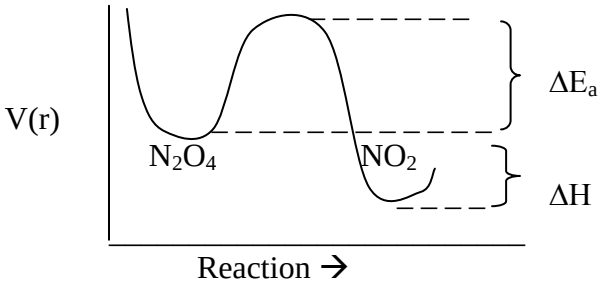
## SECTION 14: Radioactive Decay Kinetics

First-Order Kinetics

Just as in the case with atoms and molecules, the nucleus has internal structure and depending on the available energy, can undergo transformation to more stable species. A chemical analogy is the reaction

$$N_2O_4 \rightarrow 2\ NO_2\,,$$

for which we can schematically show the reaction coordinates as follows:




The corresponding **first-order rate equation** is

$$\text{Rate} = -d\left[\frac{N_2O_4}{dt}\right] = k\,[N_2O_4]\,, \qquad (14.1a)$$

where

$$k\ \alpha\ e^{-\Delta E_a/RT} x f(J,\pi\ ...)\,. \qquad (14.1b)$$

These equations describe a unimolecular decomposition; i.e. no collisional processes are involved. Since atoms and molecules are neutral, if T > 0 K , they will have 3kT/2 kinetic energy. Therefore binary collisions (second-order processes) also become possible and therefore distinguishing the reaction order becomes important for chemical reactions.

For nuclei T ~ 0 K (except in stars) and the Coulomb barrier inhibits collisions for charged particles. Therefore only first-order decay can occur, unless inaugurated by accelerated particles or neutrons (Sec. 15 – Nuclear Reactions). For nuclear decay the parameters of Eq. 14.1a are modified as follows:

- Concentration [ ] is replaced by **N**, where N is the **number of nuclei**, and
- k is replaced by $\lambda$ , the **rate constant**, which is a function of the Q value, spin and parity.

The instantaneous first-order decay rate is then

$$\text{Rate} = -\frac{dN}{dt} = \lambda N\,, \qquad \text{(Eq. 14.2)}$$

where the rate is in disintegrations per unit time (dpt). Two commonly used decay rate units are the Curie (Ci) and the Bequerel (Bq):

**1 Ci = 3.70 x $10^{10}$ dps and 1 Bq = 1 dps.**

Integrating this expression gives the time-dependent first-order rate law

$$N = N_0\, e^{-\lambda t}, \qquad \text{(Eq. 14.3)}$$

where the rate constant λ has a different value for every isotope. For a pure sample this behavior is illustrated in fig 14.1.

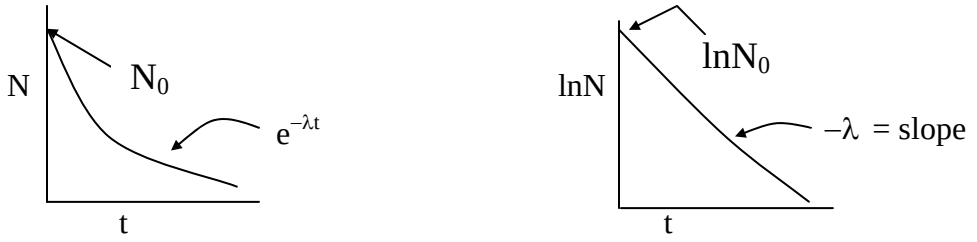



Fig. 14.1 Linear (left) and log (right) plots of Eq. 14.3, showing the decrease in the number of nuclei N as a function of time t.

A more convenient way to express the probability of decay is in terms of a **half-life, $t_{1/2}$,** i.e. a high probability corresponds to a short half-life. **The half-life is defined as the length of time required for a sample of $N_0$ nuclei to decay to $N_0/2$,** i.e. after $t = t_{1/2}$ , $N = N_0/2$. Substituting into Eq. 14.3,

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

$$\ell n\, 2 = \lambda\, t_{1/2} \;\Rightarrow\; \therefore \quad t_{1/2} = 1n\, 2/\lambda = \mathbf{0.693/\lambda = t_{1/2}} \qquad \text{(Eq. 14.4)}$$

<u>Mathematical Shortcuts</u>

Although Eq. 14.3 always works, there are several mathematical relationships that can be useful.

- If the time t is short with respect to the half-life ( $t << t_{1/2}$), then an expansion of Eq. 14.3 leads to the following result

$N/N_0 = e^{-\lambda t} = e^{-0.693 t/t_{1/2}}$ $\qquad$ $\lim(e^{-x})_{x \to 0} = 1 - x + \ldots$

$N/N_0 = 1 - \lambda t$

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

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

**$\Delta N = \lambda N_0 \Delta t$** = the number of nuclei that decay in a time interval Δt, and

**$\Delta N/\Delta t = \lambda N_0$** is the instantaneous decay rate of the initial sample.

**RULE**: if $t < 0.1\, t_{1/2}$ , the answer is good to three significant figures.

**Problem**: How many $^{238}U$ nuclei will decay in 1.0 y from a sample that contains 2.38 mg of uranium? How many will remain remain?

For $^{238}U$ : **abundance = 99.275%, $t_{1/2}$ = 4.468 × $10^9$ y**

The number of $^{238}U$ nuclei in the sample is

$$N_0 = \left(\frac{2.38\times10^{-3}\,g}{238\ g/mole}\right)(0.99275)\left(6.02\times10^{23}\,\frac{atoms}{mole}\right) = 5.98\times10^{18}\ atoms$$

$\lambda = 0.693/4.468 \times 10^9 y = 1.55\times10^{-10} y^{-1}$

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

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

i.e., there is no change at 3 significant figure level.

- If $t >> t_{1/2}$ , one obtains the trivial result

  $e^{-\lambda t} = e^{-0.693\ t/t_{1/2}} = e^{-\infty} = 0$

  i.e., $N = 0$ and $\Delta N = N_0$ ; i.e., all (or most of) sample has decayed.
  If $t >> 10\ t_{1/2}$, then $\Delta N = N_0$ to three significant figures.

- For the case of integral half-lives, where $n = t/t_{1/2}$ = 1,2,3, etc., Eq. 14.3 can more conveniently be written

  $$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n . \qquad \text{(Eq. 14.5)}$$

  Thus, the fraction of atoms that remain is just 1/2, 1/4, 1/8, etc. times $N_o$.

- Because radioactive decay follows exponential behavior, it is sometimes useful to use an average lifetime τ, defined as

  $$\tau = 1/\lambda = 1.44\ t_{1/2} \qquad \text{( Eq. 14.6)}$$

  This result is described in appendix 14.1. The **average lifetime** is frequently useful in assigning a half-life to an isotope for which only a few disintegrations are observed. It is longer than the half-life because of the exponential nature of radioactive decay, which gives decays that occur at a long time extra weight.

Rate of Energy Loss

The rate of energy loss by a radioactive source is an important quantity for numerous applications. For example, it is estimated that about 50% of the heating of the earth's crust is due to the radioactive decay of $^{40}K$, $^{232}Th$ and $^{235,238}U$. The isotope $^{238}Pu$ is valuable as a miniature power source for devices that probe remote locations on the planet and space vehicles. And of course the rate of energy loss plays an important role in efforts to determine the heating of radioactive wastes from nuclear reactors. From a chemical perspective, it is important to evaluate the spurious heating effects in studying the thermochemistry of radioactive elements.

The rate of energy loss –dE/dt for the generic emission of particle B in the equation below

$$ {}^{A}_{Z}X \rightarrow B + {}^{A'}_{Z'}Y + Q_B \; ; \; Q_B = + $$

can be written

$$ \text{Rate} = \frac{-dE}{dt} = \underbrace{\frac{dN}{dt}}_{\lambda N} \bullet \underbrace{\frac{dE}{dN}}_{Q} = Q\lambda N = Q\lambda N_0 e^{-\lambda t} = \frac{\Delta E}{\Delta t} . \qquad \text{(Eq. 14.7)} $$

Here QλN is the instantaneous energy loss rate, $Q\lambda N_o e^{-\lambda t}$ is the integral rate and $\Delta E/\Delta t$ gives the rate when $t << t_{1/2}$.

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

$^{210}$Po is an alpha emitter with a Q-value of 5.305 MeV and a half-life of 138.4 days. Since we are interested in the rate per minute, the approximation $\Delta E/\Delta t = Q_\alpha \lambda N$ can be used. Thus,

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

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

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

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

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

This amount of energy is comparable to the molar heat of reaction for many chemical processes. But in this case at the end of the day you still have nearly the same amount of $^{210}$Po that you started with. For example, after 138.4 days, the heat generation is only down to 935 kJ/min and half a mole remains to continue generating heat.

Activity –Practical Aspects of Radiation Measurement

In measuring radioactivity it is the emitted particles that are detected, not the absolute number of daughter nuclei N. Two important physical limitations are imposed on any such measurement. First, the radiation is emitted isotropically in space about a sphere of surface area $4\pi R^2$, shown schematically below

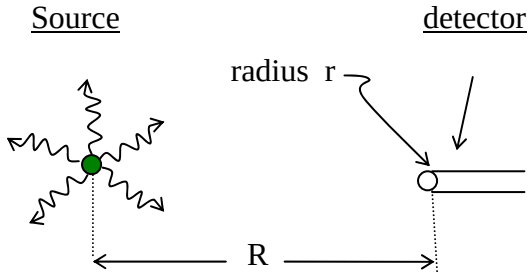



Fig. 14.2 Schematic diagram of a radiation detection measurement in which a detector of radius r intercepts radiation at a distance R from a radioactive source.

A second factor that limits measurement of the absolute disintegration rates arises from the ability of the detector to register a signal when radiation is incident upon it. Thus most measurements are relative and not absolute.

In order to relate the relative measurement to absolute values, we define a quantity called the **activity A**, where activity is the actual number of emitted particles detected by a detector. Specifically,

$$A = c(-dN/dt) = c\lambda N = \text{counts/unit time}, \qquad \text{(Eq. 14.8)}$$

where **c** is called a detection coefficient and as long as the measurement time is short with respect to the half-life**,** the counts are the number of particles detected in a time interval $\Delta t$ .

In order to obtain the absolute disintegration rate from the measured activity, it is essential to have an accurate determination of the detection coefficient. (**Accurate calibration of one's instrument is critical for any quantitative measurement ).**
In the present case, the detection coefficient can be written

$$\mathbf{c = G\varepsilon,} \qquad \text{(Eq. 14.9)}$$

where G is a geometry factor determined by the radius r of the detector and the distance R from the source

$$\mathbf{G = \pi r^2/4\pi R^2 = r^2/4R^2} \ . \qquad \text{(Eq. 14.10)}$$

Eq. 10.10 is a basic principle of radiation safety, i.e. the amount of radiation one receives decreases as the square of the distance from a radioactive source. The factor **ε** is the **detector efficiency** , which indicates the fraction of the radiation that strikes the detector and produces a measurable signal. For energetic heavy particles such as alpha particles and fission fragments, ε is usually 100%. However, for beta particles and gamma rays the detector efficiency is smaller, requiring careful calibration of the instrument for **reliable** quantitative results.

Another factor that must be taken into account is the background radiation due to residual radiation in the environment ($^{40}$K, Th, U , cosmic rays) that triggers the detector in the absence of any source. **This activity must be subtracted from that measured with the source present.**

The integral first order decay law (Eq. 14.3) can be rewritten in terms of activity (Eq. 14.8) as follows

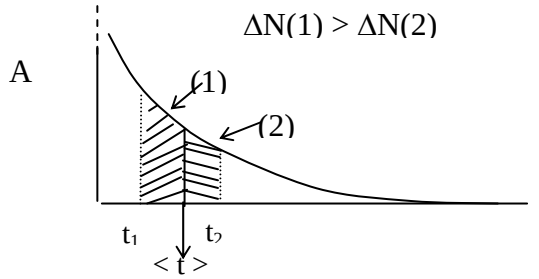
$$c\lambda N = c\lambda N_0 e^{-\lambda t} \qquad \Rightarrow \ A = A_0 e^{-\lambda t} . \qquad \text{(Eq. 14.11)}$$

By measuring a series of activities A as a function of time t and then plotting lnA versus t, a graph similar to that shown in fig. 14.1 is obtqined. The slope of this graph gives the decay constant, related to the half-life $t_{1/2}$ and the time zero intercept gives the initial activity $A_0$. The **uncertainty of each measurement** is approximately

**± the square root of the number of counts.** For example, if one measures 900 counts, the error is ± 30 or 3.3%.

For the case where the counting time is sufficiently long that it cannot be considered instantaneous, the decay curve analysis must consider that the average time

$<t> = \frac{t_2 + t_1}{2}$ is not appropriate. Because of the exponential nature of radioactive decay, more nuclei will decay in the interval between $t_1$ and $<t>$ than in the interval between $t_2$ and $<t>$, as shown below

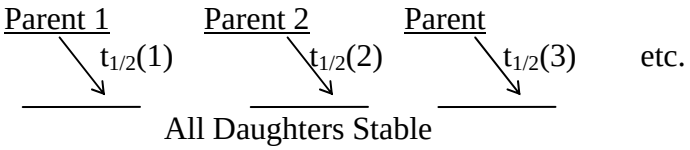



In this case the number of nuclei that decay in the interval between $t_1$ and $t_2$ is

$$\Delta N(\text{total}) = N_0 e^{-\lambda t1} - N_0 e^{-\lambda t2} .$$

Mixtures of Independent Activities

Up to this point we have dealt with a single parent nucleus that decays to a stable daughter. For a mixture of independent activities that all decay to stable daughters, as diagrammed below, a composite decay curve will be observed.




For this general case the total activity (background subtracted) is

$$A_{total} - A_{bkg} = A(1) + A(2) + A(3) + \ldots$$
$$= A_0(1)\, e^{-\lambda_1 t} + A_0(2)\, e^{-\lambda_2 t} + A_0(3)\, e^{-\lambda_3 t} + \ldots..$$

The **basic rule** when decomposing a multicomponent decay curve is that as the decay time becomes very long, the shorter-lived components will have decayed away. Thus only the longest-lived component will remain. Since we know that the logarithm of the activity is linear with time, this component can be isolated and extrapolated back to time = 0 to yield its activity at all times. This same procedure can then be followed sequentially until all additional components are resolved. There will be n–1 slope changes in the log plot of the total activity versus time, where n is the number of components. The exception occurs when two half-lives are close to one another, in which case more sophisticated methods are required.

As an example, a two-component decay curve is shown in Fig. 14.3.

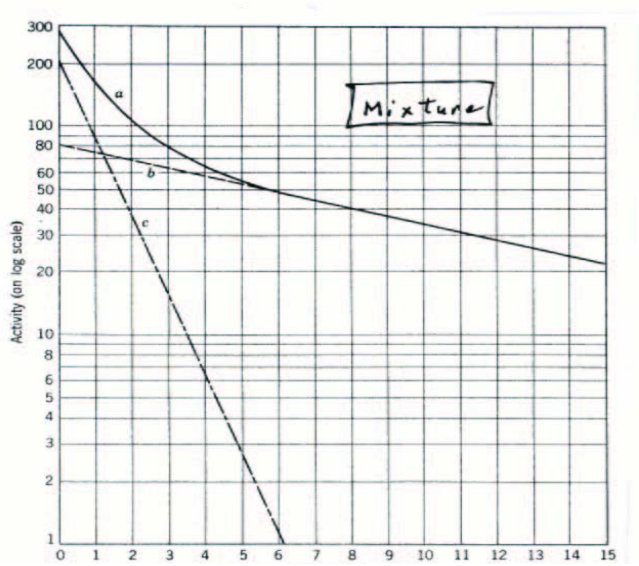
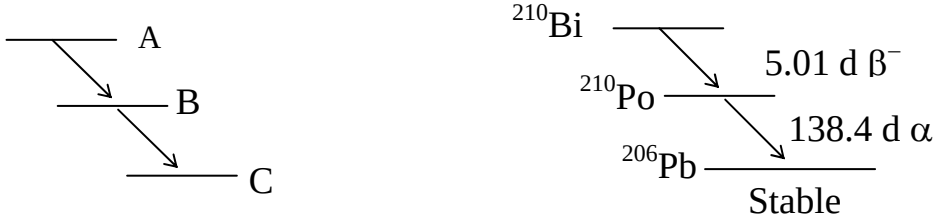



Fig. 10.3 Composite decay curve (a) for activities (b) and (c).

Curve a represents the log of the total background-subtracted activity as a function of time. For times longer than about 8 minutes, linear behavior is observed, indicating a pure longer-lived component. By extrapolating this line linearly back to time t = 0 (curve b), the initial activity of b at all times is determined. The initial activity can be read from the graph as $A_o(1) = 80$ and the half-life as 8 minutes. Curve b is then subtracted from curve a to obtain curve c, the decay curve of the shorter-lived component, for which the initial activity is found to be $A_o(2) = 200$ and the half-life 1 minute. For three or more components, the same procedure is followed until all activities have bee separated. The bottom line is that one must always start with the long-time portion of the decay curve and isolate the components sequentially.

Parent-Daughter Relationships

Finally, we examine the case of a radioactive daughter, which is identical to the case of a stepwise chemical reaction and introduces the concept of the rate-determining step. Schematically, this sequential decay is illustrated below, along with the specific example of the decay of $^{210}$Bi.




In the $^{210}$Bi example shown above, the decay of $^{210}$Po is the rate-determining step for production of $^{206}$Pb since it has the longest half-life.

The mathematics of this problem is as follows:

Parent A: decay rate = $-dN/dt = \lambda_A N_A$ ; $\mathbf{N_A} = N_A^0 \, \mathbf{e}^{-\lambda_A t}$ . (nothing new here)

Daughter B: formation rate = $+dN_B/dt = \lambda_A N_A$

decay rate = $-dN_B/dt = -\lambda_B N_B$

The net equation for the rate of rate B gives the following first-order linear differential equation:

$$\frac{dN_B}{dt} = \lambda_A N_A - \lambda_B N_B = \lambda_A N_A^0 e^{-\lambda A t} - \lambda_B N_B . \quad \text{(Eq. 14.12)}$$

The solution to the differential equation 14.12 gives the following expression for the number of B nuclei at any time:

$$N_B = \frac{\lambda_A N_A^0}{\lambda_B - \lambda_A}\left(e^{-\lambda A t} - e^{-\lambda_B t}\right) + N_B^0 e^{-\lambda_B t} . \quad \text{(Eq.14.13)}$$

Note that if sample A is initially pure, the initial number of B nuclei is zereo and the second term vanishes. Finally it should be noted that the number of daughter C nuclei is determined by the conservation nucleon number

$$\mathbf{N_C} = N_A^0 - \mathbf{N_A} - \mathbf{N_B} .$$

The long-time solution of Eq. 14.13 leads to three cases of interest:

| classification | time relationship | Rate-determining step |
|---|---|---|
| • No Equilibrium | $t > t_B > t_A$ | $B \rightarrow C$ |
| • Transient Equilibrium | $t > t_A > t_B$ | $A \rightarrow B$ |
| • Secular Equilibrium | $t_A >> t > t_B$ | $A \rightarrow B$ |

Secular equilibrium is a special case of transient equilibrium, that is of particular importance to the uranium and thorium decay series that leads to $^{206,\ 207,208}Pb$ isotopes (see fig. 3.1). Each of these cases is discussed below.

- **No Equilibrium**
  When the parent (A) half-life is shorter than that of the daughter (B), then the decay of the daughter is the rate-determining step and no equilibrium between parent and daughter decay rates can develop. In this case the parent will eventually decay to a negligible level, while the daughter nuclei will continue to decay, as shown in Fig. 14.4.

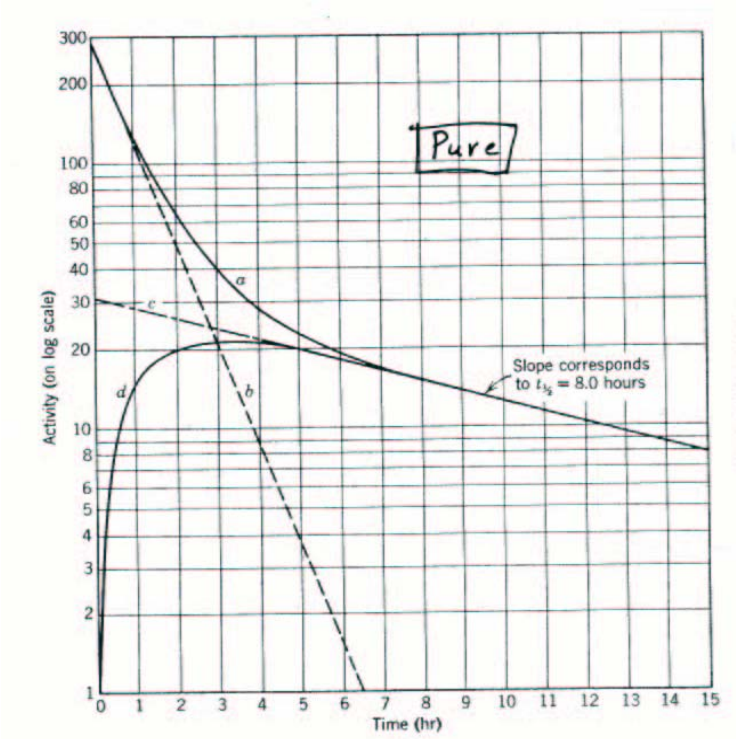



Fig.14.4 Example of no equilibrium: total activity (curve a); growth of daughter activity (curve d); long-time behavior of daughter (curve c), extrapolated to time = 0 , and decay if parent (curve b).

In Fig. 14.4 the total activity is shown by curve a, which initially is due to the parent only. Note that this curve resembles that of two independent activites. However, in this case the initial activity of component B is zero; i.e. only pure parent nuclei are initially present. Curve d represents the growth of the daughter, which reaches a maximum and then at long times becomes the only activity present. From this linear portion of the plot (line c) at long times, the half-life of the daughter can be determined. This can be shown by considering that at long times t,

$t / t_{1/2}(A) >> 1$ so that $e^{-\lambda_A t} \rightarrow 0$,

and Eq. 14.13 can be written in the long-time approximation as

$$N_B = \frac{\lambda_A N_A^0}{\lambda_B - \lambda_A}(-e^{-\lambda_B t}) . \qquad (\text{Note: } \lambda_B < \lambda_A) \qquad \text{(Eq. 14.14)}$$

Note that only the exponential involving the daughter appears in this equation. In order to obtain the half-life of the parent, it is helpful to have a means of differentiating the parent and daughter radiations, or equations 14.13 or 14.14 can be used to approximate the parent half-life, knowing the half=life of the daughter.

- **Transient Equilibrium**

In transit equilibrium the parent half-life is greater that of the daughter and thus the decay of the parent is the rate-determining step. Transient equilibrium can be readily distinguished by the fact that initially the **total activity increases with time**, rather than decreasing, as is the usual case. This behavior is demonstrated in Fig. 14.5 for the decay of a pure parent.

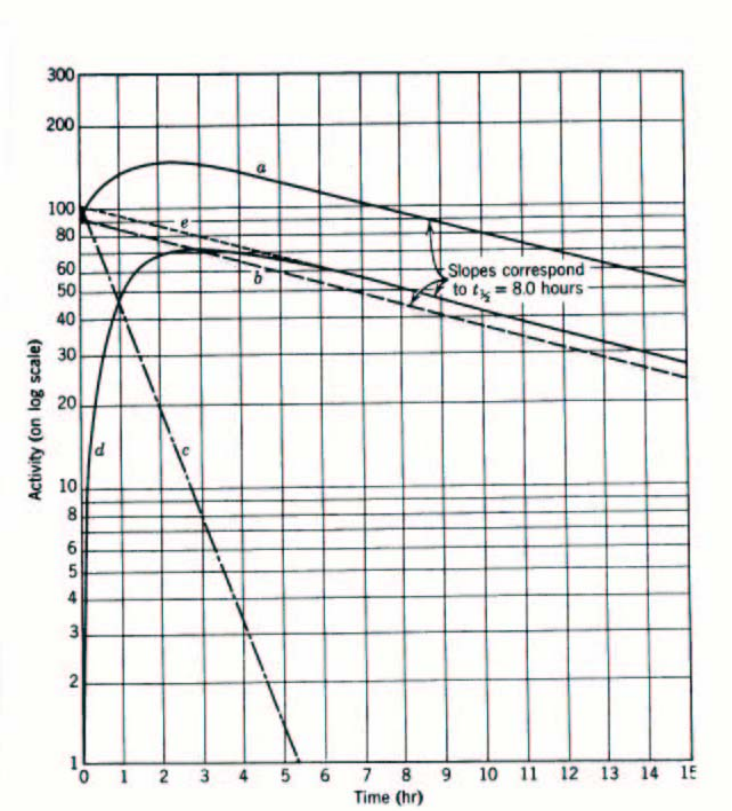



Fig. 14.5 Example of transient equilibrium: total activity (curve a); growth of daughter (curve d); decay of parent (curve b); decay of an independent sample of the daughter with intial activity of 100 cpm (curve c), and extrapolation of long-term activity to time =0 (cirve e).

The important curves a in Fig.15.5 are a, b and c. Curve a represents the total parent-daughter decay activity. Line b describes the decay of the parent and defines the half-life of the parent. The growth of the daughter activity is given by curve d, which reaches a maximum and decreases at the same rate as that of the parent; i.e. the parent and daughter decay rates assume a constant proportionality, consistent with the concept of equilibrium.

The maximum daughter activity is of significant importance in nuclear medicine. Ideally, a useful isotope for medical diagnostics or treatment will have a half-life that is long enough to enable the procedure to be administered conveniently but short enough so that it does not leave residual activity in the patient. Two methods

are commonly used for this purpose. One technique involves synthesizing the radioisotope in a particle accelerator, which requires the presence of an accelerator in the medical facility. The second method is to use a long-lived parent nucleus that decays to a shorter-lived daughter with an appropriate half-life for medical purposes. An example of such a parent-daughter pair is the decay of the fission product $^{137}$Cs

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

At appropriate intervals the daughter can be chemically separated from the mixture for medical use – a process called "milking the cow". The maximum yield of the daughter will occur when the production and decay rates are equal, at which point dN /dt = 0. By differentiating Eq. 14.13 and setting it equal to to zero, the following expression for the time at which the daughter activity is a maximum can be obtained

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

For example, in the $^{137}$Cs example above, it takes 58 minutes to reach the maximum activity from a freshly-prepared sample of $^{137}$Cs.

To demonstrate the equilibrium-like nature of the long-time behavior of systems in which the parent is the rate-determining step, eq. 14.13 can be approximated as follows. Since the half-life of the daughter is short, $t >> t_{1/2}(B)$ and therefore

$$e^{-\lambda_B t} \cong e^{-\infty} \Rightarrow 0.$$

Inserting this approximation into Eq. 14.13 yields the long-time solution

$$N_B = \frac{(\lambda_A N_A^0)}{\lambda_B - \lambda_A} e^{-\lambda_A t} \cong \frac{\lambda_A N_A}{\lambda_B - \lambda_A}, \quad \text{OR} \quad \frac{N_B}{N_A} = \frac{\lambda_A}{\lambda_B - \lambda_A}. \quad \text{(Eq. 14.15)}$$

Thus at long times the ratio of daughter to parent nuclei ($N_B/N_A$) is constant and the system appears to be in equilibrium. In terms of activity Eq. 14.15 can be written

$$c\lambda_B N_B = \frac{c\lambda_B\lambda_A N_A}{\lambda_B - \lambda_A} A_B = \left(\frac{\lambda_B}{\lambda_A - \lambda_B}\right) A_A \qquad \text{(Eq.14.16)}$$

The half-life of the daughter can be determined from the activity ratio in eq. 14.16, once the parent half-life is determined from the long-time slope in Fig. 14.5.

- **Secular equilibrium**

As mentioned previously, secular equilibrium is a special case of transient equilibrium in which the half-life of the parent is very long with respect to

possible observation times; i.e. the parent activity does not change on a measurable time scale and therefore corresponds to a constant production rate process. Secular equilibrium is especially relevant to the decay chains of $^{232}$Th ($t_{1/2}$ = 1.4x10$^{10}$ yr ), $^{235}$U ($t_{1/2}$ = 7.0x10$^{8}$ yr ) and $^{238}$U ($t_{1/2}$ = 4.5x10$^{9}$ yr ) as they decay to stable $^{208}$Pb, $^{207}$Pb and $^{206}$Pb nuclei, respectively, through a chain of much shorter-lived nuclei. One of these intermediate activities is $^{222}$Rn, a major source of environmental radioactivity, radon gas.

The behavior of a pure parent – stable daughter system under these conditions is shown in Fig. 14.6.

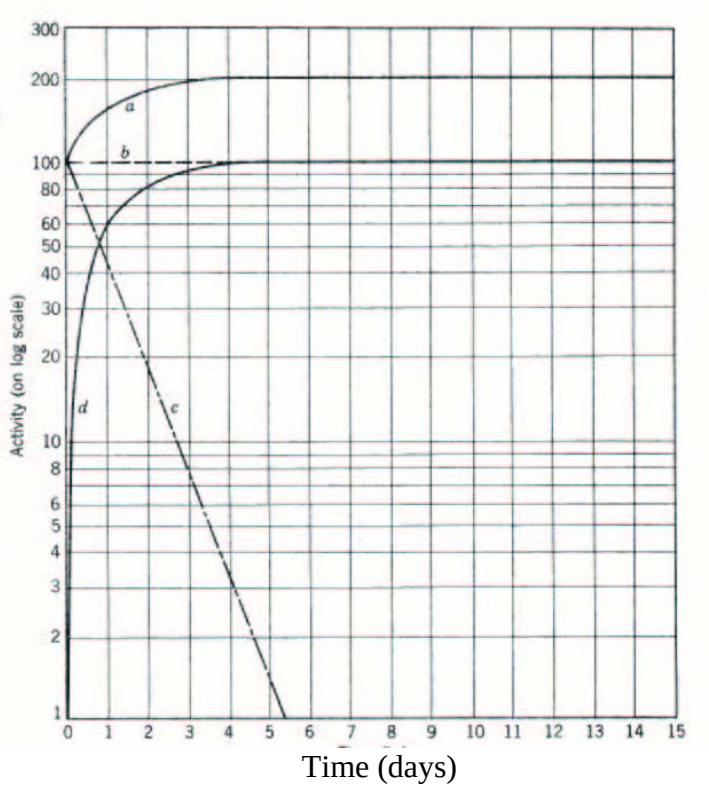



Fig. 14.6 Parent-daughter behavior for secular equilibrium: total activity (curve a); parent decay (line b); growth of the daughter (curve d), and the independent decay curve of the daughter (curve c).

As in transient equilibrium, the total activity initially increases with time, but in this case reaches a constant plateau at long times. Because of its long half-life, the parent activity remains constant. The growth of the daughter eventually assumes an activity equal to that of the parent..

Under these conditions, $t_{1/2}(A) > > t > > t_{1/2}(B)$, so that for a pure parent

$$e^{-\lambda_A t} \approx e^0 = 1 \text{ and } \lambda_B > > \lambda_A \; ; \; \lambda_B - \lambda_A \cong \lambda_B$$

and Eq. 14.13 can be rewritten

$$N_B \approx \frac{N_A^0 \lambda_A}{\lambda_B}(1 - e^{-\lambda_B t}), \qquad \text{(Eq. 14.17)}$$

or in terms of activity

$$A_B = A_A \cdot (1 - e^{-\lambda_B t}) \ . \qquad \text{(Eq. 14.18)}$$

Equations 14.17 and 14.18 describe the growth curve of the daughter. After one half-life of the daughter,

$$e^{-\lambda_B t} = \tfrac{1}{2} ,$$

Enabling determination of the daughter half-life from the time at which $A_B / A_A = 1/2$.

The long-time solution to Eq. 14.17 takes advantage of the fact that since

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

$$N_B = \frac{\lambda_A N_A^0}{\lambda_B} \Rightarrow \boxed{N_B \lambda_B = \lambda_A N_A^0} \qquad \text{(Eq. 14.19)}$$

and if $c_A = c_B$, $\boxed{A_B = A_A = A_{total/2} \ .}$

**Problem:** How many atoms of $^{222}$Rn are present in an initially pure 226 mg sample of $^{226}$Ra after three months of decay? What is the activity of the $^{222}$Rn after this time (assume c = 1)? $t_{1/2}(^{222}\text{Rn}) = 3.82$ d ; $t_{1/2}(^{226}\text{Ra}) = 1620$ y.

$$N_{Rn} = \frac{\lambda_{Ra}}{\lambda_{Rn}} \bullet N^0(\text{Ra}) = \frac{t_{1/2}(\text{Rn})}{t_{1/2}(\text{Ra})} \bullet N^0(\text{Ra}) =$$

$$N_{Rn} = \frac{(3.82 \text{ d})}{1620 \text{ y } (365 \text{ d / y})} \bullet \frac{226 \times 10^{-3} \text{g}}{226 \text{ g / mole}}$$

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

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

In order to obtain the half-life of the parent it is necessary to know the number of atoms of the parent (e.g. by weighing) and then using the relation

$$A_A = c\lambda N_A^0 \ .$$

**Several Successive Decays**

The U-Th decay series includes several successive decays

$$A \rightarrow B \rightarrow C \rightarrow D, \ldots\ldots ,$$

which leads to a series of differential equations. However, for present purposes we will only deal with the solution for secular equilibrium and the **long-time solution** which applies to the U-Th decay series. In this case a simple result is obtained

$$\lambda_A N_A^0 = \lambda_B N_B = \lambda_C N_C = \ldots\ldots \qquad \text{(Eq. 14.20)}$$

Equation 14.20 states that the disintegration rates are the same for all species in secular equilibrium and that the total activity is

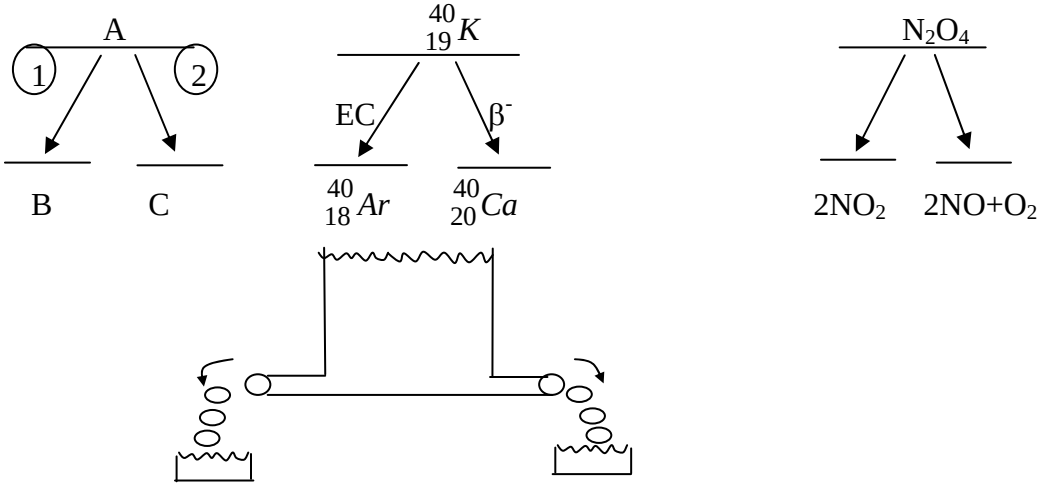
$-dN/dt(\text{total} = n\lambda_A N_A^0$ , where n is number of decays in chain.

If the detection coefficients are all equal, then $\mathbf{A_A = A_B = A_C \ldots}$

As an **exercise**, calculate the mass of $^{226}$Ra Marie Curie could have obtained from 2 tons of uranium ore (assume $U_3O_8$).

Branching Decay

As discussed in the sections on radioactive decay modes, nuclei decay by two different paths, or **branching decay**, as shown below for the general case, the decay of $^{40}$K and the chemical example of $N_2O_4$ decomposition. This mechanism is analogous to chemical reactions in which two or first-order decomposition modes compete or to the draining of a tank of liquid with two different spigots that have different-sized openings and therefore will fill the collecting containers depending on the area of the outlet.




The total decay probability for a nucleus that undergoes branching decay is

$$\lambda_{total} = \lambda_1 + \lambda_2 + \lambda_3 + \ldots$$

or in terms of half-lives,

$$\frac{1}{t_{1/2}} = \frac{1}{t_{1/2(1)}} + \frac{1}{t_{1/2(2)}} + \frac{1}{t_{1/2(3)}} + \ldots ,$$

where the $\mathbf{t_i}$ are the **partial half-lives** of the available decay modes. The partial half-life is the half-life a nucleus would have if all the competing decay modes were switched off. Partial half-lives are always longer than the total half life.

In order to determine the partial half-life for each mode, it is essential to know the **branching ratio (BR)** for each mode. The branching ratio is the fraction of total events (probability) that decay via a given path. For a nucleus with two possible branches,

$$BR(1) = \frac{\lambda_1}{\lambda_{total}} = \frac{\lambda_1}{\lambda_{total}} = \frac{t_{1/2}(total)}{t_{1/2}(1)} \quad , \qquad \text{(Eq. 14.21)}$$

and if $c_1 = c_2$,

$$BR(1) = \frac{\lambda_1 \times c_1 \times N}{\lambda_{total} \times c \times N} = \frac{A_1}{A_{total}} .$$

**Problem**: In the decay of $^{40}K$, electron capture occurs 10.7 % of the time and negatron decay 89.3 %. The half-life of $^{40}K$ is $1.28 \times 10^9$ years.

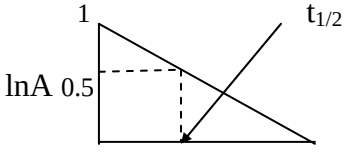
$$BR(EC) = (0.107) = \frac{t_{1/2}}{t_{EC}}; \quad t_{EC} = 1.19 \times 10^{10}$$

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

## Determination of Half-lives

Nuclear lifetimes have been measured over a range from about $10^{-23}$s to $10^{30}$y, corresponding to 60 orders of magnitude. Few other physical phenomena are amenable to measurement over such a large range. Several methods exist for determining half-lives, depending on the time scale involved.
These include :

- **Specific Activity** (>> 1year): For **long lifetimes**, measurement of the mass of the sample and its activity permits determination of the half-life from the basic equation $A = c\lambda N$. For example, 238mg of $^{238}U$ has a specific activity of 300 dps, which permits assigning this nucleus a $4.5 \times 10^9$ year half-life. The upper limit for such measurements is often determined by the background radiation, which may be greater than that from the source for very long lifetimes.
- **Decay curves** ($10y \gtrsim t_{1/2} \gtrsim 1s$): In this time range decay curves such as that shown in Fig.14.1 permit determination of the half-life by finding the time it take the activity to decrease by a factor of two.



time

- **Electronic Techniques (**$10s \gtrsim t_{1/2} \gtrsim 10$ ps**):** The time difference between the electronic signals from two events in a detector can be used to determine the lifetime.
- **Heisenberg Uncertainty Principle** ($10^{-15} \lesssim t_{1/2}$) : By measuring line widths of emitted radiation the lifetime can be determined from the Heisenberg relationship
  $\Delta t \sim h/2\pi\Delta E$
- **Additional methods** ($\sim 10^{-20}$s): Relevant lifetime information can also be derived from a number of methods involving nuclear reaction studies, for example Doppler shifts, channeling in crystals, angular distribution of emitted particles and small-angle correlations between pairs of emitted particles emitted in close proximity to one another.

All of these methods have permitted us to catalogue thousands of nuclear lifetimes that contribute to our understanding of nuclear structure and nuclear reaction mechanisms.

## Appendix 10.1

Mathematics of the average lifetime calculation

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

Changing variables $N_0 \rightarrow 0$ as $t \rightarrow \infty$

$$\tau = \frac{1}{N_0}\int_{N_0}^{0} t\,dN = \frac{1}{N_0}\int_{0}^{\infty} t\,(-\lambda N\,dt) = \frac{-\lambda}{N_0}\int_{0}^{\infty} t\,N_0(-\lambda N_0 e^{-\lambda t}\,dt = -\lambda\int_{0}^{\infty} te^{\lambda t}\,dt$$

MATH: $\int_0^\infty xe^{ax}dx = \frac{e^{ax}}{a^2}(ax - 1)$

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