Nuclear Chemistry Cumulative Examination
September 15, 2010

The examination will focus on radioactive decay kinetics. Support all answers with brief justifications where appropriate. A periodic table is available on the wall at the front of the room.

Some helpful relations:

$A = N\lambda$ $T_{1/2} = \ln 2 / \lambda$ $1\ Ci = 3.7\times10^{10}$ dps $N_t = N_o e^{-\lambda t}$ $N_A = 6.02\times10^{23}\ mol^{-1}$

Q1 (15 points): Radioactive decay follows first-order kinetics. Sketch the following:

a. Activity as a function of time.
b. Natural logarithm of the activity as a function of time.
c. Activity as a function of the natural logarithm of time.

Q2 (10 points): Determine the number of grams of radioactive atoms contained in 1 mCi of ^{24}Na, a β^- emitter with a half-life of 14.95 h.

Q3 (10 points): The half-life of ^{22}Na is 3.604 y. It decays by the emission of positrons (β^+) with a branching ratio of 89%. The competing decay branch is electron capture (EC), which happens 11% of the time. Calculate the partial decay half-life for each of the modes of decay.

Q4 (20 points): A sample of plutonium consists of ^{239}Pu ($T_{1/2} = 2.41 \times 10^4$ y) and ^{240}Pu ($T_{1/2} = 6.56 \times 10^3$ y) in unknown proportions. The specific activity was found to be 1.72×10^8 disintegrations per minute per milligram. What is the composition of the sample?

Q5 (15 points): Radioactive ^{14}C ($T_{1/2} = 5.72 \times 10^3$ y) produced in the earth's atmosphere is taken up by living things, resulting in an average ^{14}C radioactivity of 10 disintegrations per minute per gram of carbon. Wood taken from an Egyptian tomb had a ^{14}C content of 7.62 disintegrations per minute per gram of carbon.

a. Estimate the age of the wood.
b. List the assumptions made in determining the estimate.

Q6 (10 points): The activity of a radioactive nuclide at the end of an irradiation can be expressed as:

$$A = N\lambda = R\left(1 - e^{-\lambda t}\right)$$

where *R* is the production rate and *t* is the irradiation time. Sketch the activity as a function of irradiation time, and justify why an irradiation time of order 3 times the half-life is sufficient to maximize production of the product nuclide.

The final two questions focus on successive radioactive decays. For a chain of n members with the assumption that at $t = 0$ the parent nuclide is solely present (N_1^0), the general solution for the number of atoms of any member of the chain was provided by H. Bateman:

$$N_n = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} + \cdots C_n e^{-\lambda_n t}$$

$$C_1 = \frac{\lambda_1 \lambda_2 \cdots \lambda_{n-1}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \cdots (\lambda_n - \lambda_1)} N_1^0$$

$$C_2 = \frac{\lambda_1 \lambda_2 \cdots \lambda_{n-1}}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2) \cdots (\lambda_n - \lambda_2)} N_1^0, \text{and so on}$$

Q7 (10 points): Show that the time required for the daughter to reach its maximum activity in a sequential decay is:

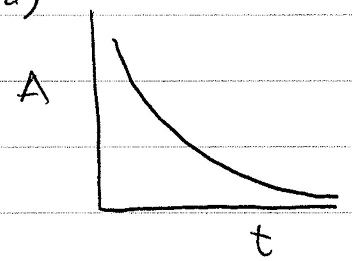
$$t_{max} = \frac{1}{\lambda_2 - \lambda_1} \ln \frac{\lambda_2}{\lambda_1}$$

for the case of non-equilibrium decay ($\lambda_1 > \lambda_2$).

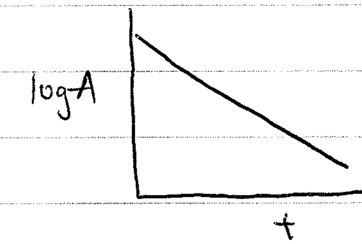
Q8 (10 points): Show that for secular equilibrium, where the parent is very much longer lived (> 10^4 times longer) than the daughter, the activities at long times of the parent and daughter are the same: that is, $A_1 = A_2$.

Nucl. Cure Exam
Key - 9/15/2010

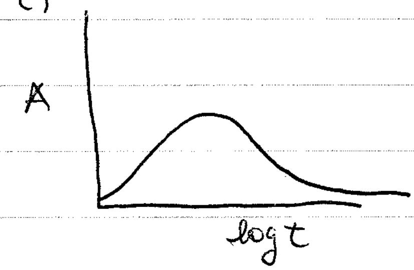
① a)



b)



c)



② $A = \lambda N = 1\,mCi = 1\times10^{-3}\,Ci = (1\times10^{-3})(3.7\times10^{10}\,dps)$

$= 3.7\times10^{7}\,dps$

$$\lambda = \frac{\ln 2}{T_{1/2}} = \frac{0.693}{14.95h} \times \frac{1h}{3600s} = 1.288\times10^{-5}\,s^{-1}$$

$$N = \frac{3.7\times10^{7}/s}{1.288\times10^{-5}/s} = \frac{2.87\times10^{12}}{6.02\times10^{23}/mol} = 4.77\times10^{-12}\,mol \times 24\,\frac{g}{mol}$$

$$= \boxed{1.14\times10^{-10}\,g}$$

③ $\lambda_T = \lambda_{\beta+} + \lambda_{EC} = \frac{0.693}{T_{1/2}}$

$\frac{\lambda_{\beta+}}{\lambda_{EC}} = \frac{0.89}{0.11}$ $\quad \lambda_\beta = 8.09\,\lambda_{EC}$

$\lambda_T = \frac{0.693}{3.604y} = 8.09\lambda_{EC} + \lambda_{EC}$

$0.1922 = 9.09\,\lambda_{EC}$

$0.02115\,y^{-1} = \lambda_{EC}$

$T_{1/2}(EC) = \frac{0.693}{0.02115\,y^{-1}}$

$\boxed{= 32.7\,y}$

$\lambda_\beta = 8.09\,\lambda_{EC}$

$= 8.09(0.02115\,y^{-1})$

$= 0.1711\,y^{-1}$

$T_{1/2}(\beta^+) = \frac{0.693}{0.1711\,y^{-1}}$

$\boxed{= 4.05\,y}$

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(4) assume 1 mg of sample

composition in mass = 1 mg = $\# mol\ ^{239}Pu \cdot 239\frac{g}{mol} + \# mol\ ^{240}Pu \cdot 240\frac{g}{mol}$

$$\text{Activity of } 1mg = 1.72\times 10^{8}\ dps = A_T = A(^{239}Pu) + A(^{240}Pu)$$
$$= N_{(^{239}Pu)}\lambda_{^{239}Pu} + N_{(^{240}Pu)}\lambda_{(^{240}Pu)}$$

Two equations, two unknowns. Can solve for $N_{(^{239}Pu)}$

$$\lambda(^{239}Pu) = \frac{0.693}{T_{1/2}(^{239}Pu)} = \frac{0.693}{2.41\times 10^{4}\,y} = 2.87\times 10^{-5}\,y^{-1}\cdot\frac{1\,y}{3.15\times 10^{7}\,s} = 9.10\times 10^{-13}\,s^{-1}$$

$$\lambda(^{240}Pu) = \frac{0.693}{T_{1/2}(^{240}Pu)} = \frac{0.693}{6.56\times 10^{3}\,y} = 1.056\times 10^{-4}\,y^{-1}\cdot\frac{1\,y}{3.15\times 10^{7}\,s} = 3.35\times 10^{-12}\,s^{-1}$$

$$1.72\times 10^{8}\,\cancel{dps} = N_{(^{239}Pu)}(9.10\times 10^{-13}\,\cancel{s^{-1}}) + N_{(^{240}Pu)}(3.35\times 10^{-12}\,\cancel{s^{-1}})$$

$$\left(1\times 10^{-3}\,g = \frac{N(^{239}Pu)}{\cancel{N_A}}\cdot 239\frac{g}{\cancel{mol}} + \frac{N(^{240}Pu)}{\cancel{N_A}}\cdot 240\frac{g}{\cancel{mol}}\right)N_A$$

$$6.02\times 10^{20}\,\cancel{g} = N(^{239}Pu)(239\,\cancel{g}) + N(^{240}Pu)\ 240\,\cancel{g}$$

$$N(^{240}Pu)(240) = 6.02\times 10^{20} - N(^{239}Pu)(239)$$

$$1.72\times 10^{8}\,\cancel{dps} = N(^{239}Pu)(9.10\times 10^{-13}) + \left[6.02\times 10^{20} - N(^{239}Pu)(239)\right](3.35\times 10^{-12})$$

$$1.72\times 10^{8} = N(^{239}Pu)(9.10\times 10^{-13}) + 2.017\times 10^{9} - N(^{239}Pu)\ 8.00\times 10^{-10}$$

$$+1.845\times 10^{9} = +N(^{239}Pu)(7.99\times 10^{-10})$$

$$\boxed{2.31\times 10^{18} = N(^{239}Pu)}$$

$$N(^{240}Pu) = \frac{(6.02\times 10^{20}) - (2.31\times 10^{18})(239)}{(240)}$$

$$\boxed{= 2.07\times 10^{17}}$$

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(5) $SA_t = SA_0 e^{-\lambda t}$ $\lambda = \frac{0.693}{T_{1/2}} = \frac{0.693}{5.72 \times 10^3 y} = 1.211 \times 10^{-4} y^{-1}$

$7.62 = 10.0\, e^{-(1.211 \times 10^{-4} y^{-1})t}$ $SA_t = 7.62$ dpm/g

$0.762 = e^{-1.1211 \times 10^{-4} y^{-1} t}$ $SA_0 = 10.0$ dpm/g

$\ln(0.762) = -1.1211 \times 10^{-4} y^{-1} t$

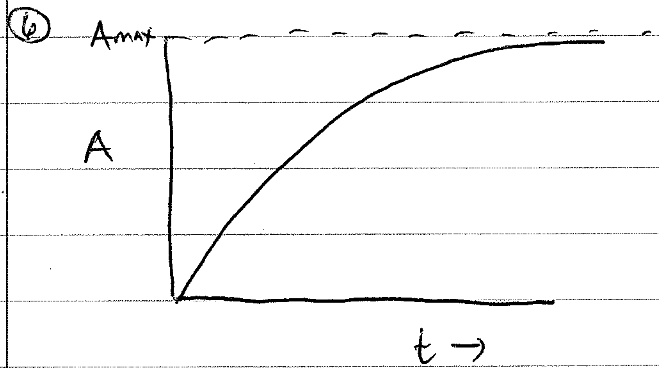
$-2.718 = -1.1211 \times 10^{-4} y^{-1} t$

$\boxed{t = 2.244 \times 10^3 y}$

assume – no carbon-14 uptake after death

– no leakage of C-14 from sample

(6)



$A_{max} = R$, when

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

when $\lambda t \approx 1$

$t \approx \frac{1}{\lambda}$

$\approx \frac{t_{1/2}}{0.693}$

$\approx 1.44\, t_{1/2}$

when t exceeds $1.44\, t_{1/2}$, starting to reach saturation. At $t = 3 t_{1/2}$ no longer making activity beyond maximum allowed.

(7) $N_1 = N_1^0 e^{-\lambda_1 t}$

$N_2 = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t}$ $C_1 = \frac{\lambda_1}{(\lambda_2 - \lambda_1)} N_1^0$

$C_2 = \frac{\lambda_1}{(\lambda_1 - \lambda_2)} N_1^0$

$N_2 = \frac{\lambda_1}{(\lambda_2 - \lambda_1)} N_1^0 e^{-\lambda_1 t} + \frac{\lambda_1}{(\lambda_1 - \lambda_2)} N_1^0 e^{-\lambda_2 t}$

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$$N_2 = \frac{\lambda_1}{(\lambda_2-\lambda_1)}\left(N_1^0 e^{-\lambda_1 t} - N_2^0 e^{-\lambda_2 t}\right)$$

$$\frac{dN_2}{dt} = 0 = \frac{\lambda_1}{(\lambda_2-\lambda_1)} N_1^0 \frac{d}{dt}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

$$0 = \frac{d}{dt}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

$$= -\lambda_1 e^{-\lambda_1 t} + \lambda_2 e^{-\lambda_2 t}$$

$$\lambda_1 e^{-\lambda_1 t} = \lambda_2 e^{-\lambda_2 t}$$

$$\frac{\lambda_2}{\lambda_1} = \frac{e^{-\lambda_1 t}}{e^{-\lambda_2 t}}$$

$$\ln\left(\frac{\lambda_2}{\lambda_1}\right) = -\lambda_1 t + \lambda_2 t$$

$$= t(\lambda_2-\lambda_1)$$

$$\boxed{t_{max} = \frac{1}{(\lambda_2-\lambda_1)} \ln\left(\frac{\lambda_2}{\lambda_1}\right)}$$

⑧ Secular Equilibrium $(T_{1/2})_1 >> (T_{1/2})_2$

$$\lambda_2 >> \lambda_1$$

Parent Activity $= A_1 = \lambda_1 N_1 = \lambda_1 N_1^0 e^{-\lambda_1 t}$

Daughter Activity $= A_2 = \lambda_2 N_2 = \frac{\lambda_2 \lambda_1}{(\lambda_2-\lambda_1)}\left(N_1^0 e^{-\lambda_1 t} - N_1^0 e^{-\lambda_2 t}\right)$

if $\lambda_2 >> \lambda_1$

$$A_2 = \frac{\cancel{\lambda_2}\lambda_1}{\cancel{\lambda_2}}\left(N_1^0 e^{-\lambda_1 t} - N_1^0 e^{-\lambda_2 t}\right)$$

$$= \lambda_1 N_1^0 \left[e^{-\lambda_1 t} - e^{-\lambda_2 t}\right]$$

if $\lambda_2 >> \lambda_1$

$$\boxed{A_2 = \lambda_1 N_1^0 e^{-\lambda_1 t} = A_1}$$