Chapter 23 - Nuclear Chemistry

Chemical reactions: reactions in which elements maintain their identity and interact only through electronic changes (changes in the number of outer electrons etc).

Nuclear reactions involve
(1) changes in the composition of nuclei
(2) release (usually) of tremendous amounts of energy
(3) transmutation of elements ($element_1 \rightarrow element_2$)

Recall the characteristics of the nucleus of an atom; the nucleus makes up only a very small part of the total volume - but it contains most of the mass of an atom hence it is very dense. (Rutherford's expt - Ch 5)
It is known now that there are many subatomic particles in the nucleus - not just protons and neutrons - that help overcome the coulombic proton-proton repulsion and bind the nuclear particles (nucleons) together.

Nuclear reactions are the result of the instability of the nucleus of an atom. The more unstable the nucleus is, the faster it will decay or decompose and release radiation (radioactivity).

Nuclear stability can be related to the ratio of the number of neutrons to the number of protons (n/p) in the nucleus. The most stable nuclides (the set of all the isotopes of all the elements) are those with an even number of both neutrons and protons.

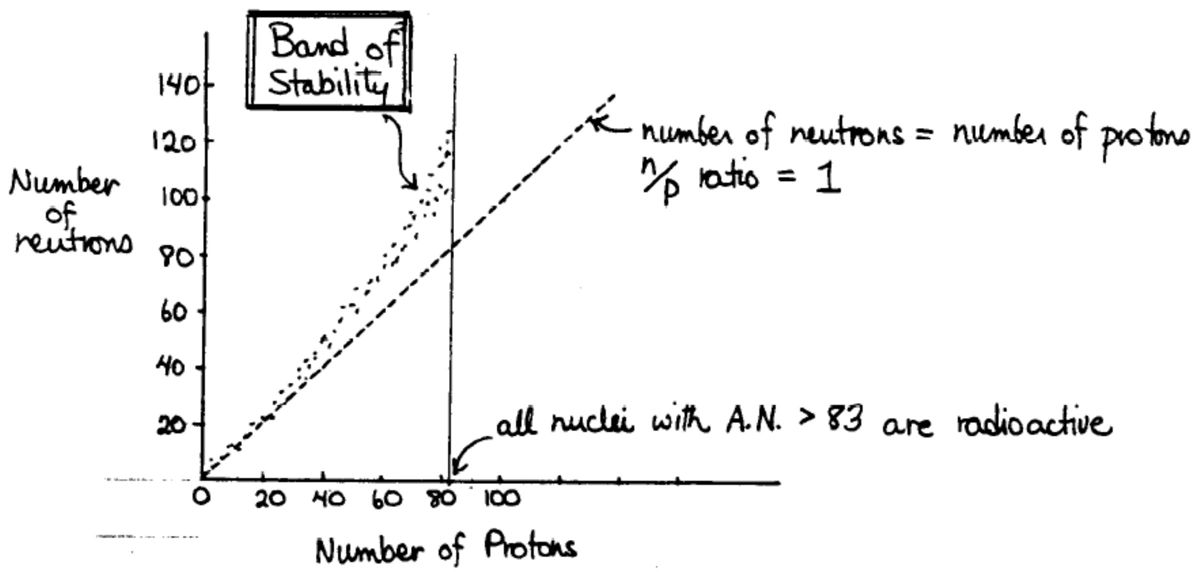
Consider all the naturally occurring stable nuclides

protons	even	even	odd	odd
neutrons	even	odd	even	odd
number of nuclides	153	52	50	5

Moreover, there are magic numbers which appear to impart exceptional stability. Nuclides with a number of protons OR a number of neutrons OR a sum of these two equal to 2, 8, 20, 28, 50, 82, 126 have unusual stability, eg.

	# p	# n	# p + # n
$^{4}_{2}He$	2	2	4
$^{16}_{8}O$	8	8	16
$^{42}_{20}Ca$	20	22	42
$^{88}_{38}Sr$	38	50	88
$^{208}_{82}Pb$	82	126	208

Figure 23.3 p.1117 shows a plot of the number of neutrons (N) versus number of protons (Z = atomic number) for the stable nuclides



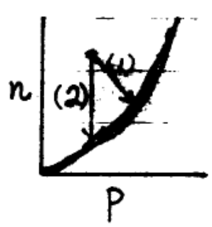
Above an atomic number of 20, most stable nuclides have n/p ratio > 1. Nuclei whose n/p ratios lie outside the band of stability emit particle(s) and/or electromagnetic rays in order to get back into the band of stability. These nuclei lying outside the band of stability are called radioactive and undergo spontaneous radioactive decay.

Common Radioactive Emissions

Type	Symbol	Identity	Charge	Penetrating Power
beta	β^- $\;{}^{0}_{-1}\beta$ $\;{}^{0}_{-1}e$	electron	−1	low to moderate
positron	${}^{0}_{+1}\beta$ $\;{}^{0}_{+1}e$	positively charged electron	+1	low to moderate
alpha	α $\;{}^{4}_{2}\alpha$ $\;{}^{4}_{2}He$	helium nucleus (no electrons)	+2	low
proton	${}^{1}_{1}p$ $\;{}^{1}_{1}H$	proton, hydrogen nucleus	+1	low to moderate
neutron	${}^{1}_{0}n$	neutron	0	very high (has no charge)
gamma ray	${}^{0}_{0}\gamma$	electromagnetic radiation	0	high

Lets look at the ways in which nuclides outside the band of stability return to the band of stability.

I. Nuclei Above Band of Stability: n/p ratio is too large



(1) beta emission ≡ gain a proton + lose a neutron

due to ${}^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}^{0}_{-1}\beta$

A lone neutron does undergo spontaneous decay to a proton and an electron.

$${}^{228}_{88}Ra \longrightarrow {}^{228}_{89}Ac + {}^{0}_{-1}\beta$$

#p	88	89
#n	228−88 = 140	228−89 = 139

(2) neutron emission

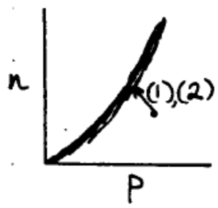
$${}^{137}_{53}I \longrightarrow {}^{136}_{53}I + {}^{1}_{0}n$$

Note : to balance nuclear reactions,

$\sum$ mass numbers of reactants = $\sum$ mass numbers of products

$\sum$ atomic numbers of reactants = $\sum$ atomic numbers of products

II. Nuclei Below Band of Stability : n/p ratio is too small



(1) positron emission due to ${}^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{1}\beta$

$${}^{38}_{19}K \rightarrow {}^{38}_{18}\underline{Ar} + {}^{0}_{1}\beta$$

#p	19	18	∴ #p ↓
#n	38−19 " 19	38−18 " 20	#n ↑

(2) electron capture ("K" electron capture)

- an electron from n=1 orbital (K shell) is captured by the nucleus

$${}^{106}_{47}Ag + {}^{0}_{-1}e \rightarrow {}^{106}_{46}Pd$$

III. Nuclei with Atomic Number (A.N.) > 83

all are radioactive

many decay by alpha emission

$${}^{226}_{88}Ra \rightarrow {}^{222}_{86}\underline{Rn} + {}^{4}_{2}He$$
$$(\text{or } {}^{4}_{2}\alpha)$$

Radiation can be detected in many ways : (Section 30-8)

1. photographic detection
2. detection by fluorescence using scintillation counter – very routine
3. cloud chamber
4. gas ionization counters (eg Geiger-Müller counter)

USA today: April 24, 1986

Element	U-238 Series						
Neptunium							
Uranium	U-238 4.49×10^9 yrs		U-234 2.48×10^5 yrs				
Protactinium		Pa-234 1.18 min					
Thorium	Th-234 24.1 days		Th-230 7.5×10^4 yrs				
Actinium							
Radium			Ra-226 1622 yrs				
Francium							
Radon			Rn-222 3.825 days				
Astatine							
Polonium			Po-218 3.05 min		Po-214 1.6×10^{-4} sec		Po-210 138.4 days
[illegible]uth				Bi-214 19.7 min		Bi-210 50 days	
Lead			Pb-214 26.8 min		Pb-210 21.4 yrs		Pb-206 stable lead (isotope)
Thallium							

Across state lines

Source: *New Shelter Magazine* USA TODAY

Homeowners at peril from deadly radon gas

Stanley Watras sympathizes with the 70 Clinton, N.J., homeowners who this week begin trying to eliminate high levels of radiation from their houses.

Eighteen months ago Watras, of Boyertown, Pa., set off radiation monitors as he walked into a nuclear power plant. He also set off a wave of concern that radon — radioactive gas linked to lung cancer — could be seeping from underground rock formations into millions of USA homes.

"I just kept thinking 'What have I done to my kids?' " said Watras, 35, a construction engineer and father of two. "My son Christopher lived 12 of his first 15 months in that environment. What have we done to him?"

Home contamination from commercial uranium operations is well documented. But Clinton and Boyertown involve a newer and perhaps more pervasive threat — radioactivity from natural radon-bearing rock, including granite, phosphate, shale and uranium.

Watras was forced to leave his home for more than a year during repairs. Clinton residents likely can remain. The U.S. Environmental Agency this week began an effort to remedy radiation in 10 Clinton homes. Other homeowners likely will have to pay $2,000-$10,000 for repairs. Most work involves ventilation improvements and sealing foundation cracks.

The EPA also is sampling the USA to determine the enormity of the problem. Estimates range from a million to several million homes.

"The potential exists for many, many more problems," said health physicist Christie Eheman of the National Center for Disease Control. Some state efforts:

- New Jersey hopes next month to begin a statewide geological study and testing of thousands of homes.
- In Florida, special ventilation requirements for homes being built in high-risk areas go into effect Thursday.
- Idaho this month said homes tested in Blaine and Kootenai counties average double the federal standard.
- In New Mexico, a small sampling revealed several homes above the federal standard. Funding is a problem.
- Bonneville Power Administration offers free testing in Idaho, Montana, Oregon, Washington and Wyoming.

Health officials found a radiation level in Watras' home of about 3,200 picocuries per liter — the equivalent to smoking about 100 packs of cigarettes a day. Four picocuries is generally considered the acceptable limit.

In Clinton, 70 houses registered between four and 1,000 picocuries. Gerry Nichols of the state Bureau of Radiation Protection said most were about 200 picocuries.

"Nobody is panicking," said Clinton Mayor Robert Nulman, who said he doesn't expect values to drop on the $100,000-plus homes. More houses will be tested.

Watras admits he's bitter, but says there is no one to blame. "You can't sue God," said Watras. "And he's . . . put it there."

3200/L = 7100 dpm/L

— John Bacon

10 dpm is acceptable limit

1 curie = 3.7×10^{10} dps

most ~ 400 dpm.

In a 1.0 L sample of air, the concentration of Rn-222 was measured to be 200 dpm (disintegrations per minute).

(7000 dpm/L is high #)

xtra → (a) How many atoms, moles, grams of ^{222}Rn does this represent?

Or better yet, use the equations we've used before: ln (A/Ao) = -kt Where $t_{1/2}$ = 0.693/k

$$\text{rate of decay} = -\frac{dA}{dt} = kA$$

$$200 \text{ dpm} = kA$$

∴ must find the rate constant k in minute^{-1}

$$k = \frac{0.693}{t_{1/2} \text{ (in min)}} = \frac{0.693}{3.82 \text{d} \times 24 \frac{\text{hours}}{\text{d}} \times 60 \frac{\text{min}}{\text{h}}}$$

$$= 1.26 \times 10^{-4} \text{ min}^{-1}$$

$$\therefore A = \frac{200 \text{ dpm}}{1.26 \times 10^{-4} \text{ min}^{-1}}$$

$$= 1.59 \times 10^{6}$$

∴ 1.59×10^6 atoms are in the sample (1 L)

$$A \text{ (mol)} = \frac{1.59 \times 10^6 \text{ atoms}}{6.023 \times 10^{23} \text{ atom/mole}} = 2.64 \times 10^{-18} \text{ moles radon}$$

$$A \text{ (g)} = 2.64 \times 10^{-18} \text{ moles} \times 222 \text{ g/mole} = 5.86 \times 10^{-16} \text{ g}$$ in 1 liter sample.

(b) What % of ^{222}Rn has decayed away after 8.00 days?

Estimation using 4d: 200 dpm $\xrightarrow[4d]{}$ 100 dpm $\xrightarrow[4d]{}$ 50 dpm

∴ after 8d, we have ~ ¼ left

∴ ~75% has decayed away.

$$\log\left(\frac{A}{A_o}\right) = \frac{-kt}{2.303}$$

$$k(d) = \frac{0.693}{3.82 \text{ d}} = 0.181 \text{ d}^{-1}$$

$$\log\left(\frac{A}{A_o}\right) = \frac{-0.181 \text{ d}^{-1} \times 8 \text{d}}{2.303}$$

$$= -0.629$$

$$\left(\frac{A}{A_o}\right) = 0.235 = \text{fraction remaining}.$$

∴ 23.5 % of Rn remains
∴ 76.5 % of Rn has decayed away.

(c) How long (in days) before 1 liter of sample is reading a safe level: 10 dp,

$$\log \frac{A}{A_o} = -\frac{kt}{2.303}$$

$$\log \frac{10}{200} = -\frac{0.181\ t}{2.303}$$

$$-1.301 = -\frac{0.181\ t}{2.303}$$

$$t = 16.6 \text{ days}$$

Why can't a person just wait 17 days until their home air reading is down to 10 dp
^{238}U is present in building material and keeps producing more.

Uses of Radionuclides

There are many practical applications of radionuclides because they decay at known rates. Rates of decay are independent of external factors such as concentration, temperature, pressure, catalyst etc.
These include
(1) radioactive dating
(a) radiocarbon dating : objects < 50,000 years old
$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}\beta \quad t_{\frac{1}{2}} = 5730$ years

(b) uranium - lead dating : objects several billion years old
$^{238}U \rightarrow\rightarrow\rightarrow ^{206}Pb \quad t_{\frac{1}{2}} = 4.5 \times 10^9$ years
used to determine age of the earth at 4.6×10^9 years.

(2) medical uses : radioactive tracers, energy for pacemakers, ^{60}Co treatments for canc
(3) research :

(4) agricultural uses : investigating nutrient uptake
(5) industrial uses

Artificial Transmutation of Elements (Nuclear bombardment)

The first artificially induced nuclear reaction happened in 1915 by Rutherford.

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{1}_{1}H + ^{17}_{8}O$$

The abbreviated form of this reaction is

$$^{14}_{7}N\ (^{4}_{2}\alpha\ ,\ ^{1}_{1}p)\ ^{17}_{8}O$$

1. bombardment with positive ions

positive ions :

$^{1}_{1}H$	hydrogen nucleus (ion)	+1 charge
$^{2}_{1}H$	deuterium nucleus (ion)	+1 charge
$^{4}_{2}He$	helium nucleus (ion)	+2 charge

problem : since the nucleus is positively charged, a great deal of energy is required to bombard it with a positively charged ion. Cyclotrons and linear accelerators are needed.

examples :

$$^{230}_{90}Th + ^{1}_{1}H \rightarrow ^{223}_{87}Fr + 2\ ^{4}_{2}He$$

$$^{96}_{42}Mo + ^{2}_{1}H \rightarrow ^{97}_{43}Tc + ^{1}_{0}n$$

2. Neutron bombardment :

Since neutrons have no charge, they need not be accelerated to produce bombardment reactions. Neutrons can be produced in nuclear reactors.

Types of reactions

(a) fast neutrons – have high kinetic energies – cause subsidiary particles to be ejected

$$^{142}_{60}Nd + ^{1}_{0}n \rightarrow ^{143}_{61}Pm + ^{0}_{-1}\beta$$

(b) slow neutrons are captured by the nucleus

$$^{200}_{80}Hg + ^{1}_{0}n \rightarrow ^{201}_{80}Hg + ^{0}_{0}\gamma$$: a (n, γ) reaction

Nuclear Fission and Fusion

nuclear fission : the process in which a heavy nucleus (A.N. > 80) split into nuclei of intermediate masses and one or more neutrons are emitted. E.g.

$$^{235}_{92}U + ^{1}_{0}n \rightarrow [^{236}U] \rightarrow ^{160}_{62}Sm + ^{72}_{30}Zn + 4\,^{1}_{0}n + \underline{\text{energy}}$$

short-lived intermediate ↘ ~~ ↘ ~~

nuclear fusion : the process in which light nuclei combine together to produce a heavier nucleus. Eg

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

deuterium, tritium (more energy than fission produces)

Where does this energy that is produced come from? ANSWER: in both reactions, the products have a total mass that is slightly less than the sum of the masses of reactants. ie there is a decrease in mass that accompanies the reaction. This difference in mass between products and the reactants is equivalent to the energy released in the nuclear reaction by $E = mc^2$ (Einstein's equation)

It is an experimental fact that the mass of an atom is ALWAYS less than the sum of the masses of its constituent particles. The difference in masses is the MASS DEFICIENCY or DEFECT..

mass defect = (sum of masses of all e^-, p^+ and n°) − (actual mass of atom)

this mass defect is equivalent to the energy required to bind the electrons, protons and neutrons together – called the NUCLEAR BINDING ENERGY using $E = mc^2$.

Example: Calculate for $^{35}_{17}Cl$ whose atomic weight is 34.9689 amu.

(a) mass defect : in ^{35}Cl there are 17 protons, 17 electrons, 18 neutrons

the sum of masses of constituent particles :	17 p^+	:	17×1.0073 =	17.1241 amu
	17 e^-	:	17×0.00055 =	0.0093
	18 n°	:	18×1.0087 =	18.1566
				35.2900 amu

but the actual mass is only 34.9689 amu.

∴ mass defect = 35.2900 − 34.9689
= 0.3211 amu / atom of ^{35}Cl

(b) nuclear binding energy (J/mol) is energy required to separate 1 mole of ^{35}Cl atoms into its parts.

mass defect = 0.3211 g / mole of ^{35}Cl by definition of amu.

$$E = mc^2$$
$$= (3.211 \times 10^{-4}\ kg)(3.00 \times 10^8\ \tfrac{m}{s})^2$$
$$= 2.89 \times 10^{13}\ J/mole$$
$$= 2.89 \times 10^{10}\ kJ/mol$$

E: energy (J)
m: mass (kg)
c: speed of light (3.00×10^8 m/s)

Note: this is a lot of energy.

Another way to express nuclear binding energy is in MeV per nucleon. (mega electron volts) The conversion factor (given when needed) is 931 MeV/amu. (from $E = mc^2$)

Note: A nucleon is a particle making up the nucleus – a neutron or a proton. The number of nucleons in a particular isotope is equal to the mass number, (the sum of protons + neutrons). E.g. the number of nucleons in ^{35}Cl = 35.

$$\therefore \text{nuclear binding energy (MeV/nucleon)} = 0.3211 \frac{\text{amu}}{\text{atom}} \times \frac{1 \text{ atom}}{35 \text{ nucleons}} \times 931 \frac{\text{MeV}}{\text{amu}}$$
$$= 8.54 \text{ MeV/nucleon.}$$

So, how much energy is released in fusion? ΔE for the reaction below.

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

Plan (1) find Δmass in reaction (amu)
(2) use conversion factor, 931 MeV/amu

mass of $^{2}_{1}H$ = 2.0140 amu
$^{3}_{1}H$ = 3.01605
$^{4}_{2}He$ = 4.00260
$^{1}_{0}n$ = 1.0087

$$\therefore \Delta\text{mass for reaction} = (2.0140 + 3.01605) - (4.00260 + 1.0087)$$
$$= 0.01875 \text{ amu}$$

$$\Delta E = 0.01875 \text{ amu} \times 931 \text{ MeV/amu}$$
$$= 17.5 \text{ MeV}$$

What is the meaning of this number: 17.5 MeV of energy released when 1 atom of deuterium reacts with 1 atom of tritium to form helium and a neutron?

Using conversion factor: $1 \text{ eV} = 1.60 \times 10^{-19}$ J

on an atomic scale, this reaction produces $17.5 \times 10^{6} \text{ eV} \times 1.60 \times 10^{-19} \text{ J/eV}$
or 2.80×10^{-12} J

but if 1mol of ${}^{2}_{1}H$ (~2 g) reacts with ${}^{3}_{1}H$ (~3 g),
then $2.80 \times 10^{-12} \text{ J/atom} \times 6.02 \times 10^{23}$ atoms/mol
$= 1.74 \times 10^{12}$ J of energy are produced.

How much energy is this?

To calculate the mass of $H_2O(g)$ that can be heated from 20°C to boiling it away.

heat = (Sp Ht H_2O × mass × ΔT) + (Ht vap H_2O × mass)
1.74×10^{12} J = [4.18 J/g°C × mass × (100-20)°C) + (2260 J/g × mass)
mass = 6.71×10^{8} g water
volume = 6.71×10^{8} cm^3 water (Density of H_2O = 1.00)

How much water can be boiled? using 1.74×10^{12} J of heat

$$? \text{ ft}^3 = 6.71 \times 10^{8} \text{ cm}^3 \times \left(\frac{1 \text{ in}}{2.54 \text{ cm}}\right)^3 \times \left(\frac{1 \text{ ft}}{12 \text{ in}}\right)^3 = 2.37 \times 10^{4} \text{ ft}^3$$

which is the approximate volume of a swimming pool that is 6 ft deep, 40 ft wide, 100 ft long.

If we plot binding energy against mass numbers for all the nucleons, we obtain the following:

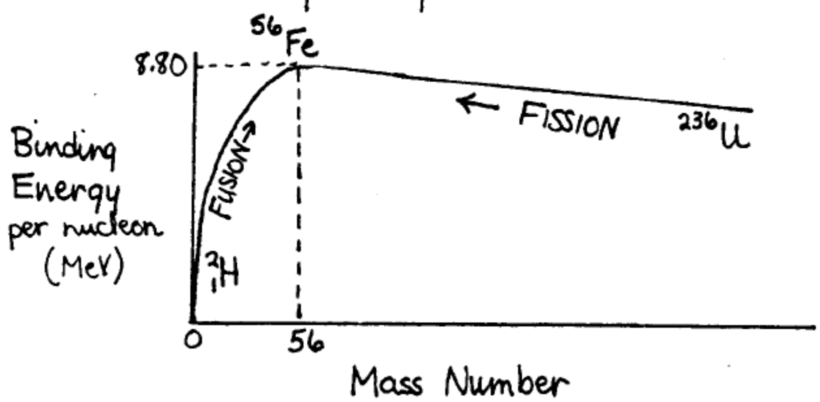


Figure 23.4

^{56}Fe is the most stable atom since it has the highest binding energy. In fact, all atoms with intermediate mass numbers have the greatest stability.

Atoms with high mass numbers, eg ^{236}U, will undergo fission to produce atoms with intermediate mass numbers.
Atoms with low mass numbers, eg $^{2}_{1}H$, will undergo fusion readily to form atoms with greater mass and hence greater stability.

Most Nuclear reactors today use fission reactions to produce useful energy. (see figure on next page)

Inside the reactor, energy is released when the nucleus of a heavy atom (eg U-235) is split apart by a slow moving neutron into lighter fission fragments plus 2 or more neutrons. These neutrons are slowed down when they pass thru a MODERATOR (graphite or water) and are used to split other U-235 nuclei. The result is a self containing nuclear chain reaction that steadily releases tremendous amounts of energy. The fission rate of U-235 is controlled by moving neutron-absorbing control rods (usually Cd) in + out of fuel core.

A meltdown occurs when (1) fuel rods overheat, (2) the reactors uranium core goes into uncontrolled reaction + core melts (3) radioactive molten metal burns thru containment vessel and enters earth, (4) heat hits water table (5) steam rises carrying radiation.

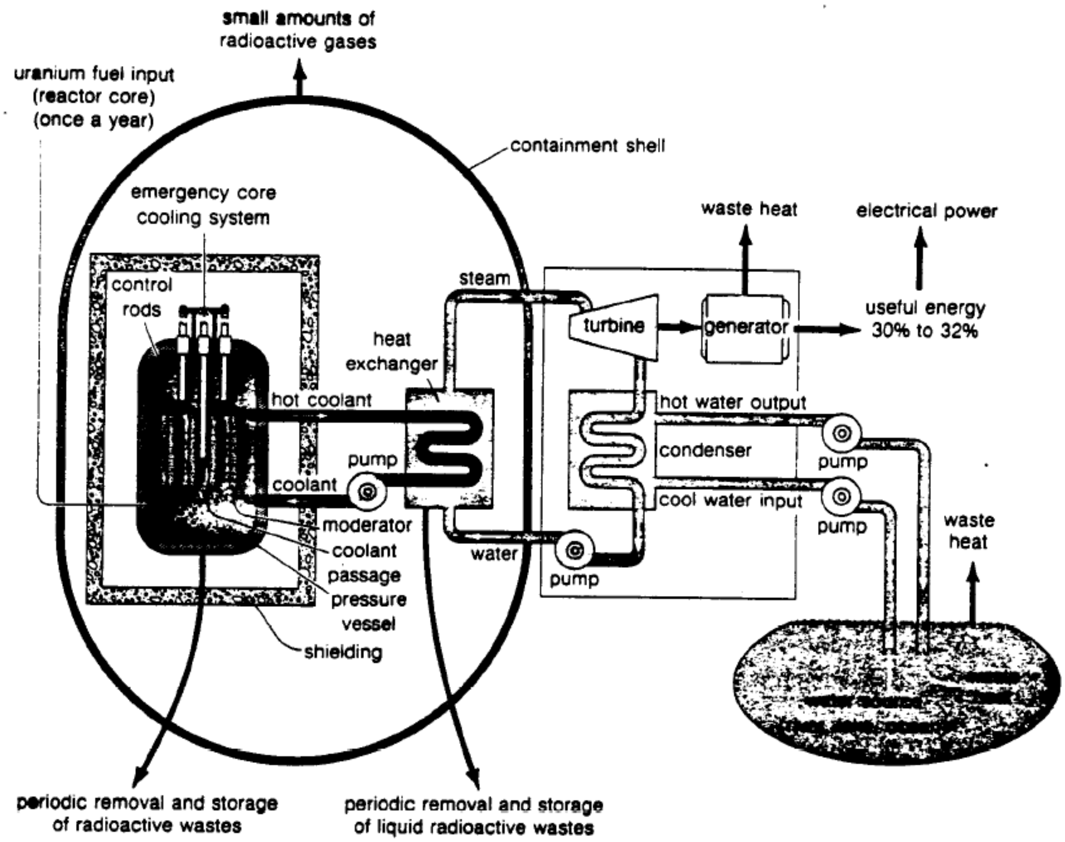


Figure 17.8 A nuclear power plant with a pressurized water reactor.