Elements & Isotopes
Not in this text – See lecture slides & Gen.Chem. textbook
Genesis of the Elements, Nuclear Reactions & Radioactivity

Why you should care about inorganic chemistry (one example…):

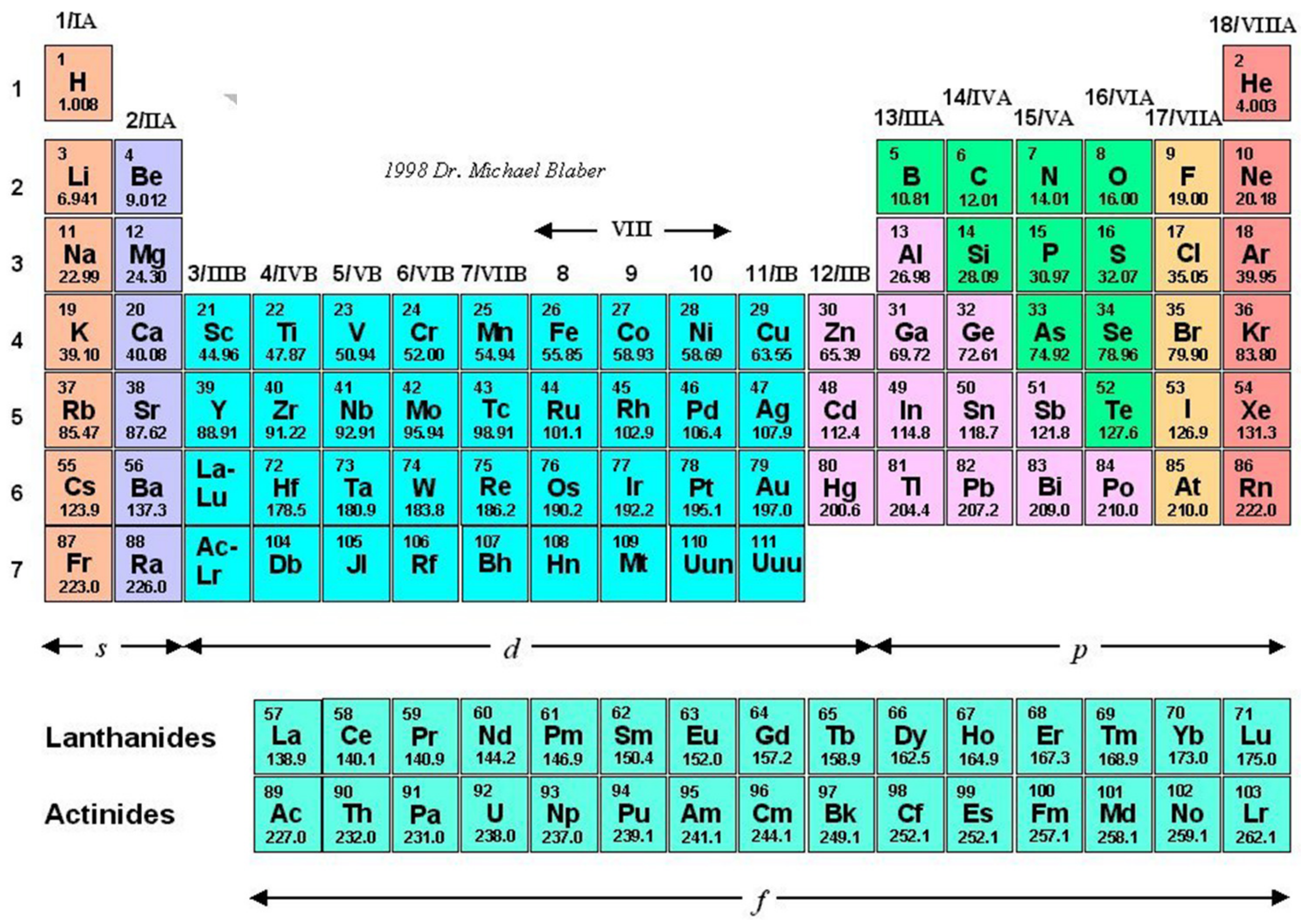
Industrial synthesis of ammonia: $N_{2(g)} + 3\,H_{2(g)} \rightarrow 2\,NH_{3(g)}$

- Haber-Bosch process (developed in 1913)
  - metal oxide catalysis, 350-550 °C, 150-350 atm
  - modern version still has only 15% yield of NH_3 (a crucial feedstock)
  - responsible for ~1% of world's total energy consumption!
- Huge interest in finding ways to fix nitrogen under mild conditions
  - nitrogenase enzyme catalyzes same reaction (0.8 atm N_2, ambient T)
  - enzyme's active site contains a complex iron-molybdenum-sulfur site
  - mimicking this is a very active area of inorganic chemistry research

What is inorganic chemistry?

Inorganic chemistry = the chemistry of the elements other than carbon

but… organometallic chemistry (involves metal-C bonds)
bioinorganic chemistry (bridges biochemistry & inorganic)
environmental chemistry (includes both organic & inorganic)



I. Elements and Compounds

CLASSES OF ELEMENTS:

Metals - have metallic lustre, are usually solids which are often easy to beat into different shapes (malleable) and stretch into wires (ductile), and *they conduct electricity*.

Non-metals - can come as gases (e.g. O_2, Cl_2), liquids (Br_2) or solids (S_8, I_2), and *they do not conduct electricity*.

AND WHEN ELEMENTS COMBINE:

Metals can combine (or just mix) with each other: they form alloys which usually have metallic properties (e.g. brass - Cu and Zn).

Non-metals combine with each other to form compounds which are generally covalent compounds, and often molecular in structure, though not always. They can be gases (NO), liquids (H_2O), or solids (N_2O_5), and they are usually electrical insulators.

Metallic elements combine with non-metallic elements to form hard, non-volatile solids which are usually electrical insulators in the solid state (e.g. NaCl). They are often quite predominantly ionic in their bonding.

Types of Substances (based on bonding)

Covalent	Ionic	
Covalent	Ionic with Complex Ions	Ionic with Simple Ions
Molecular: N_2, P_4, S_8, C_{60}, $B_{12}H_{12}$ $W(CO)_6$ *"Infinite" Chains:* $(BeCl_2)_n$, S_n *"Infinite" Sheets:* graphite black phosphorus *3D Structures:* diamond SiO_2	*Ionic with smallish ions:* $(Na^+)_2\ SO_4^{2-}$ $NH_4^+\ Cl^-$ $(NH_4^+)_2\ SO_4^{2-}$ $[Cr(NH_3)_6]^{3+}\ (Cl^-)_3$ *Ionic with polymeric complex ions:* Pyroxene $CaMg(SiO_3)_2$ Chrysotile (asbestos) $Mg_3(Si_2O_5)(OH)_4$ Talc $Mg_3(Si_2O_5)_2(OH)_2$ Aluminosilicates, zeolites $M_{x/n}[(AlO_2)_x(SiO_2)_y].zH_2O$	*Simple Ionic:* Rock salt $Na^+\ Cl^-$ Blende, wurtzite $Zn^{2+}\ S^{2-}$ Cesium chloride $Cs^+\ Cl^-$ Rutile $Ti^{4+}\ (O^{2-})_2$ Fluorite $Ca^{2+}\ (F^-)_2$

For rotatable molecular models of most of these, and more, see the Moodle site.

Inorganic *vs.* Organic Compounds

- Most organic structures → tetrahedral and simpler units

  Inorganic structures → linear, trigonal, all five "platonic" solids (tetrahedron, octahedron, cube, dodecahedron and icosahedron), less regular shapes such as the trigonal and pentagonal bipyramids

- Covalent molecules → solids, liquids or gases

  Ionic compounds (Partially or completely) → solids (generally)

  In addition:

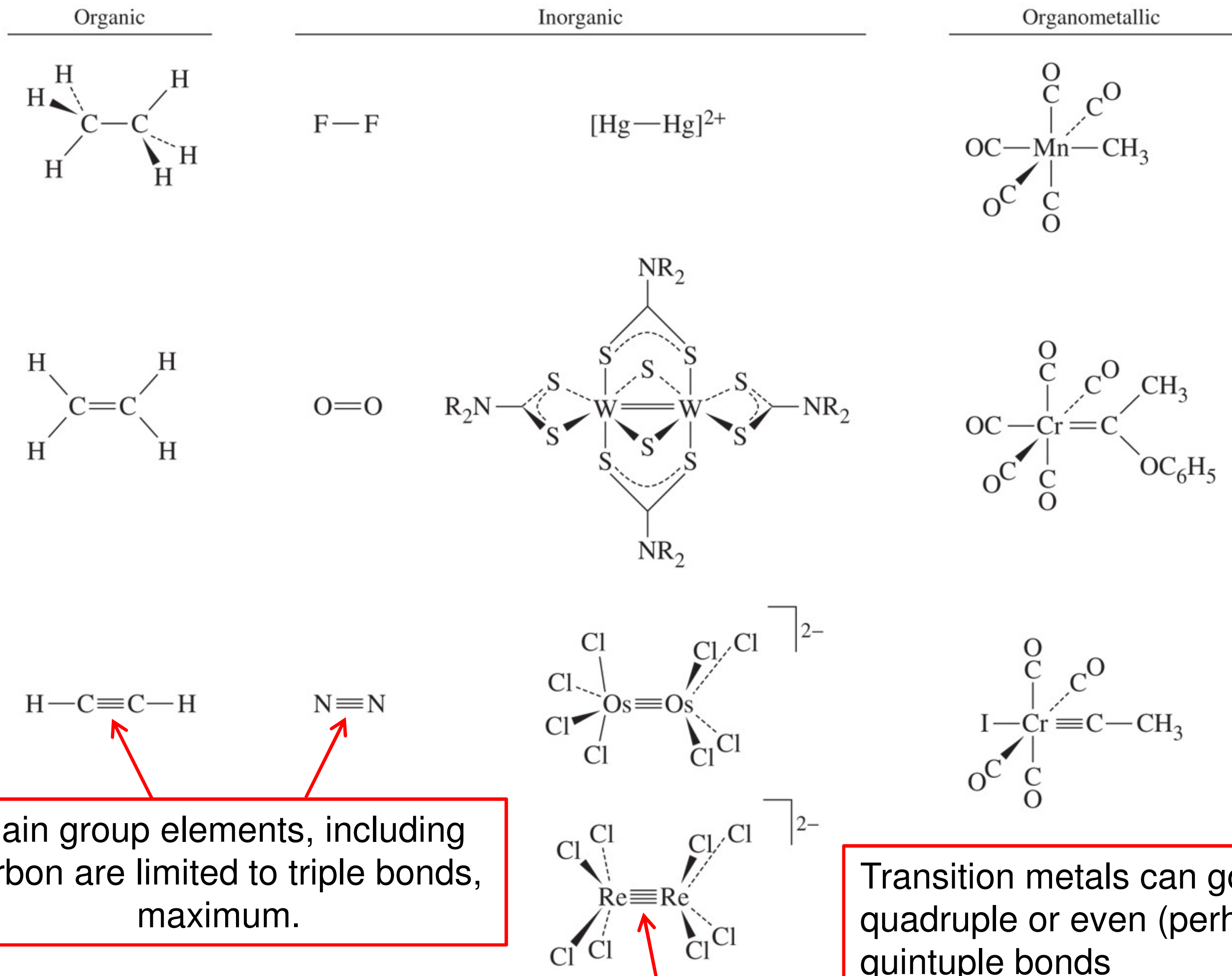
  Noble gases → monoatomic

  Metallic elements → solids except Hg and Ga (on warm days)

  Certain alloys are liquids: some Hg alloys (amalgams) and Na/K alloys

The following figures from the text illustrate the structural richness in inorganic chemistry by making comparisons with organic chemistry. The complicated structures are the topics of Chem 341 (not 241…).

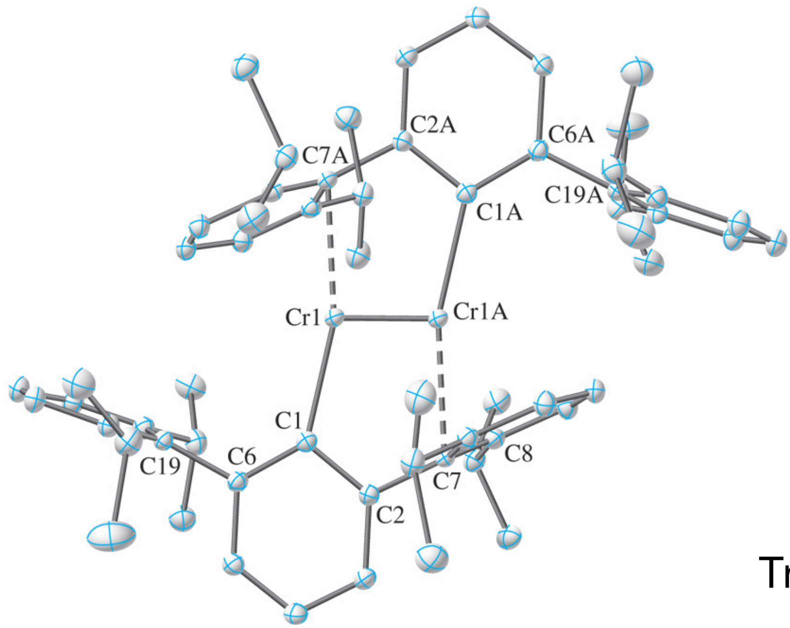
Multiple bonds

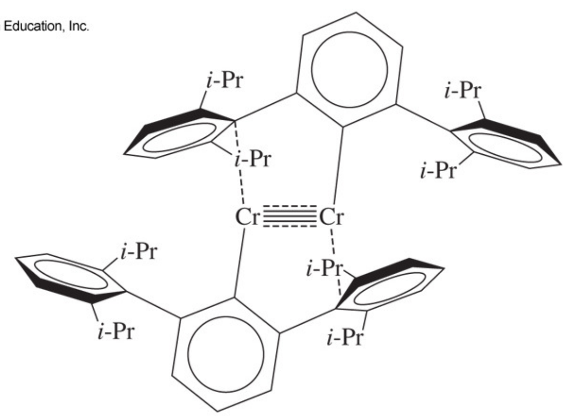


Main group elements, including carbon are limited to triple bonds, maximum.

Transition metals can go to quadruple or even (perhaps) quintuple bonds

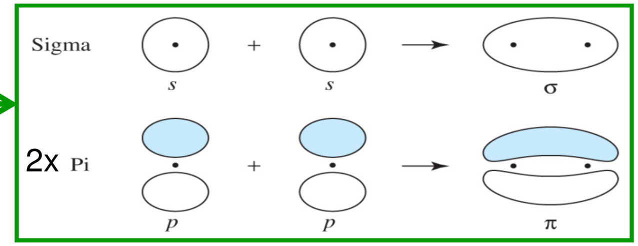
Multiple bonds (cont.)



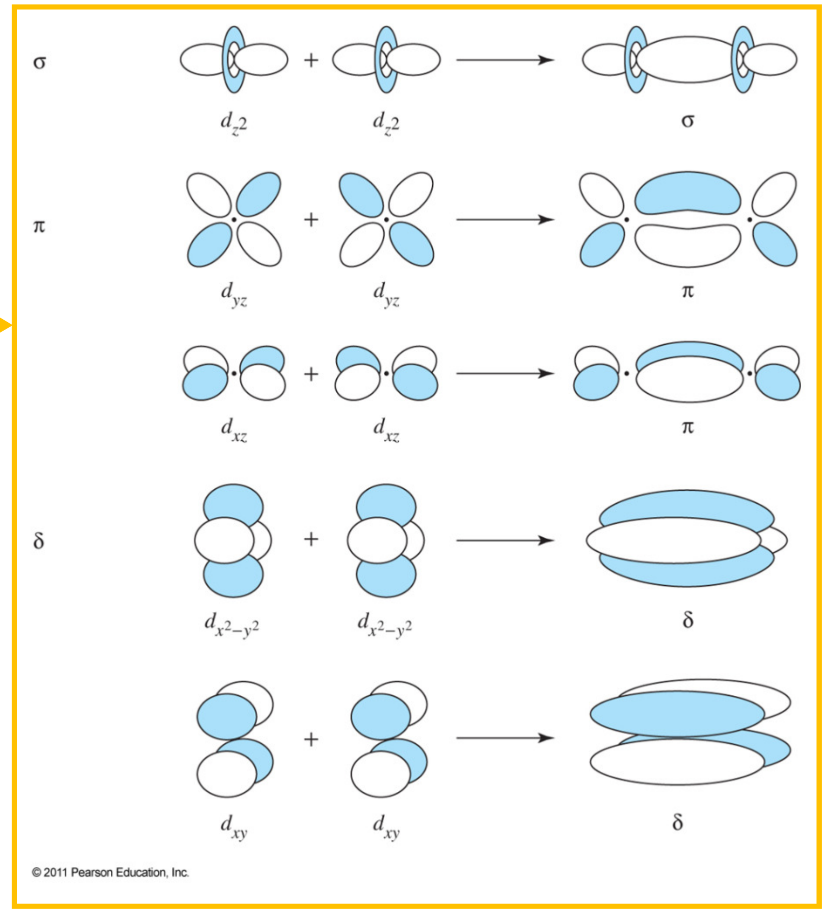


Cr – Cr single bond: ~2.5 Å
This compound: 1.835 Å
http://www.sciencemag.org/cgi/content/full/310/5749/844

Light Main Group Elements



Transition Metals

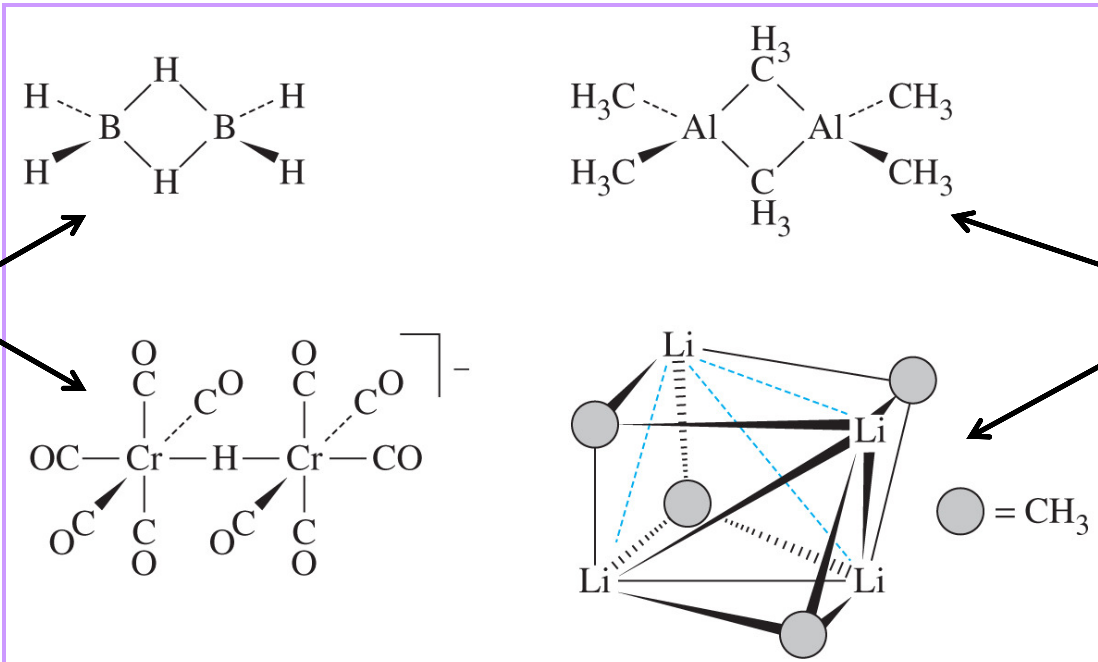


use valence d-orbitals to make sigma bonds, pi bonds & ***delta bonds***

Non-Classical Bonds

Hydrogen and alkyl groups can form non classical bonds (*i.e.,* 3-centered, 2-electron bonds):

Bridging Hydrogen



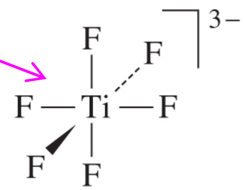
Each CH_3 bridges a face of the Li_4 tetrahedron.

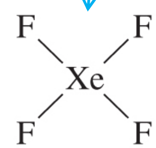
Bridging Alkyl

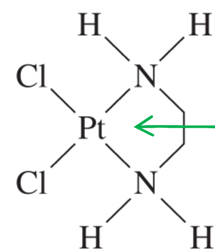
Various Inorganic Geometries

Octahedral

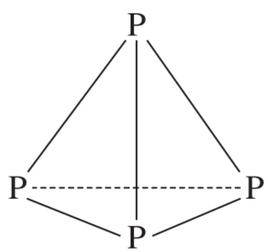
Square-Planar

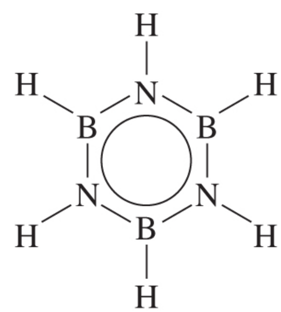


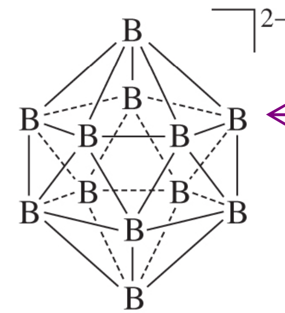




Tetrahedral (1 lone-pair on each P)





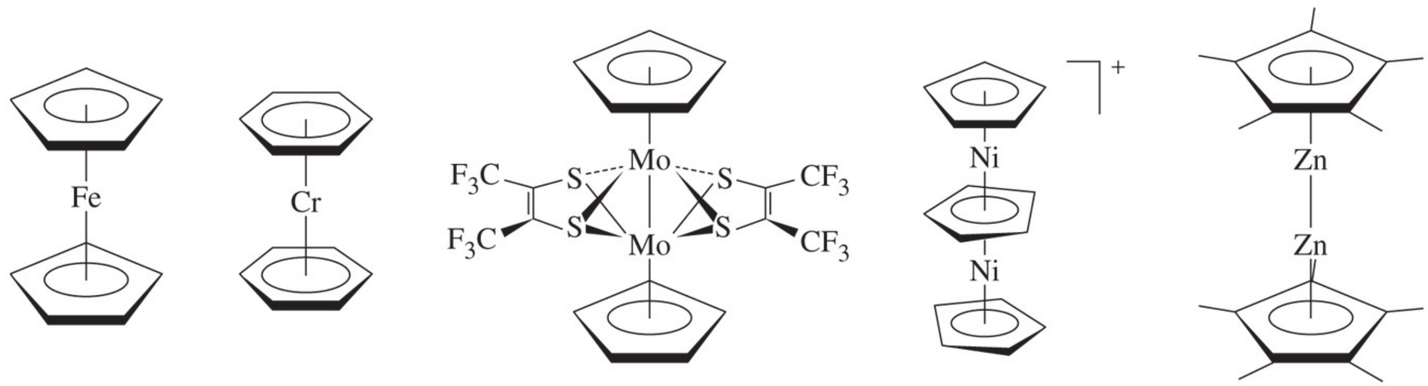


$B_{12}H_{12}^{2-}$ (not shown: one hydrogen on each boron)

Tetrahedral (1 hydrogen on each B)

a benzene "look-alike"
(but not very aromatic in its properties)

π-Bonded Aromatic Rings

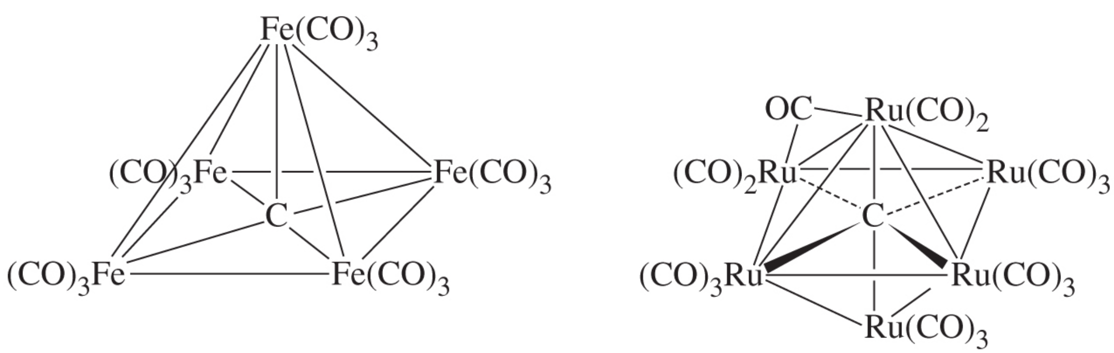


"Sandwiches"

"Triple-decker Sandwich"

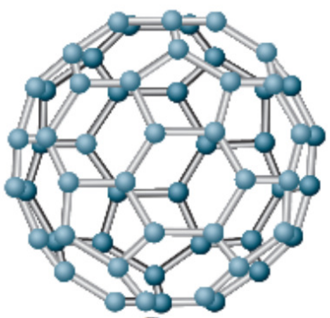
"Piano stool"

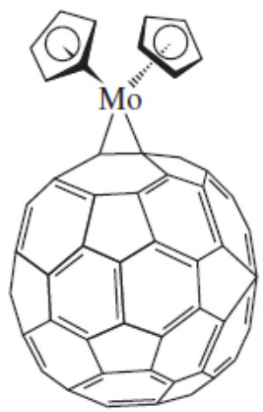
Unusual Carbon Geometries



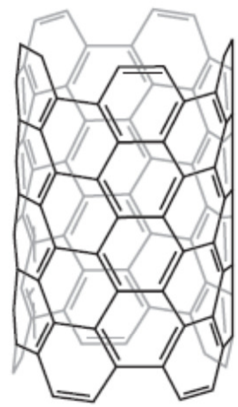
Carbon-based Architectures

Buckminster Fullerene
“Bucky Ball”

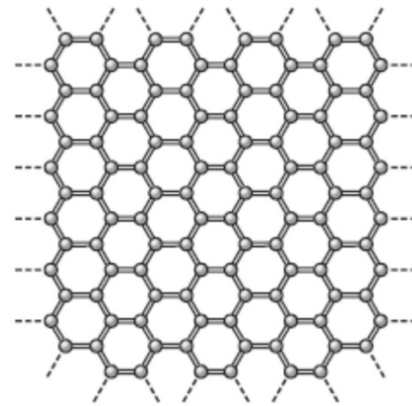


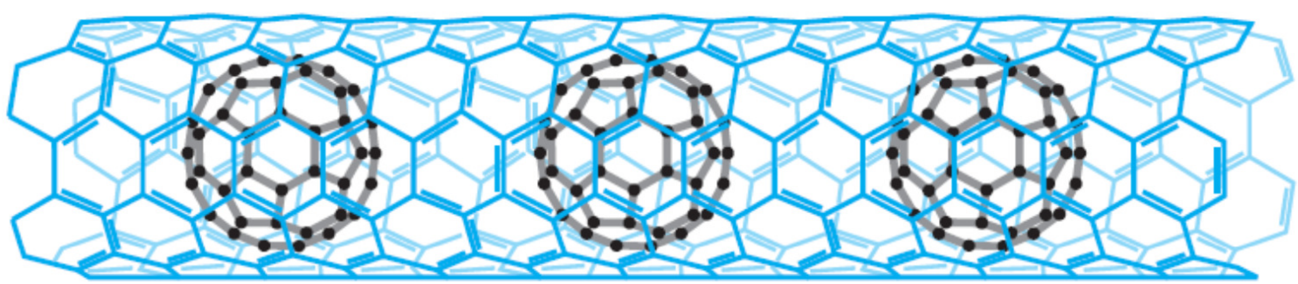


Carbon
Nanotube

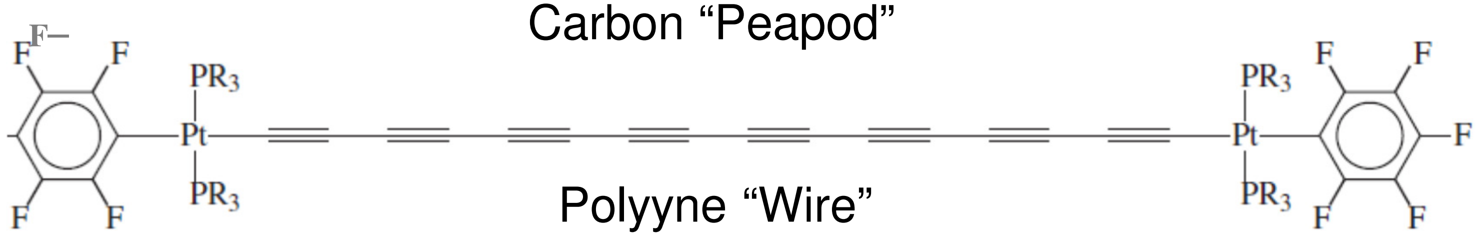


Graphene





Carbon “Peapod”



Polyyne “Wire”

Genesis of the Elements & Nuclear Reactions

For related readings: Gen. Chem. text, e.g., Kotz 8th Ed. Ch.23 - Nuclear Chemistry

Subatomic Particles – Review

Particle	Symbol	Mass (u)	Mass No.	Charge (e)	Spin
electron	e^- (or $^{0}_{-1}e$)	5.486×10^{-4}	0	–1	½
proton	p (or $^{1}_{1}H$)	1.0073	1	+1	½
neutron	n (or $^{1}_{0}n$)	1.0087	1	0	½
neutrino	ν_e	≈ 0	0	0	½
antineutrino	$\overline{\nu}_e$	≈ 0	0	0	½
positron	e^+ (or $^{0}_{1}e$)	5.486×10^{-4}	0	+1	½
α-particle	α	He^{2+} nucleus	4	+2	0
β-particle	β or β^-	e^- from nucleus	0	–1	½
β^+-particle	β^+	e^+ from nucleus	0	+1	½
photon		0	0	0	1
γ-photon	γ	(from nucleus)	0	0	1

Masses are expressed in atomic units (u or amu) where 1 u = 1.6605×10^{-27} kg
Charges are expressed in electrons (e), where 1 e = 1.602×10^{-19} C

Atoms and Isotopes – Review

There are about 110 known elements which are distinguished by their atomic number: Z = number of protons in their nucleus.

Many elements have isotopes: same atomic number, different number of neutrons.

Isotopes have different mass numbers: A = sum of the number of protons and neutrons, also called the nucleon number.

A nuclide's full symbol is written: $^{A}_{Z}X$

Because the value of Z is specified by the symbol of the element (X), it is often omitted.

Examples:

$^{1}_{1}H$ or ^{1}H or H (hydrogen nuclide = proton)

$^{2}_{1}H$ or ^{2}H or D (deuterium nuclide)

$^{3}_{1}H$ or ^{3}H or T (tritium nuclide)

$^{35}_{17}Cl$ or ^{35}Cl

$^{37}_{17}Cl$ or ^{37}Cl

Balancing Nuclear Reactions (clicker)

Nuclear rxns: ≥1 atomic nuclei undergoing spontaneous conversion or absorption of subatomic particles ⇨ change in identity of atoms/isotopes

Rule: the mass numbers and the charges must balance.

Example: the nucleosynthesis of technetium, Tc (not naturally occurring):

Synthesis step 1: $^{98}_{42}Mo + {}^{A}_{Z}X \rightarrow {}^{99}_{42}Mo + \gamma$

What is $^{A}_{Z}X$?

A. It is $^{1}_{1}H$

B. It is $^{0}_{0}n$

C. It is $^{1}_{0}n$

Synthesis step 2: $^{99}_{42}Mo \rightarrow {}^{A}_{Z}Tc + \beta^{-} + \overline{\nu}_{e}$

What are A and Z ?

A. A = 98 and Z = 43

B. A = 99 and Z = 43

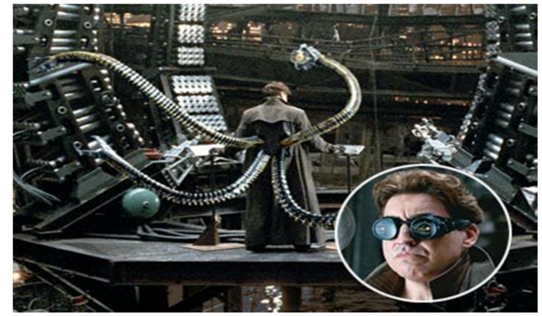
C. A = 100 and Z = 43

Nuclear Fusion Reactions

Experimental

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

Lasers focused on a frozen pellet, or a high current in a contained plasma. Requires a temperature >10^8 K



The Sun - "the Carbon Cycle"

Requires a temperature >10^6 K

$$^{12}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{13}_{7}\mathrm{N} + \gamma$$

$$^{13}_{7}\mathrm{N} \rightarrow {}^{13}_{6}\mathrm{C} + {}^{0}_{1}\mathrm{e} + \nu_e$$

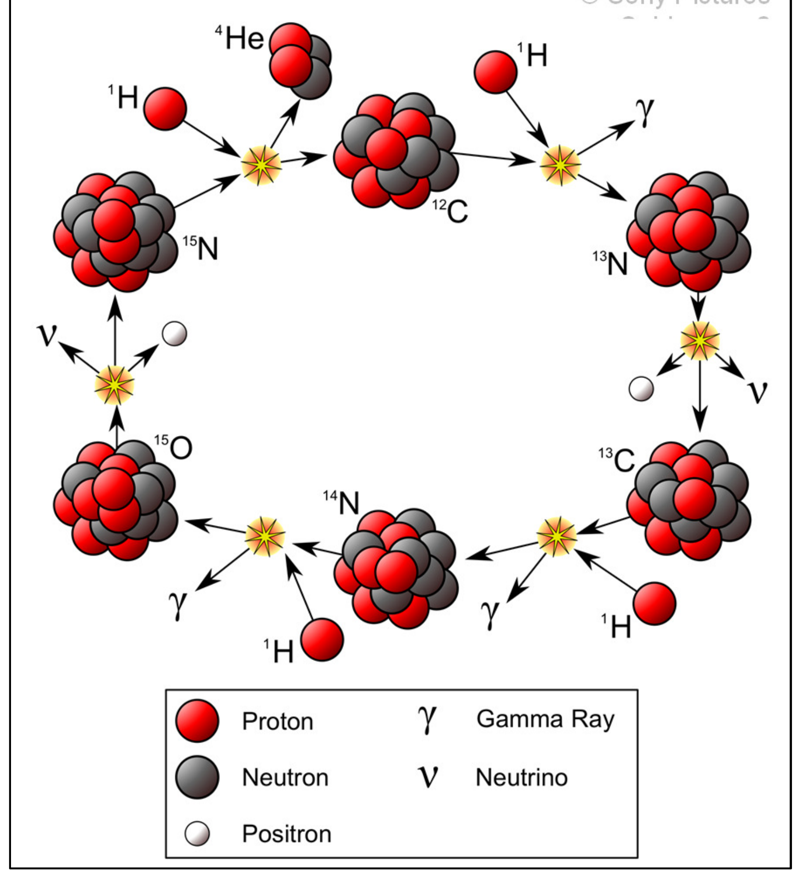
$$^{13}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{14}_{7}\mathrm{N} + \gamma$$

$$^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{15}_{8}\mathrm{O} + \gamma$$

$$^{15}_{8}\mathrm{O} \rightarrow {}^{15}_{7}\mathrm{N} + {}^{0}_{1}\mathrm{e} + \nu_e$$

$$^{15}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{12}_{6}\mathrm{C}$$

$$4\ {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\ {}^{0}_{1}\mathrm{e} + 2\ \nu_e + 3\ \gamma$$



http://en.wikipedia.org/wiki/CNO_cycle

Origins of the Universe

About 1.37 x 10^{10} years ago, bang! Supposedly, the first particles were neutrons. Then:

$$n \longrightarrow p + e^{-} + \overline{\nu}_e \qquad (t_{1/2} = 11.3 \text{ min})$$

also written as: $${}^{1}_{0}n \rightarrow {}^{1}_{1}H + {}^{0}_{-1}e^{-} + \overline{\nu}_e$$

Universe expands, and temperature drops to 10^9 K. Then, in minutes:

${}^{1}_{1}H + {}^{1}_{0}n \rightleftharpoons {}^{2}_{1}H + \gamma$	$p + n \rightleftharpoons D + \gamma$
${}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{1}H + {}^{1}_{1}H$	$D + D \longrightarrow T + H$
${}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He + {}^{1}_{0}n$	$D + D \longrightarrow {}^{3}_{2}He + n$
${}^{3}_{2}He + {}^{1}_{0}n \rightarrow {}^{4}_{2}He + \gamma$	${}^{3}_{2}He + n \longrightarrow {}^{4}_{2}He + \gamma$

First step is rate-determining step (reverse is fast…step 1 equilibrates),

thus final He:H ratio is 1:10

Origins of the Universe

Temperature continues to drop, background residual radiation is formed, stars begin to form, & atom–atom reactions begin during the next 30–60 min, called "hydrogen burning":

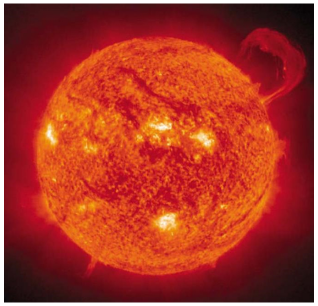
http://en.wikipedia.org/wiki/Proton-proton_chain

① fusion + β⁺-emission: $^{1}_{1}H + ^{1}_{1}H \rightarrow ^{2}_{1}H + ^{0}_{1}e + \nu_e$

② fusion (p⁺-capture): $^{2}_{1}H + ^{1}_{1}H \rightarrow ^{3}_{2}He + \gamma$

③ fusion: $^{3}_{2}He + ^{3}_{2}He \rightarrow ^{4}_{2}He + 2\,^{1}_{1}H$

NET (2x①)+(2x②)+③: $3\,^{1}_{1}H \rightarrow ^{4}_{2}He + 2\,^{0}_{1}e + 2\gamma + \nu_e$



Kotz 8th Ed. Brooks/Cole

Galaxies and denser stars form. In stars with T = 10^7-10^8 K, hydrogen burning continues but heavier elements are created from "helium burning":

① fusion: $^{4}_{2}He + ^{4}_{2}He \rightleftarrows ^{8}_{4}Be + \gamma$

② fusion: $^{4}_{2}He + ^{8}_{4}Be \rightarrow ^{12}_{6}C + \gamma$

③ p⁺-capture: $^{12}_{6}C + ^{1}_{1}H \rightarrow ^{13}_{7}N + \gamma$

④ β⁺-emission: $^{13}_{7}N \rightarrow ^{13}_{6}C + ^{0}_{1}e + \nu_e$

NET ①+②+③+④: $3\,^{4}_{2}He + ^{1}_{1}H \rightarrow ^{13}_{6}C + ^{0}_{1}e + 3\gamma + \nu_e$

http://en.wikipedia.org/wiki/Helium_fusion

Origins of the Universe (cont.)

In massive stars, (T = 6 × 10⁸ K or higher), the carbon-nitrogen-oxygen (CNO) cycle is possible:

$$^{12}_{6}C \rightarrow ^{13}_{7}N \rightarrow ^{13}_{6}C \rightarrow ^{14}_{7}N \rightarrow ^{15}_{8}O \rightarrow ^{15}_{7}N \rightarrow ^{12}_{6}C$$

This cycle generates a lot of energy.

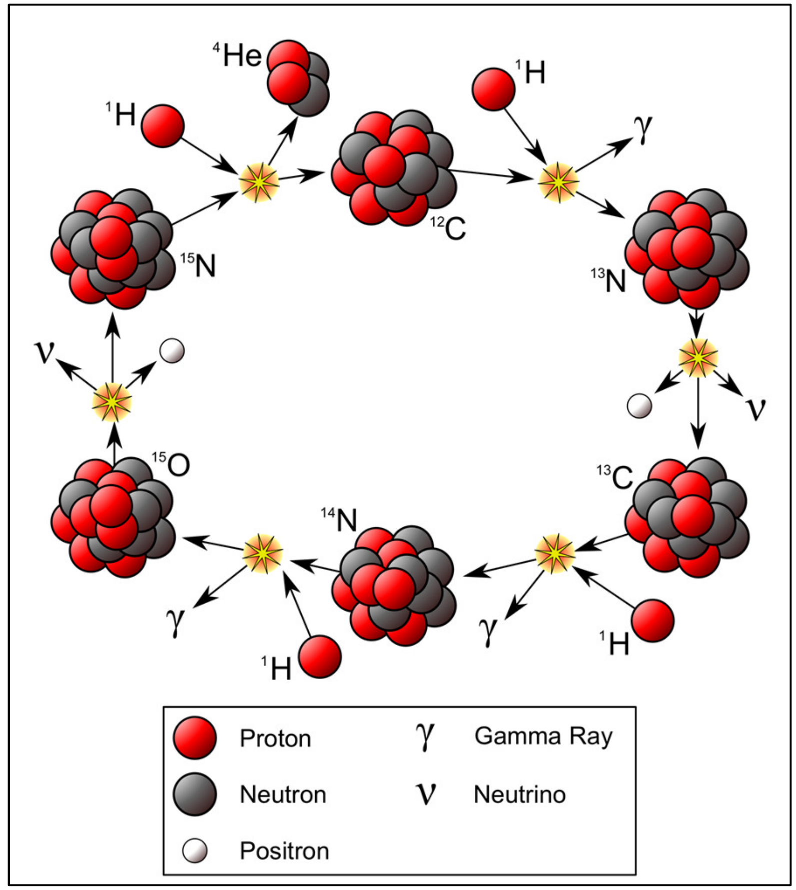
Also, heavier elements are created, such as:

$$^{12}_{6}C + ^{12}_{6}C \rightarrow ^{20}_{10}Ne + ^{4}_{2}He$$

$$2\ ^{16}_{8}O \rightarrow ^{28}_{14}Si + ^{4}_{2}He$$

$$2\ ^{16}_{8}O \rightarrow ^{31}_{16}S + ^{1}_{0}n$$

And so on…

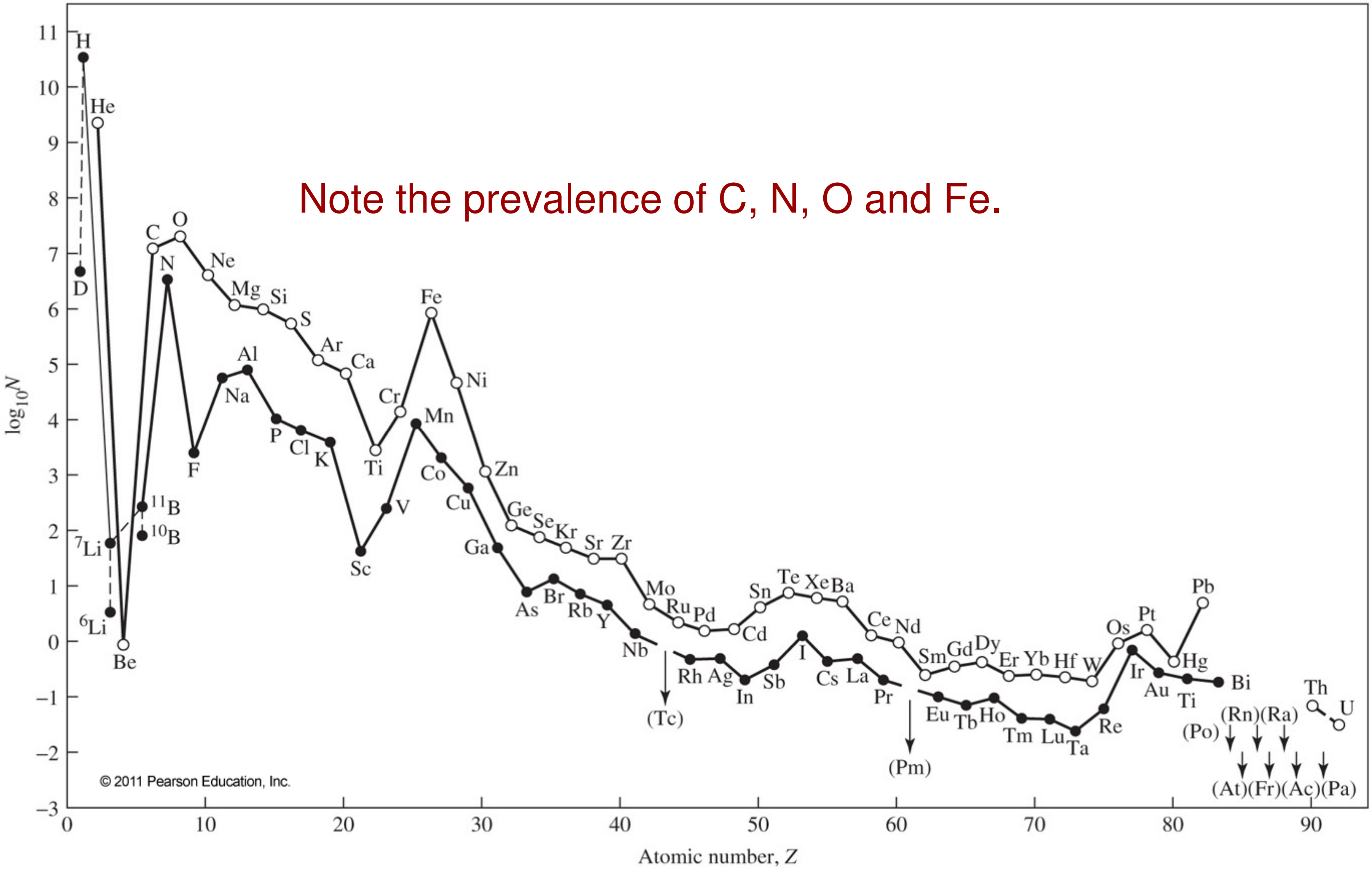


http://en.wikipedia.org/wiki/CNO_cycle

Origins of the Universe (cont.)

Overall, the final abundances of the elements in the universe are:

Note the prevalence of C, N, O and Fe.



Nuclear Binding Energy

The mass of a nuclide of any element (except H) is *less* than the sum of the masses of its individual particles ("mass defect").

Example:	Observed mass of	$^{7}_{3}Li$ = 7.010600 u = 1.16503×10^{-26} kg
	Expected mass of	3 p + 4 n = $\underline{1.17177 \times 10^{-26}\ kg}$
	Difference in mass	0.00674×10^{-26} kg
	is converted to energy:	$E = mc^2 = 6.06 \times 10^{-12}$ J/atom.

This energy is called the nuclear binding energy.

For making comparisons between elements, it is more useful to look at the binding energy *per nuclear particle* (nucleon). This quantity is shown graphically on the next slide.

The nuclear binding energy reaches a maximum at ^{56}Fe.

- To the left of Fe: nuclear ***fusion:*** *combining* lighter elements generally releases energy (binding E).
- To the right of Fe: nuclear ***fission:*** *breaking up* heavier elements generally releases energy (binding E).

Nuclear Binding Energy per Nucleon

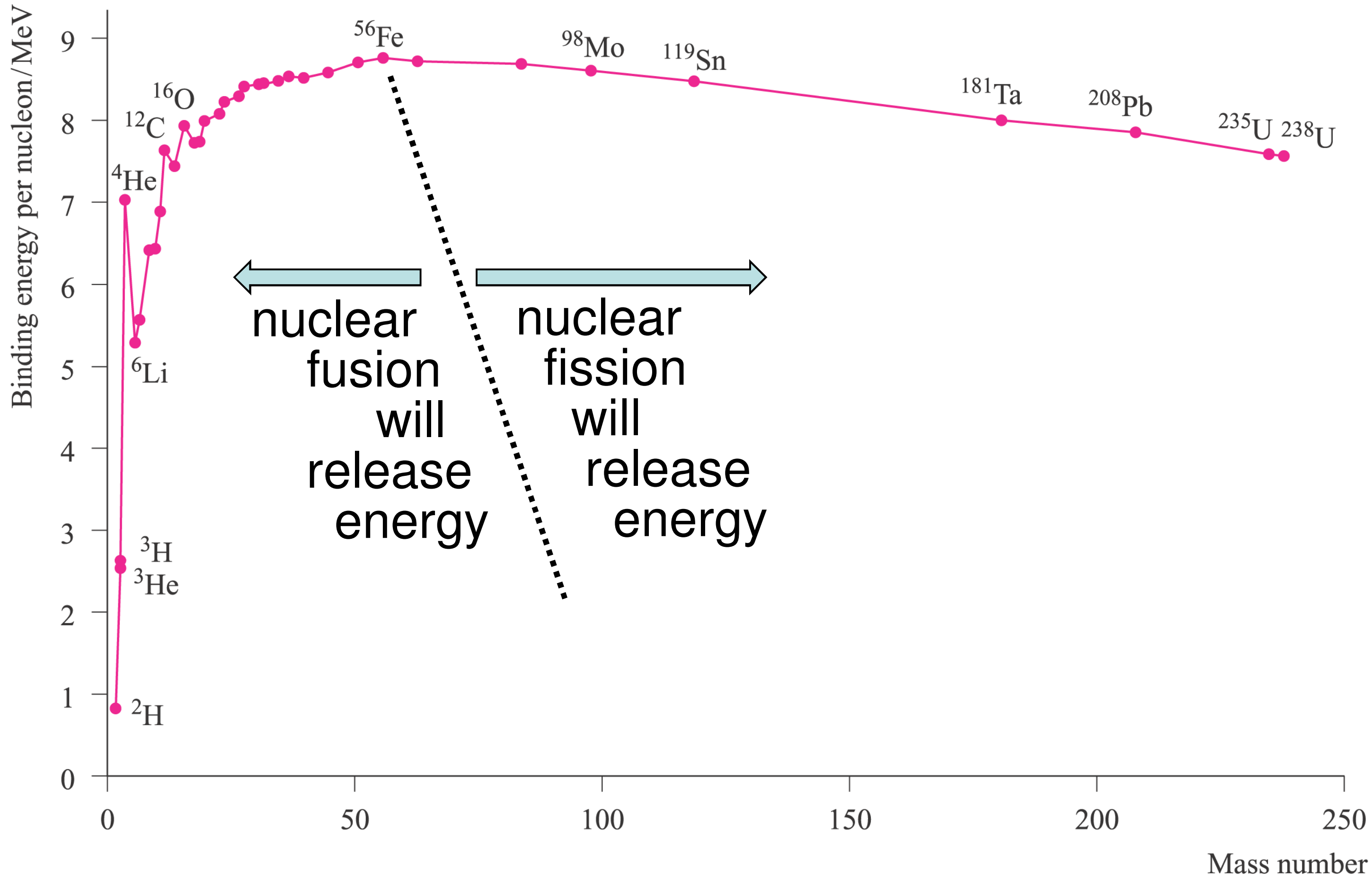


Fig. 2.1 Variation in average binding energy per nucleon as a function of mass number. Note that the energy scale is positive, meaning that the nuclei with the highest values of the binding energies release the greatest amount of energy upon formation.

Nuclear Fission Reactions

One of many product possibilities…

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n$$

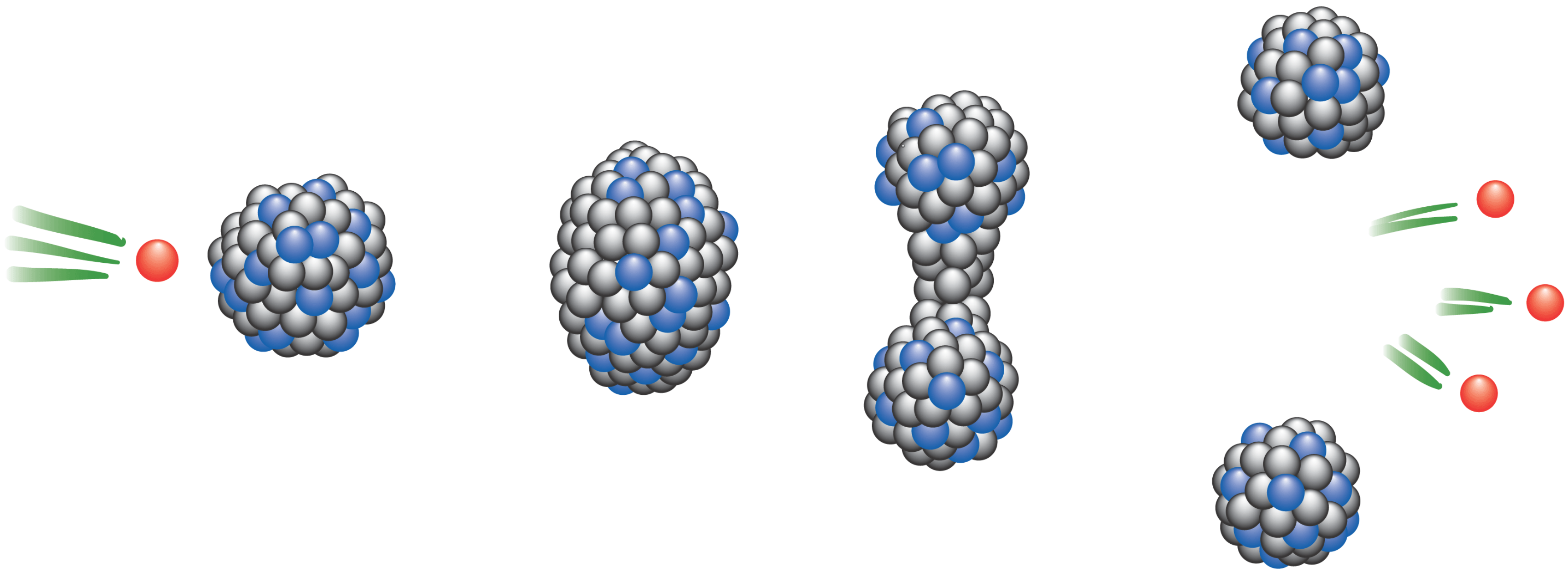
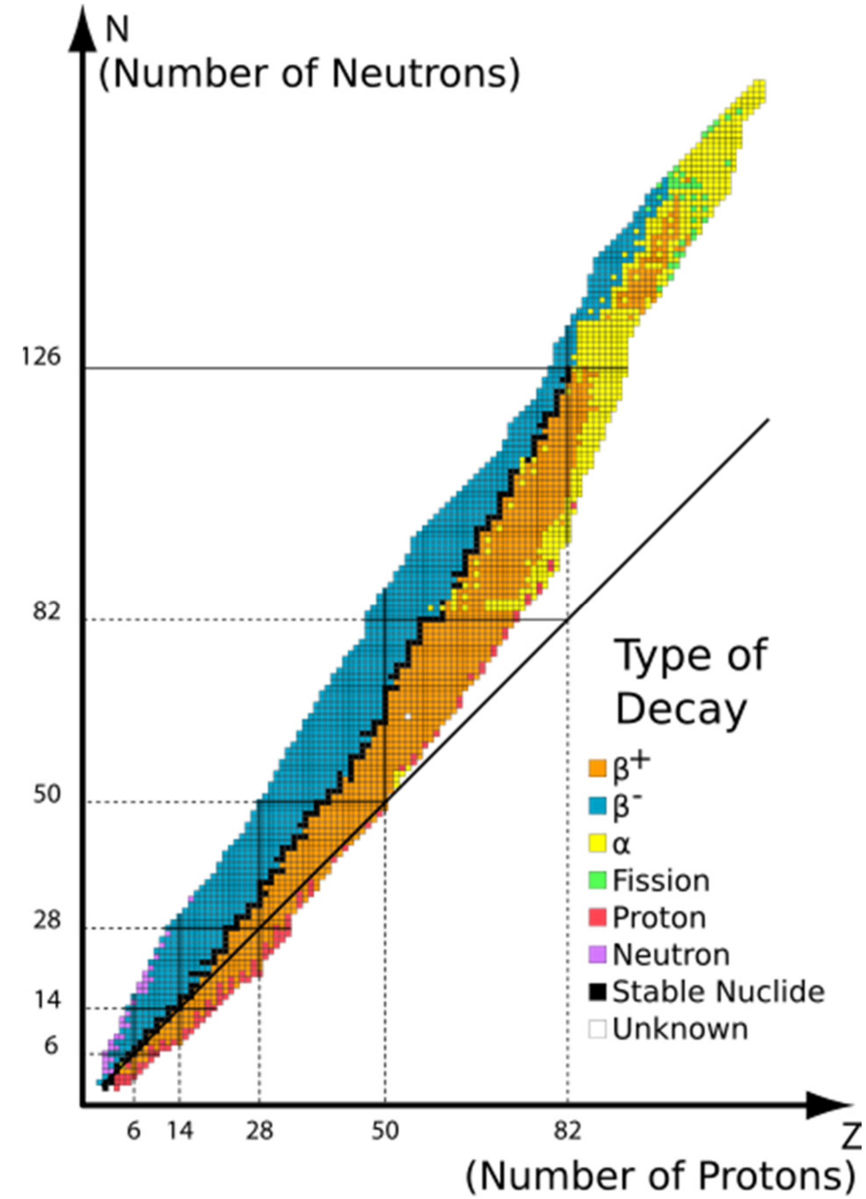


Fig. 2.5 A schematic representation of the collision of a thermal neutron with a heavy nuclide leading to fission into two nuclides of lower mass numbers and the release of (in this case) three neutrons. The fission is accompanied by the release of large amounts of energy. [Redrawn from P. Fenwick (1990) *Reprocessing and the Environment*, Hobsons, Cambridge.]

Radioactive Decay & Band of Stability



http://en.wikipedia.org/wiki/Stable_nuclide

α-emission involves loss of ^{4}He (⇨ A-4, Z-2). All elements beyond Bi, Z=83, are unstable & subject to α-emission.

$$^{243}_{95}Am \rightarrow \, ^{239}_{93}Np + \, ^{4}_{2}He$$

β⁻-emission (n^0 converts to p$^+$ ⇨ A same, Z+1) occurs if n/p ratio is high, i.e. elements above band of stability (black dots).

$$n \rightarrow p + e^- + \overline{\nu}_e$$

$$^{60}_{27}Co \rightarrow \, ^{60}_{28}Ni + \, ^{0}_{-1}e + \overline{\nu}_e$$

β⁺-emission or **e⁻-capture** (K-capture) (p$^+$ converts to n^0, 1 of 2 ways ⇨ A same, Z-1) occur for atoms with low n/p ratio.

$$energy + p \rightarrow n + e^+ + \nu_e$$

$$^{13}_{7}N \rightarrow \, ^{13}_{6}C + \, ^{0}_{+1}e + \nu_e$$

$$energy + p + e^- \rightarrow n + \nu_e$$

$$^{41}_{20}Ca + \, ^{0}_{-1}e \rightarrow \, ^{41}_{19}K$$

more common for Z > 35ish, & ^{7}Be

Shell Model of Nucleus & Nuclear Stability

A few "factoids":

- The protons and neutrons comprising the nucleus also have energy levels governed by 4 quantum numbers.
- The rules governing quantum numbers are different to those for electrons.
- Filled shells occur for 2, 8, 20, 28, 50, 82, and 126 nucleons of each kind.
- Nuclei tend to be more stable (lower energy level) if they have even numbers of each nucleon (protons, neutrons), rather than odd numbers.
- "Even-even" nuclides are most stable; "odd-odd" nuclides are rare (highly unstable with respect to β-decay, to produce even-even product nuclides).

THUS:

- Helium with 2 neutrons and 2 protons is a common product (α-particle) in radioactive decay of elements beyond bismuth.
- Elements beyond Bi often decay to isotopes of Pb (lead) with 82 protons.
- Sn (tin), with 50 protons, has the largest number of stable isotopes (10).
- There are 6 stable (well almost!) elements with 50 neutrons:
  ^{86}Kr, ^{87}Rb ($t_{1/2} = 5 \times 10^{11}$ years, β^- emission), ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Mo

Summary – Nuclear Reactions

NUCLEAR PROCESS	Cause	Reaction equation	Effect
α-emission	ejects $2n^0 + 2p^+$		Z-2 & A-4
β-emission	n^0 converts to p^+		Z+1, A same
positron emission	p^+ converts to n^0		Z-1, A same
electron capture	absorbs e^-		Z-1, A same
neutron capture	absorbs n^0		Z same, A+1
fission	gross fragmentation		massive daughters
Less common			
neutron emission	ejects n^0		
proton capture	absorbs p^+		
α-capture	absorbs $2n^0 + 2p^+$		

Clicker Question

Which one of the following processes occurs naturally?

A. $^{11}_{6}C + ^{1}_{0}n \rightarrow ^{12}_{6}C$

B. $^{11}_{6}C \rightarrow ^{7}_{5}B + ^{4}_{2}He$

C. $^{11}_{6}C + ^{0}_{-1}e \rightarrow ^{11}_{5}B$

D. $^{11}_{6}C \rightarrow ^{11}_{5}C + ^{0}_{+1}e$

E. $^{11}_{6}C \rightarrow ^{11}_{5}B + ^{0}_{+1}e$

Applications of nuclear chemistry

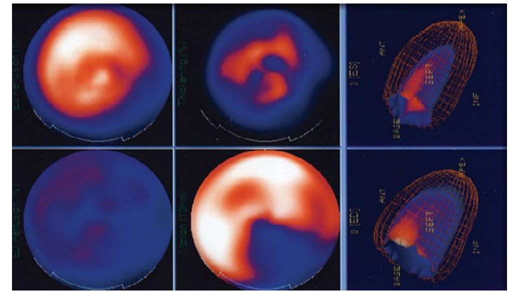
- Food science: food irradiation
  - Food can be irradiated with γ rays from ^{60}Co or ^{137}Cs.
  - Irradiation retards the growth of bacteria, molds and yeasts.
  - Irradiated milk has a shelf life of 3 months without refrigeration.
  - USDA has approved irradiation of meats and eggs.
- Analytical methods: radioactive tracers
  - ^{32}P, β-emitter with $t_{1/2}$ 14.3 d, is often used as a biochemical tracer.
  - Nutrient uptake by plants can be traced using $^{32}PO_4^{3-}$ fertilizer.
  - Pesticide accumulation in soil & run-off can be traced with labelled pesticides.
- Nuclear medicine: medical imaging, radiation therapy (next 2 slides)

Nuclear medicine: medical imaging

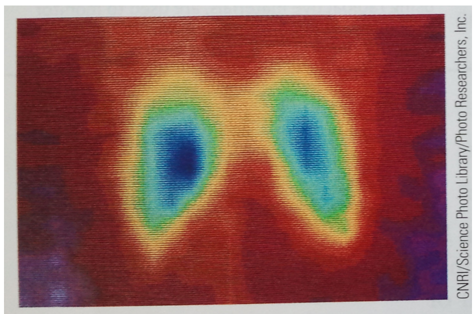
Table 23.4 Radioisotopes Used in Medical Diagnostic Procedures (Kotz 8th Ed.)

Radioisotope	Half-Life (h)	Imaging
^{99m}Tc	6.0	Thyroid, brain, kidneys
^{201}Tl	73.0	Heart
^{123}I	13.2	Thyroid
^{67}Ga	78.2	Various tumors and abscesses
^{18}F	1.8	Brain, sites of metabolic activity

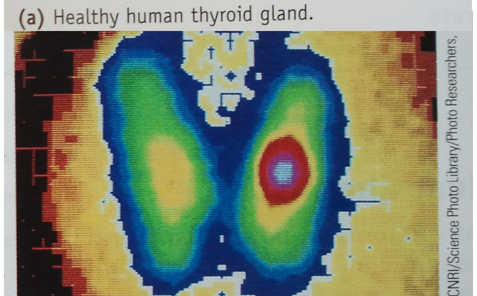
Kotz 8th Fig.23.12: Tc-99m image of heart before & after exercise



Kotz Ch.23 Closer Look: Tc-99m thyroid images



(a) Healthy human thyroid gland.



(b) Thyroid gland showing effect of hyperthyroidism.

Example: Technetium-99m is used in more than 85% of the diagnostic scans done in hospitals each year (synthesized on-site from Mo-99).

$$^{99}_{42}\text{Mo} \rightarrow {}^{99m}_{43}\text{Tc} + {}^{0}_{-1}\beta$$

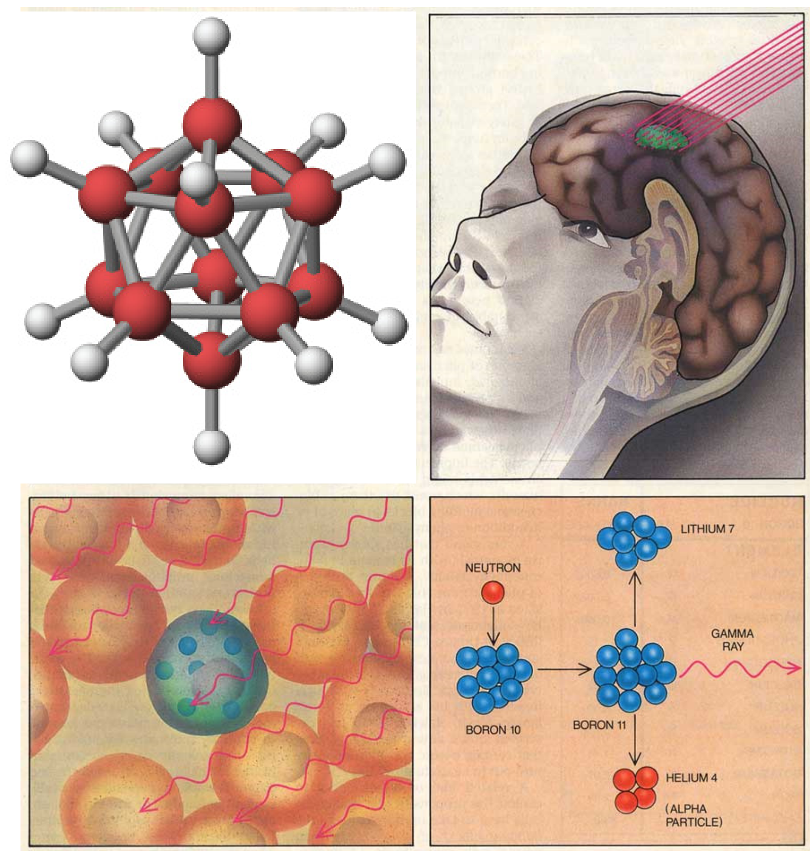
$^{99m}{}_{43}$Tc decays to $^{99}{}_{43}$Tc giving off a γ -ray, with half-life of 6.01 hrs. Once ingested, Tc-99m concentrates in areas of high activity (e.g., thyroid) & is detected via γ -ray imagining.

Nuclear medicine: radiation therapy

BNCT: Boron Neutron Capture Therapy

$$^{10}B + {}^{1}n \rightarrow {}^{7}Li + \alpha + \text{photon}$$

- non-radioactive ^{10}B (not typical ^{11}B) can efficiently capture slow neutrons via reaction shown above, to produce high E products
- tumor cells preferentially take up a B compound (*e.g.,* $Na_2[B_{12}H_{12}]$), normal cells take up much less
- subsequent irradiation by slow neutrons causes above reaction, which releases high E α-particles
- damages & kills nearby cells only, because penetration power of α-particles is low (2 cell diameter)
- experimental treatment in past 10-15 years, with fewer side effects…



Structure: J. Mack (Cal.State U.) lecture slides for Kotz 8th Ed., Brooks-Cole Publishing.

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Suggested problems for Chapter 1 material:

- any non-half-life radiochemistry questions from a general chemistry textbook (*e.g.*, Kotz, Zumdahl, Petrucci…).

Sample Exam Questions (1): Fall 2015 midterm & Fall 2014 final

Which ***one*** statement below about nuclear chemistry is FALSE?

a) Radioactive nuclei that are heavier than Fe tend to release energy via fusion reactions.
b) Electron capture converts a proton into a neutron, and thereby raises the n^0:p^+ ratio of the nucleus.
c) Nuclides with n^0:p^+ ratio lower than the band of stability often decay via positron-emission.
d) Even-even nuclides (even numbers of p^+ & n^0) are more stable than even-odd or odd-odd nuclides.

Which of these nuclides likely decay by β-emission: ^{3}H, ^{16}O, ^{20}F, ^{13}N?

a) ^{13}N and ^{16}O
b) ^{20}F and ^{16}O
c) ^{3}H and ^{16}O
d) ^{3}H and ^{20}F

What sequence of radioactive decay events occurs when radon-222 decays to polonium-218, then to lead-214, then to bismuth-214?

a) β^-, α, β^-
b) α, α, β^-
c) α, β^-, α
d) β^-, α, α
e) α, α, α

Be prepared to answer ALL questions in full explanatory format, not just MCQ.