Lecture 14 Nuclear Decay kinetics: Transient and Secular Equilibrium

![Graph showing activity over time for a mixture of decay processes.](image)

**Fig. 3-1** Analysis of composite decay curve:
IV. Parent-Daughter Relationships
⇒ (The Rate-Determining Step) ⇐

A. Case of Radioactive Daughter

\[ \begin{align*}
\text{A} & \quad \Downarrow \quad \text{B} \\
& \quad \Downarrow \\
& \quad \text{C}
\end{align*} \]

\[ \text{e.g.} \quad 210^{\text{Bi}} \quad 5.01 \text{ d } \beta^- \]

\[ \begin{align*}
210^{\text{Po}} & \quad 138.4 \text{ d } \alpha \\
\text{Stable} & \quad 206^{\text{Pb}}
\end{align*} \]

Same problem as a stepwise chemical reaction

B. Mathematics of the Problem

1. Parent: A
   \[ \text{Decay: } -dN/dt = \lambda_A N_A ; \quad N_A = N_A^0 e^{-\lambda_A t} \quad \text{(nothing new)} \]

2. Daughter: B
   \[ \begin{align*}
   \text{Formation: } & \quad dN_B/dt = \lambda_A N_A \\
   \text{Decay: } & \quad dN_B/dt = -\lambda_B N_B \\
   \text{NET: } & \quad \frac{dN_B}{dt} = \lambda_A N_A - \lambda_B N_B = \lambda_A N_A^0 e^{-\lambda_A t} - \lambda_B N_B
   \end{align*} \]
   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 pure A initially, \( N_B^0 = 0 \) and second term vanishes

4. Daughter: C
   \[ \begin{align*}
   N_A^0 & = N_A + N_B + N_C
   \end{align*} \]
5. **Special Cases: Long time solutions**

<table>
<thead>
<tr>
<th>Classification</th>
<th>Time Relationship</th>
<th>Rate-determining step</th>
</tr>
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<tbody>
<tr>
<td>a. No Equilibrium</td>
<td>t &gt; t_B &gt; t_A</td>
<td>B → C</td>
</tr>
<tr>
<td>b. Transient Equilibrium</td>
<td>t &gt; t_A &gt; t_B</td>
<td>A → B</td>
</tr>
<tr>
<td>c. Secular Equilibrium</td>
<td>t_A &gt;&gt; t &gt; t_B</td>
<td>A → B</td>
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</table>

(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. **Fig. 3-4**

   a. Curve a: Total activity of initially **PURE** sample of A

   NOTE: resembles two-component independent decay curve. **NOT !!!**

   \[ A(\text{total}) = A(A) + A(B) \]

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

   d. Curve d: Daughter activity, A(B); note growth curve
2. **Curve c**: Long-term behavior: \( t > t_{1/2} (A) \)
\[ \therefore \frac{t}{t_{1/2}(A)} = \infty \quad \text{and} \quad e^{-\lambda A t} \Rightarrow 0 \]

OR
\[ N_B = \frac{\lambda A^0}{\lambda_B - \lambda_A} (-e^{-\lambda_B t}) \]
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**
   a. Curve a: Total activity of initially pure sample of A
   \[ A(\text{total}) = A(A) + A(B) \]
   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 \( A(A) \) and then decay according to the half-life of the parent.
2. Maximum Daughter Activity

a. Maximum occurs when $dN_B/dt = 0$
∴ differentiate equation for $N_B$ and set this equal to zero; this defines $t_{\text{max}}$ as
\[
t_{\text{max}} = \frac{\ln(\lambda_B / \lambda_A)}{\lambda_B - \lambda_A}; \text{ i.e., } N_B \text{ is maximum when } t = t_{\text{max}}
\]

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

c. Example: $^{137}\text{Cs} \rightarrow ^{137m}\text{Ba} \rightarrow ^{137}\text{Ba} \text{ (stable)}$
\[
t_{\text{max}} = \frac{\ln(\lambda_B / \lambda_A)}{\ln\left(\frac{t_{1/2}(A)/t_{1/2}(B)}{0.693 \frac{30 \text{ y}}{2.6 \text{ m}}} \times \frac{5.3 \times 10^5 \text{ min/y}}{2.6 \text{ m}}\right)} \approx 0.693 \text{ y/2.6m}
\]
\[
t_{\text{max}} = 58 \text{ min}
\]

3. Long-Time Solution: Curve e

a. For initially pure A, $t >> t_{1/2}(B)$
\[
\therefore e^{-\lambda_B t} = e^{-\infty} \Rightarrow 0
\]
or
\[
N_B = \frac{\lambda_A N_A^0}{\lambda_B - \lambda_A} e^{-\lambda_A t}
\]
\[
\therefore \frac{\lambda_A N_A}{\lambda_B - \lambda_A}, \text{ or } \frac{N_B}{N_A} = \frac{\lambda_A}{\lambda_B - \lambda_A}
\]
i.e., at long time, ratio $N_B/N_A$ is CONSTANT with time
∴ 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)**

![Secular Equilibrium Graph](image)

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

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 **PURE** Sample

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

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

2. General Solution

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

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

\[ \lambda_B > > \lambda_A ; \lambda_B - \lambda_A \approx \lambda_B \]

\[ N_B = \frac{N_A^0 \lambda_A}{\lambda_B} (1 - e^{-\lambda_B t}) \]

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 $c_A = c_B \quad A_B = A_A = A_{total/2}$

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

\[ N_{Rn} = \frac{\lambda_A}{\lambda_{Rn}} \cdot N_A^0 = \frac{t_{1/2}(Rn)}{t_{1/2}(Ra)} \cdot N_A^0 = \frac{(3.82 d)}{1620 y (365 d / y)} \cdot \frac{226 \times 10^{-3} g}{226 g / mole} \]

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

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

3. Points to keep in mind
a. \( A_A = A_A^0 \) = constant

b. \( A_B = A_{\text{total}} - A_A^0 \)

c. Half-life of A

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

\[ \downarrow \quad \text{counts} \quad \uparrow \quad \text{wt} \]

d. Half-life of B

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

\[ N_B = \frac{\lambda_A N_A^0}{\lambda_B} (1 - 1/2) = \frac{\lambda_A N_A^0}{2\lambda_B} , \quad \text{or} \quad A_B = \frac{1}{2} A_A^0 ; \text{this time corresponds to } t_{1/2}(B) \]

Since \( A(\text{total}) = A_A^0 + A_B \), \( t_{1/2}(B) \) is also time at which \( A(\text{total}) = (3/2) A_A^0 \)

F. Several Successive Decays

\( A \rightarrow B \rightarrow C \rightarrow D \), etc.

1. Bateman Solutions

\[ \begin{cases} \frac{dN_c}{dt} = \lambda_B N_B - \lambda_c N_c \end{cases} \]

2. For Secular Equilibrium -- ONLY CASE WE WILL USE THIS LONG-TIME SOLUTION

\( t_{1/2}(A) >> t \)
\( t_{1/2}(A) > t_{1/2}(B) > t_{1/2}(C) \) etc.

a. \( \lambda_A N_A^0 = \lambda_B N_B = \lambda_C N_C = ... \)

&

b. \(-dN/dt(\text{total}) = n\lambda_A N_A^0 \), where \( n \) is number of decays in chain
c. IF \( c_A = c_B = c_C \) etc. \( A_A = A_B = A_C \) ...

d. Marie Curie: \( N^{(238}\text{U}) = \left[ t_{1/2}(\text{U})/t_{1/2}(\text{Ra})\right] \bullet N_{\text{Ra}} \)

IV. Branching Decay

Competitive Decay Modes for the same nucleus

A. Total Probability = \( \lambda \)
\[
\lambda = \lambda_1 + \lambda_2 + \lambda_3 + \ldots
\]
or \[
\frac{1}{t_{1/2}} = \frac{1}{t_{1/2}(1)} + \frac{1}{t_{1/2}(2)} + \frac{1}{t_{1/2}(3)} + \ldots ; t_i = \text{partial half-lives}
\]

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)
\[
\left\{ \begin{array}{c}
BR = \frac{\lambda_1}{\lambda_{\text{total}}} = \frac{t_{1/2}(1)}{t_{1/2}(\text{total})} \\
\end{array} \right. 
\]

2. Measurement; if \( c_1 = c_2 \)
\[
BR = \frac{\lambda_1 \times c_1 \times N}{\lambda_{\text{total}} \times c \times N} = \frac{A_1}{A_{\text{total}}}
\]
3. Example: $^{40}\text{K}; \ t_{1/2} = 1.28 \times 10^9 \text{y}$

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

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

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

V. \textbf{Determination of Half-lives}

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

A. \(T_{1/2} \gtrsim 1\) year: \textbf{Specific Activity}

1. \(A = c\lambda N\) \quad A = \text{counts/unit time}
   \(N = \text{weight of sample}\)
   \(c = \text{detection coefficient}\)

\爆发\begin{align*}
\text{Measure} & \Rightarrow \lambda = \frac{0.693}{t_{1/2}} \\
\text{e.g., 238 mg of }^{238}\text{U has a specific activity of } \sim 300 \text{ dps} \quad & c = 1
\end{align*}

2. Limit: Natural background radiation; when \(A(\text{sample} - A(\text{bkg}) \approx 0, \text{large errors}\)

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

\[
\begin{array}{c}
\text{ln} A \\
\hline
\text{t}
\end{array}
\]

\[
\text{t}_{1/2}
\]

C. \textbf{Electronic Techniques}

D. \textbf{Doppler Shift}

E. \textbf{Channeling in Crystals}

F. \textbf{Heisenberg Uncertainty Principle}

G. \textbf{Angular Distributions of Emitted Particles}

H. \textbf{Small Angle Correlations}
1. Pure Activity

\[ \frac{\text{d}N}{\text{d}t} = \lambda N \]

\[ N = N_0 e^{-\lambda t} \]

\[ A = A_0 e^{-\lambda t} \]

\[ \frac{\text{d}}{\text{d}t} \sqrt{A} = \text{uncertain} \]

2. Mixture of Independent Activities

\[ A = A_1 + A_2 + A_3 + \ldots \]

3. Parent–Daughter Relationships

\[ N_B = \frac{\lambda A}{\lambda_B - \lambda_A} N_A \left[ e^{-\lambda_B t} - e^{-\lambda_A t} \right] e^{-\lambda_B t} e^{-\lambda_A t} \]

No Equilibrium

[\[ N = N_0 \]

B–rate determining

Transient Equilibrium

Secular Equilibrium

A–rate determining

4. Branching Decay

\[ \frac{1}{T_{12}} = \frac{1}{T_{120}} + \frac{1}{T_{122}} \]

\[ \text{BR} = \frac{\lambda 0}{\lambda_{124}} = \frac{T_{122}}{T_{120}} \]