Energy Generation, Storage, and Transformation

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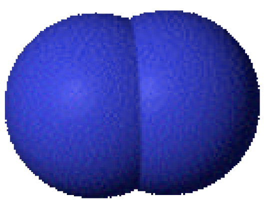
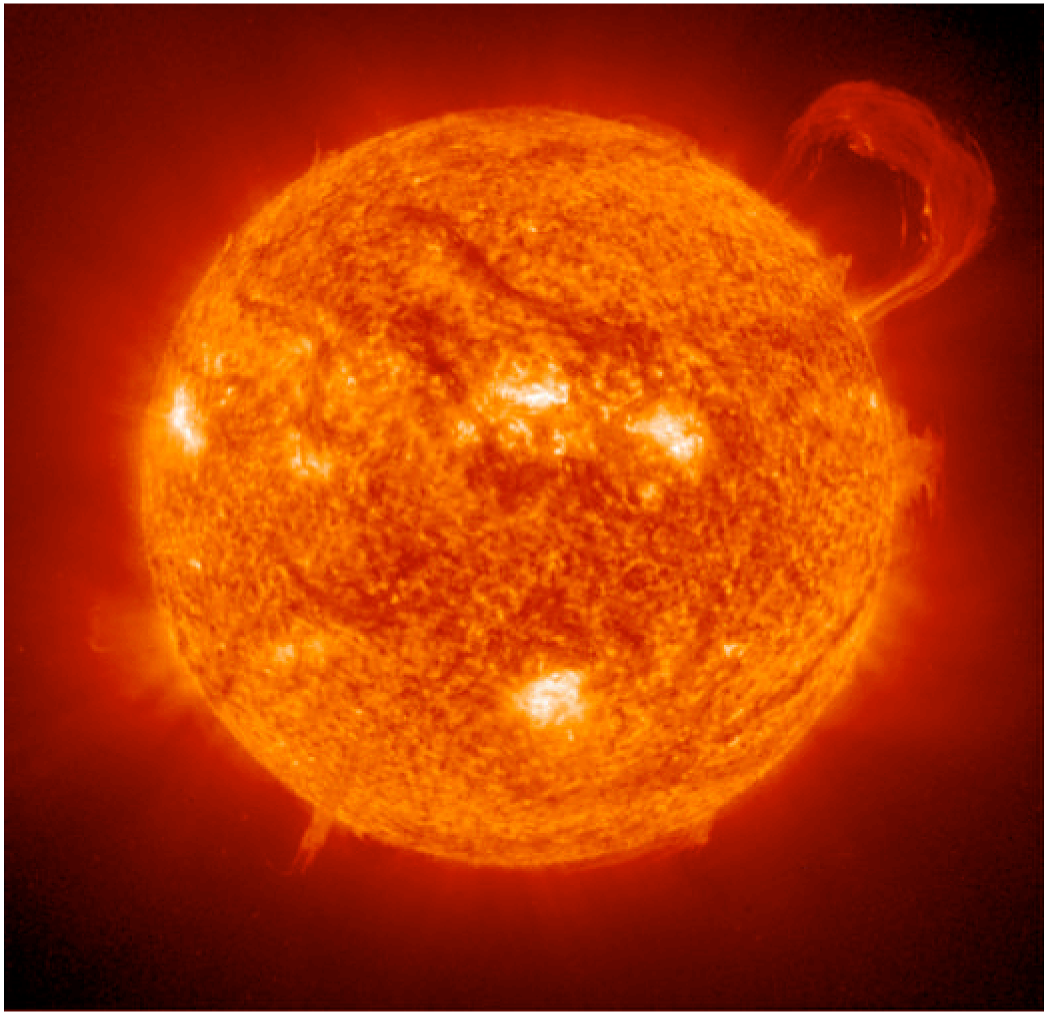
6. Energy from Hydrogen



Hydrogen: The Sun



In a sense, we already get almost all our energy from hydrogen

Hydrogen: Chemical Energy

$H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l)$ $\Delta H^\circ = -285.8\ \text{kJ mol}^{-1}$

$\Delta G^\circ = -237.2\ \text{kJ mol}^{-1}$

If obtained directly (e.g. in fuel cell) $\eta_{ideal} = \frac{\Delta G}{\Delta H} = 0.83$

However, H_2 is not readily available on Earth - must be generated somehow.

$H_2O(l) \longrightarrow H_2(g) + 1/2\ O_2(g)$ $\Delta H^\circ = +285.8\ \text{kJ mol}^{-1}$

$\Delta G^\circ = +237.2\ \text{kJ mol}^{-1}$

Hydrogen: Chemical Energy

Pro: Hydrogen has the highest energy density among chemical fuels:

Gasoline	46.4 MJ/kg
E85	33.1 MJ/kg
Hydrogen	143 MJ/kg

Water is the only product of hydrogen combustion (or reaction in a fuel cell).

Although water vapor is a greenhouse gas, atmospheric [H_2O] is limited by the hydrological cycle, and by the fact that H_2O is a liquid at ambient temperatures (VP = 2338 Pa at 293 K).

Con: Compression and liquefaction of hydrogen carry a fairly heavy energy cost in addition to that of the electrolytic production of H_2.

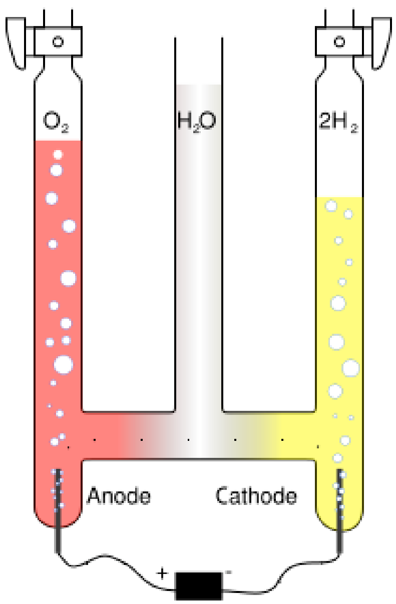
Hydrogen: Chemical Energy

Hydrogen generation - water electrolysis:

$$\begin{array}{lrl} \text{Anode (oxidation):} & 2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^- & E^o_{ox} = -1.23\ \text{V} \\ \text{Cathode (reduction):} & 2H^+\ (aq) + 2e^- \rightarrow H_2\ (g) & E^o_{red} = 0.00\ \text{V} \end{array}$$

Overall E° = -1.23 V i.e. ΔG° = +237 kJ mol^{-1}

Not quite as straightforward as it seems - electrolyte must be chosen appropriately to avoid undesirable anode reactions. ($NaHCO_3$ is suitable; other alternatives include H_2SO_4 or KOH.)



Hofmann voltameter

Energy for electrolysis can be provided by solar panels.

Hydrogen: Hazards

Sam Shere, Burning of the Hindenburg, Lakehurst, New Jersey, May 6, 1937

Hydrogen: Hazards

hydrogen

vs

gasoline

burns rapidly

rises (lighter than air)

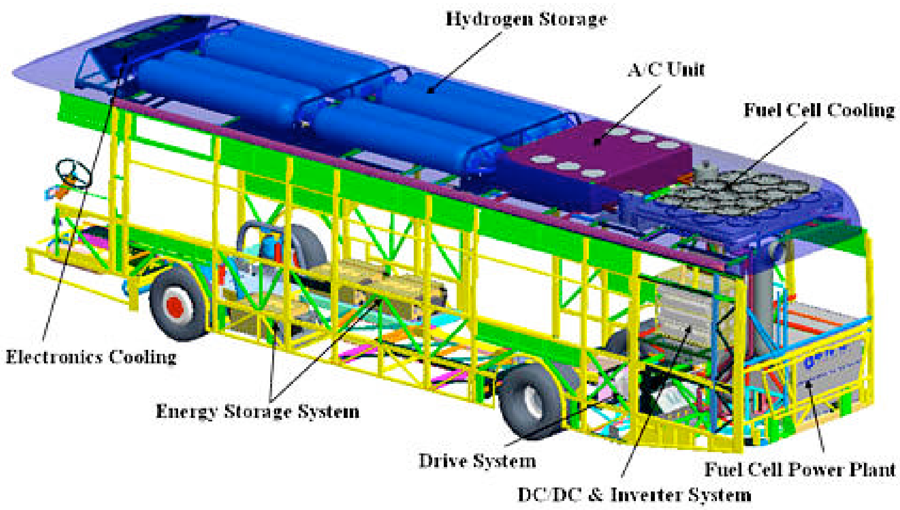
burns rapidly

spreads on ground (liquid)

Hydrogen: Vehicles

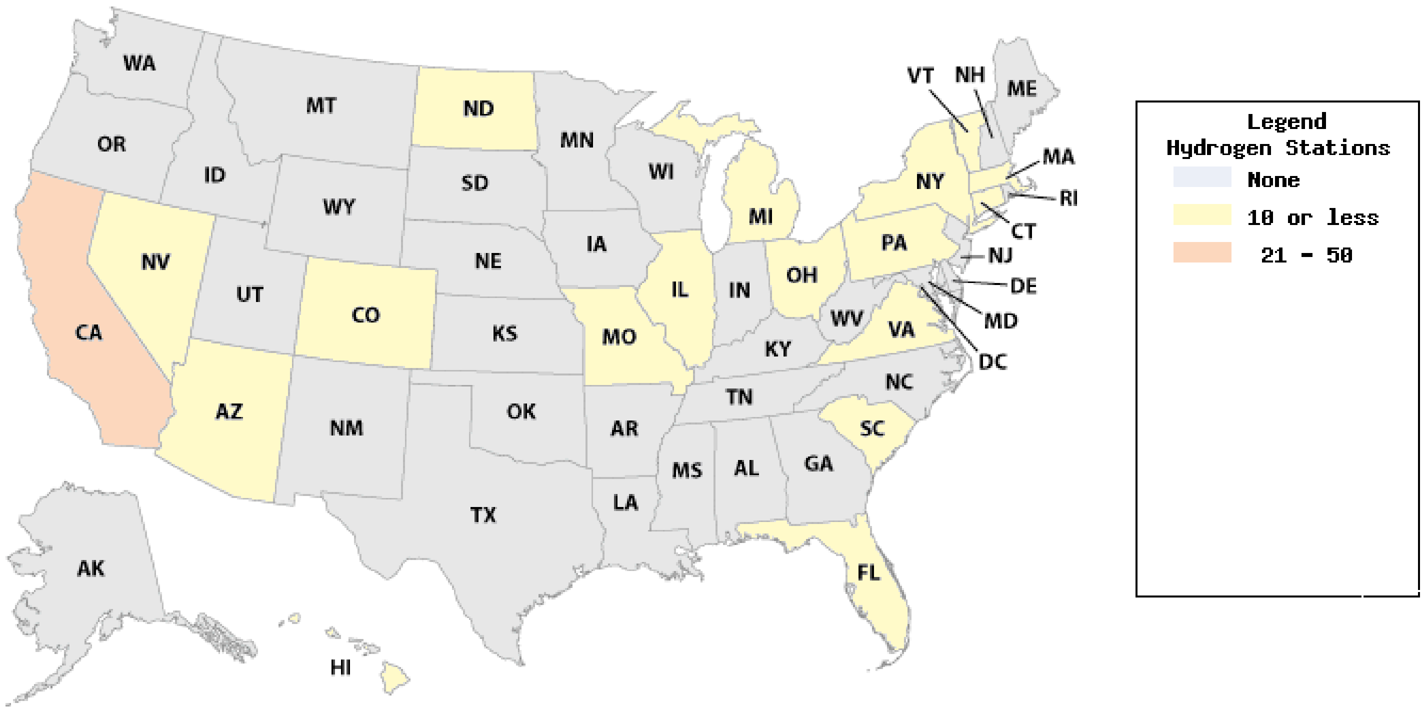
While the majority of hydrogen vehicles utilize fuel cells, some are flex-fuel internal combustion vehicles.

Idea has been around for several decades - Jack Nicholson drove a (solar-power-generated) hydrogen-powered Chevy in 1978.



Hydrogen-powered buses are more common than private cars, and have been adopted in several countries (e.g. Brazil).

Hydrogen: Availability (as transportation fuel)



Alternative Fuels and Advanced Vehicles Data Center

http://www.afdc.energy.gov/afdc/

Hydrogen: Storage

U.S. DEPARTMENT OF ENERGY

Hydrogen Program

http://www.hydrogen.energy.gov/

DOE Targets:

•6 wt. % storage (15% by 2010)

•operate near room temperature

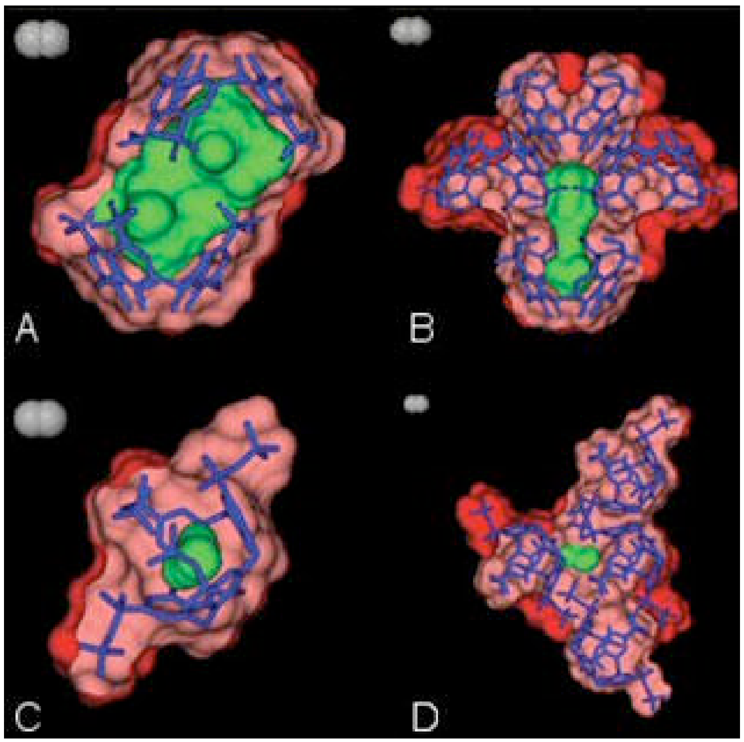
•reversible absorption/adsorption

These criteria require that candidate materials be light in weight, and place thermodynamic/kinetic constraints on adsorption energetics.

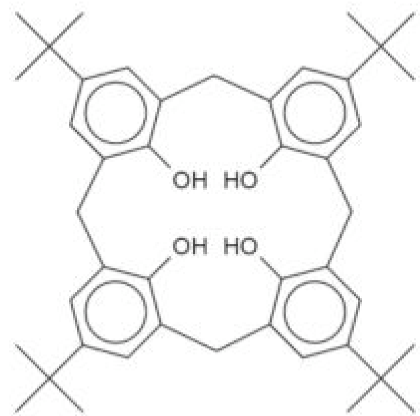
Next: Some candidate systems

Hydrogen: Storage

A few strategies: Organic Clathrates



Clathrate complex: A lattice of molecules of one type trapping molecules of another type.

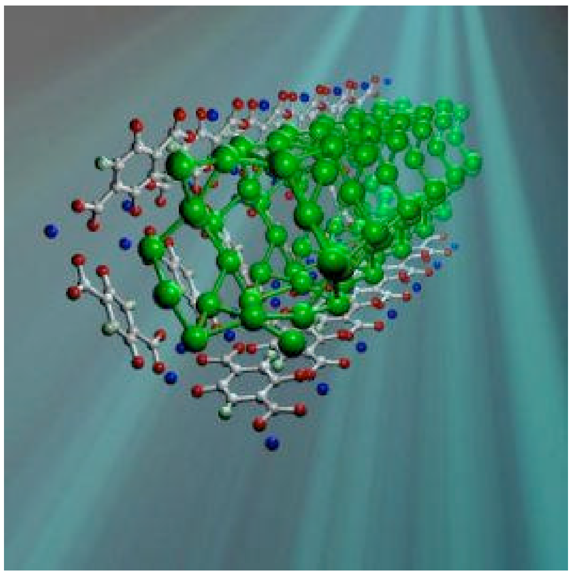


p-tert-butyl-calix[4]arene

P. K. Thallapally, G. O. Lloyd, T. B. Wirsiga, M. W. Bredenkamp, J. L. Atwood, and L. J. Barbour. Organic crystals absorb hydrogen gas under mild conditions. *The Royal Society of Chemistry: Chemical Communications*: (2005) 5272-5274.

Hydrogen: Storage

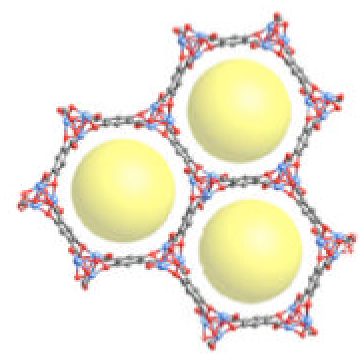
A few strategies: Metal-Organic Frameworks (MOFs)



MOF-74 (Zn_2(dhBDC))

Absorbs H_2 at a higher density than solid hydrogen!

(at 77 K.)

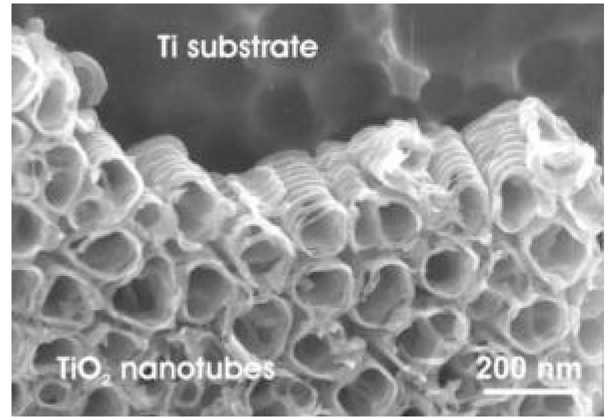


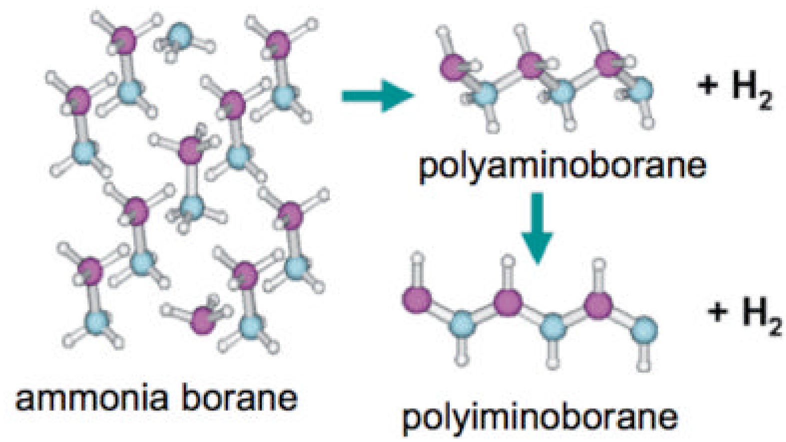
Citation: Y. Liu, H. Kabbour, C.M. Brown, D.A. Neumann and C.C. Ahn. Increasing the density of adsorbed hydrogen with coordinatively unsaturated metal centers in metal-organic frameworks. *Langmuir*, ASAP Article 10.1021/la703864a. Published March 27, 2008.

Hydrogen: Storage

A few strategies: Others

- Lithium nitrides, amides, and imides;
- TiO_2 nanotubes;
- Sodium alanate ($NaAlH_4$);
- Ammonia borane (NH_3BH_3);





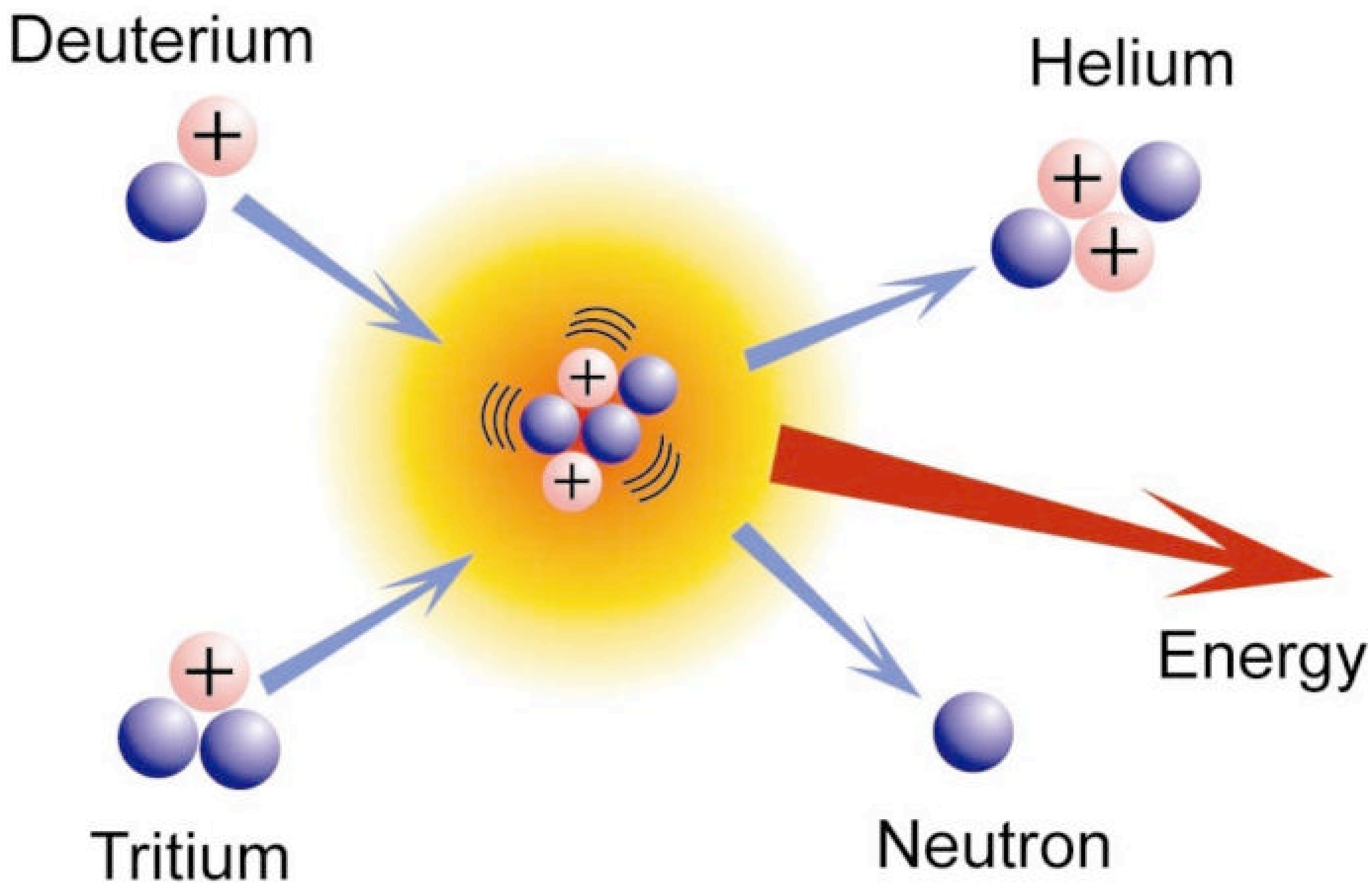
Muons have been helpful:

PRL **100**, 026401 (2008) PHYSICAL REVIEW LETTERS week ending 18 JANUARY 2008

Hydrogen Bonding in Sodium Alanate: A Muon Spin Rotation Study

R. Kadono,[1,2] K. Shimomura,[1] K. H. Satoh,[2] S. Takeshita,[1] A. Koda,[1,2] K. Nishiyama,[1] E. Akiba,[3] R. M. Ayabe,[4] M. Kuba,[4] and C. M. Jensen[4]

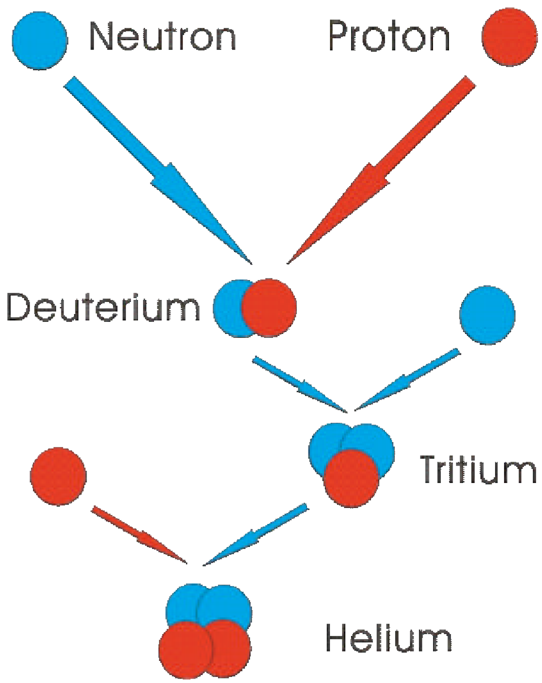
Hydrogen: Nuclear Fusion

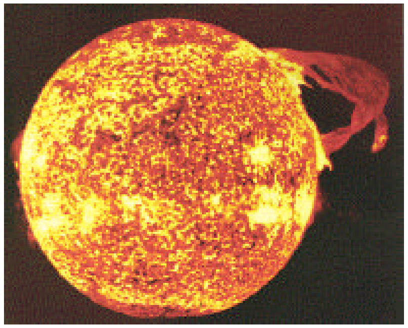


Nuclear Chemistry

Where do the elements come from?

Nucleosynthesis in stars proceeds mainly by *nuclear fusion*.





The main process is hydrogen fusion, which produces He.

Hydrogen fusion

A multi-step process

Occurs at 4×10^7 K

(1) Two protons fuse to form a deuteron (and a *positron*).

$$\boxed{{}^{1}_{1}H + {}^{1}_{1}H \rightarrow {}^{2}_{1}H + {}^{0}_{1}e}$$

(2) A deuteron and a proton fuse to form a ^{3}He nucleus.

$$\boxed{{}^{2}_{1}H + {}^{1}_{1}H \rightarrow {}^{3}_{2}He}$$

(3) Two ^{3}He nuclei combine to yield ^{4}He and $2 \times {}^{1}$H.

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

Note - deuteron formed in (2) is consumed in (3) - it is an *intermediate* in the overall process.

Combining all individual reactions:

$$2 \times \left(2\,{}^{1}_{1}H \rightarrow {}^{2}_{1}H + {}^{0}_{1}e \right)$$

$$+2 \times \left({}^{1}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He \right)$$

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

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

Cancelling terms…

$$\boxed{4\,{}^{1}_{1}H \rightarrow {}^{4}_{2}He + 2\,{}^{0}_{1}e}$$

The sun also contains many free electrons - these annihilate with the positrons produced in the H fusion reaction to produce energy in the form of γ-rays.

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

At higher temperatures (higher particle velocities), He-He fusion can be initiated.

$\boxed{2\text{x}10^{8}\ \text{K}}$

Core temperature of stars much larger than the sun

Q: Why are higher temperatures needed?

A: To overcome the (4xgreater) repulsion between nuclei with charge +2.

The energy produced in H fusion is offset by a loss of mass according to

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

$$4\,{}^{1}_{1}H \rightarrow {}^{4}_{2}He + 2\,{}^{0}_{1}e$$

m = 4x1.00728 amu

= 4.02912 amu

m = 4.00150 amu

Difference Δm = 0.02762 amu

$$\Delta E = \Delta mc^2 = 0.02762 \text{ amu} \times \frac{1.6604\times10^{-27} \text{ kg}}{1 \text{ amu}} \times 2.9979\times10^{8} \text{ m s}^{-1}$$

= 4.12×10^{-12} J (about 26 MeV)

(large compared to chemical energies)

Nuclear Binding Energies

When protons and neutrons combine to form a nucleus, the total mass of the nucleus is *less* than the sum of the individual particle masses by an amount called the **mass defect** (Δm).

The mass defect is related to the **binding energy** of the nucleus by the equation

$$\boxed{E = \left(\Delta m\right) c^2}$$

Example: Beryllium-8

Example: Beryllium-8

$^{8}_{4}Be$ ← Z=4

i.e. 4p + 4n

$$\left.\begin{array}{l}\text{masses: proton } 1.67263\text{x}10^{-27}\text{ kg} \\ \text{neutron } 1.67494\text{x}10^{-27}\text{ kg} \\ \text{electron } 9.1094\text{x}10^{-31}\text{ kg}\end{array}\right\} \quad 4p + 4n = 1.33903 \text{ x } 10^{-26}\text{ kg}$$

Be atom: ^{8}Be 8.0053 amu = 8 x 1.66054x10^{-27} kg = 1.32843x10^{-26} kg

Be nucleus: 8Be^{4+} 1.32843x10^{-26} kg - (4 x 9.1094x10^{-31} kg)

= 1.3281x10^{-26} kg

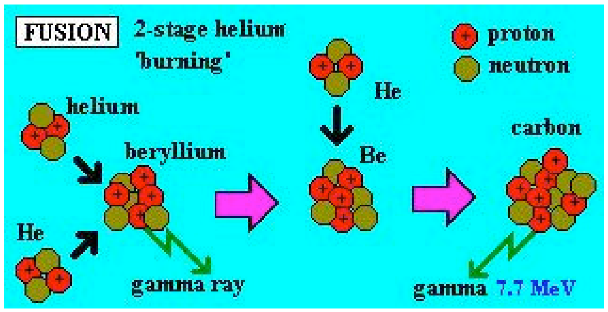
Mass defect: Δm = 1.3390 x 10^{-26} kg - 1.3277 x 10^{-26} kg

= 1.09 x 10^{-28} kg

Binding energy: E = (Δm)c^2 = 1.13 x 10^{-28} kg x (2.9979 x 10^{8} ms^{-1})^2

= 9.827 x 10^{-12} J

In giant stars, repeated fusion events lead to generation of successively heavier nuclei.



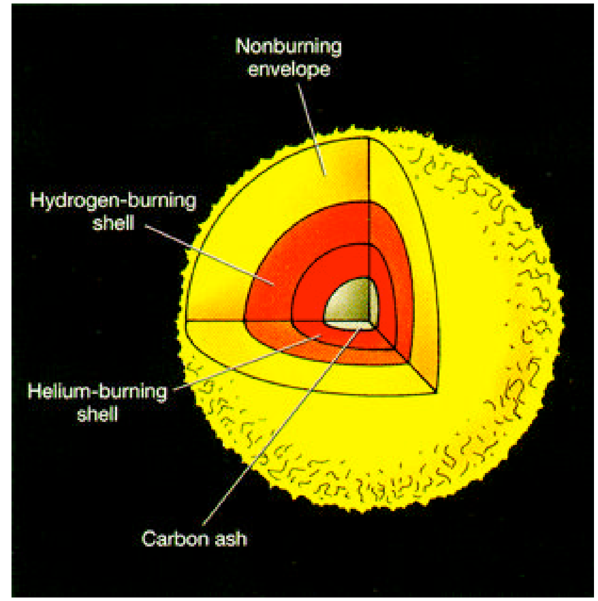
$$^{4}_{2}He + ^{4}_{2}He \rightarrow ^{8}_{4}Be$$

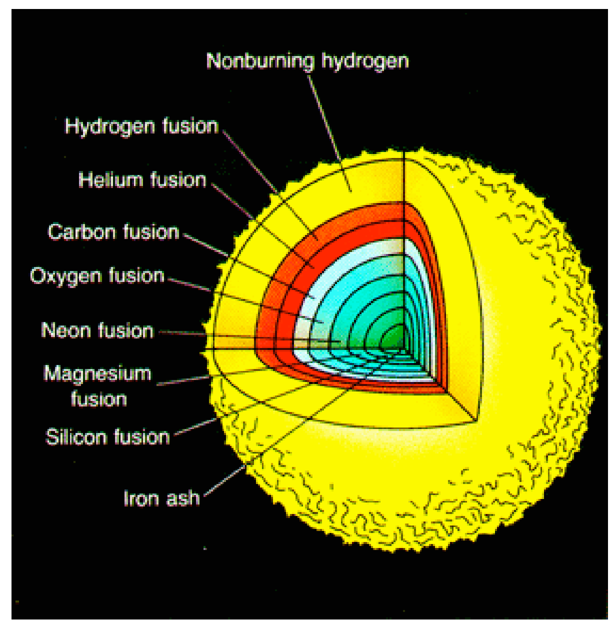
$$^{4}_{2}He + ^{8}_{4}Be \rightarrow ^{12}_{6}C$$

$$^{4}_{2}He + ^{12}_{6}C \rightarrow ^{16}_{8}O$$

As Z increases, more energy is required to initiate fusion.

Core temperatures up to ~3x10^{9} K can produce nuclei up to Z~26.



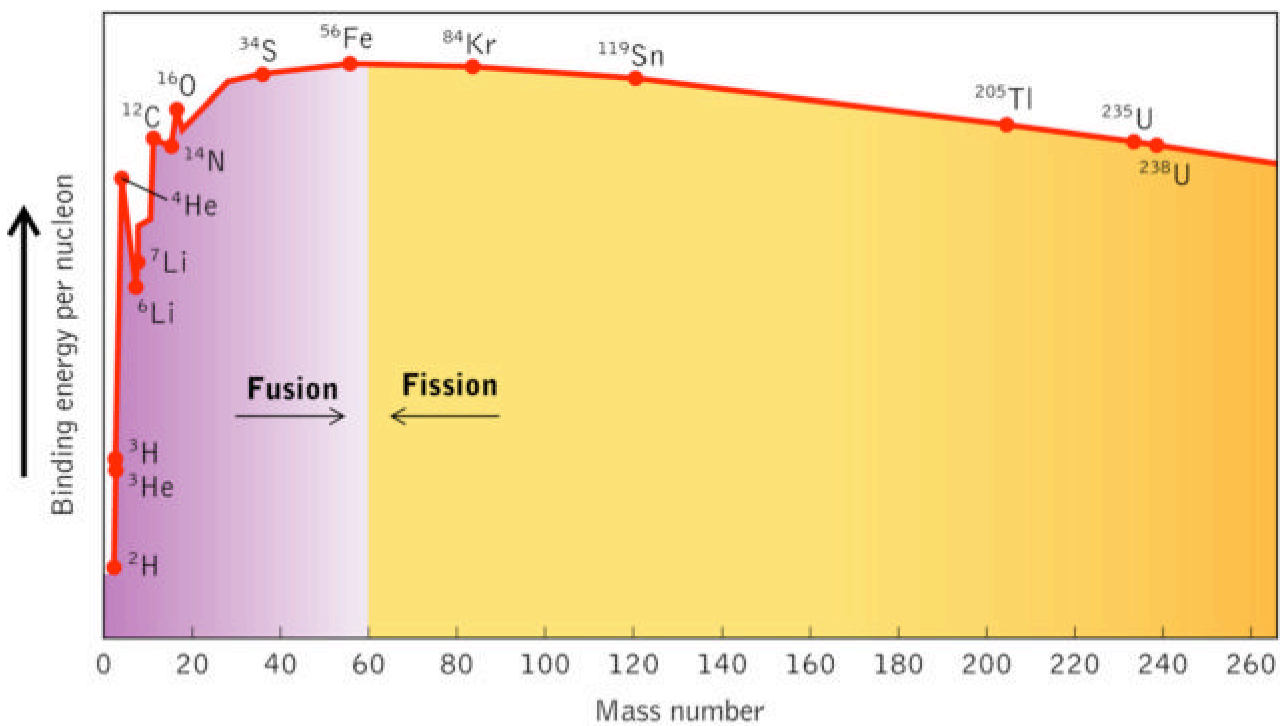


Binding energy per nucleon

A useful indicator of stability

Example: ^{8}Be B.E. = 9.83×10^{-12} J

Divide by 8 nucleons… B.E. per nucleon = 1.228×10^{-12} J



B.E. per nucleon goes through a maximum at Z = 26 (^{56}Fe).

Processes resulting in a release of energy are usually more probable - fusion in stars is only useful up to Z~26.

Hydrogen: Nuclear Fusion - Fusion for Energy

To be useful for energy generation, a fusion reaction must:

•**be exothermic**: limits the reactants to $Z < 26$, and makes helium-4 and helium-3 the most common products;

•**involve low *Z* nuclei**: to minimize the coulomb repulsion barrier;

•**have (only) two reactants**: three body collisions are improbable at low density;

•**have two or more products**: to allow conservation of energy and momentum in a straightforward fashion;

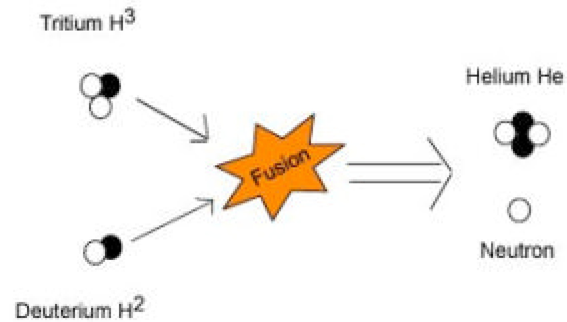
•**conserve both protons and neutrons**: cross sections for weak interaction processes are too small.

Hydrogen: Nuclear Fusion - Fusion for Energy

Main fusion type under exploration is deuterium-tritium fusion:

d-d
$$\begin{cases} {}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He + {}^{1}_{0}n & \Delta E=-3.27\ \text{MeV} \\ {}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{1}T + {}^{1}_{1}H & \Delta E=-4.03\ \text{MeV} \end{cases}$$

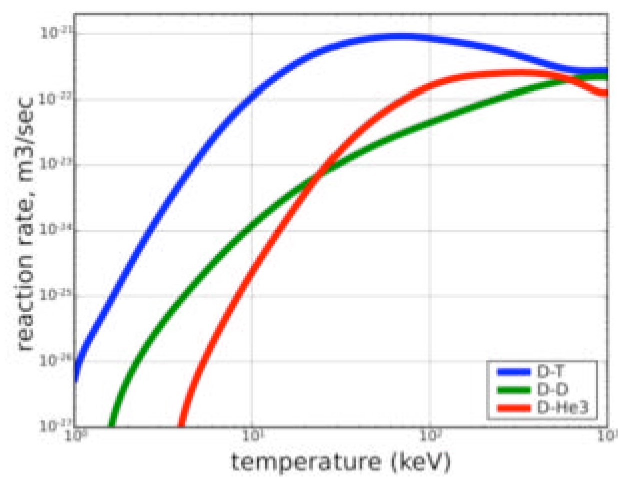
d-t
$$\left\{ {}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n \right. \qquad \Delta E=-17.59\ \text{MeV}$$



Energy requirement:

Can be triggered below 10 keV

Peak rate at 66 keV (7.3 x 10^8 K)



Hydrogen: Nuclear Fusion - Fusion for Energy

"Deuterium cycle"

$${}_{1}^{2}H + {}_{1}^{2}H \rightarrow {}_{2}^{3}He + {}_{0}^{1}n$$ ΔE=-3.37 MeV

$${}_{1}^{2}H + {}_{1}^{2}H \rightarrow {}_{1}^{3}T + {}_{1}^{1}H$$ ΔE=-4.0 MeV

$${}_{1}^{2}H + {}_{1}^{3}H \rightarrow {}_{2}^{4}He + {}_{0}^{1}n$$ ΔE=-17.6 MeV

$${}_{1}^{2}H + {}_{2}^{3}He \rightarrow {}_{2}^{4}He + {}_{1}^{1}H$$ ΔE=-18.3 MeV

Overall:

$$6\,{}_{1}^{2}H \rightarrow 2\,{}_{2}^{4}He + 2\,{}_{1}^{1}H + 2\,{}_{0}^{1}n$$ ΔE=-43.2 MeV

Hydrogen: Nuclear Fusion - Tokamaks

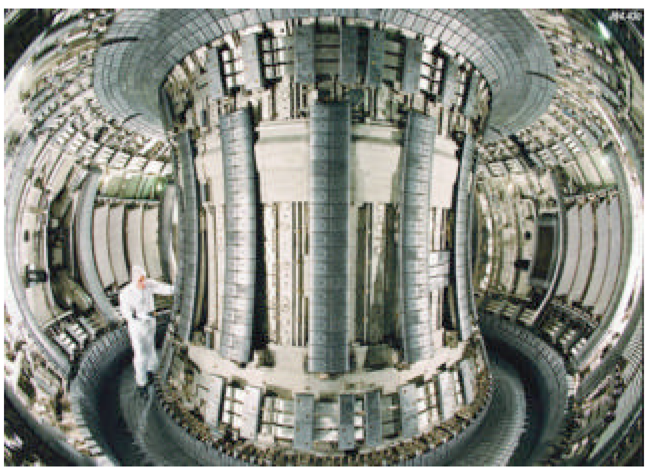
Fusion reactor containing toroidally confined plasma

d-t plasma heated to 10 keV (about 10^8 K)

d-t fusion yields about 17.6 MeV per event

"neutronicity" (fraction of E released in form of neutrons) of d-t fusion about 0.8

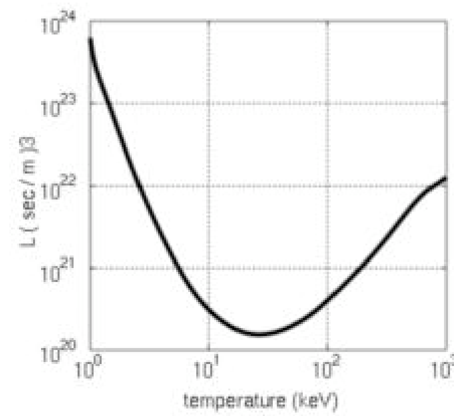
"Lawson criterion" - fusion heating must exceed power loss



JET project, Culham, UK

$$n_e \tau_E \geq L \equiv \frac{12}{E_{ch}} \frac{k_B T}{\langle \sigma v \rangle}$$

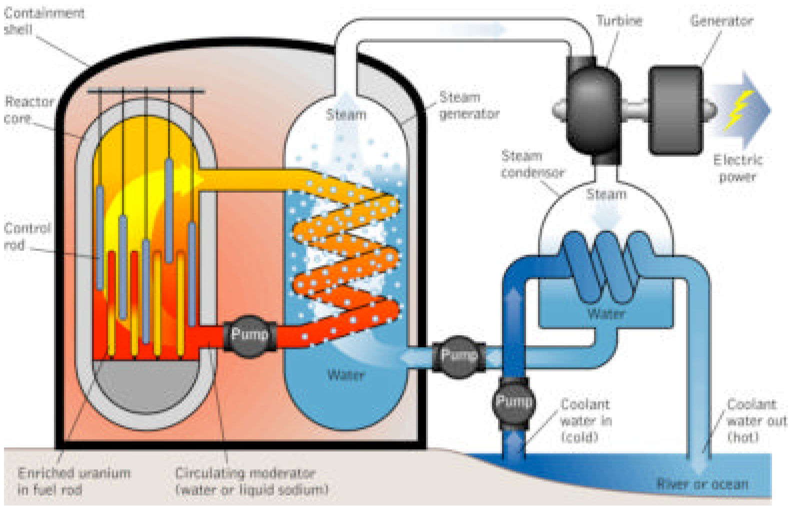
E_{ch} = energy of charged products (because n do not contribute to heating) = 3.5 MeV for d-t

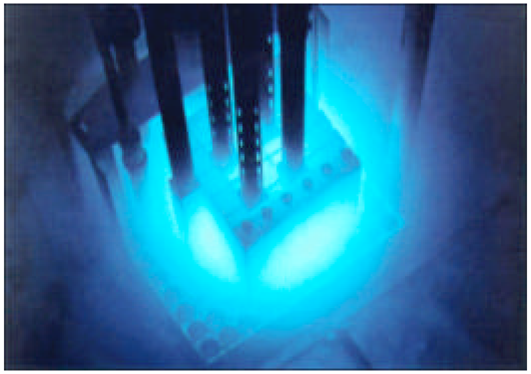


Hydrogen: Nuclear Fusion

Q: Where does the tritium come from?

A: Nuclear fission reactors.





Hydrogen: Nuclear Fusion

Tritium production

1. Atmospheric - from cosmic rays

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{12}_{6}C + ^{3}_{1}T$$

E > 4 MeV

Not a significant source of useful tritium.

2. In fission reactors

e.g. Neutron activation ("breeding")) of lithium-6 (exothermic, releasing 4.8 MeV)

$$^{6}_{3}Li + ^{1}_{0}n \longrightarrow \underset{2.05\ \text{MeV}}{^{4}_{2}He} + \underset{2.75\ \text{MeV}}{^{3}_{1}T}$$

^{6}Li natural abundance 7.5%
Exothermic by 4.8 MeV

$$^{7}_{3}Li + ^{1}_{0}n \longrightarrow ^{4}_{2}He + ^{3}_{1}T + ^{1}_{0}n$$

^{7}Li natural abundance 92.5%
Endothermic by 2.466 MeV
Requires high energy n

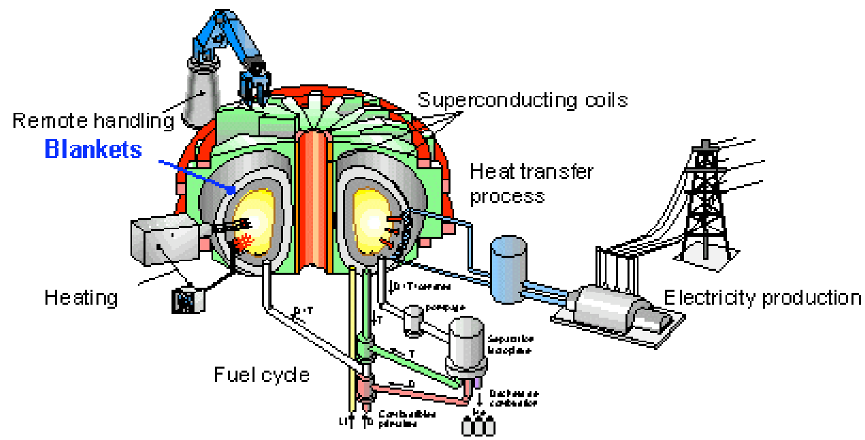
As fission reactors depend on a supply of uranium (or perhaps thorium), and stocks are limited, fusion may not be the panacea it is sometimes thought to be.

Hydrogen: Nuclear Fusion

Tritium production

It may be possible to produce tritium within the tokamak itself by the use of *tritium breeding blankets* just beyond the first reactor wall.

$$D + T \rightarrow {}^{4}He + n + \text{energy}$$
$$Li + n \rightarrow {}^{4}He + T + \text{energy}$$
$$D + Li \rightarrow 2\,{}^{4}He + \text{energy}$$

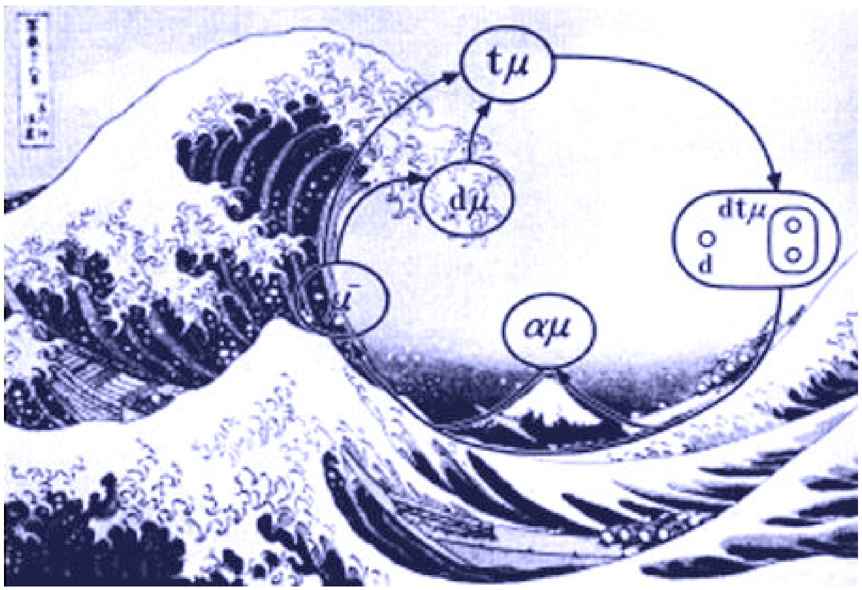


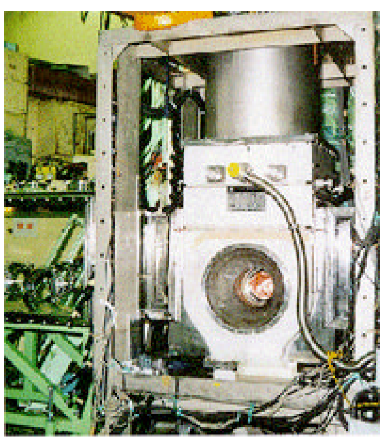
These can be liquid (e.g. LiPb) or solid (e.g. Li_4SiO_4), and serve the dual purpose of tritium breeding and protection of the magnets and vacuum vessel from neutron radiation.

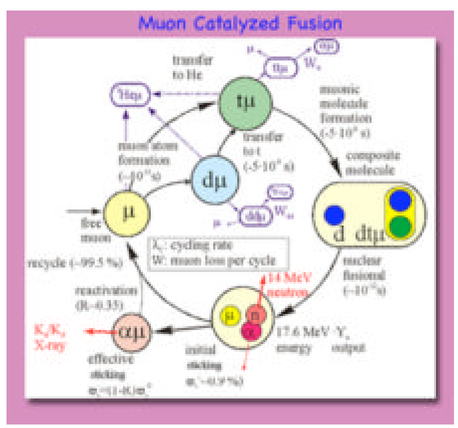
Other fusion options: proton-boron (aneutronic fusion) - requires high temperature (600 keV) and plasma density

Hydrogen: Nuclear Fusion

Muon-catalyzed fusion ("the real cold fusion")







•First suggested by Sakharov and Frank in 1947;

•Relies on the capture of a *negative muon* into the 1s orbit of deuterium or tritium; the Bohr radius is smaller than that of H by a factor of 207;

•The nucleus now "sees" a charge of Z=0, i.e. the Coulomb barrier is overcome;

•A single muon can catalyze around 200 d-t fusion events;

•This is still nowhere near energy breakeven (or $ breakeven) due to "α-sticking" and other issues;

•Further technical refinements are possible based on new physics.

Bohr radius: $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c\alpha}$