Alternatives to Petroleum

‘Synthetic’ gasoline: Fischer-Tropsch (or C_1) Chemistry

$$n\,CO + (2n+1)\,H_2 \xrightarrow{Fe/Co} C_nH_{(2n+2)} + n\,H_2O$$

Other reactions relevant to this chemistry:

$$CO + H_2O \xrightarrow{Fe_2O_3\ /\ CuO} CO_2 + H_2$$ **Water-gas shift reaction**

Methane feed

$$CH_4 + H_2O \xrightarrow{Ni} CO + 3\,H_2$$ **Steam reforming**

syngas

Coal feed

$$C + H_2O \xrightarrow{\text{limited } O_2} CO + H_2$$ **Coal gasification**

Chemistry in Context 6th Edition, ACS, McGraw-Hill

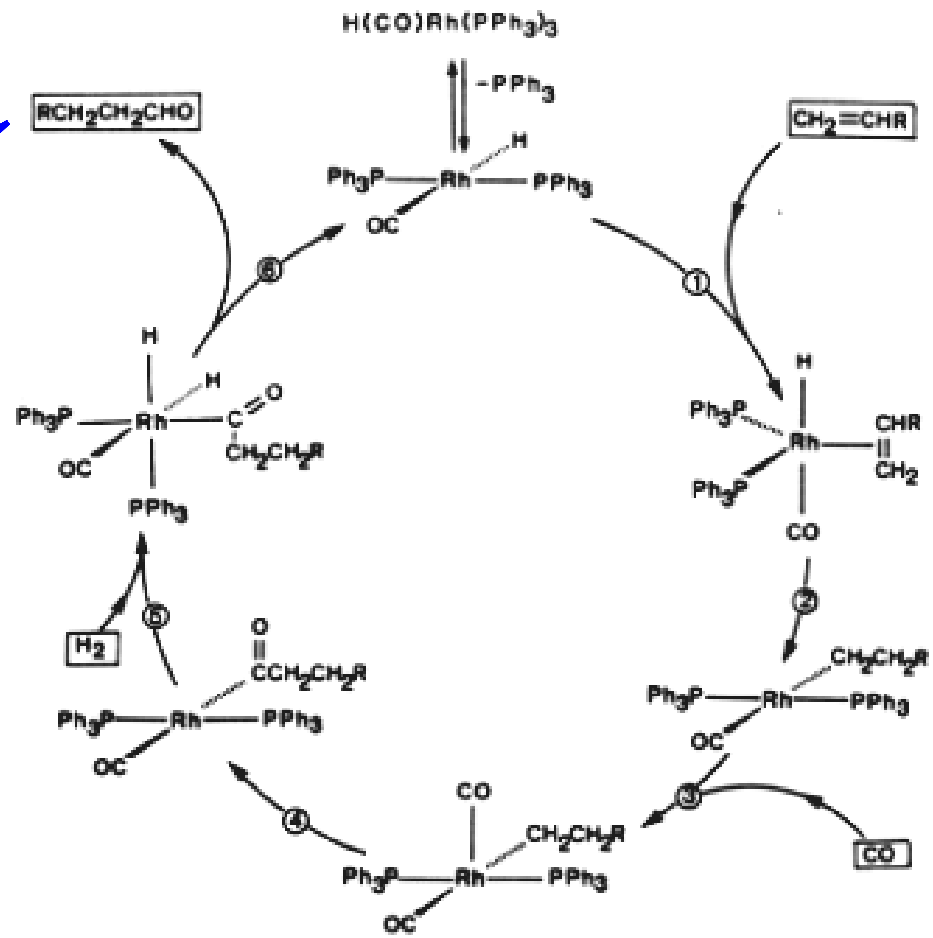
Syngas: A versatile starting material for synthesis

Hydroformylation: converting alkenes to functionalized products

Alcohols

Acids

Detergents



Union Carbide hydroformylation process

Sasol: played an important role in 'synthetic' gasoline development

S. Africa: limited oil but abundant coal reserves

From the Sasol corporate website: www.sasol.com

GTL = gas to liquid

Oil Shale: rebirth of US petroleum production

Oil shale: actually organic matter known as **kerogen** that produces a **low grade crude oil when heated to 450-500 C**. *(In contrast, '**oil-bearing shales'** actually DO contain oil)*

Largest oil shale deposit in the world:

Eocene Green River Formation of Colorado, Utah, and Wyoming is estimated to contain about **800 billion barrels of oil**

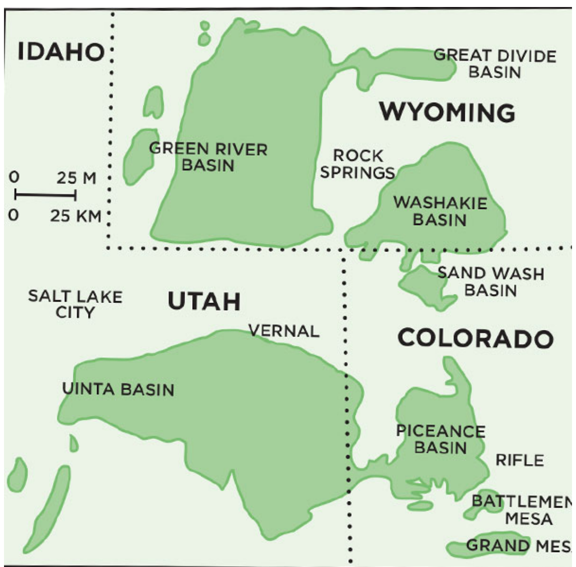
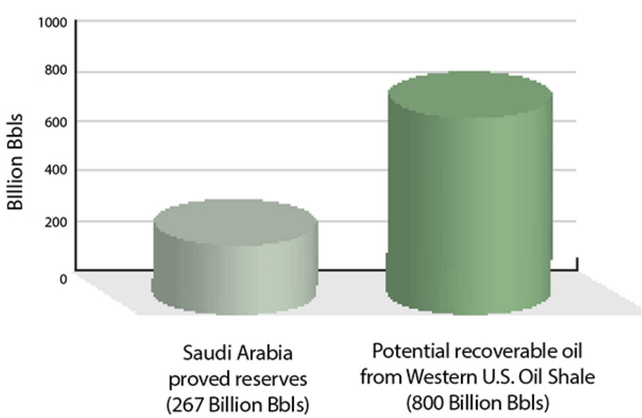
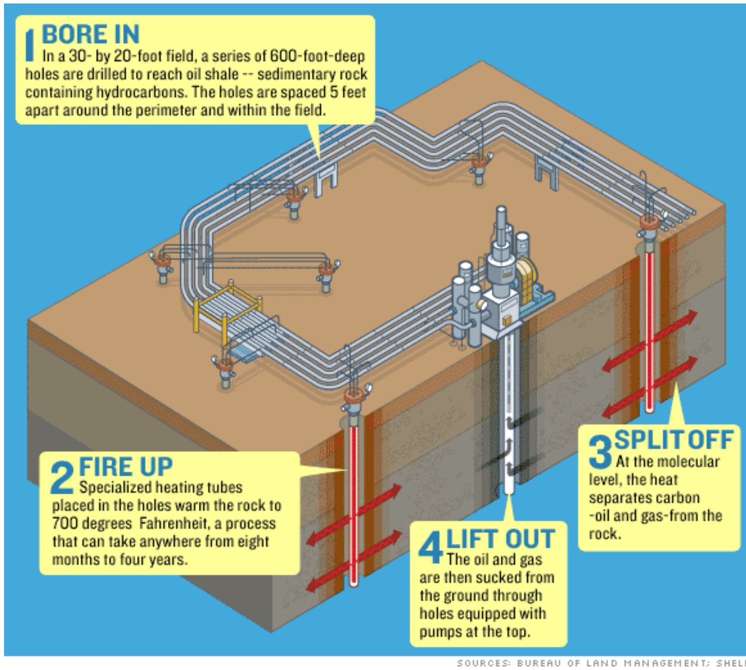


Figure 2. Oil reserves of Saudi Arabia vs. Western U.S. oil shale potential.



From: API – US Oil Shale Factsheet

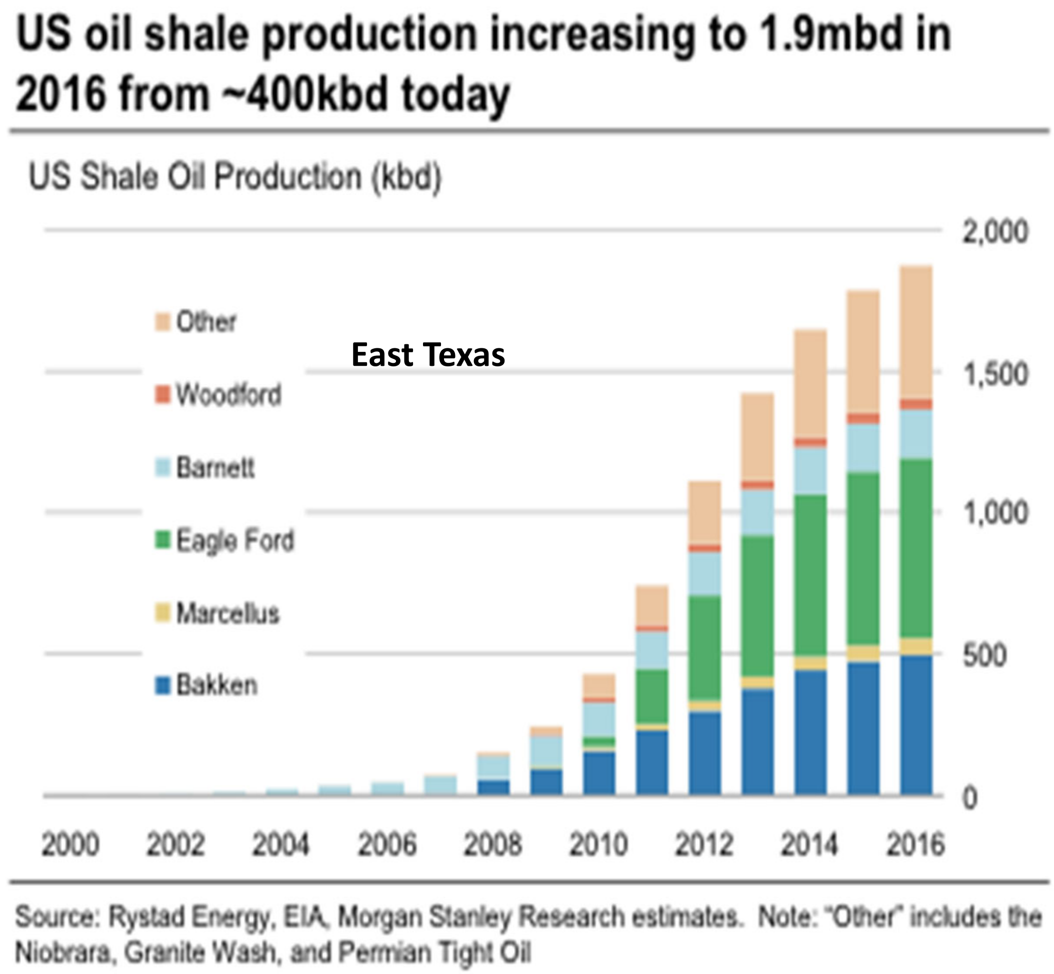


from Permanent Culture Now *from www.evsroll.com*

Shale Oil: fracking R Us

This IS actually oil trapped in shale formations: many large deposits in US and Russia

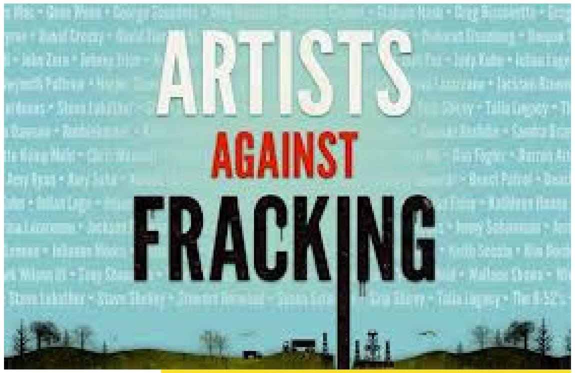
Technique based on extraction by **fracking:** ***hydraulic fracturing of the surrounding rock***



Fracking fluid:
90% water
9.5% sand/ceramic
and
0.5% chemical additives that can include:
HCl, gums, ethylene glycol, isopropanol, methanol or gelling agents

Fracking concerns?

- Consumes large quantities of water
  - True, but water is not ‘lost’ in the process
- Fracking fluid generally not recovered so environmental contamination
  - True, but most components are water and sand plus organic gums
- Groundwater contamination
  - Aquifer depths are far closer to the surface than frack zone so less likely that contamination will occur
- Release of trapped gases to air
  - Volume levels insignificant
- Increased seismic activity: micro-quakes
  - True but is this good or bad?



Video (from American Petroleum Institute):

https://www.api.org/oil-and-natural-gas/wells-to-consumer/exploration-and-production/hydraulic-fracturing/fracking-safe-oil-gas-extraction

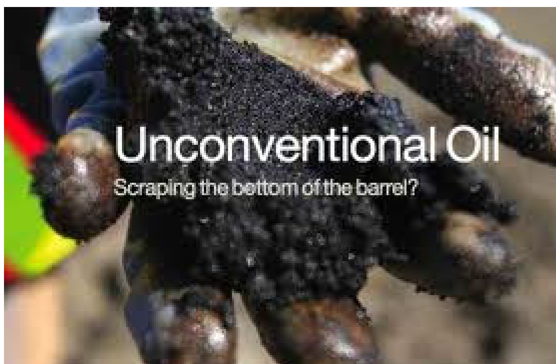
Tar Sands: Oil Recovery

Athabasca tar sands deposits are largest in the world and close to surface

Bitumen (tarry oil and sand) → **Hot water for sand separation** → **Extraction: naphtha used to further separate oil from sand/water**

↓ **Transport as 'dilbit': pipeline**

Upgrader: catalytic cracking and reforming



Tar Sands: Issues

- **Dirty process**
- **Very energy intensive**
- **Uses a huge amount of water**
- **Strip mining defaces environment**
- **Located far from ports and refineries: pipelines (Keystone XL, Northern Gateway)**

from the Huffington Post

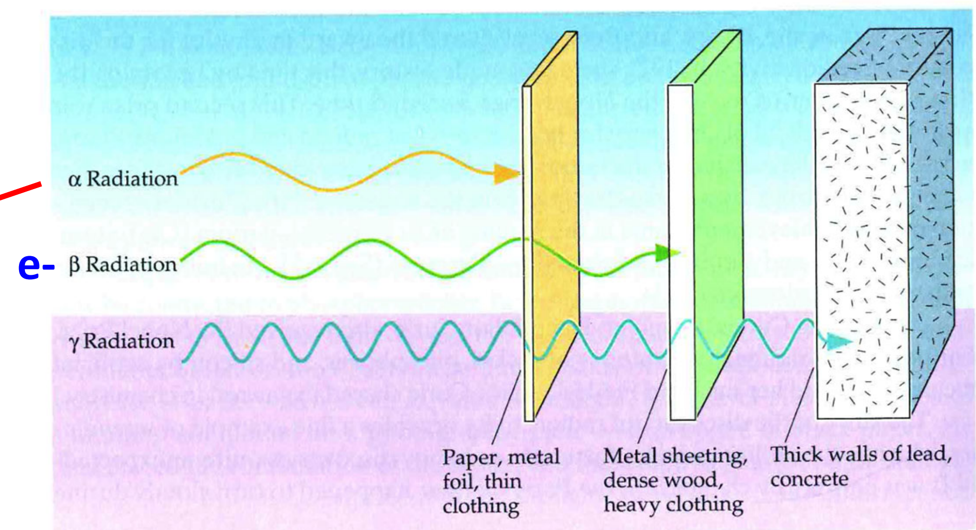
Nuclear Energy

Notation => mass number, atomic number and charge

- 39 Mass number
- 19 Atomic number
- 1+ Charge

Protium	$^{1}_{1}H$
Deuterium	$^{2}_{1}H$
Tritium	$^{3}_{1}H$
Helium atom	$^{4}_{2}He$
Helium nucleus	$^{4}_{2}He^{2+}$
Uranium–235	$^{235}_{92}U$
Potassium atom	$^{39}_{19}K$
Potassium cation	$^{39}_{19}K^{1+}$

Radioactive decay



The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Nuclear reactions

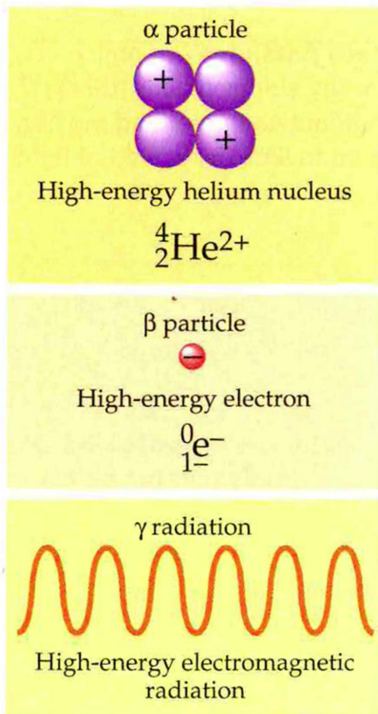
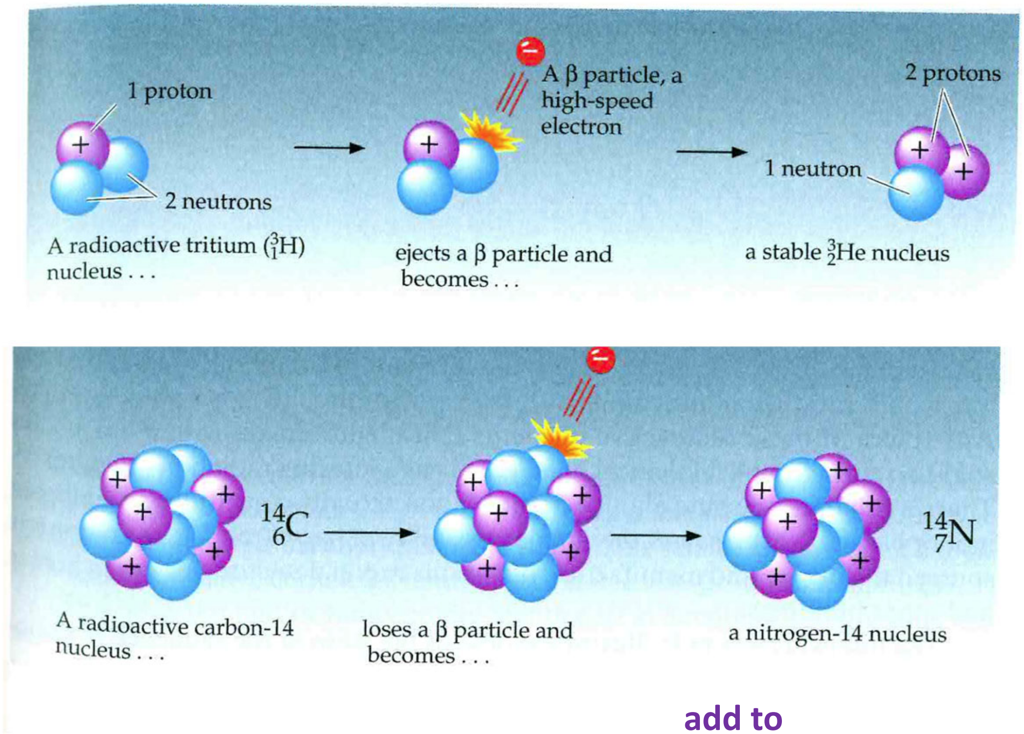


Figure 4.4 The components of α rays, β rays, and γ rays.

Beta decay: neutron converts to a proton and an electron (ejected):

tritium $^{3}_{1}H \longrightarrow ^{3}_{2}He + ^{0}_{1-}\beta$



Alpha emission: ejection of a helium nucleus

add to balance

$^{238}_{92}U \longrightarrow ^{234}_{90}Th + ^{4}_{2}He$

The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Nuclear reactions (*cont*)

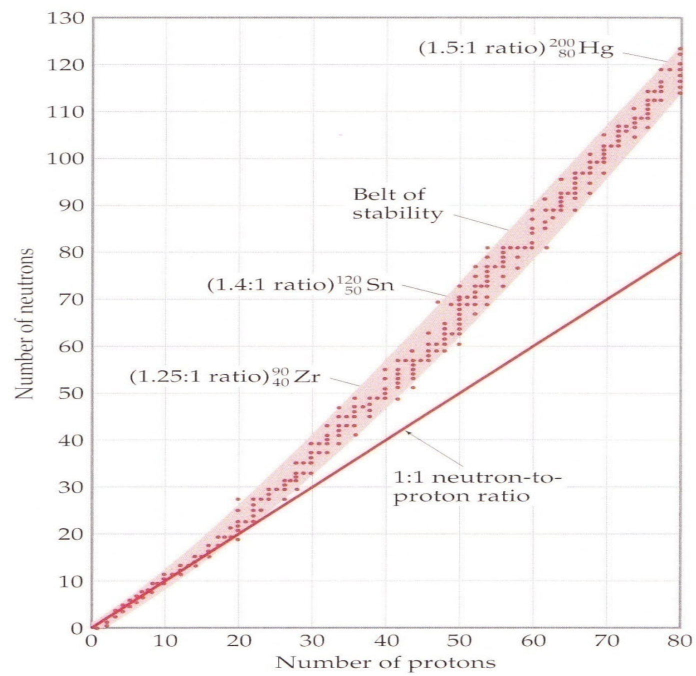
Things that happen to protons…

positron emission (β+): $^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{+1}e$ $^{18}_{9}F \rightarrow {}^{18}_{8}O + {}^{0}_{+1}e$

electron capture (EC): $^{1}_{1}p + {}^{0}_{-1}e \rightarrow {}^{1}_{0}n$ $^{125}_{53}I + {}^{0}_{-1}e \rightarrow {}^{125}_{52}Te$

And also note: $^{0}_{+1}e + {}^{0}_{-1}e \rightarrow 2\ {}^{0}_{0}\gamma$

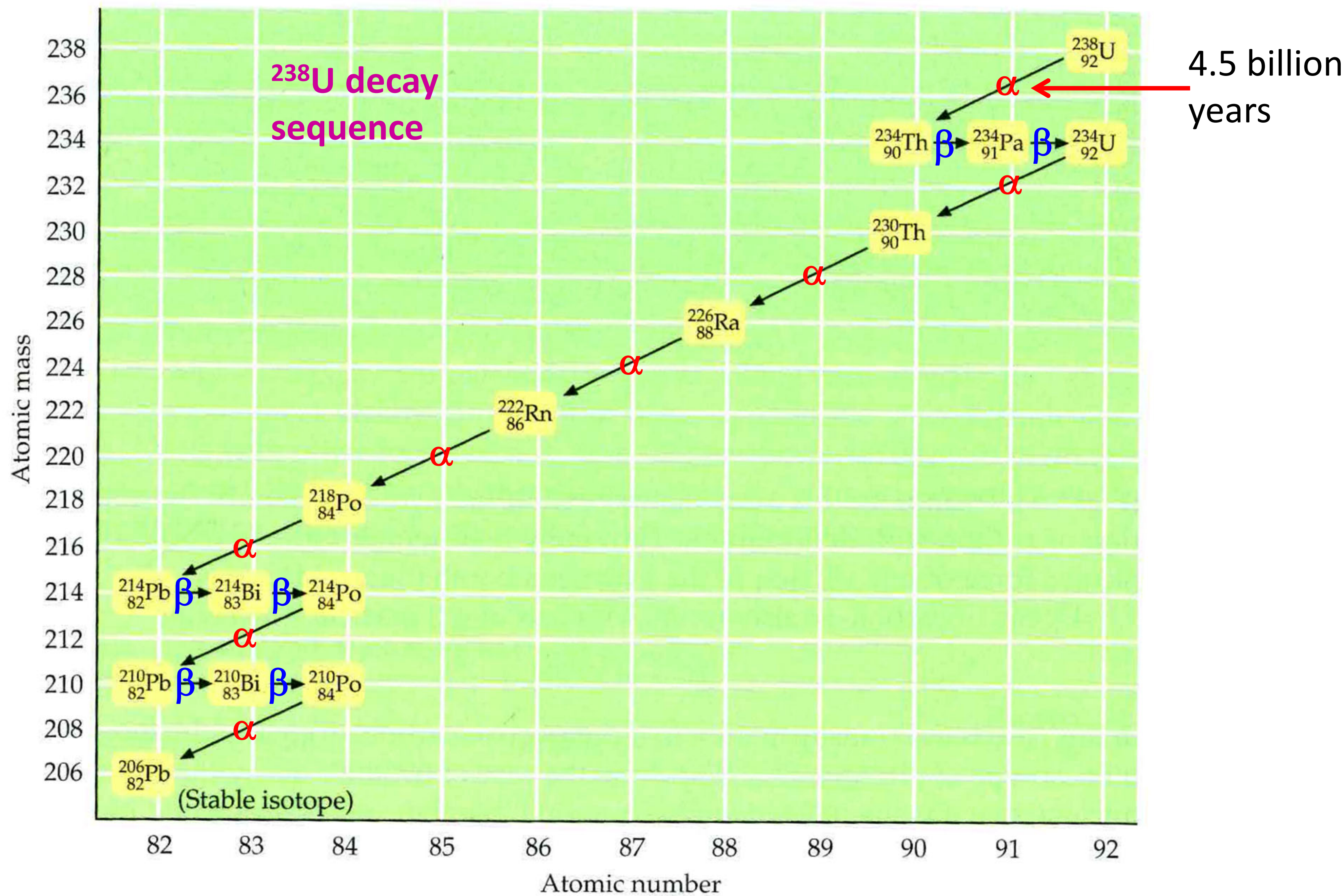
positrons and electrons annihilate one another
producing two gamma rays
(that travel in exactly opposite directions)



Belt of stability: only certain ratios of neutrons and protons are stable

from Westlake, OH school resources website

Decay occurs through many steps until a stable atom is formed



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Why is there energy released – nuclear fission

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{140}_{56}Ba + ^{93}_{36}Kr + 3\,^{1}_{0}n$$ + a LOT of heat

1 gets you 3

$E = mc^2$

$M_{U235} + M_n$ = 236.053 amu

$M_{Ba140} + M_{Kr93} + 3M_n$ = 235.869 amu *so-called 'mass defect'*

Mass lost = 0.184 amu or 0.078% of U235 mass is ***converted to energy***

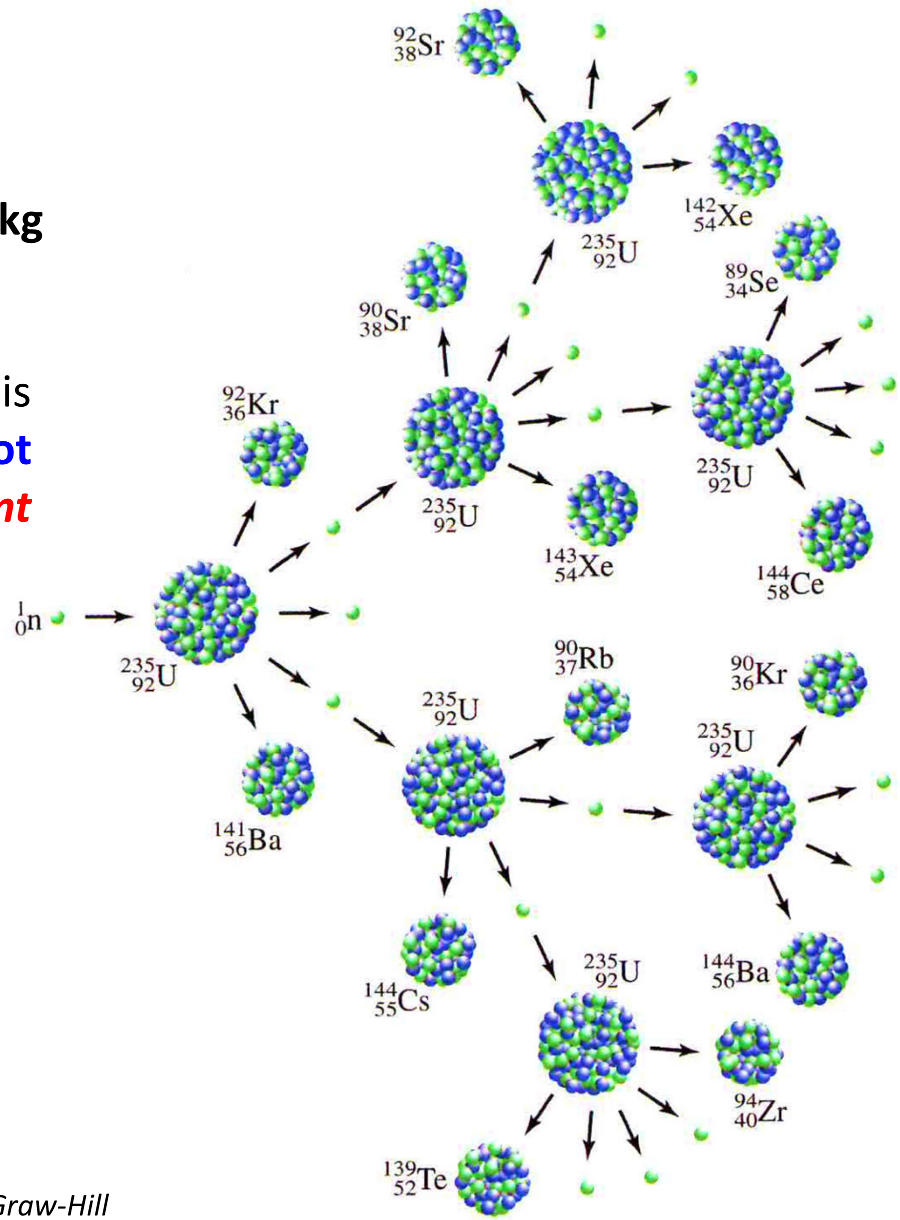
1kg of U235 = 9.0 x 10^{10} kJ equivalent to 33,000 tons of TNT

The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Chain reaction

^{235}U critical mass is *ca.* 4 kg

Most U is **^{238}U** which is **radioactive but not fissionable** so ***enrichment*** is required



Chemistry in Context 6th Edition, ACS, McGraw-Hill

Enrichment in ^{235}U required for:

- Reactors: 3-5%
- Bombs: 90%

$$UF_4(g) + F_2(g) \longrightarrow UF_6(g)$$

- **Membrane diffusion**
- **Centrifugation**

Plutonium production and breeder reactors

$$^{1}_{0}n + {}^{238}_{92}U \longrightarrow [{}^{239}_{92}U] \longrightarrow {}^{239}_{93}Np + {}^{0}_{-1}e$$

$$^{239}_{93}Np \longrightarrow {}^{239}_{94}Pu + {}^{0}_{-1}e$$

^{239}Pu is fissile:
Core of ^{239}Pu surrounded by ^{238}U gives ***in situ creation (breeding)*** of ^{239}Pu from non-fissile ^{238}U

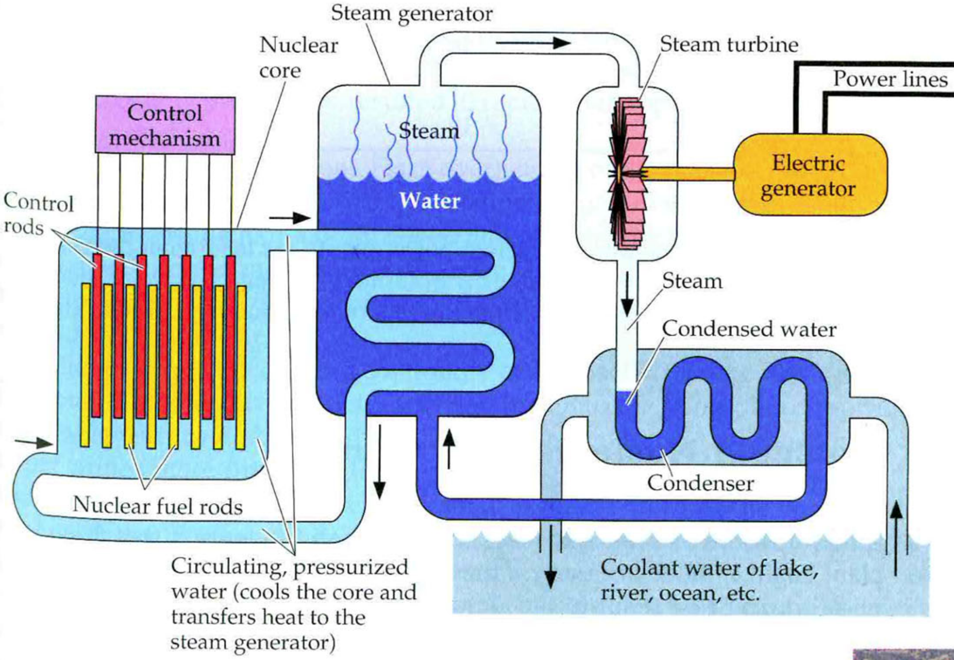
Concerns about breeder reactors:

- plutonium is low melting so cooling is critical (core meltdown is a major risk)
- ^{239}Pu has a long half life (25,000y) and is v. toxic
- reactor grade ^{239}Pu easily used in bombs

'Fat Man' ^{239}Pu bomb dropped on Nagasaki, Japan

from Chemistry in Context 6th Edition, ACS, McGraw-Hill and Chemistry for Changing Times, 9th Ed., Prentice-Hall

Nuclear Reactors

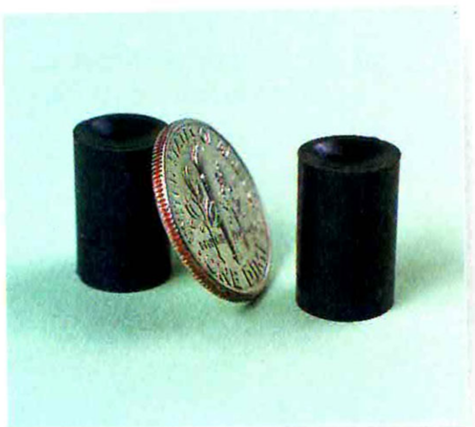


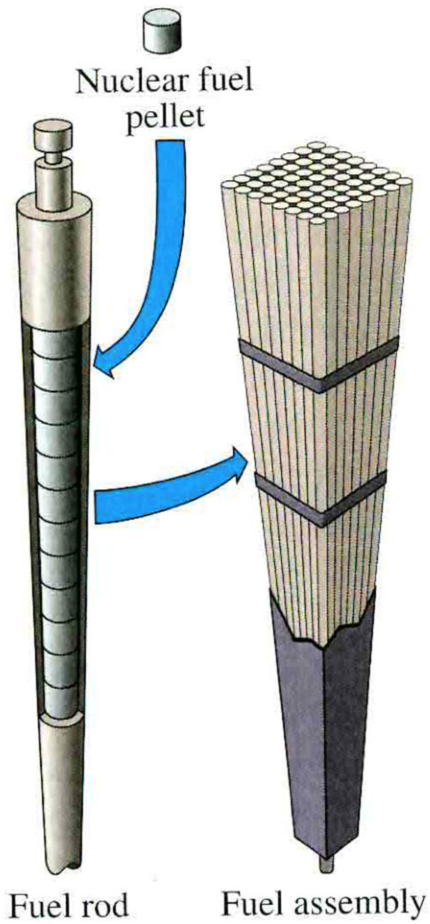
Pressurized water reactor

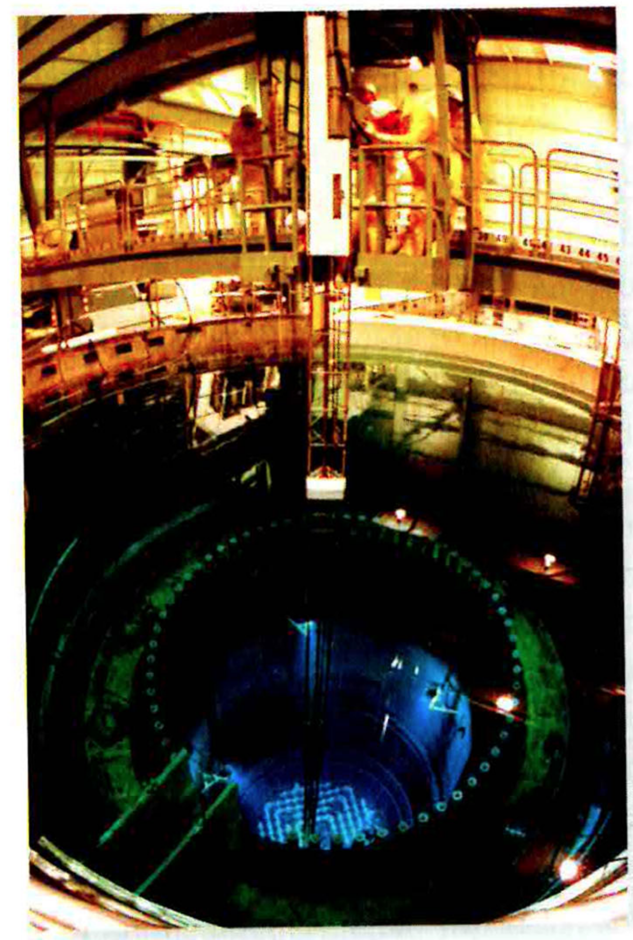
The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Chemistry in Context 6th Edition, ACS, McGraw-Hill

Fuel pellets and rods



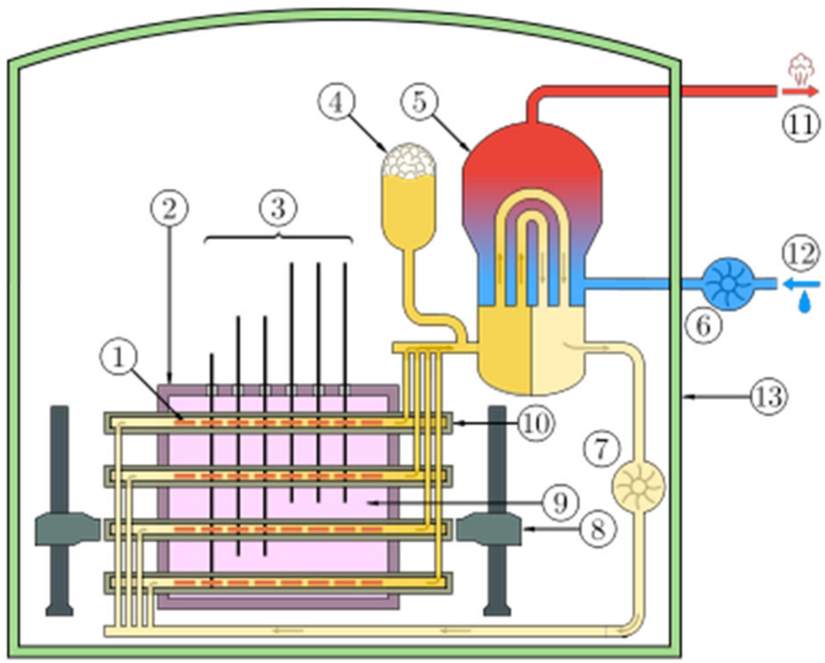




Chemistry in Context 6th Edition, ACS, McGraw-Hill

CANDU Reactor

D_2O as moderator: low neutron capture cross section allows use of natural uranium fuel

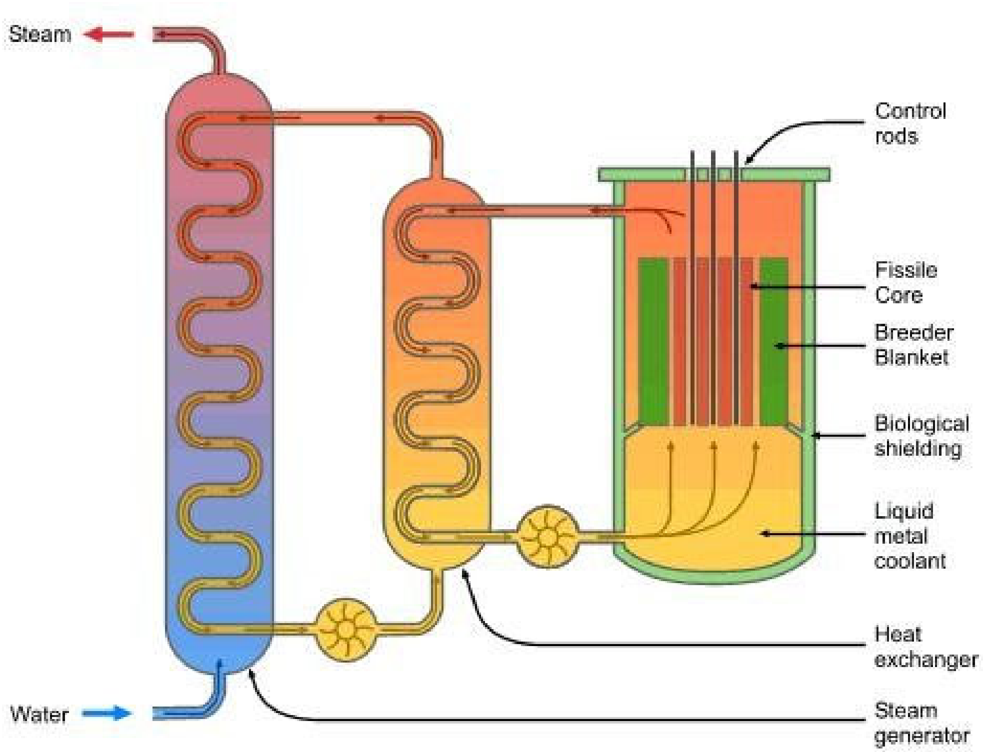


wikipedia

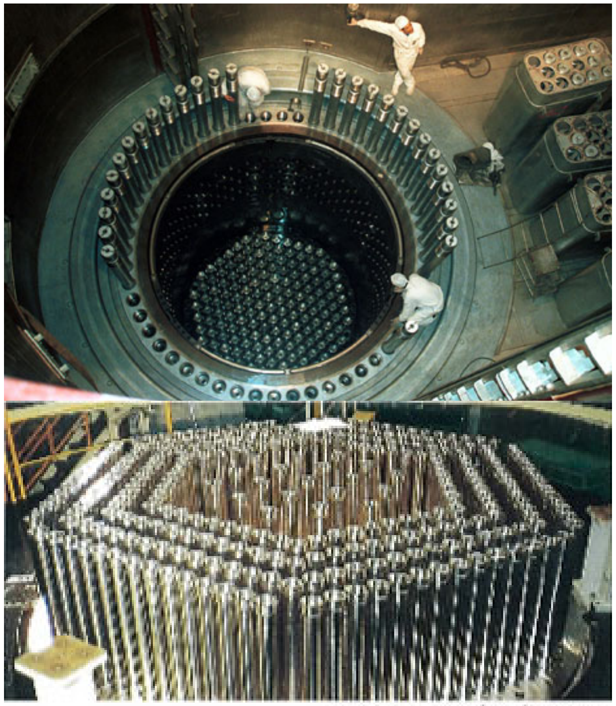
Pickering – 8 units of 540 MW each

http://www.nucleartourist.com/world/canada.htm

Breeder Reactors: generate their own fuel *(sort of…)*



From: universe-review.ca



Core internals of Monju
—Core support plate and connecting pipes—

Monju: liquid Na cooled breeder reactor:
decommissioned after liquid Na leak and fire

From: Mitsubishi Heavy Industries

Monju

Risks of nuclear energy

Risk is of **explosions (non-nuclear)** and **escape of radioactive materials**

Three Mile Island – Harrisburg, PA, Mar ‘79
partial meltdown, stuck control valve
From: www.atomicarchive.com

Chernobyl – Ukraine, Apr ‘86
total meltdown, power surge, steam explosion
31 direct fatalities, long term effects on hundreds of thousands

For some other remarkable photos like this see Timm Seuss’ article in businessinsider: http://www.businessinsider.com/chernobyl-disaster-photos-timm-suess-2012-4?op=1

Fukushima – Japan, Mar ‘11
partial meltdown of multiple reactors,
power failure caused by tsunami,
Hydrogen and pressure explosions released gases
(from: http://www.sciencemediacentre.co.nz)

Sources:

Eubanks, L.P., Middlecamp, C.H. Hetzel, C.E. and Keller, S.W. “Chemistry in Context: Applying Chemistry to Society” 6th edition (2009), A Project of the American Chemical Society, McGraw Hill Higher Education

Snyder, C.H. “The Extraordinary Chemistry of Ordinary Things” (2003), Wiley.

For examples of the process used in the tar sands see: www.syncrude.ca web site

The Economist: see the January 20, 2011 article, ‘Muck and Brass’ at: http://www.economist.com/node/17959688

Waldron, K. “The Chemistry of Everything” (2009), Prentice-Hall.

Hill, J.W., Kolb, D.K. “Chemistry for Changing Times”, 9th Ed. (2001), Prentice-Hall.