

CHAPTER 17

NUCLEAR CHEMISTRY

17.1 $\lambda = \frac{c}{\nu}$, $E = N_A h\nu$, $1 \text{ Hz} = 1 \text{ s}^{-1}$

(a) $\lambda = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{5.3 \times 10^{20} \text{ s}^{-1}} = 5.7 \times 10^{-13} \text{ m}$

$$E = 6.02 \times 10^{23} \text{ mol}^{-1} \times 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \times 5.3 \times 10^{20} \text{ s}^{-1}$$

$$= 2.1 \times 10^{11} \text{ J} \cdot \text{mol}^{-1}$$

(b) $\lambda = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{4.7 \times 10^{22} \text{ s}^{-1}} = 6.4 \times 10^{-15} \text{ m}$

$$E = 6.02 \times 10^{23} \text{ mol}^{-1} \times 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \times 4.7 \times 10^{22} \text{ s}^{-1}$$

$$= 1.9 \times 10^{13} \text{ J} \cdot \text{mol}^{-1}$$

(c) $\lambda = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{2.8 \times 10^{21} \text{ s}^{-1}} = 1.1 \times 10^{-13} \text{ m}$

$$E = 6.02 \times 10^{23} \text{ mol}^{-1} \times 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.8 \times 10^{21} \text{ s}^{-1}$$

$$= 1.1 \times 10^{12} \text{ J} \cdot \text{mol}^{-1}$$

(d) $\lambda = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{6.5 \times 10^{19} \text{ s}^{-1}} = 4.6 \times 10^{-12} \text{ m}$

$$E = 6.02 \times 10^{23} \text{ mol}^{-1} \times 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \times 6.5 \times 10^{19} \text{ s}^{-1}$$

$$= 2.6 \times 10^{10} \text{ J} \cdot \text{mol}^{-1}$$

17.3 We assume that all the change in energy goes into the energy of the γ ray emitted. Then, in each case,

$$\nu = \frac{\Delta E}{h}, \quad \lambda = \frac{c}{\nu}$$

$$\begin{aligned}\text{energy of 1 MeV} &= \left(\frac{10^6 \text{ eV}}{1 \text{ MeV}} \right) \left(\frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) \\ &= 1.602 \times 10^{-13} \text{ J} \cdot \text{MeV}^{-1}\end{aligned}$$

$$(a) \quad \Delta E = (1.33 \text{ MeV}) \left(\frac{1.602 \times 10^{-13} \text{ J}}{1 \text{ MeV}} \right) = 2.13 \times 10^{-13} \text{ J}$$

$$\nu = \frac{\Delta E}{h} = \frac{2.13 \times 10^{-13} \text{ J}}{6.63 \times 10^{-34} \text{ J} \cdot \text{s}} = 3.21 \times 10^{20} \text{ s}^{-1} = 3.21 \times 10^{20} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{3.21 \times 10^{20} \text{ s}^{-1}} = 9.35 \times 10^{-13} \text{ m}$$

$$(b) \quad \Delta E = (1.64 \text{ MeV}) \left(\frac{1.602 \times 10^{-13} \text{ J}}{1 \text{ MeV}} \right) = 2.63 \times 10^{-13} \text{ J}$$

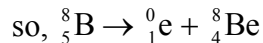
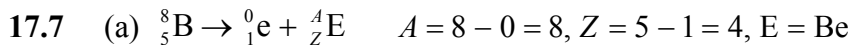
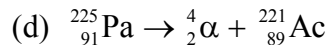
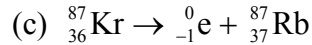
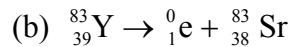
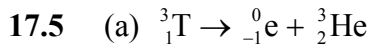
$$\nu = \frac{\Delta E}{h} = \frac{2.63 \times 10^{-13} \text{ J}}{6.63 \times 10^{-34} \text{ J} \cdot \text{s}} = 3.97 \times 10^{20} \text{ s}^{-1} = 3.97 \times 10^{20} \text{ Hz}$$

$$\lambda = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{3.95 \times 10^{20} \text{ s}^{-1}} = 7.59 \times 10^{-13} \text{ m}$$

$$(c) \quad \Delta E = (1.10 \text{ MeV}) \left(\frac{1.602 \times 10^{-13} \text{ J}}{1 \text{ MeV}} \right) = 1.76 \times 10^{-13} \text{ J}$$

$$\nu = \frac{\Delta E}{h} = \frac{1.76 \times 10^{-13} \text{ J}}{6.63 \times 10^{-34} \text{ J} \cdot \text{s}} = 2.65 \times 10^{20} \text{ s}^{-1} = 2.65 \times 10^{20} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{2.65 \times 10^{20} \text{ s}^{-1}} = 1.13 \times 10^{-12} \text{ m}$$



$$(b) \quad {}_{28}^{63}\text{Ni} \rightarrow {}_{-1}^0\text{e} + {}_Z^A\text{E} \quad A = 63 - 0 = 63, \quad Z = 28 - (-1) = 29, \quad \text{E} = \text{Cu}$$

$$\text{so, } {}_{28}^{63}\text{Ni} \rightarrow {}_{-1}^0\text{e} + {}_{29}^{63}\text{Cu}$$

$$(c) \quad {}_{79}^{185}\text{Au} \rightarrow {}_2^4\alpha + {}_Z^A\text{E} \quad A = 185 - 4 = 181, \quad Z = 79 - 2 = 77, \quad \text{E} = \text{Ir}$$

$$\text{so, } {}_{79}^{185}\text{Au} \rightarrow {}_2^4\alpha + {}_{77}^{181}\text{Ir}$$

$$(d) \quad {}_4^7\text{Be} + {}_{-1}^0\text{e} \rightarrow {}_Z^A\text{E} \quad A = 7 + 0 = 7, \quad Z = 4 - 1 = 3, \quad \text{E} = \text{Li}$$

$$\text{so, } {}_4^7\text{Be} + {}_{-1}^0\text{e} \rightarrow {}_3^7\text{Li}$$

17.9 (a) ${}_{11}^{24}\text{Na} \rightarrow {}_{12}^{24}\text{Mg} + {}_{-1}^0\text{e}$; a β particle is emitted.

(b) ${}_{50}^{128}\text{Sn} \rightarrow {}_{51}^{128}\text{Sb} + {}_{-1}^0\text{e}$; a β particle is emitted.

(c) ${}_{57}^{140}\text{La} \rightarrow {}_{56}^{140}\text{Ba} + {}_1^0\text{e}$; a positron (β^+) is emitted.

(d) ${}_{90}^{228}\text{Th} \rightarrow {}_{88}^{224}\text{Ra} + {}_2^4\alpha$; an α particle is emitted.

17.11 (a) ${}_{5}^{11}\text{B} + {}_2^4\alpha \rightarrow 2 {}_0^1\text{n} + {}_7^{13}\text{N}$

(b) ${}_{17}^{35}\text{Cl} + {}_1^2\text{D} \rightarrow {}_0^1\text{n} + {}_{18}^{36}\text{Ar}$

(c) ${}_{42}^{96}\text{Mo} + {}_1^2\text{D} \rightarrow {}_0^1\text{n} + {}_{43}^{97}\text{Tc}$

(d) ${}_{21}^{45}\text{Sc} + {}_0^1\text{n} \rightarrow {}_2^4\alpha + {}_{19}^{42}\text{K}$

17.13 (a) $A/Z = 68/29 = 2.34 > (A/Z)_{\text{based}}$; hence, ${}_{29}^{68}\text{Cu}$

is neutron rich, and β decay is most likely. ${}_{29}^{68}\text{Cu} \rightarrow {}_{-1}^0\text{e} + {}_{30}^{68}\text{Zn}$

(b) $A/Z = 103/48 = 2.15 < (A/Z)_{\text{based}}$; therefore,

${}_{48}^{103}\text{Cd}$ is proton rich, and β^+ decay is most likely. ${}_{48}^{103}\text{Cd} \rightarrow {}_1^0\text{e} + {}_{47}^{103}\text{Ag}$

(c) ${}_{97}^{243}\text{Bk}$ has $Z > 83$ and is proton rich; therefore, α decay is most likely.

$${}_{97}^{243}\text{Bk} \rightarrow {}_2^4\alpha + {}_{95}^{239}\text{Am}$$

(d) ${}_{105}^{260}\text{Db}$ has $Z > 83$; therefore, α decay is most likely.

$${}_{105}^{260}\text{Db} \rightarrow {}_2^4\alpha + {}_{103}^{256}\text{Lr}$$

$$17.15 \quad \alpha \quad {}_{92}^{235}\text{U} \rightarrow {}_2^4\alpha + {}_{90}^{231}\text{Th}$$

$$\beta \quad {}_{90}^{231}\text{Th} \rightarrow {}_{-1}^0\text{e} + {}_{91}^{231}\text{Pa}$$

$$\alpha \quad {}_{91}^{231}\text{Pa} \rightarrow {}_2^4\alpha + {}_{89}^{227}\text{Ac}$$

$$\beta \quad {}_{89}^{227}\text{Ac} \rightarrow {}_{-1}^0\text{e} + {}_{90}^{227}\text{Th}$$

$$\alpha \quad {}_{90}^{227}\text{Th} \rightarrow {}_2^4\alpha + {}_{88}^{223}\text{Ra}$$

$$\alpha \quad {}_{88}^{223}\text{Ra} \rightarrow {}_2^4\alpha + {}_{86}^{219}\text{Rn}$$

$$\alpha \quad {}_{86}^{219}\text{Rn} \rightarrow {}_2^4\alpha + {}_{84}^{215}\text{Po}$$

$$\beta \quad {}_{84}^{215}\text{Po} \rightarrow {}_{-1}^0\text{e} + {}_{85}^{215}\text{At}$$

$$\alpha \quad {}_{85}^{215}\text{At} \rightarrow {}_2^4\alpha + {}_{83}^{211}\text{Bi}$$

$$\beta \quad {}_{83}^{211}\text{Bi} \rightarrow {}_{-1}^0\text{e} + {}_{84}^{211}\text{Po}$$

$$\alpha \quad {}_{84}^{211}\text{Po} \rightarrow {}_2^4\alpha + {}_{82}^{207}\text{Pb}$$

17.17 To determine the charge and mass of the unknown particle, it helps to write ${}_1^1\text{p}$ and ${}_0^1\text{n}$ for the proton and neutron, respectively; and ${}_{-1}^0\text{e}$ and ${}_1^0\text{e}$ for the β particle and positron, respectively.

$$(a) \quad {}_7^{14}\text{N} + {}_2^4\alpha \rightarrow {}_8^{17}\text{O} + {}_1^1\text{p}$$

$$(b) \quad {}_{96}^{248}\text{Cm} + {}_0^1\text{n} \rightarrow {}_{97}^{249}\text{Bk} + {}_{-1}^0\text{e}$$

$$(c) \quad {}_{95}^{243}\text{Am} + {}_0^1\text{n} \rightarrow {}_{96}^{244}\text{Cm} + {}_{-1}^0\text{e} + \gamma$$

$$(d) \quad {}_6^{13}\text{C} + {}_0^1\text{n} \rightarrow {}_6^{14}\text{C} + \gamma$$

$$17.19 \quad (a) \quad {}_{10}^{20}\text{Ne} + {}_2^4\alpha \rightarrow {}_4^8\text{Be} + {}_8^{16}\text{O}$$

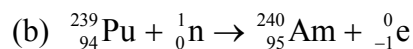
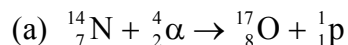
$$(b) \quad {}_{10}^{20}\text{Ne} + {}_{10}^{20}\text{Ne} \rightarrow {}_8^{16}\text{O} + {}_{12}^{24}\text{Mg}$$

$$(c) \quad {}_{20}^{44}\text{Ca} + {}_2^4\alpha \rightarrow \gamma + {}_{22}^{48}\text{Ti}$$

$$(d) \quad {}_{13}^{27}\text{Al} + {}_1^2\text{H} \rightarrow {}_1^1\text{p} + {}_{13}^{28}\text{Al}$$

17.21 In each case, identify the unknown particle by performing a mass and charge balance as you did in the solutions to Exercises 17.5 and 17.7.

Then write the complete nuclear equation.



17.23 (a) untriquadium, Utq (b) unquadpentium, Uqp (c) binilunium, Bnu

17.25 $\text{activity} = (4.7 \times 10^5 \text{ Bq}) \left(\frac{1 \text{ Ci}}{3.7 \times 10^{10} \text{ Bq}} \right) = 1.3 \times 10^{-5} \text{ Ci}$

17.27 1 Bq = 1 disintegration per second (dps)

(a) $(2.5 \text{ } \mu\text{Ci}) \left(\frac{10^{-6} \text{ Ci}}{1 \text{ } \mu\text{Ci}} \right) \left(\frac{3.7 \times 10^{10} \text{ dps}}{1 \text{ Ci}} \right) = 9.2 \times 10^4 \text{ dps}$
 $= 9.2 \times 10^4 \text{ Bq}$

(b) $142 \text{ Ci} = (142)(3.7 \times 10^{10} \text{ dps}) = 5.3 \times 10^{12} \text{ Bq}$

(c) $(7.2 \text{ mCi}) \left(\frac{10^{-3} \text{ Ci}}{1 \text{ mCi}} \right) \left(\frac{3.7 \times 10^{10} \text{ dps}}{1 \text{ Ci}} \right) = 2.7 \times 10^8 \text{ dps}$
 $= 2.7 \times 10^8 \text{ Bq}$

17.29 $\text{dose in rads} = 1.0 \text{ J} \cdot \text{kg}^{-1} \times \left(\frac{1 \text{ rad}}{10^{-2} \text{ J} \cdot \text{kg}^{-1}} \right) = 1.0 \times 10^2 \text{ rad}$

dose equivalent in rems = $Q \times$ dose in rads

$$= \left(\frac{1 \text{ rem}}{1 \text{ rad}} \right) (1.0 \times 10^2 \text{ rad}) = 1.0 \times 10^2 \text{ rem}$$

$$1.0 \times 10^2 \text{ rem} \div 100 \text{ rem/Sv} = 1.0 \text{ Sv}$$

17.31 $1.0 \text{ rad} \cdot \text{day}^{-1} = (1.0 \text{ rad} \cdot \text{day}^{-1}) \left(\frac{1 \text{ rem}}{1 \text{ rad}} \right) = 1 \text{ rem} \cdot \text{day}^{-1}$

$$100 \text{ rem} = 1 \text{ rem} \cdot \text{day}^{-1} \times \text{time}$$

$$\text{time} = 100 \text{ day}$$

$$17.33 \quad k = \frac{0.693}{t_{1/2}}$$

$$(a) \quad k = \frac{0.693}{12.3 \text{ a}} = 5.63 \times 10^{-2} \text{ a}^{-1}$$

$$(b) \quad k = \frac{0.693}{0.84 \text{ s}} = 0.83 \text{ s}^{-1}$$

$$(c) \quad k = \frac{0.693}{10.0 \text{ min}} = 0.0693 \text{ min}^{-1}$$

17.35 We know that initial activity $\propto N_0$, and final activity $\propto N$. Therefore,

$$\frac{\text{final activity}}{\text{initial activity}} = \frac{N}{N_0} = e^{-kt}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.26 \text{ a}} = 0.132 \text{ a}^{-1}$$

$$\begin{aligned} \text{final activity} &= \text{initial activity} \times e^{-kt} \\ &= 4.4 \text{ Ci} \times e^{-(0.132 \text{ a}^{-1} \times 50 \text{ a})} \\ &= 6.0 \times 10^{-3} \text{ Ci} \end{aligned}$$

17.37 In each case, $k = \frac{0.693}{t_{1/2}}$, $N = N_0 e^{-kt}$, $\frac{N}{N_0} = e^{-kt}$, and the percentage

remaining

$$= 100\% \times (N/N_0)$$

$$(a) \quad k = \frac{0.693}{5.73 \times 10^3 \text{ a}} = 1.21 \times 10^{-4} \text{ a}^{-1}$$

$$\text{percentage remaining} = 100\% \times e^{-(1.21 \times 10^{-4} \text{ a}^{-1} \times 2000 \text{ a})} = 78.5\%$$

$$(b) \quad k = \frac{0.693}{12.3 \text{ a}} = 0.0563 \text{ a}^{-1}$$

$$\text{percentage remaining} = 100\% \times e^{-(0.0563 \text{ a}^{-1} \times 11.0 \text{ a})} = 53.8\%$$

17.39 (a) From Table 17.5, $t_{1/2} = 4.5 \times 10^9 \text{ a}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ a}} = 1.54 \times 10^{-10} \text{ a}^{-1}$$

$$\begin{aligned} \text{fraction remaining} &= \frac{N}{N_0} = e^{-kt} \\ &= e^{-(1.54 \times 10^{-10} \text{ a}^{-1} \times 4.5 \times 10^9 \text{ a})} \\ &= e^{-1.4} = 0.50 \end{aligned}$$

After 1 half-life, 50% remains.

$$\text{(b) fraction remaining} = \frac{N}{N_0} = \frac{3}{5};$$

$$t_{1/2} = 1.26 \times 10^9 \text{ a}, k = \frac{0.693}{1.26 \times 10^9 \text{ a}} = 5.50 \times 10^{-10} \text{ a}^{-1}$$

$$\frac{3}{5} = e^{-kt}$$

$$\frac{3}{5} = e^{-(5.50 \times 10^{-10} \text{ a}^{-1} \times x)}$$

$$x = 9.3 \times 10^8 \text{ a}$$

17.41 Let dis = disintegrations

$$\text{activity from "old" sample} = \frac{1500 \text{ dis}/0.250 \text{ g}}{10.0 \text{ h}} = 600 \text{ dis} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$$

$$\text{activity from current sample} = 921 \text{ dis} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.73 \times 10^3 \text{ a}} = 1.21 \times 10^{-4} \text{ a}^{-1}$$

"old" activity $\propto N$, current activity $\propto N_0$

$$\frac{\text{"old" activity}}{\text{current activity}} = \frac{N}{N_0} = e^{-kt}, \frac{N_0}{N} = e^{kt}, \ln \left(\frac{N_0}{N} \right) = kt$$

Solve for t (= age):

$$t = \frac{\ln\left(\frac{N_0}{N}\right)}{k} = \frac{\ln\left(\frac{921}{600}\right)}{1.21 \times 10^{-4} \text{ a}^{-1}} = 3.54 \times 10^3 \text{ a}$$

17.43 In each case, $k = \frac{0.693}{t_{1/2} \text{ (in s)}}$, activity in $Bq = k \times N$

$$\text{activity in Ci} = \frac{\text{activity in Bq}}{3.7 \times 10^{10} \text{ Bq} \cdot \text{Ci}^{-1}}$$

Note: Bq (= disintegrating nuclei per second) has the units of $\text{nuclei} \cdot \text{s}^{-1}$

$$(a) \quad k = \left(\frac{0.693}{1.60 \times 10^3 \text{ a}}\right) \left(\frac{1 \text{ a}}{3.17 \times 10^7 \text{ s}}\right) = 1.37 \times 10^{-11} \text{ s}^{-1}$$

$$N = (1.0 \times 10^{-3} \text{ g}) \left(\frac{1 \text{ mol}}{226 \text{ g}}\right) \left(\frac{6.02 \times 10^{23} \text{ nuclei}}{1 \text{ mol}}\right) = 2.7 \times 10^{18} \text{ nuclei}$$

$$\begin{aligned} \text{activity} &= 1.37 \times 10^{-11} \text{ s}^{-1} \times 2.7 \times 10^{18} \text{ nuclei} \times \left(\frac{1 \text{ Ci}}{3.7 \times 10^{10} \text{ Bq}}\right) \\ &= 1.0 \times 10^{-3} \text{ Ci} \end{aligned}$$

$$(b) \quad k = \left(\frac{0.693}{28.1 \text{ a}}\right) \left(\frac{1 \text{ y}}{3.17 \times 10^7 \text{ s}}\right) = 7.80 \times 10^{-10} \text{ s}^{-1}$$

$$N = (2.0 \times 10^{-6} \text{ g}) \left(\frac{1 \text{ mol}}{90 \text{ g}}\right) \left(\frac{6.02 \times 10^{23} \text{ nuclei}}{1 \text{ mol}}\right) = 1.3 \times 10^{16} \text{ nuclei}$$

$$\begin{aligned} \text{activity} &= (7.80 \times 10^{-10} \text{ s}^{-1})(1.3 \times 10^{16} \text{ nuclei}) \left(\frac{1 \text{ Ci}}{3.7 \times 10^{10} \text{ Bq}}\right) \\ &= 2.7 \times 10^{-4} \text{ Ci} \end{aligned}$$

$$(c) \quad k = \left(\frac{0.693}{2.6 \text{ a}}\right) \left(\frac{1 \text{ y}}{3.17 \times 10^7 \text{ s}}\right) = 8.4 \times 10^{-9} \text{ s}^{-1}$$

$$N = (0.43 \times 10^{-3} \text{ g}) \left(\frac{1 \text{ mol}}{147 \text{ g}}\right) \left(\frac{6.02 \times 10^{23} \text{ nuclei}}{1 \text{ mol}}\right) = 1.8 \times 10^{18} \text{ nuclei}$$

$$\text{activity} = (8.4 \times 10^{-9} \text{ s}^{-1})(1.8 \times 10^{18} \text{ nuclei}) \left(\frac{1 \text{ Ci}}{3.7 \times 10^{10} \text{ Bq}}\right) = 0.41 \text{ Ci}$$

$$17.45 \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{8.05 \text{ d}} = 0.0861 \text{ d}^{-1}$$

$$N = N_0 e^{-kt} \text{ and } \frac{N}{N_0} = e^{-kt}$$

Taking natural log of both sides gives

$$\ln \left(\frac{N}{N_0} \right) = -kt$$

Because activity is proportional to N (Eq. 2), we can write

$$\ln \left(\frac{\text{final activity}}{\text{initial activity}} \right) = -kt$$

Solving for t gives

$$t = -\left(\frac{1}{k} \right) \ln \left(\frac{\text{final activity}}{\text{initial activity}} \right) = -\left(\frac{1}{0.0861 \text{ d}^{-1}} \right) \ln \left(\frac{10}{500} \right) = 45 \text{ d}$$

$$17.47 \quad (\text{a}) \text{ activity} \propto N; \text{ and, because } \ln \left(\frac{N}{N_0} \right) = -kt$$

$$\ln \left(\frac{\text{final activity}}{\text{initial activity}} \right) = -kt$$

$$\ln \left(\frac{32}{58} \right) = -k \times 12.3 \text{ d}$$

$$k = 0.048 \text{ d}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.048 \text{ d}^{-1}} = 14 \text{ d}$$

$$(\text{b}) \quad \ln \left(\frac{N}{N_0} \right) = -0.048 \text{ d}^{-1} \times 30 \text{ d} = -1.4$$

$$\frac{N}{N_0} = \text{fraction remaining} = 0.25$$

$$17.49 \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.27 \text{ a}} = 0.131 \text{ a}^{-1}$$

$$\frac{N}{N_0} = e^{-kt} = e^{-(0.131 \text{ a}^{-1})(2.50 \text{ a})} = \frac{0.266 \text{ g}}{N_0}$$

$$N_0 = 0.370 \text{ g}$$

$$\frac{0.370 \text{ g}}{1.40 \text{ g}} \times 100 = 26.4\%$$

17.51 Since radioactive decay follows first-order kinetics, the rate of loss of X is

$$\frac{d[X]}{dt} = -k_1[X]$$

(1) Y, which is an intermediate, is lost in the first reaction but formed in the second one, so its rate equation can be expressed as

$$\frac{d[Y]}{dt} = k_1[X] - k_2[Y]$$

(2) Z is the final product of the two consecutive reactions so its rate law is

$$\frac{d[Z]}{dt} = k_2[Y]$$

(3) As discussed in Chapter 13, the integrated form of equation (1) is

$$[X] = [X]_0 e^{-k_1 t}$$

(4) Substituting this expression into the rate law for Y and rearranging gives

$$\frac{d[Y]}{dt} + k_2[Y] = k_1[X]_0 e^{-k_1 t}$$

(5) This linear first-order differential equation has the solution

$$[Y] = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) [X]_0 \quad \text{when } [Y]_0 = 0.$$

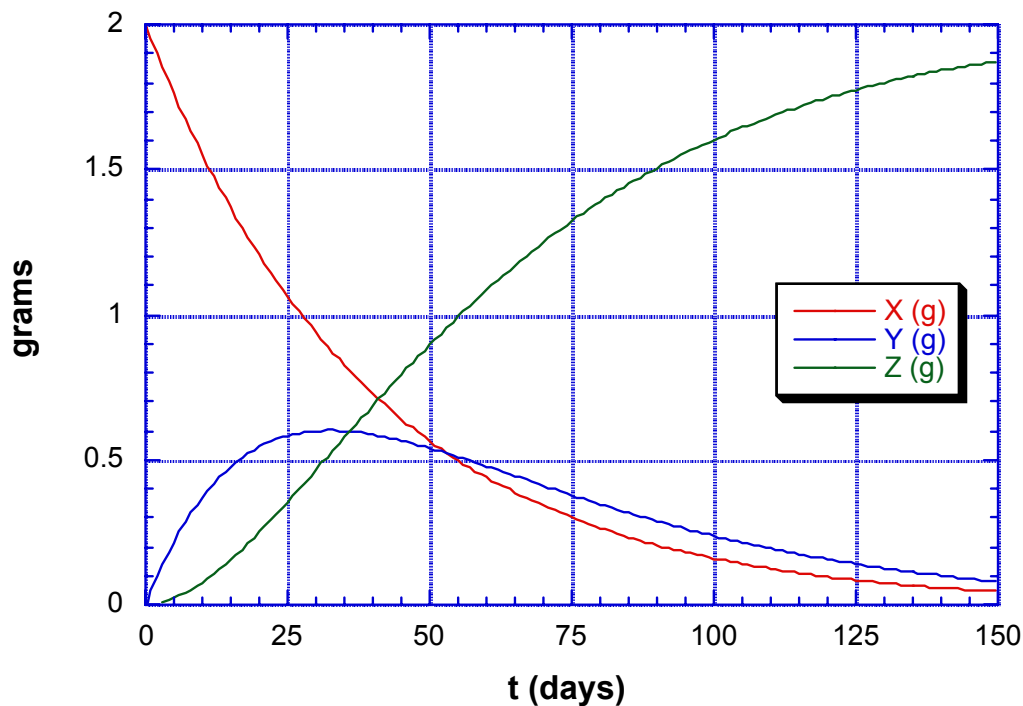
(6) Since $[X] + [Y] + [Z] = [X]_0$ at all times, $[Z] = [X]_0 - ([X] + [Y])$, or

$$[Z] = [X]_0 - \left([X]_0 e^{-k_1 t} + \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) [X]_0 \right) = [X]_0 \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right)$$

(7) The values of the rate constants can be found from the half-lives:

$$k_1 = \frac{0.693}{27.4 \text{ d}} = 0.0253 \text{ d}^{-1} \quad k_2 = \frac{0.693}{18.7 \text{ d}} = 0.0371 \text{ d}^{-1}$$

Using these constants and assuming $[X]_0 = 2.00$ g, equations (4), (6) and (7) are graphed below.



17.53 If isotopically enriched water, such as H_2^{18}O , is used in the reaction, the label can be followed. Once the products are separated, a suitable technique, such as vibrational spectroscopy or mass spectrometry, can be used to determine whether the product has incorporated the ^{18}O . For example, if the methanol ends up with the O atom from the water molecules, then its molar mass would be $34 \text{ g} \cdot \text{mol}^{-1}$, rather than $32 \text{ g} \cdot \text{mol}^{-1}$ found for methanol with elements present at their natural isotopic abundance.

17.55 The vibrational frequency is proportional to the reduced mass of the two atoms that form the bond according to the equation:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{where } \mu = \frac{m_A m_B}{m_A + m_B}$$

Because we are not given ν , it is easiest to make a relative comparison by taking the ratio of ν for the C—D molecule versus ν for the C—H molecule:

$$\begin{aligned} \frac{\nu_{\text{C-D}}}{\nu_{\text{C-H}}} &= \frac{\frac{1}{2\pi} \sqrt{\frac{k}{\mu_{\text{C-D}}}}}{\frac{1}{2\pi} \sqrt{\frac{k}{\mu_{\text{C-H}}}}} = \sqrt{\frac{\mu_{\text{C-H}}}{\mu_{\text{C-D}}}} = \sqrt{\frac{\frac{m_{\text{C}} m_{\text{H}}}{m_{\text{C}} + m_{\text{H}}}}{\frac{m_{\text{C}} m_{\text{D}}}{m_{\text{C}} + m_{\text{D}}}}} = \sqrt{\frac{\frac{(12.011)(1.0078)}{12.011 + 1.0078}}{\frac{(12.011)(2.0140)}{12.011 + 2.0140}}} \\ &= \sqrt{\frac{\left(\frac{12.105}{13.019}\right)}{\left(\frac{24.190}{14.025}\right)}} = 0.73422 \end{aligned}$$

We would thus expect the vibrational frequency for the C—D bond to be approximately 0.73 times the value for the C—H bond (lower in energy).

17.57 Remember to convert g to kg.

$$\begin{aligned} \text{(a)} \quad E &= mc^2 = (1.0 \times 10^{-3} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 \\ &= 9.0 \times 10^{13} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 9.0 \times 10^{13} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad E &= mc^2 = (9.109 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 \\ &= 8.20 \times 10^{-14} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 8.20 \times 10^{-14} \text{ J} \end{aligned}$$

$$\text{(c)} \quad E = mc^2 = (1.0 \times 10^{-15} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = 90 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 90 \text{ J}$$

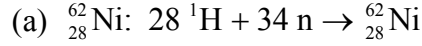
$$\text{(d)} \quad E = mc^2$$

$$E = (1.673 \times 10^{-27} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = 1.51 \times 10^{-10} \text{ J}$$

$$\text{17.59} \quad \Delta m = \frac{\Delta E}{c^2} = \frac{-3.9 \times 10^{26} \text{ J} \cdot \text{s}^{-1}}{(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2} = -4.3 \times 10^9 \text{ kg} \cdot \text{s}^{-1}$$

$$\text{17.61} \quad 1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg}$$

In each case, calculate the difference in mass between the nucleus and the free particles from which it may be considered to have been formed. Then obtain the binding energy from the relation $E_{\text{bind}} = \Delta mc^2$.

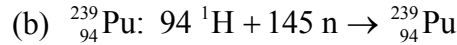


$$\Delta m = 61.928 \text{ u} - (28 \times 1.0078 \text{ u} + 34 \times 1.0087 \text{ u}) = -0.5862 \text{ u} = -0.586 \text{ u (SF)}$$

$$\Delta m = (-0.5862 \text{ u}) \left(\frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = -9.7339 \times 10^{-28} \text{ kg}$$

$$E_{\text{bind}} = -(9.7339 \times 10^{-28} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 \\ = -8.7605 \times 10^{-11} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = -8.7605 \times 10^{-11} \text{ J}$$

$$E_{\text{bind}}/\text{nucleon} = \frac{-8.7605 \times 10^{-11} \text{ J}}{62 \text{ nucleons}} = -1.41 \times 10^{-12} \text{ J} \cdot \text{nucleon}^{-1}$$

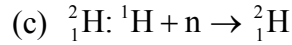


$$\Delta m = 239.0522 \text{ u} - (94 \times 1.0078 \text{ u} + 145 \times 1.0087 \text{ u}) = -1.9425 \text{ u}$$

$$\Delta m = -1.9425 \text{ u} \times \left(\frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = -3.2255 \times 10^{-27} \text{ kg}$$

$$E_{\text{bind}} = -3.2255 \times 10^{-27} \text{ kg} \times (2.997 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = -2.897 \times 10^{-10} \text{ J}$$

$$E_{\text{bind}}/\text{nucleon} = \frac{-2.897 \times 10^{-10} \text{ J}}{239 \text{ nucleons}} = -1.212 \times 10^{-12} \text{ J} \cdot \text{nucleon}^{-1}$$

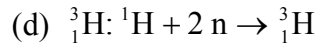


$$\Delta m = 2.0141 \text{ u} - (1.0078 \text{ u} + 1.0087 \text{ u}) = -0.0024 \text{ u}$$

$$\Delta m = -0.0024 \text{ u} \times \left(\frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = -4.0 \times 10^{-30} \text{ kg}$$

$$E_{\text{bind}} = -4.0 \times 10^{-30} \text{ kg} \times (3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = -3.6 \times 10^{-13} \text{ J}$$

$$E_{\text{bind}}/\text{nucleon} = \frac{-3.6 \times 10^{-13} \text{ J}}{2 \text{ nucleons}} = -1.8 \times 10^{-13} \text{ J} \cdot \text{nucleon}^{-1}$$



$$\Delta m = 3.01605 \text{ u} - (1.0078 \text{ u} + 2 \times 1.0087 \text{ u}) = -0.00915 \text{ u}$$

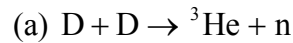
$$\Delta m = -0.00915 \text{ u} \times \left(\frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = -1.52 \times 10^{-29} \text{ kg}$$

$$E_{\text{bind}} = -1.52 \times 10^{-29} \text{ kg} \times (3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = -1.37 \times 10^{-12} \text{ J}$$

$$E_{\text{bind}}/\text{nucleon} = \frac{-1.37 \times 10^{-12} \text{ J}}{3 \text{ nucleons}} = -4.57 \times 10^{-13} \text{ J} \cdot \text{nucleon}^{-1}$$

(e) ^{62}Ni is the most stable, because it has the largest binding energy per nucleon.

17.63 In each case, we first determine the change in mass, $\Delta m = (\text{mass of products}) - (\text{mass of reactants})$. We then calculate the energy released from $\Delta E = (\Delta m)c^2$.



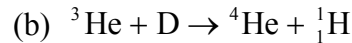
$$2.0141 \text{ u} + 2.0141 \text{ u} \rightarrow 3.0160 \text{ u} + 1.0087 \text{ u}$$

$$4.0282 \text{ u} \rightarrow 4.0247 \text{ u}$$

$$\Delta m = (-0.0035 \text{ u}) \left(\frac{1.661 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = -5.8 \times 10^{-30} \text{ kg}$$

$$\Delta E = \Delta mc^2 = (-5.8 \times 10^{-30} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = -5.2 \times 10^{-13} \text{ J}$$

$$\left(\frac{-5.2 \times 10^{-13} \text{ J}}{4.0282 \text{ u}} \right) \left(\frac{1 \text{ u}}{1.661 \times 10^{-24} \text{ g}} \right) = -7.8 \times 10^{10} \text{ J} \cdot \text{g}^{-1}$$



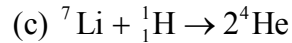
$$3.0160 \text{ u} + 2.0141 \text{ u} \rightarrow 4.0026 \text{ u} + 1.0078 \text{ u}$$

$$5.0301 \text{ u} \rightarrow 5.0104 \text{ u}$$

$$\Delta m = (-0.0197 \text{ u}) \left(\frac{1.661 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = -3.27 \times 10^{-29} \text{ kg}$$

$$\Delta E = \Delta mc^2 = -(3.27 \times 10^{-29} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = -2.94 \times 10^{-12} \text{ J}$$

$$\left(\frac{-2.94 \times 10^{-12} \text{ J}}{5.0301 \text{ u}} \right) \left(\frac{1 \text{ u}}{1.661 \times 10^{-24} \text{ g}} \right) = -3.52 \times 10^{11} \text{ J} \cdot \text{g}^{-1}$$



$$7.0160 \text{ u} + 1.0078 \text{ u} \rightarrow 2(4.0026 \text{ u})$$

$$8.0238 \text{ u} \rightarrow 8.0052 \text{ u}$$

$$\Delta m = (-0.0186 \text{ u}) \left(\frac{1.661 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = -3.09 \times 10^{-29} \text{ kg}$$

$$\Delta E = \Delta mc^2 = (-3.09 \times 10^{-29} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = -2.78 \times 10^{-12} \text{ J}$$

$$\left(\frac{-2.78 \times 10^{-12} \text{ J}}{8.0238 \text{ u}} \right) \left(\frac{1 \text{ u}}{1.661 \times 10^{-24} \text{ g}} \right) = -2.09 \times 10^{11} \text{ J} \cdot \text{g}^{-1}$$

$$(d) \text{ D} + \text{T} \rightarrow {}^4\text{He} + \text{n}$$

$$2.0141 \text{ u} + 3.0160 \text{ u} \rightarrow 4.0026 \text{ u} + 1.0087 \text{ u}$$

$$5.0301 \text{ u} \rightarrow 5.0113 \text{ u}$$

$$\Delta m = (-0.0188 \text{ u}) \left(\frac{1.661 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = -3.12 \times 10^{-29} \text{ kg}$$

$$\Delta E = \Delta mc^2 = (-3.12 \times 10^{-29} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = -2.81 \times 10^{-12} \text{ J}$$

$$\left(\frac{-2.81 \times 10^{-12} \text{ J}}{5.0301 \text{ u}} \right) \left(\frac{1 \text{ u}}{1.661 \times 10^{-24} \text{ g}} \right) = -3.36 \times 10^{11} \text{ J} \cdot \text{g}^{-1}$$

$$17.65 \quad {}^{24}_{11}\text{Na} \rightarrow {}^{24}_{12}\text{Mg} + {}^0_{-1}\text{e}$$

$$\text{mass } ({}^{24}_{11}\text{Na}) = 23.990\,96 \text{ u}$$

$$\text{mass } ({}^{24}_{12}\text{Mg}) = 23.985\,04 \text{ u}$$

The mass of the electron does not need to be explicitly included in the calculation because it is already included in the mass of Mg.

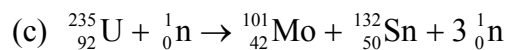
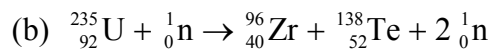
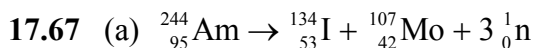
$$\begin{aligned} \Delta m &= \text{mass } ({}^{24}_{12}\text{Mg}) - \text{mass } ({}^{24}_{11}\text{Na}) = 23.985\,04 \text{ u} - 23.990\,96 \text{ u} \\ &= -5.92 \times 10^{-3} \text{ u} \end{aligned}$$

$$\Delta m \text{ (in kg)} = -5.92 \times 10^{-3} \text{ u} \times 1.661 \times 10^{-27} \text{ kg u}^{-1} = -9.83 \times 10^{-30} \text{ kg}$$

$$(a) \quad \Delta E = \Delta mc^2 = -(9.83 \times 10^{-30} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = -8.85 \times 10^{-13} \text{ J}$$

$$(b) \quad \Delta E \text{ (per nucleon)} = \frac{-8.85 \times 10^{-13} \text{ J}}{24 \text{ nucleons}} = -3.69 \times 10^{-14} \text{ J} \cdot \text{nucleon}^{-1}$$

This simple calculation works because the number of nucleons is the same on both sides of the equation.



17.69 (a) $1 \text{ Ci} = 3.7 \times 10^{10} \text{ decays per second (dps)}$

decays per minute (dpm) for

$$4 \text{ pCi} = 4 \times 10^{-12} \text{ Ci} \times 3.7 \times 10^{10} \text{ dps} \times \left(\frac{60 \text{ s}}{1 \text{ min}} \right)$$

$$= 9 \text{ dpm}$$

(b) $\text{volume(L)} = (2.0 \times 3.0 \times 2.5) \text{ m}^3 \times \left(\frac{10^3 \text{ L}}{1 \text{ m}^3} \right) = 1.5 \times 10^4 \text{ L}$

$$\text{number of decays} = (1.5 \times 10^4 \text{ L}) \left(\frac{4 \text{ pCi}}{1 \text{ L}} \right) \left(\frac{9 \text{ decays} \cdot \text{min}^{-1}}{4 \text{ pCi}} \right) (5.0 \text{ min})$$

$$= 7 \times 10^5 \text{ decays}$$

17.71 $N_0 = \text{number of } {}^{222}\text{Rn atoms} = 2.0 \times 10^{-5} \text{ mol} \times 6.0 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}$

$$= 1.2 \times 10^{19} \text{ atoms}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{3.82 \text{ d}} = 0.181 \text{ d}^{-1}$$

(a) $\text{rate of decay} = k \times N = \left(\frac{0.181}{\text{d}} \right) \left(\frac{1 \text{ d}}{8.64 \times 10^4 \text{ s}} \right) (1.2 \times 10^{19} \text{ atoms})$

$$= 2.52 \times 10^{13} \text{ atoms} \cdot \text{s}^{-1} \text{ (dps or Bq)}$$

$$\text{initial activity} = (2.52 \times 10^{13} \text{ Bq}) \left(\frac{1 \text{ Ci}}{3.7 \times 10^{10} \text{ Bq}} \right) \left(\frac{1 \text{ pCi}}{10^{-12} \text{ Ci}} \right)$$

$$\times \left(\frac{1}{2000 \text{ m}^3} \right) \left(\frac{1 \text{ m}^3}{10^3 \text{ L}} \right)$$

$$= 3.4 \times 10^8 \text{ pCi} \cdot \text{L}^{-1}$$

(b) $N = N_0 e^{-kt} = 1.2 \times 10^{19} \text{ atoms} \times e^{-0.181 \text{ d}^{-1} \times 1 \text{ d}} = 1.0 \times 10^{19} \text{ atoms}$

$$(c) \ln \left(\frac{\text{activity}}{\text{initial activity}} \right) = -kt$$

$$t = -\left(\frac{1}{k}\right) \ln \left(\frac{\text{activity}}{\text{initial activity}} \right) = -\left(\frac{1}{0.181 \text{ d}^{-1}}\right) \ln \left(\frac{4}{3.4 \times 10^8} \right) \\ = 1 \times 10^2 \text{ days}$$

17.73 (a) At first thought, it might seem that a fusion bomb would be more suitable for excavation work, because the fusion process itself does not generate harmful radioactive waste products. However, in practice, fusion cannot be initiated in a bomb in the absence of the high temperatures that can only be generated by a fission bomb. So, there is no environmental advantage to the use of a fusion bomb. The fission bomb has the advantage that its destructive power can be more carefully controlled. It is possible to make small fission bombs whose destructive effect can be contained within a small area.

(b) The principal argument for the use of bombs in excavation is speed, and therefore cost-effectiveness, of the process. The principal argument against their use is environmental damage.

$$\mathbf{17.75} \quad k = \frac{0.693}{4.5 \times 10^9 \text{ a}} = 1.5 \times 10^{-10} \text{ a}^{-1}$$

$$t(= \text{age}) = -\left(\frac{1}{k}\right) \ln \left(\frac{N}{N_0} \right)$$

$$\frac{N}{N_0} = \frac{\text{mass of } ^{238}\text{U}}{\text{initial mass of } ^{238}\text{U}} = \frac{1}{1 + \frac{\text{mass of } ^{206}\text{Pb}}{\text{mass of } ^{238}\text{U}}}$$

$$(a) \quad \frac{N}{N_0} = \frac{1}{1 + 1.00} = \frac{1}{2.00}, \text{ therefore age} = t_{1/2} = 4.5 \times 10^9 \text{ a}$$

$$(b) \quad \frac{N}{N_0} = \frac{1}{1 + \frac{1}{1.25}} = 0.556$$

$$t(= \text{age}) = -\left(\frac{1}{1.5 \times 10^{-10} \text{ a}^{-1}}\right) \ln (0.556) = 3.9 \times 10^9 \text{ a}$$

17.77 (a) activity = (17.3 Ci) $\left(\frac{3.7 \times 10^{10} \text{ Bq}}{1 \text{ Ci}}\right)$
 $= 6.4 \times 10^{11} \text{ Bq} = 6.4 \times 10^{11} \text{ nuclei} \cdot \text{s}^{-1}$

$$N = (2.0 \times 10^{-6} \text{ g}) \left(\frac{1 \text{ u}}{1.661 \times 10^{-24} \text{ g}}\right) \left(\frac{1 \text{ nucleus}}{24 \text{ u}}\right) = 5.0 \times 10^{16} \text{ nuclei}$$

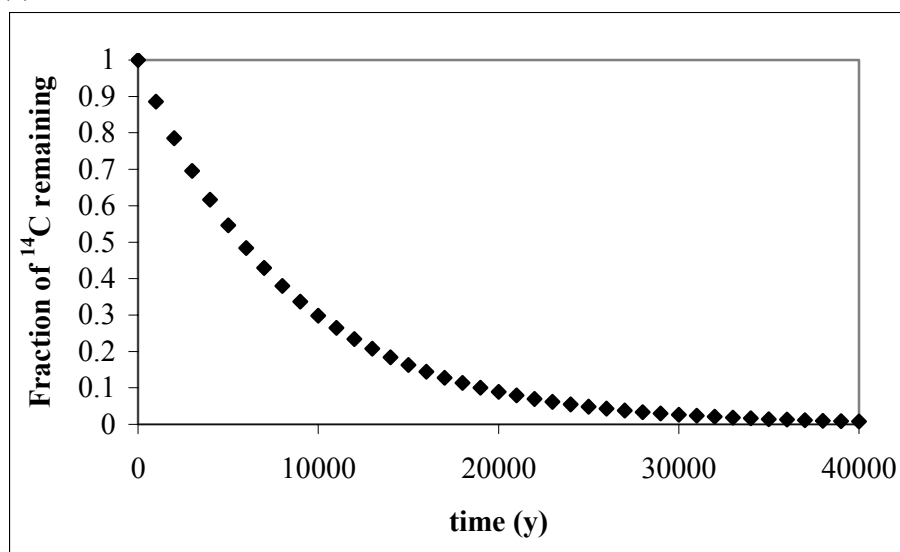
$$k = \frac{\text{activity}}{N} = \frac{6.4 \times 10^{11} \text{ nuclei} \cdot \text{s}^{-1}}{5.0 \times 10^{16} \text{ nuclei}} = 1.3 \times 10^{-5} \text{ s}^{-1} = 1.1 \text{ d}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.3 \times 10^{-5} \text{ s}^{-1}} = 5.3 \times 10^4 \text{ s} = 15 \text{ h} = 0.63 \text{ d}$$

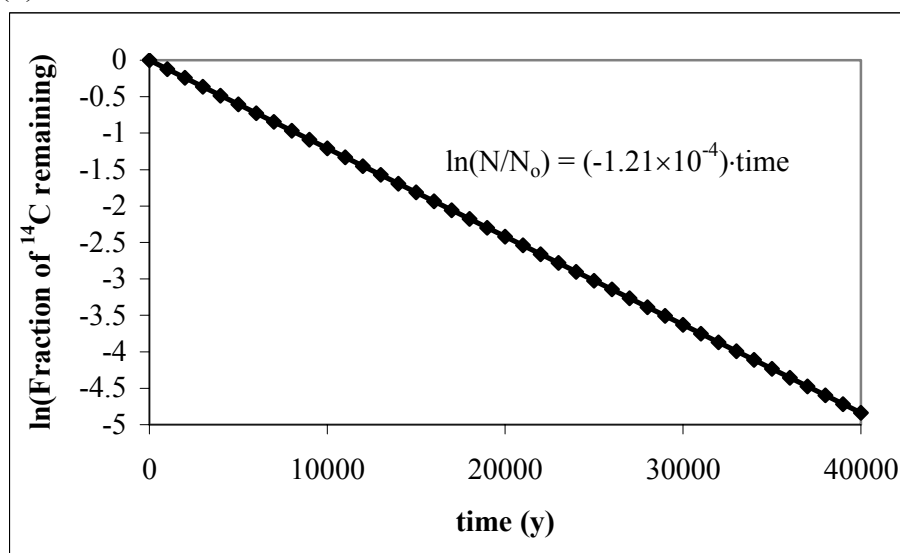
(b) $m = m_0 e^{-kt} = 2.0 \text{ mg} \times e^{-1.11 \text{ d}^{-1} \times 2.0 \text{ d}} = 0.22 \text{ mg}$

- 17.79** (a) Radioactive substances which emit γ radiation are most effective for diagnosis because they are the least destructive of the types of radiation listed. Additionally, γ rays pass easily through body tissues and can be counted, whereas α and β particles are stopped by the body tissues.
- (b) α particles tend to be best for this application because they cause the most destruction. (c) and (d) ^{131}I , 8d (used to image the thyroid); ^{67}Ga , 78 h (used most often as the citrate complex); $^{99\text{m}}\text{Tc}$, 6 h (used for various body tissues by varying the ligands attached to the Tc atom).

17.81 (a)



(b)



(c) The information can be obtained from the graphs or from the equation

$$-\ln \frac{N}{N_0} = kt$$

If we want to have less than 1% of the original amount of ^{14}C present, then we will want the value for which N/N_0 is 0.01 or less.

$$-\ln 0.01 = (1.21 \times 10^{-4} \text{ a}^{-1})(t)$$

$$t = 3.8 \times 10^4 \text{ a}$$

17.83 Radon-222 decays to polonium-218 by alpha emission with a half-life of 3.824 days.



An alpha particle is the nucleus of ${}^4\text{He}$. Assuming that (1) the alpha particles are captured inside the container, (2) they behave as an ideal gas and (3) the temperature is constant at 298 K, we can find the volume of the container by calculating the number of moles of ${}^4_2\alpha$ formed in 15 days and then applying the ideal gas law.

$$n_{\text{He}} = n_{\text{Po}} = n_{\text{initial Rn}} - n_{\text{final Rn}} \quad n_{\text{final Rn}} \propto N_{15 \text{ days}}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.824 \text{ d}} = 0.181 \text{ d}^{-1}$$

$$N_{15 \text{ days}} = N_0 e^{-kt} = (2.5 \text{ g})e^{-(0.181 \text{ d}^{-1})(15 \text{ d})} = 0.165 \text{ g}$$

$$\begin{aligned} n_{\text{final Rn}} &= (0.165 \text{ g } {}^{222}\text{Rn}) \left(\frac{1 \text{ mol } {}^{222}\text{Rn}}{222.0175 \text{ g } {}^{222}\text{Rn}} \right) \\ &= 7.43 \times 10^{-4} \text{ mol } {}^{222}\text{Rn} \end{aligned}$$

$$\begin{aligned} n_{\text{initial Rn}} &= (2.5 \text{ g } {}^{222}\text{Rn}) \left(\frac{1 \text{ mol } {}^{222}\text{Rn}}{222.0175 \text{ g } {}^{222}\text{Rn}} \right) \\ &= 1.13 \times 10^{-2} \text{ mol } {}^{222}\text{Rn} \end{aligned}$$

$$\begin{aligned} n_{\text{He}} &= n_{\text{initial Rn}} - n_{\text{final Rn}} = 1.13 \times 10^{-2} \text{ mol} - 7.43 \times 10^{-4} \text{ mol} \\ &= 1.06 \times 10^{-2} \text{ mol} \end{aligned}$$

$$PV = nRT$$

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(1.06 \times 10^{-2} \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{1.00 \text{ atm}} \\ &= 0.26 \text{ L} \end{aligned}$$

17.85 (a) The rate will decrease because the heavier D atom makes the zero-point energy of the X-D bond lower than that of the X-H bond. The X-D bond energy is deeper in the potential energy well and requires slightly more energy for dissociation.

(b) The activation energy would correspond to the bond dissociation energy. As long as the force constant for the transition state is low, the

bond dissociation energies for C-H and C-D will be the same except for the small difference in their zero-point energies.

$$E_{a(C-D)} = E_{a(C-H)} + \frac{1}{2}h(\nu_{C-H} - \nu_{C-D})$$

Recall from problem 17.55:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{where } \mu = \frac{m_A m_B}{m_A + m_B}$$

$$\frac{\nu_{C-D}}{\nu_{C-H}} = \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}} = 0.73422$$

The ratio of rates will be the same as the ratio of the rate constants.

$$\frac{k_{C-H}}{k_{C-D}} = \frac{Ae^{-\frac{E_{a(C-H)}}{RT}}}{Ae^{-\frac{E_{a(C-D)}}{RT}}} = e^{\frac{E_{a(C-D)}}{RT}} \cdot e^{-\frac{E_{a(C-H)}}{RT}} = e^{\frac{E_{a(C-D)} - E_{a(C-H)}}{RT}}$$

$$\begin{aligned} E_{a(C-D)} - E_{a(C-H)} &= \frac{1}{2}h(\nu_{C-H} - \nu_{C-D}) = \frac{1}{2}h(\nu_{C-H} - 0.73422\nu_{C-H}) \\ &= \frac{1}{2}h(0.26578\nu_{C-H}) \end{aligned}$$

Noting that a typical C-H stretching frequency is about

3000 cm⁻¹ or 9 × 10¹³ Hz (see, for example, Exercise 2.101)

$$\frac{k_{C-H}}{k_{C-D}} = e^{\frac{\frac{1}{2}(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(0.26578)(9 \times 10^{13} \text{ s}^{-1})(6.02 \times 10^{23} \text{ mol}^{-1})}{(8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298 \text{ K})}} = e^{1.925} = 6.86 \approx 7$$

(c) If the carbon atom is infinitely heavy, then it acts like a stationary wall and does not vibrate. In that case, the H or D atomic mass can be used instead of the reduced mass since only that atom is moving.

$$\frac{\nu_D}{\nu_H} = \sqrt{\frac{m_H}{m_D}} = 0.70739$$

$$E_{a(D)} - E_{a(H)} = \frac{1}{2}h(\nu_H - \nu_D) = \frac{1}{2}h(\nu_H - 0.70739\nu_H) = \frac{1}{2}h(0.29261\nu_H)$$

$$\frac{k_{C-H}}{k_{C-D}} = e^{\frac{\frac{1}{2}(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(0.29261)(9 \times 10^{13} \text{ s}^{-1})(6.02 \times 10^{23} \text{ mol}^{-1})}{(8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298 \text{ K})}} = e^{2.119} = 8.32 \approx 8$$

This result suggests that the kinetic isotope effect can become even more pronounced for heavier molecules.

$$\begin{aligned}
 \mathbf{17.87} \quad m_{tot} &= m_{e^-} + m_{e^+} \\
 &= 2m_{e^-} = 2(9.109\,39 \times 10^{-31} \text{ kg}) \\
 &= 1.821\,88 \times 10^{-30} \text{ kg}
 \end{aligned}$$

$$\begin{aligned}
 E &= mc^2 \\
 &= (1.821\,88 \times 10^{-30} \text{ kg})(2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 \\
 &= 1.637\,42 \times 10^{-13} \text{ J}
 \end{aligned}$$

17.89 (a) ${}^8_2\text{He} \rightarrow {}^8_3\text{Li} + {}^0_{-1}\text{e}$ followed by ${}^8_3\text{Li} \rightarrow {}^8_4\text{Be} + {}^0_{-1}\text{e}$ followed by

