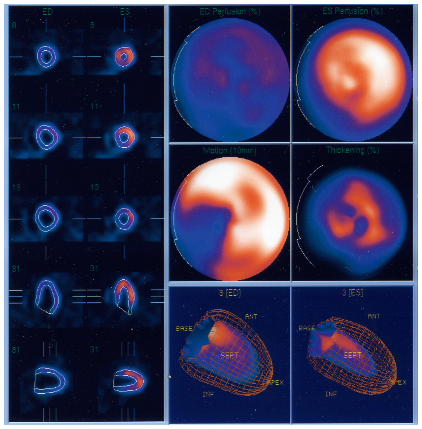
Nuclear Chemistry

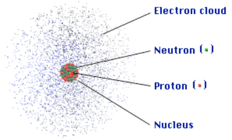
Chapter 21

Chemistry 222
Professor Michael Russell

MAR *Last update: 4/29/24*



Nuclear Chemistry: *the study of the nucleus*



Nucleus = neutrons and protons
Differs from "normal" electron chemistry

MAR

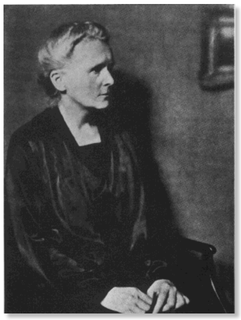
Early Nuclear Chemistry Pioneers:

Marie Curie
Pierre Curie
Henri Becquerel

Noticed beams of light on photographic plates

Danger (and potential) of nuclear chemistry poorly understood

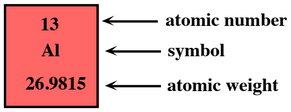
Marie Curie



MAR

Atomic Number, Z

All atoms of the same element have the same number of protons in the nucleus, Z.



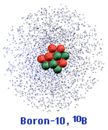
MAR

Mass Number, A

Mass Number
= # protons + # neutrons

A boron atom can have
A = 5 p + 5 n = 10 *and*
Z = 5 protons = 5

$$\begin{matrix} A \rightarrow 10 \\ Z \rightarrow 5 \end{matrix} B$$



Isotopes of boron have **different # of neutrons** but **same # of protons** *(Boron-10, Boron-11)*

MAR

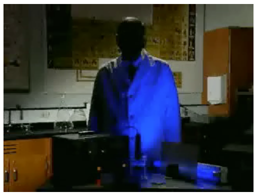
Radioactive Particles

ALPHA	helium nucleus	${}^{4}_{2}He$ *or* ${}^{4}_{2}\alpha$
BETA	electron	${}^{0}_{-1}e$ *or* ${}^{0}_{-1}\beta$
GAMMA	*energy (massless)*	γ
PROTON	proton	${}^{1}_{1}p$ *or* ${}^{1}_{1}H$
NEUTRON	neutron	${}^{1}_{0}n$
POSITRON	antielectron	${}^{0}_{+1}e$ *or* ${}^{0}_{+1}\beta$

MAR *see: Nuclear Chemistry Guide*

Radioactive Particles

Each particle has different properties



Alpha - stopped by clothes
Beta - stopped by skin
Gamma - stopped by lead

MAR

Balancing Nuclear Reactions

* Number of *reactant* protons must equal the number of *product* protons

* Number of *reactant* neutrons must equal the number of *product* neutrons

Example:

$${}^{226}_{88}\mathrm{Ra} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{222}_{86}\mathrm{Rn}$$

$$\begin{aligned} \mathrm{A}&: \ 226 = 4 + 222 \\ \mathrm{Z}&: \ 88 = 2 + 86 \end{aligned}$$

MAR

Balancing Nuclear Reactions

Problem: Uranium-235 decomposes through beta decay to a new product. Find the identity of the new product.

Solution:

Uranium has 92 protons, so: ${}^{235}_{92}\mathrm{U}$

Beta decay means "losing a beta particle", or generating a beta particle as a product, so:

$${}^{235}_{92}\mathrm{U} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{A}_{Z}\mathrm{X}$$

MAR

Balancing Nuclear Reactions

Problem: Uranium-235 decomposes through beta decay to a new product. Find the identity of the new product.

$${}^{235}_{92}\mathrm{U} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{A}_{Z}\mathrm{X}$$

Solution:

235 = 0 + A, therefore A = 235
92 = -1 + Z, therefore Z = 93
If Z = 93, X = Neptunium (Np), and

$$\boxed{{}^{235}_{92}\mathrm{U} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{235}_{93}\mathrm{Np}}$$

The "inner reaction":

$${}^{1}_{0}\mathrm{n} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{1}_{1}\mathrm{p}$$

MAR

Emission, Decay and Capture

Emission and **Decay** imply a *product* particle

An example of positron emission:

$$\boxed{{}^{207}_{84}\mathrm{Po} \longrightarrow {}^{0}_{+1}\beta + {}^{207}_{83}\mathrm{Bi}}$$

Capture implies a *reactant* particle

An example of neutron capture:

$$\boxed{{}^{19}_{9}\mathrm{F} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{20}_{9}\mathrm{F}}$$

Many types of "particles" and "decays"

MAR

Positrons and Antimatter

Paul Dirac first predicted antimatter in 1928, identical to "regular" matter except for opposite charge

Positrons are **antielectrons**; combining with electrons leads to **annihilation** *(gamma)*

$$\boxed{{}^{0}_{-1}\mathrm{e} + {}^{0}_{+1}\mathrm{e} \longrightarrow 2\gamma}$$

electron + positron ---> gamma radiation
Used in Positron Emission Tomography (PET)

Many examples of **annihilation reactions** are known:

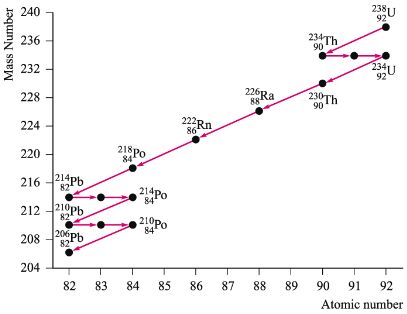
$$\boxed{\nu + \bar{\nu} \longrightarrow 2\gamma}$$

neutrino + antineutrino ---> gamma radiation

Neutrino first postulated by Pauli (CH 221)

MAR

Decay Scheme for Uranium-238



MAR

Metastable Nuclei

When *electrons* are excited in an atom, they relax and emit UV, IR and visible radiation

A **metastable nuclei** is created when a ***nucleus*** is excited. Relaxation results in high energy gamma ray emission

$$^{99m}_{43}\mathrm{Tc} \longrightarrow {}^{99}_{43}\mathrm{Tc} + \gamma$$

metastable Tc ---> "regular" Tc + gamma ray
Note the "m" for "metastable" and no change in atomic or mass numbers

Metastable nuclei (*especially Technetium-99m*) used extensively in medical imaging

MAR

The Four Forces of Nature

Gravitation: weak, long range force

Weak nuclear: short range, gives beta decay

Electromagnetic (E/M): long range, keeps electrons around nucleus, 10^{36} times more powerful than gravity (*aka* electrostatic, Coulombic, etc.)

Strong nuclear: 10^{6} times more powerful than E/M, *very* short range (10^{-15} m); overpowers E/M repulsion between protons. Strong keeps (protons + neutrons) and (neutrons + neutrons) together. "**Glue**" that keeps nucleus together

MAR

Nuclear Stability

Why are nuclei unstable? **E/M Force** (long range) begins overpowering strong force (short range)

Magnetic dilution (more neutral neutrons than positive protons) helps stabilize nuclei - *to a point*

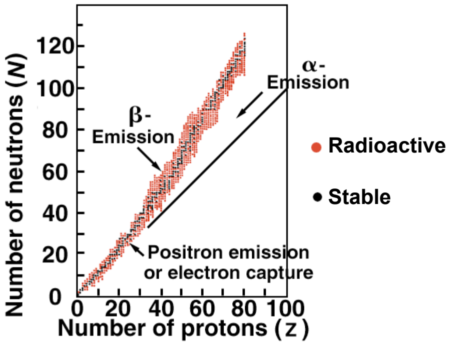
Up to calcium (Z = 20), most stable nuclei occur when **# protons = # neutrons**

Exceptions: helium-3 and hydrogen-1

Up to lead (Z = 82), most stable nuclei occur when **# protons < # neutrons**

Beyond lead, **all isotopes unstable and radioactive**

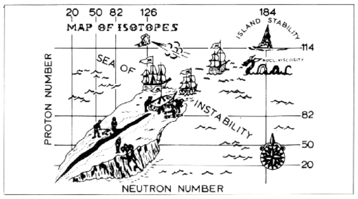
MAR



A "peninsula of stability" (black dots) in a "sea of instability" (red dots)

MAR

An "Island of Stability"?



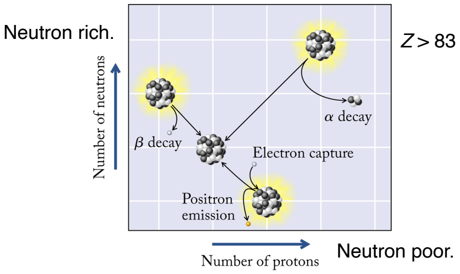
Glenn Seaborg and **Ken Moody** believe that heavier elements can be made - *exciting!*

Interested? See: http://www.pbs.org/wgbh/nova/sciencenow/3313/02.html

MAR

Nuclear Stability

Isotopes *often* decay based on their number of neutrons:



Nuclear Stability

β-decay occurs in isotopes with a high neutron to proton ratio. *Result:* higher atomic number, same mass number

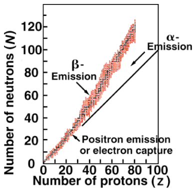
$$^{235}_{92}\text{U} \longrightarrow {}^{0}_{-1}\text{e} + {}^{235}_{93}\text{Np}$$

Low neutron to proton ratio: **positron emission** or **electron capture**. *Result:* lower atomic number, same mass number

$$^{13}_{7}\text{N} \longrightarrow {}^{0}_{+1}\text{e} + {}^{13}_{6}\text{C}$$

All elements beyond Bi decay, usually by **α-decay**

$$^{226}_{88}\text{Ra} \longrightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$



Nuclear Stability

Energy required to overcome positive-positive repulsion of protons is substantial - use strong *(and weak)* forces

- *Strong and weak forces much stronger than electromagnetic force or gravity*

Nuclear binding energy, E_b, used to estimate force contribution

- **E_b is the negative of the energy change if nucleus formed directly from individual protons and neutrons**

Nuclear Stability

Problem: Calculate the binding energy, E_b, for deuterium (hydrogen-2).

Solution:

The process: $^{1}_{1}\text{p} + {}^{1}_{0}\text{n} \longrightarrow {}^{2}_{1}\text{H}$

Note that: $\text{mass}_p + \text{mass}_n \neq \text{mass}_D$

$$1.007825 + 1.00865 \neq 2.01410$$

$$2.016475 \neq 2.01410$$

$$\Delta m = -0.00239 \text{ g/mol}$$

mass is *not* conserved!

Nuclear Stability

Problem: Calculate the binding energy, E_b, for deuterium (hydrogen-2). $\Delta m = -0.00239$ g/mol

Solution:

Now use Einstein's equation: $\Delta E = \Delta mc^2$

$\Delta E = (-2.39 \times 10^{-6}\ \text{kg mol}^{-1})(2.998 \times 10^{8}\ \text{m s}^{-1})^2$

$\Delta E = -2.15 \times 10^{11}\ \text{J mol}^{-1}$, ***and***

$E_b = -\Delta E$, **so**

$E_b = 2.15 \times 10^{8}\ \text{kJ mol}^{-1}$

E very negative (exothermic) - lots of energy produced. E_b very positive - lots of energy saved through stabilization

Nuclear Stability

Problem: Calculate the binding energy, E_b, for deuterium (hydrogen-2). $\Delta m = -0.00239$ g/mol

Solution:

Now use Einstein's equation: $\Delta E = \Delta mc^2$

$\Delta E = (-2.39 \times 10^{-6}\ \text{kg mol}^{-1})(2.998 \times 10^{8}\ \text{m s}^{-1})^2$

$\Delta E = -2.15 \times 10^{11}\ \text{J mol}^{-1}$, ***and***

$E_b = -\Delta E$, **so**

$E_b = 2.15 \times 10^{8}\ \text{kJ mol}^{-1}$

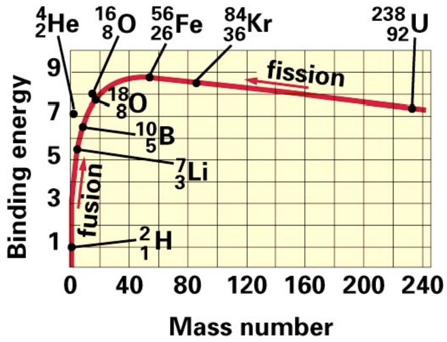
***E_b per nucleon** = 2.15×10^{8} / (1 p + 1 n) nucleons*

= $1.08 \times 10^{8}\ \text{kJ mol}^{-1}\ \text{nucleon}^{-1}$

This is the strong force contribution in the nucleus!

Nuclear Stability

Can use Binding energy (E_b) to calculate stability of nuclei:



MAR

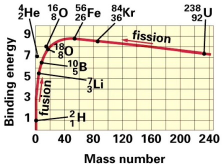
Nuclear Stability

Note that iron-56 is the most stable element *thermodynamically* - end of solar cycles, etc.

Elements with Z < 26 can use fusion to become more like iron-56

Elements with Z > 26 can use fission to become more like iron-56

Kinetics of nuclear reactions important - half life, rate of decay, etc.



MAR

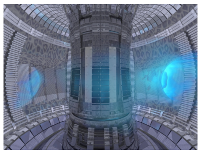
Tremendous amounts of energy are generated when light nuclei combine to form heavier nuclei - nuclear fusion

"Clean" energy, used in stars and bombs, requires *plasma* and/or high temperatures - high activation energy barrier

No "meltdown" - reaction just stops, no waste

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

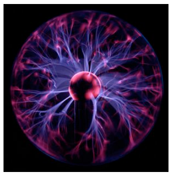
E = -1.7*10⁹ kJ/mol



Fusion

MAR

Plasma

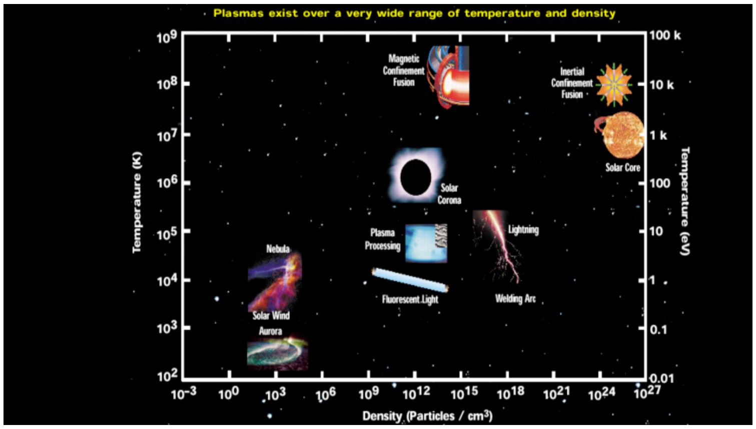


Plasma is the fourth state of matter - along with solids, liquids and gases

Plasma is an electrically conducting fluid composed of freely roaming electrons and ions; strong magnetic and electric fields; hot!

Plasmas comprise the vast majority of the apparent universe, and only in occasional "islands" (like the planet Earth) is matter found in condensed forms (solids, liquids, gases)!

MAR



Plasma - *in your microwave?*

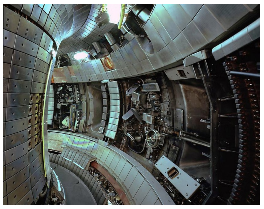
Video by Sergiu and Ben Todor 2010

Grape microwave "plasma" - ?!?

MAR

Fusion - *Tokamak Reactor*

Tokamak reactor uses magnetic fields to constrict plasma for fusion in "donut" shape; most promising "future" magnetic fusion device



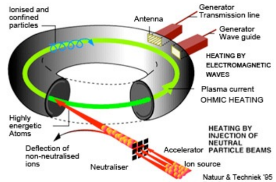
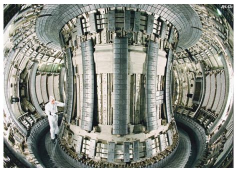
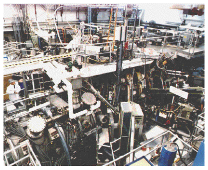


Figure 2: Various tokamak plasma heating techniques

MAR

Fusion - *Tokamak Reactor*





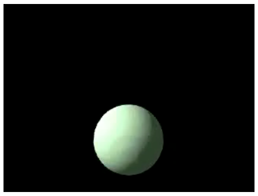
Tokamak reactors - *inside* and *outside* views

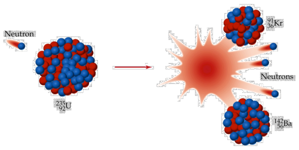
MAR

Fission

Tremendous amounts of energy *(electricity)* generated when heavy nuclei split to form lighter nuclei - *nuclear fission*

Generally requires a "neutron trigger"





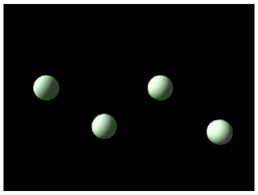
MAR

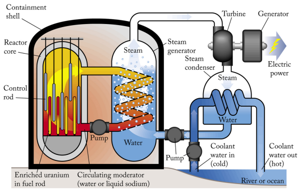
Fission

Excess neutrons *must* be controlled! *Supercritical chain reactions* can result without proper caution

Waste products from fission messy and virtually perpetual

More than 400 nuclear fission plants in 30 different countries!





MAR

Uses for Nuclear Chemistry

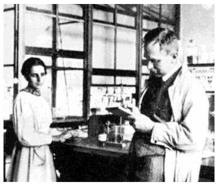
Energy: Fission (commercial) *and* Fusion (coming!)

Nuclear fission "problem events":

- SL-1, Idaho Falls (1961)
- Three Mile Island, Pennsylvania (1979)
- Chernobyl, Ukraine (1986)
- Fukushima Daiichi, Japan (2011)
- Hanford, Washington (ongoing!)

LISE MEITNER - *unsung hero*

With Otto Hahn



Meitner and colleagues Otto Hahn, Fritz Strassmann & Otto Frisch explained the process of fission (1938)

Meitnerium (Mt, #109) named after her

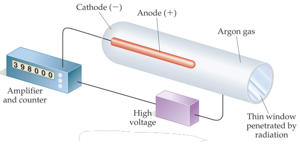
Forced to work in basement, never got Nobel Prize (but Hahn did!)

Pioneering woman in a male-dominated field; deserves more credit for her work

MAR

Radiation and Health

Some radiation is around us all of the time



Geiger counters measure the amount of radioactive activity present in a sample. The radiation creates ions which conduct a detectable current.

MAR

Radiation and Health

Many units for radiation exposure - röntgen (R), curie (Ci), rad, rem, *others*

The röntgen is a measure of radiation exposure proportional to air ionization (*X*- and γ-rays)

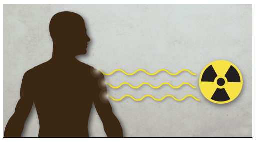
***Ex:* chest X-ray = 0.1 R**

rem = röntgen equivalent man

One curie = quantity of any isotope that undergoes 3.7 * 10^{10} *dps* (disintegrations per second)

One rad = 1.00 * 10^{-5} J absorbed per gram of material.

A whole-body dose of 450 rad = LD_{50} for humans

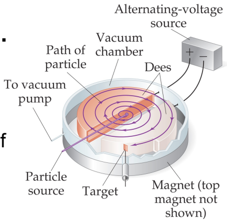


MAR

Nuclear Transformations

Nuclear transformations can be induced by accelerating a particle and colliding it with the nuclide.

- **Linear accelerator**—uses alternating electric fields to accelerate particle.
- **Cyclotron**—uses combination of electric and magnetic fields to accelerate particles in spiral pathway.



Cyclotron

MAR

Particle Accelerators

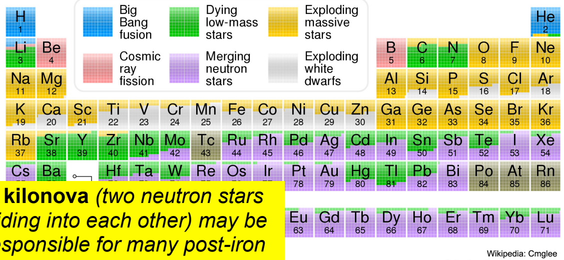
These particle accelerators are *enormous*, having circular tracks with radii that are miles long. New elements created by "smashing" smaller nuclei together.

CERN Particle Accelerator, Geneva, Switzerland

MAR

Uses for Nuclear Chemistry

Astronomers and chemists work together to define the origin of elements. Many made through fusion, some via fission, much not understood



*A **kilonova** (two neutron stars sliding into each other) may be responsible for many post-iron elements on the Earth*

Wikipedia: Cmglee
Data: Jennifer Johnson (OSU)

MAR

NSCL = *National Superconducting Cyclotron Laboratory at Michigan State University (http://www.nscl.msu.edu/)*

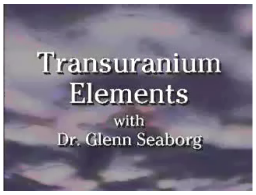
Full video *available here:* **https://youtu.be/677ZmPEFIXE**

MAR

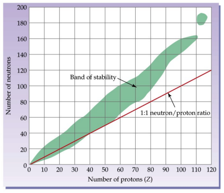
Uses for Nuclear Chemistry

Uses for Nuclear Chemistry

Expanding the Frontiers of Science




(271) 106
+6
Sg
Seaborgium
[Rn] $7s^2 5f^{14} 6d^4$
Transition Metal



Dr. Glenn Seaborg (1912 - 1999)

MAR

Uses for Nuclear Chemistry

Radiocarbon Dating

$t_{1/2}$ = 5730 years for carbon-14
Accurate up to 60,000 years old!

MAR

Uses for Nuclear Chemistry

Medicine: PET *and* MRI

Tc (in PET) not found in nature, created via Mo:

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

- Tc-99*m*: metastable; $t_{1/2}$ = 6.0 hrs.
- Can be incorporated into variety of compounds to target specific organs (heart, etc.).

PET = Positron Emission Tomography
MRI = Magnetic Resonance Imaging

MAR

End of Chapter 21

See:
- *Chapter Twenty-one Study Guide*
- *Chapter Twenty-one Concept Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

MAR

Important Equations, Constants, and Handouts from this Chapter:

- **all** *of the* **first order kinetics** *equations apply. See the* **Nuclear Chemistry Guide** *(handout)*
- **decay** *or* **emission = product**
- **capture = reactant**
- **know how to balance nuclear reactions**

$$-E_b = \Delta E = \Delta mc^2$$

c = *speed of light* = **2.998 x 10^8 m/s**
use **kg/mol** *for* **Δm**

1st Order Integrated Rate Law;

$$ln\frac{[R]}{[R_0]} = -kt$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

MAR

End of Chapter Problems: *Test Yourself*

1. What particle is emitted when Gold-198 decays to mercury-198?
2. What particle is emitted when radon-222 decays to polonium-218?
3. What particle is emitted when indium-110 decays to cadmium-110?
4. What is emitted when hafnium-178m decays?
5. Boron has two stable isotopes, ^{10}B and ^{11}B. Calculate the binding energies per nucleon of these two nuclei. The required masses (in grams per mole) are proton = 1.00783, neutron = 1.00867, boron-10 = 10.01294, and boron-11 = 11.00931.
6. Gold-198 is used in the diagnosis of liver problems. The half-life of ^{198}Au is 2.69 days. If you begin with 2.8 μg of this gold isotope, what mass remains after 10.8 days?

MAR

End of Chapter Problems: *Answers*

1. beta particle
2. alpha particle
3. positron particle
4. hafnium-178
5. boron-10: 6.26×10^8 kJ/mol·nucleons; boron-11: 6.70×10^8 kJ/mol·nucleons
6. 0.17 µg

MAR