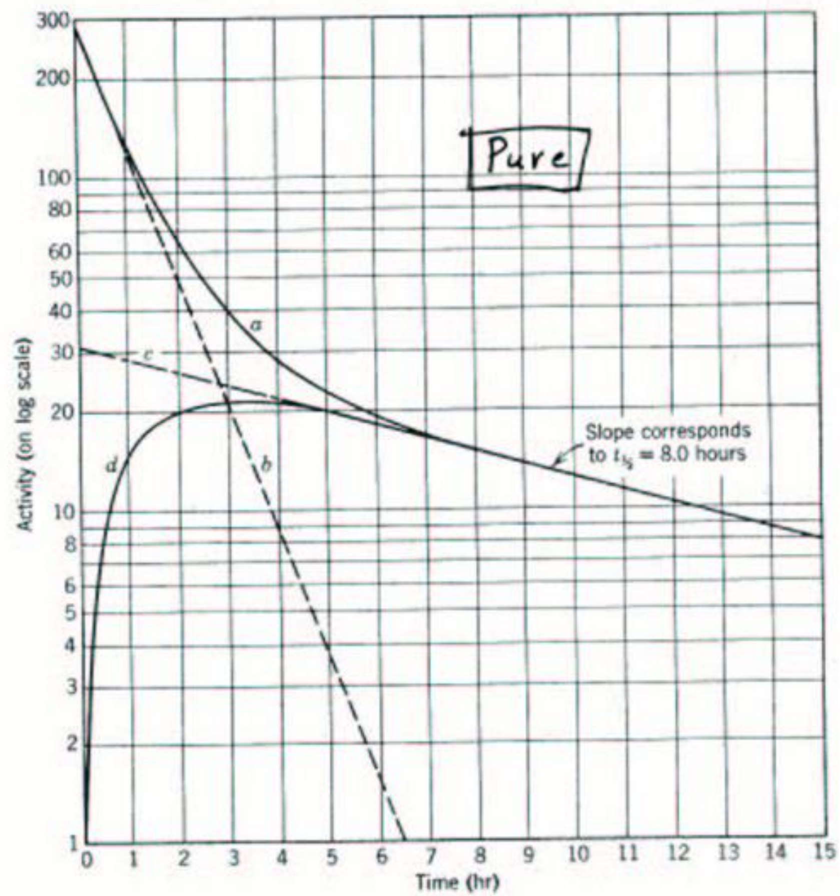


Fig. 3-4 The case of no equilibrium:

2. Curve c: Long-term behavior: $t >> t_{1/2}$ (A)

Therefore, $t/t_{1/2}(A) = \infty$

$$e^{-\lambda_A t} \rightarrow 0$$

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

Note: $\lambda_B < \lambda_A$; $\therefore$ (–)(–) = +

3. Long term curve: All of A has disappeared ; this defines $t_{1/2}$(B)

D. Transient Equilibrium

Parent decay is rate-determining step

$t_{1/2}$ (A) > $t_{1/2}$ (B

1. Fig. 3-2 (on right)

a. Curve a: Total activity of initially pure sample of A

$$A(total) = A(A) + A(B)$$

A decay curve that initially increases with time is a signature of transient or secular equilibrium.

b. Curve b: Parent Activity: A(A)

c. Curve d: Daughter Activity: A(B)

d. Initial growth of A(total) and then decay according to the half-life of the parent.

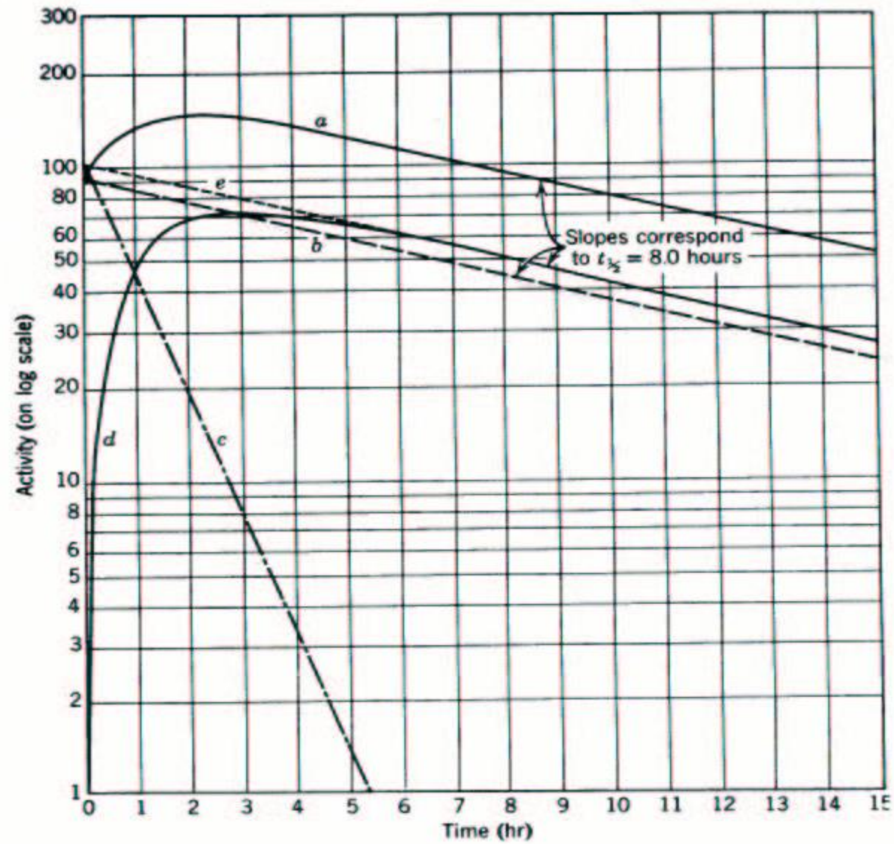


Fig. 3-2 Transient equilibrium:

2. Maximum Daughter Activity

a. Maximum occurs when $dN_B/dt = 0$

Therefore, differentiate equation for N_B and set this equal to zero; this defines t_{max} as

$$t_{\max} = \frac{\ln(\lambda_B / \lambda_A)}{\lambda_B - \lambda_A}$$

N_B is maximum when $t = t_{max}$

b. Importance

Medical isotopes – Milking a cow – how long must one wait before extracting the daughter activity again?

c. Example: $^{137}_{55}\text{Cs} \xrightarrow[30\text{ y}]{1\beta} {}^{137m}_{50}\text{Ba} \xrightarrow[2.6\text{m}]{\gamma} {}^{137}\text{Ba}$ (stable)

$$t_{\max} = \frac{\ln(\lambda_B / \lambda_A)}{\lambda_B - \lambda_A} = \frac{\ln[t_{1/2}(A) / t_{1/2}(B)]}{\frac{0.693}{2.6m} - \frac{0.693}{30y}} = \frac{\ln[(30y / 2.6\,\text{min}) \times 5.3 \times 10^5\,\text{min}/y]}{0.693 / 2.6\,\text{min}}$$

$t_{max} = 58$ min

3. Long-Time Solution: Curve e

a. For initially pure A, $t >> t_{1/2}(B)$

$$e^{-\lambda_B t} \rightarrow 0$$

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

$$N_B = \frac{\lambda_A N_A}{\lambda_B - \lambda_A}$$

$$\frac{N_B}{N_A} = \frac{\lambda_A}{\lambda_B - \lambda_A}$$

i.e., at long time, ratio N_B/N_A is CONSTANT with time

$\therefore$ SYSTEM APPEARS TO BE IN EQUILIBRIUM

4. Consequences

a. Long term decay is governed by parent

b. Activity: multiply equation in 3a. above by $c\lambda_B$

$$c\lambda_B N_B = \frac{c\lambda_B \lambda_A N_A}{\lambda_B - \lambda_A} = A_B = \left(\frac{\lambda_B}{\lambda_A - \lambda_B}\right) A_A$$

c. Half-life of B can be determined by combining:

- long term behavior – $t_{1/2}(A)$
- activity ratio above

E. Secular Equilibrium (Fig. 3-3)

$t_{1/2}(A) >> t >> t_{1/2}(B)$

Special Case of Transient Equilibrium; e.g., U-Th Decay Series

Rn gas problem; natural background from U and Th decay products; dating

1.

a. Curve a – Total activity of initially **<u>PURE</u>** Sample

NOTE: at long time, ACTIVITY IS CONSTANT ; signifies special case

b. Curve b – Parent activity ; since $t/t_{1/2} \sim 0$, $\Delta N/\Delta t = \lambda N_0$ = constant

c. Curve d – Daughter activity growing in

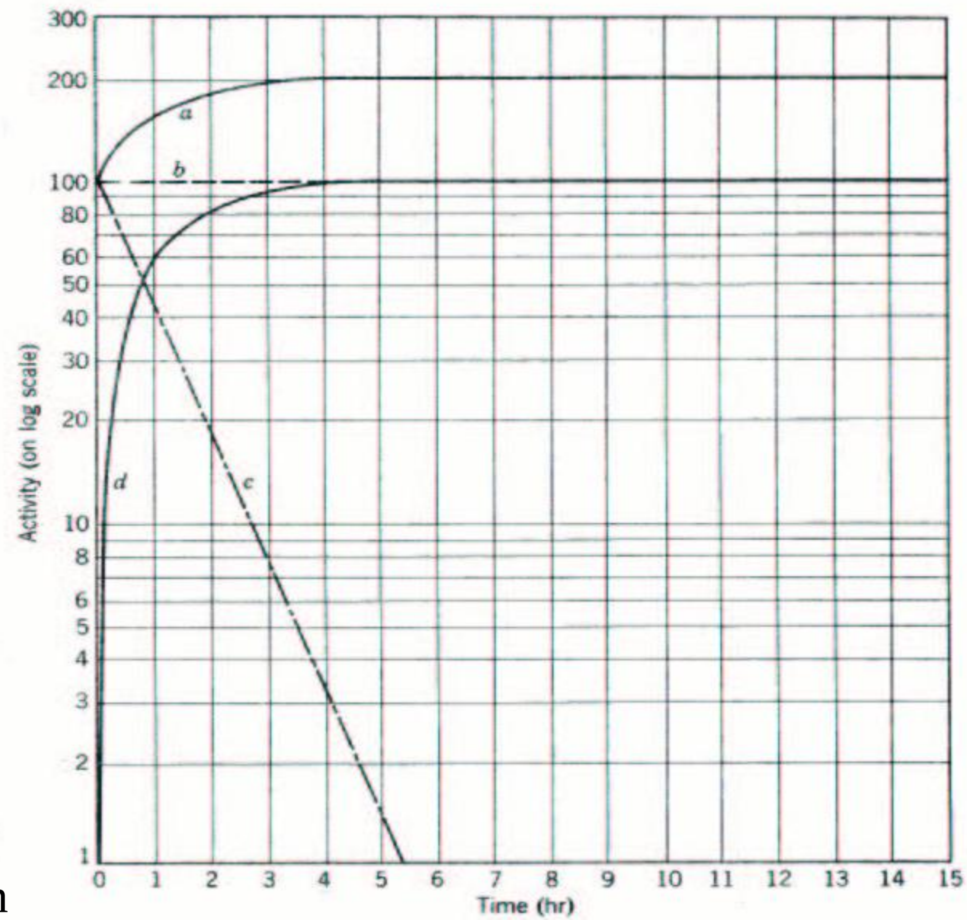


Fig. 3-3 Secular equilibrium:

2. General Solution

a. Assume $N_B^0 = 0$ (i.e., pure A) ; $t_{1/2}(A) >> t$

$$e^{-\lambda_A t} \approx e^0 = 1$$

$$\lambda_B >> \lambda_A \Rightarrow \lambda_B - \lambda_A \cong \lambda_B$$

$$N_B = \frac{\lambda_A N_A^0}{\lambda_B}\left(1 - e^{-\lambda_B t}\right)$$

Growth curve

b. Long-time solution

$t >> t_{1/2}(B)$; $e^{-\lambda B t} \Rightarrow e^{-\infty} = 0$

$$N_B = \frac{\lambda_A N_A^0}{\lambda_B} \Rightarrow N_B \lambda_B = \lambda_A N_A^0$$

c. If $c_A = c_B$ $A_B = A_A = A_{total/2}$

d. Example:

How many atoms of ^{222}Rn are present in an initially pure sample of ^{226}Ra after 3 months? Assume 226 mg of ^{226}Ra;

What is the activity?

$t_{1/2}(^{222}Rn) = 3.82$ d ; $t_{1/2}(^{226}Ra) = 1620$ y

Solution :

$$N_{Rn} = \frac{\lambda_{Ra}}{\lambda_{Rn}} \bullet N^{0}(Ra) = \frac{t_{1/2}(Rn)}{t_{1/2}(Ra)} \bullet N^{0}(Ra) = \frac{(3.82\ d)}{1620\ y\ (365\ d/y)} \bullet \frac{226 \times 10^{-3} g}{226\ g/mole}$$

$$N_{Rn} = 3.94 \times 10^{15}\ \text{atoms} = 6.54 \times 10^{-9}\ \text{moles} = 1.46 \times 10^{-4}\ \text{mL @ STP}$$

$$\frac{-dN_{Rn}}{dt} = \lambda N = \left(\frac{0.693}{3.82\ d}\right)\left(\frac{3.94 \times 10^{15}\ \text{atoms}}{1440\ m/d}\right) \cong 5.0 \times 10^{11}\ \text{d/min}$$

3. Points to keep in mind

a. $A_A = A_A^0 = const.$

b. $A_B = A_{total} - A_A^0$

c. Half-life of A

Weigh and determine from $A_A = c\lambda N_A^0$

Measure counts (→ A_A)

weigh (→ N_A^0)

d. Half-life of B

at $t = t_{1/2}(B)$; $e^{-\lambda_B t} = 1/2$

$$\therefore\ N_B = \frac{\lambda_A N_A^0}{\lambda_B}(1 - 1/2) = \frac{\lambda_A N_A^0}{2\lambda_B},\ \text{or}\ \boxed{A_B = \frac{1}{2}A_A^0}$$

corresponds to $t_{1/2}$ (B)

Since A(total) = $A_A^0 + A_B$, $t_{1/2}$ (B) is also time at which

$$A(total) = (3/2)\ A_A^0$$

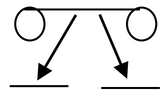
F. Several Successive Decays

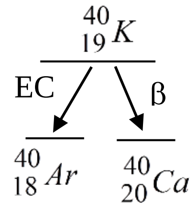
$A \rightarrow B \rightarrow C \rightarrow D$, etc.

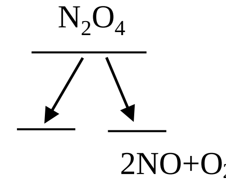
1. Bateman Solutions

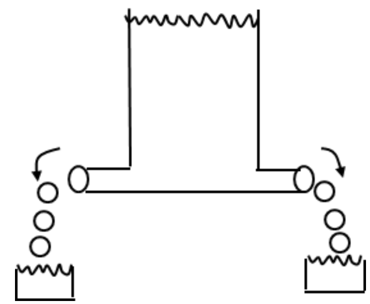
$$\frac{dN_c}{dt} = \lambda_B N_B - \lambda_c N_c$$

IV. Branching Decay
Competitive Decay Modes
for the same nucleus









A. Total Probability = λ

$$\lambda = \lambda_1 + \lambda_2 + \lambda_3 + \ldots$$

$$\text{or } \frac{1}{t_{1/2}} = \frac{1}{t_{1/2(1)}} + \frac{1}{t_{1/2(2)}} + \frac{1}{t_{1/2(3)}} + \ldots \text{ ; } t_i = \text{partial half-lives}$$

B. Partial Half-Life

Definition: The half-life a nucleus would have if the competing decay modes were switched off. (but NO switch).

C. Determination of Partial half-lives

1. Branching Ratio: BR (Assume two branches, 1 & 2)

$$BR = \frac{\lambda_1}{\lambda_{total}} = \frac{\lambda_1}{\lambda_{total}} = \frac{t_{1/2}(total)}{t_{1/2}(1)}$$

2. Measurement; if $c_1 = c_2$

$$BR = \frac{\lambda_1 \times c_1 \times N}{\lambda_{total} \times c \times N} = \frac{A_1}{A_{total}}$$

3. Example: ^{40}K ; $t_{1/2} = 1.28 \times 10^9$ y

$$\therefore \ BR(EC) = (0.107) = \frac{t_{1/2}}{t_{EC}}; \quad t_{EC} = 1.19 \times 10^{10} \text{ y}$$

$$BR(\beta^-) = 0.893) = \frac{t_{1/2}}{t_{\beta^-}}; \quad t_{\beta^-} = 1.43 \times 10^9 \text{ y}$$

NOTE: $t_{1/2} < t_{1/2}(\beta^-) < t_{1/2}(EC)$

V. Determination of Half-lives

Measurable range: 10^{-23} s to ~ 10^{30} y (60 orders of magnitude)

A. $T_{1/2} \gtrsim 1$ year: Specific Activity

1. $A = c\lambda N$ — A = counts/unit time

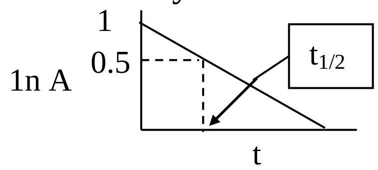
   N = weight of sample — Measure $\Rightarrow$ $\lambda = \dfrac{0.693}{t_{1/2}}$

   c = detection coefficient

   e.g., 238 mg of ^{238}U has a specific activity of ~300 dps — c = 1

2. Limit: Natural background radiation; when A(sample – A(bkg) ≈ 0, large errors

B. Decay Curves: $10\ y \gtrsim t_{1/2} \gtrsim 1\ s$



C. Electronic Techniques

D. Doppler Shift

E. Channeling in Crystals

F. Heisenberg Uncertainty Principle

G. Angular Distributions of Emitted Particles

H. Small Angle Correlations