

### Problem 1: Proton – antiproton atom

We can use the expression for hydrogen-like atoms to calculate the energy levels.

$$E_n = -\frac{2\pi Z^2 e^4 \mu}{(4\pi\epsilon_0)^2 h^2 n^2}$$

where  $Z$  is the total number of charges in the nucleus ( $= 1$ ),  $e$  is

the electron charge ( $= 1.6022 \times 10^{-19}$  C),  $\mu$  is the reduced mass of the system with  $\mu = (m_1^{-1} + m_2^{-1})^{-1}$  and  $m_1 = m_2 = m_p = 1.6726 \times 10^{-27}$  kg, thus  $\mu = \frac{1}{2} m_p$ ,  $\epsilon_0$  is the permittivity of vacuum ( $= 8.8542 \times 10^{-12}$  C<sup>2</sup> J<sup>-1</sup> m<sup>-1</sup>) [note:  $(4\pi\epsilon_0)^{-1}$  is Coulomb's constant],  $h$  is the Planck constant ( $= 6.626076 \times 10^{-34}$  J s) and  $n$  is the principal quantum number of the system taking values 1, 2, ...

For  $n = 1$ ,  $E_1 = -m_p \left( \frac{e^2}{4h\epsilon_0} \right)^2 = -2.00129 \times 10^{-15}$  J and for  $n = 2$ ,  $E_2 = \frac{E_1}{4}$ , hence

$$\Delta E \equiv E_2 - E_1 = \frac{3}{4} E_1 = 1.50097 \times 10^{-15} \text{ J}$$

$$\Delta E = h\nu, \text{ hence } \nu = \frac{\Delta E}{h} = \frac{1.50097 \times 10^{-15} \text{ J}}{6.626076 \times 10^{-34} \text{ J s}} = 2.2652 \text{ s}^{-1}.$$

$$c = \lambda\nu, \text{ hence } \lambda = c/\nu = \lambda = \frac{c}{\nu} = \frac{2.997925 \times 10^8 \text{ m s}^{-1}}{2.2652 \text{ s}^{-1}} = 1.3234 \times 10^{-10} \text{ m} = 1.3234 \text{ \AA}.$$

The Bohr radius is given by

$$\alpha = \frac{h^2(4\pi\epsilon_0)}{4\pi^2\mu e^2} = \frac{2h^2\epsilon_0}{\pi m_p e^2} = 5.76397 \times 10^{-14} \text{ m}$$

which is 1836/2 times smaller than the

hydrogen radius due to the difference in reduced mass of the "atom".

### Problem 2: Annulene

The number of  $\pi$  electrons is 18. Two electrons can occupy each state due to the Pauli exclusion principle. Each state above the lowest is two-fold degenerate. Based on these pieces of information, we can fill this table:

N	max number of e <sup>-</sup> per state	total e <sup>-</sup> up to this state
0	2	2
1	4	6
2	4	10
3	4	14
4	4	18

States up to  $N = 4$  are fully occupied with 18 electrons. The lowest possible transition is from state  $N = 4$  to state  $N = 5$ . The path forming a circular well is  $L = 18 \times 1.4 \text{ \AA}$ . Hence

$$\Delta E = E_5 - E_4 = (5^2 - 4^2) \frac{(6.6260755 \times 10^{-34} \text{ J s})^2}{2 \times (18 \times 1.4 \text{ \AA})^2 \times 9.109389 \times 10^{-31} \text{ kg}} = 3.415 \times 10^{-19} \text{ J}$$

The transition frequency is  $\nu = \Delta E/h = 5.1544 \times 10^{14} \text{ s}^{-1}$  and the corresponding wavelength is  $\lambda = c/\nu = 581.6 \text{ nm}$ .

### Problem 3: Chemical bonding: The molecular ion $\text{O}_2^{2+}$

- 171.9 kcal/mol
- No

3. Yes

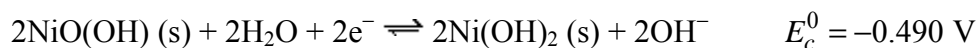
4. 85.6 kcal/mol

5.  $(171.9 - 85.6)$  kcal/mol = 86.3 kcal/mol or  $(86.3/N_A)$  kcal/molecule =  $1.43 \times 10^{-23}$  kcal/molecule.

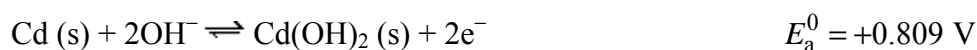
6.  $\sim 1.1 \text{ \AA}$

7.  $\sim 1.6 \text{ \AA}$

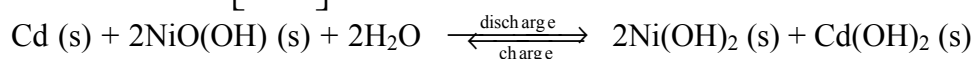
#### Problem 4: Electrochemistry: Nicad batteries



$$E_c = E_c^0 - \frac{RT}{2F} \ln [\text{OH}^-]^2$$



$$E_a = E_a^0 - \frac{RT}{2F} \ln \frac{1}{[\text{OH}^-]^2}$$



$$E = E_a - E_c = E_a^0 - E_c^0 = 0.809 \text{ V} - (-0.490 \text{ V}) = 1.299 \text{ V}.$$

$$700 \text{ mAh} = 0.700 \text{ A} \times 3600 \text{ s} = 2520.0 \text{ C}$$

$$2520.0 \text{ C} \rightarrow \frac{2520.0}{2 \cdot 96485} \text{ moles of Cd} = 0.013 \text{ moles of Cd} \rightarrow 0.013 \times 112.4 = 1.47 \text{ g of Cd.}$$

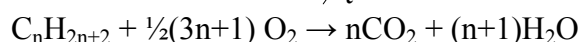
#### Problem 5: Boiler

$$\text{Tank capacity: } m = V \rho = 4 \text{ m}^3 \times 0.73 \text{ g cm}^{-3} = 2920 \text{ kg}$$

$$\text{Heating power } P = 116 \text{ kW}$$

$$\text{Consumption rate } \frac{m}{t} = \frac{P}{\Delta h / m} = \frac{116 \text{ kJ s}^{-1}}{4.3 \times 10^7 \text{ J kg}^{-1}} = 2.70 \times 10^{-3} \text{ kg s}^{-1} (= 9.73 \text{ kg h}^{-1})$$

$$\text{Operation duration } t = \frac{m}{m/t} = \frac{2920 \text{ kg}}{2.70 \times 10^{-3} \text{ kg s}^{-1}} = 1.08 \times 10^8 \text{ s} = 300 \text{ h} = 12.5 \text{ days}$$



$$\frac{m_{\text{CO}_2}}{m_{\text{C}_n\text{H}_{2n+2}}} = \frac{44n}{14n+2} = \frac{22}{7 + \frac{1}{n}} \quad \text{This ratio does not depend heavily on } n; \text{ for a}$$

representative value of  $n = 10$ , the ratio takes the value of 3.1.

$$\text{Since } \frac{m_{\text{C}_n\text{H}_{2n+2}}}{t} = 9.73 \text{ kg h}^{-1},$$

$$m_{\text{CO}_2} = \frac{m_{\text{C}_n\text{H}_{2n+2}}}{t} \frac{m_{\text{CO}_2}}{m_{\text{C}_n\text{H}_{2n+2}}} = 9.73 \text{ kg h}^{-1} \times 3.1 = 30.2 \text{ kg h}^{-1}$$

#### Problem 6: Ammonium nitrate

Mixing is endothermic and the process is adiabatic, thus heat has to be provided by the solution itself. Since water is at its freezing point, it will tend to freeze, but the solution created will experience a depression of freezing point due to the presence of

dissolved ions. The large amount of heat required for solvation will necessitate some freezing of water.

A Hess cycle of 3 steps will be considered.

A. mixing at 0 °C with  $\Delta H_1 > 0$

B. lowering of the temperature of the mixture to its final temperature with  $\Delta H_2 < 0$

C. freezing of some water  $m_s$  with  $\Delta H_3 < 0$

The final temperature is given by  $\theta_2 = -K_f 2 \frac{n}{m - m_s}$  where  $K_f$  is the cryoscopy

constant, 2 is the number of particles per formula weight for  $\text{NH}_4\text{NO}_3$ ,  $n$  the number

of moles of  $\text{NH}_4\text{NO}_3$   $n = \frac{80 \text{ g}}{80 \text{ g mol}^{-1}} = 1 \text{ mol}$ ,  $m = 1000 \text{ g}$ .

$$\Delta H_1 = \Delta h_s n = -25.69 \text{ kJ mol}^{-1} \times 1 \text{ mol} = -25.69 \text{ kJ}$$

$\Delta H_2 = c_p \frac{m}{M} \theta_2$  where  $c_p$  is the molar heat capacity of water and  $M$  its molecular mass ( $18 \text{ g mol}^{-1}$ ).

$\Delta H_3 = -\Delta h_f \frac{m_s}{M}$  where  $\Delta h_f$  is the molar enthalpy of fusion.

$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{\text{total}} = 0$  because no heat is allowed to be exchanged between the system and its surroundings.

Substituting for  $\theta_2$  and solving for  $m_s$  yields the following expression

$$m_s = \frac{m}{2} + \frac{\Delta h_s}{\Delta h_f} \frac{nM}{2} \pm \sqrt{\left( \frac{m}{2} - \frac{\Delta h_s}{\Delta h_f} \frac{nM}{2} \right)^2 + \frac{2nK_f c_p m}{\Delta h_f}}$$

We discount the solution derived from the + sign as unphysical ( $m_s > m$ ) and arrive at the result  $m_s = 28.52 \text{ g ice}$ .

Hence  $\theta_2 = -3.83 \text{ }^\circ\text{C}$ .

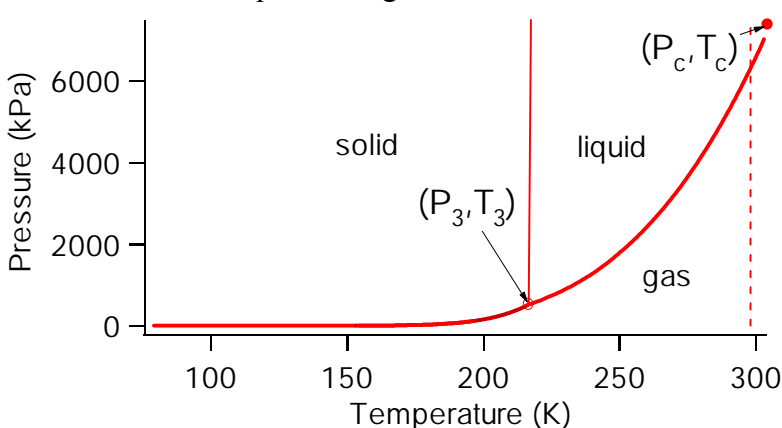
If we made the simplification that we expect  $m_s \ll m$ , then  $\theta_2$  is immediately calculated as  $-3.72 \text{ }^\circ\text{C}$ , which yields a value for  $m_s = 29.9 \text{ g}$ . If this result is used to improve the  $\theta_2$  value using the exact expression, we get  $\theta_2 = -3.83 \text{ }^\circ\text{C}$ . Then,  $m_s$  can be further improved to  $28.5 \text{ g}$ .

The process is spontaneous, irreversible, one where separation of components is possible, adiabatic, isobaric, isenthalpic, nearly isoenergetic.

The equation  $\Delta G = \Delta H - T \Delta S$  can be used here because  $T$  varies less than 2%.  $\Delta G < 0$  because the process is spontaneous and  $\Delta H = 0$ , hence  $\Delta S > 0$ . This is also to be expected from stability criteria under the constraint  $\Delta H = 0$ .

### Problem 7: Carbon dioxide

A rather accurate phase diagram for  $\text{CO}_2$  is shown here using data from Landolt-



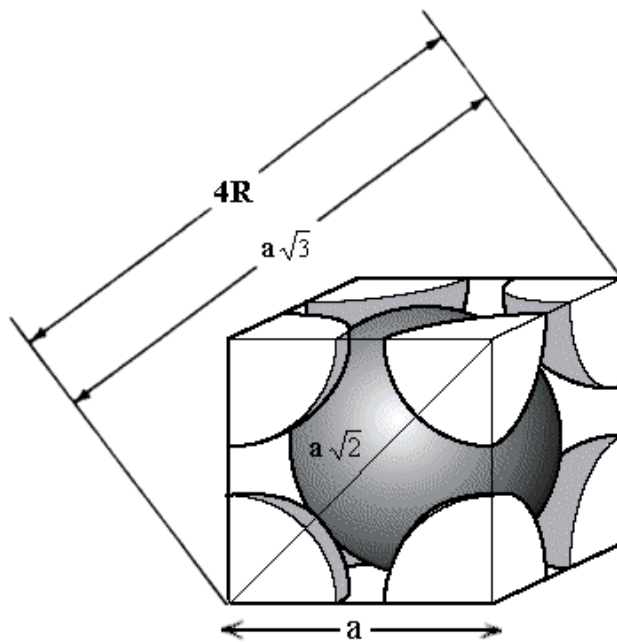
Börnstein New Series IV/20B, p. 22 which has been based on Dykyi, J. Repas, M.: Saturated Vapor Pressure of Organic Compounds, Bratislava, Czech.: Slovakian Academy of Science, 1979.

A qualitative one can be drawn based on the triple and the critical points. Since the room temperature is well above the triple point, there is no way there can be any solid CO<sub>2</sub> in the fire extinguisher. At 298 K, the CO<sub>2</sub> vapor pressure is 63.1 bar. This value can be estimated by drawing a straight line between the triple and the critical points. It can be calculated also based on the empirical Antoine equation, viz.,

$$\log \frac{P}{\text{kPa}} = A - \frac{B}{C + T/\text{K}} \quad \text{with } A = 6.46212, B = 748.28 \text{ and } C = -16.9.$$

**Problem 8: Iron crystal**

(a) Let  $R$  be the atomic radius of iron and  $a = 2.87 \text{ \AA}$  the length of the unit cell edge.



Then, as atoms touch each other along the body diagonal and from a Pythagorean theorem in the cube:

$$a\sqrt{3} = 4R \Rightarrow R = (a\sqrt{3})/4 \Rightarrow R = 1.24 \text{ \AA}$$

The Avogadro number ( $N_A$ ) can be calculated from the density ( $\rho$ ) formula. The latter is obtained by finding the number of atoms per unit cell, multiplying this number by the mass of each atom ( $\frac{\text{mole of atoms (g/mol)}}{N_A \text{ (atoms/mol)}}$ ) and,

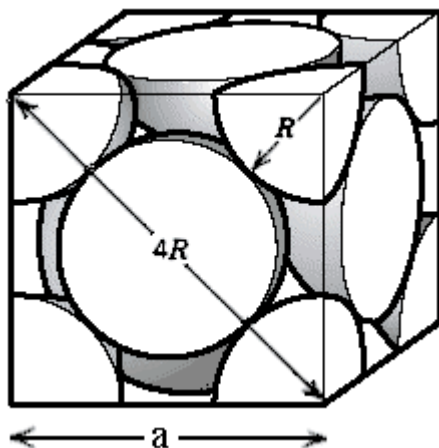
eventually, dividing the result by the volume of the unit cell ( $a^3$ ). Note that each bcc unit

cell contains two whole spheres, that is 2 Fe atoms.

$$\rho(\text{g/cm}^3) = \frac{2 \times (55.847 / N_A) \text{ g}}{a^3 (\text{cm}^3)} \Rightarrow$$

$$N_A = \frac{2 \times 55.847 \text{ g}}{7.86 \times (2.87 \times 10^{-8})^3 \frac{\text{g}}{\text{cm}^3} \text{ cm}^3} \Rightarrow N_A \approx 6.01 \times 10^{23}$$

(b) By applying the Pythagorean theorem in the cube, one finds:



$$a^2 + a^2 = (4R)^2 \Rightarrow a = 2R\sqrt{2} \Rightarrow R = \frac{a\sqrt{2}}{4} \Rightarrow R = 1.27 \text{ \AA} \text{ (slightly different from the}$$

value found above for bcc structure, because of the different packing, having an influence on the atomic radius or at least its estimation).

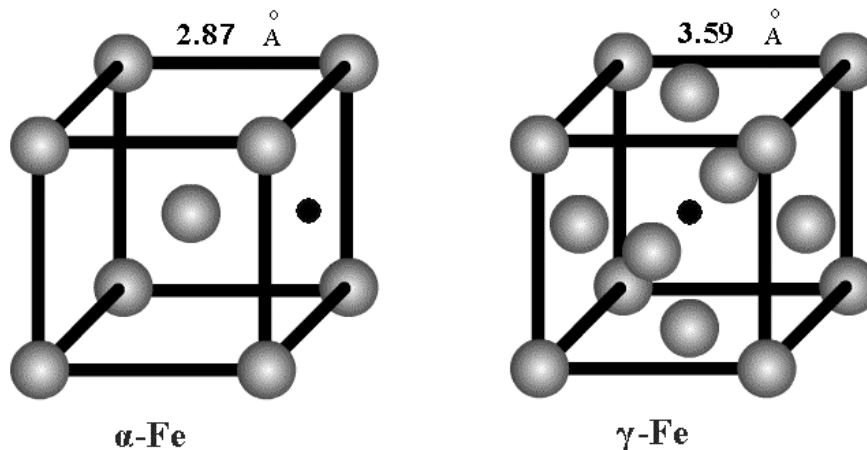
As for the density, recalling that each fcc unit cell contains four whole spheres, that is 4 Fe atoms, once again one has:

$$\rho(\text{g/cm}^3) = \frac{4 \times (55.847 / N_A) \text{ g}}{a^3 (\text{cm}^3)} =$$

$$\frac{4 \times 55.847 \text{ g}}{6.023 \times 10^{23} \times (3.59 \times 10^{-8})^3 \text{ cm}^3} = 8.02 \text{ g/cm}^3$$

The higher value of  $\gamma$ -Fe density, as compared with  $\alpha$ -Fe, points at the fact that the fcc structure is denser than bcc. fcc represents the, so called, *cubic close packed* structure which, together with the *hexagonal close packed*, are the most efficient ways of packing together equal sized spheres in three dimensions.

(c) and (d) The unit cells below are illustrated by using reduced size spheres. Note that, in hard spheres packing model the represented atoms must be in contact one to each other.



According to the left figure, a perfectly fitted interstitial atom centered at  $(\frac{1}{2}, 0, \frac{1}{2})$  in an  $\alpha$ -Fe cell, would have a radius of:

$$R_{\text{interstitial}} = \frac{1}{2} a - R_{\text{Fe}}, \text{ where } a = 2.87 \text{ \AA} \text{ and } R_{\text{Fe}} = 1.24 \text{ \AA} \quad [(\text{see question (a)})].$$

Therefore:  $R_{\text{interstitial}} (\alpha\text{-Fe}) \approx 0.20 \text{ \AA}$

Similarly, according to the figure in right, a perfectly fitted interstitial atom centered at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  in an  $\gamma$ -Fe cell, would have a radius of:

$$R_{\text{interstitial}} = \frac{1}{2} a - R_{\text{Fe}}, \text{ where } a = 3.59 \text{ \AA} \text{ and } R_{\text{Fe}} = 1.27 \text{ \AA} \quad [(\text{see question (b)})].$$

Therefore:  $R_{\text{interstitial}} (\gamma\text{-Fe}) \approx 0.53 \text{ \AA}$

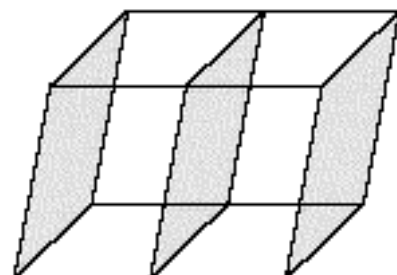
(e)  $1 \text{ nm} = 10 \text{ \AA}$ . Thus:

$$\text{For } \alpha\text{-Fe: } \frac{R_{\text{carbon}}}{R_{\text{interstitial}}} = \frac{0.77 \text{ \AA}}{0.20 \text{ \AA}} = 3.85$$

$$\text{For } \gamma\text{-Fe: } \frac{R_{\text{carbon}}}{R_{\text{interstitial}}} = \frac{0.77 \text{ \AA}}{0.53 \text{ \AA}} = 1.45$$

Therefore, the carbon atom is roughly four times too large to fit next to the nearest iron atoms in  $\alpha$ -Fe without strain, while it is only 1.5 times oversized to fit in the  $\gamma$ -Fe structure. The above estimations explain well the low solubility of carbon in  $\alpha$ -Fe ( $< 0.1 \%$ ).

(f) The wavelength ( $\lambda$ ) of the X-rays will be calculated from Bragg's law, assuming first order diffraction:  $2d \sin\theta = \lambda$ , where  $\theta$  is the angle of diffraction equal to  $32.6^\circ$  and  $d$  is the interplanar spacing of the (200) set of parallel lattice planes, that is, the perpendicular distance between any pair of adjacent planes in the set. The (200) planes are shown



shaded in the figure.

Let  $a$  be the length of the cubic unit cell edge. Then, from previous data for  $\alpha$ -Fe:  $a = 2.87 \text{ \AA}$ , so the distance between adjacent (200) planes is:  $d = \frac{a}{2} = 1.44 \text{ \AA}$  Therefore,

from Bragg's law:  $\lambda = 2d \sin\theta = 2 \times 1.44 \times \sin(32.6^\circ) \Rightarrow \lambda \approx 1.55 \text{ \AA}$

This value corresponds to the  $K_{\alpha 1}$  transition of iron.

### Problem 9: Cyclodextrine

a)  $V = a \times c \cdot b = a b c \sin(\beta) = 7474 \text{ \AA}^3$ ,  $V_m = 7474 \text{ \AA}^3 / 4 = 1868 \text{ \AA}^3$

b)  $FW = 1535.4 \text{ g mol}^{-1}$ ,  $\rho = FW / (V N_A)$ , hence  $\rho = 1.3646 \text{ g cm}^{-3}$

### Problem 10: Infrared spectroscopy

1. The number of vibrational modes is given by  $3N-6$  for non-linear and  $3N-5$  for linear molecules, where  $N$  is the number of atoms in the molecule. Hence

CO: 1,  $H_2O$ : 3,  $C_6H_6$ : 30,  $C_{60}$ : 174

2. The fact that the molecules have a vibrational infra red absorption implies that the molecules have a permanent dipole moment, hence these diatomic molecules must be heteronuclear.

For a simple harmonic oscillator-type diatomic molecule, the eigen frequency is given

by the equation  $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ , where  $k$  is the force constant and  $\mu$  the reduced mass of

the molecule. In the absence of any further information, nothing can be said about the reduce masses or the force constants (though bond strength is not related to  $k$ , but more likely to bond dissociation energy). The eigen frequency is equal to the frequency of the absorbed photons because the vibrational energy is given by  $E_v = (v+1/2) h \nu$  and the energy for the resonance transition is  $\Delta E = E_{v=1} - E_{v=0} = h \nu$ .

### Problem 11: Radioactivity and chemical reactivity

1.  $\gamma$ -rays are a form of high energy electromagnetic radiation.
2. There are no stable (non-radioactive) isotopes beyond Bi.
3. There are numerous light isotopes that are radioactive.
4. Xe compounds such as  $XeF_2$  are commercially available.
5. Cs is the element with the lowest ionization potential (3.89 eV).

### Problem 12: Carbon dating

a) Let  $N_0$  be the  $^{14}C/^{12}C$  ratio in living systems and  $N$  the same ratio found in a sample coming from a system that died  $t$  years ago. Then, the following relation between them is true:  $N = N_0 e^{-\lambda t}$ , where  $\lambda (= \ln 2 / t_{1/2})$  the disintegration constant for  $^{14}C$ . The above equation becomes

$$t = \frac{-\ln \frac{N}{N_0}}{\lambda} = -\frac{t_{1/2}}{\ln 2} \ln \frac{N}{N_0} = -5700y \frac{\ln 0.25}{\ln 2} = 11400y$$

b) The  $\beta$  decay scheme is based on the nuclear reaction  $n \rightarrow p + \beta + \bar{\nu}_e$ , where  $p$  is a proton and  $\bar{\nu}_e$  an electron antineutrino. In the case of  $^{14}C$  we have



hence C becomes a (common)  $^{14}N$  atom.

c) If an organic molecule contains  $^{14}C$ , the consequence of its disintegration can be grave for the structure of the molecule, causing great damage to the molecule in

the vicinity of the  $^{14}\text{C}$  atom. At least the chemical bond is ruptured since  $^{14}\text{N}$  is a chemically different atom than  $^{14}\text{C}$ . Free radicals may also be created.

- d) The total carbon inside a human body of 75 Kg is  $75 \text{ kg} \times 0.185 = 13.9 \text{ kg}$ . The total radioactivity (R) is  $R = 0.277 \text{ Bq} / \text{g} \times 13.9 \text{ kg} = 3850 \text{ Bq}$

The amount of  $^{14}\text{C}$  present is estimated from the total radioactivity as follow:

$$R \equiv -\frac{dN}{dt} = \lambda N$$

Then

$$N = \frac{A}{\lambda} = A \frac{t_{1/2}}{\ln 2} = 3850 \text{ s}^{-1} \frac{5700 \text{ y} \cdot 60 \times 60 \times 24 \times 365.25 \text{ s}}{0.693} = 1.00 \times 10^{15} \text{ atoms} = 1.66 \text{ nmol}$$

### Problem 13: Uranium

- a) alpha decay:  $X(A, Z) \rightarrow X(A-4, Z-2) + {}^4\text{He}^{2+} (2p+2n)$  ( $\Delta A = -4, \Delta Z = -2$ )

beta decay:  $X(A, Z) \rightarrow X(A, Z+1) + \beta + \bar{\nu}_e$  ( $\Delta A = 0, \Delta Z = +1$ )

Since changes in the mass number ( $\Delta A$ ) are due to the emission of alpha particles only, in each series we have:

$$\text{total alpha particles emitted} = \Delta A_{\text{total}}/4$$

Alpha emission also changes the atomic number ( $Z$ ) ( $\Delta Z = -2$ ), so the total decrease in  $Z$  due to the total alpha particles emitted would be twice their total number. But  $Z$  of the final (stable) element of the radioactive series is higher than the expected  $Z$  based on alpha emission. This difference in  $Z$  is due to the number of beta particle emitted. Thus

$${}^{238}\text{U} \rightarrow {}^{206}\text{Pb}, \alpha = \Delta A/4 = (238-206)/4 = 32/4 = 8, \beta = 2\alpha - \Delta Z = 18 - (92-82) = 6$$

$${}^{235}\text{U} \rightarrow {}^{207}\text{Pb}, \alpha = \Delta A/4 = (235-207)/4 = 28/4 = 7, \beta = 2\alpha - \Delta Z = 14 - (92-82) = 4$$

- b) This occurs when an alpha decay ( $\Delta Z = -2$ ) is followed by two successive beta decays ( $\Delta Z = +2$ ).

- c) For each radioisotope of uranium we can write

$${}^{235}\text{N} = {}^{235}\text{N}_0 \exp(-\lambda_{235} t) \text{ and } {}^{238}\text{N} = {}^{238}\text{N}_0 \exp(-\lambda_{238} t)$$

where  $N$  the number of nuclei at time  $t$ ,  $N_0$  at time  $t = 0$  and  $\lambda = \ln 2 / t_{1/2} = 0.693 / t_{1/2}$  the disintegration constant.

At  $t = 0$ ,  ${}^{235}\text{N}_0 = {}^{238}\text{N}_0$ , then

$$\frac{\exp(-\lambda_{238} t)}{\exp(-\lambda_{235} t)} = \frac{{}^{238}\text{N}}{{}^{235}\text{N}} = \frac{99.3}{0.7} = 142$$

Thus

$$\lambda_{235} t - \lambda_{238} t = \ln 142 = 4.95$$

$$\lambda_{238} = 0.693/t_{1/2} = 0.693/4.5 \times 10^9 = 1.54 \times 10^{-10} \text{ y}^{-1}$$

$$\lambda_{235} = 0.693/t_{1/2} = 0.693/7.1 \times 10^8 = 9.76 \times 10^{-10} \text{ y}^{-1}$$

$$t = \frac{4.95}{(9.76 - 1.54) \times 10^{-10} \text{ y}^{-1}} = \frac{4.95 \times 10^{10} \text{ y}}{8.22} = 6.0 \times 10^9 \text{ y}$$

- d) The energy released by the complete fission of  $1 \text{ g } {}^{235}\text{U}$  is

$$E = (1/235) \times 6.022 \times 10^{23} \times 200 \text{ MeV} = 5.13 \times 10^{23} \text{ MeV}$$

and the energy released upon combustion of  $1 \text{ g C}$  is

$$E = (1/12) \times 6.022 \times 10^{23} \times 4.1 \text{ eV} = 2.06 \times 10^{23} \text{ eV} = 2.06 \times 10^{17} \text{ MeV}$$

Hence the amount of carbon that would release the same amount of energy as the fission of  $1 \text{ g } {}^{235}\text{U}$  is

$$m = (5.13 \times 10^{23}) / (2.06 \times 10^{17}) = 2.49 \times 10^3 \text{ kg C}$$