

INTRODUCTION TO CHEMISTRY

(SC-230)

UNIT 10. NUCLEAR CHEMISTRY

1. Radioactivity
 2. Types of nuclear reactions
 3. Rate of Radioactive Decay and Half life
 4. Nuclear Energy -- fission and fusion
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UNIT 10. NUCLEAR CHEMISTRY

- In **chemical reactions**, only the outer electrons of the atoms are disturbed (i.e. the electron configuration)
 - Valence electrons are transferred (in ionic reactions) or shared (in covalent reactions) between different elements (the nucleus remains unchanged)
 - The energy emitted or absorbed in a chemical reaction is much less than the one emitted in nuclear reactions
- In **nuclear reactions**, the nuclear changes that occur are independent of the chemical environment of the atom
 - It involves changes in the composition of the “nuclei”. This process releases tremendous amounts of energy.

1. Radioactivity

- Protons and neutrons are found in the nucleus of the atom; the electrons are in orbit evolving around the nucleus of the atom. The atomic mass is the sum of the number of protons and neutrons found in the nucleus. **Isotopes** of an element vary in the number of neutrons found in the nucleus.
- **Radioactivity** –Is the process by which unstable isotopes decompose (*decay*); during such decay, the nucleus releases energy under the form of “**radiation**”
 - The unstable isotopes who undergo nuclear decay are referred to as “radioactive isotopes”.
 - There are over 300 naturally occurring isotopes. Of these, 264 are stable, the remainders are unstable.
- Different forms of radiation may be emitted from an unstable radioactive nucleuse. Energy is released and a new, more stable nucleus is formed.
- There are three major types of radiation:
 - **Alpha radiation (α)** --- weakest; Alpha particles are not very penetrating: paper, clothing or a few centimeters of air can block alpha particles ; (An Alpha particle is an Helium nucleus, the electrons have been removed; thus, they are positively charged)
 - **Beta radiation (β)** – stronger; Beta particles may travel 2 to 3 meters through air; they are stopped by a layer of clothing, glass, thick cardboard, one inch thick wood, or aluminum; (Beta particles are high –speed electrons emitted from the nuclei of decaying radioisotopes; since they are electrons, they have negative charges)
 - **Gamma radiation (γ)** – strongest and most dangerous; it can travel over 500 meters through the air; it can pass through your body and several cm of lead, or nearly a meter of concrete. (Gamma radiation is similar to x-rays except they have higher energy and shorter wavelengths; it has no charge)
- Besides alpha, beta, and gamma radiation, other types of particles have been found to be emitted by radioactive isotopes. These include: positron emission; electron capture...

2. Types of Nuclear Reactions

There are 2 types of nuclear reactions.

1. **Radioactive decay** = *the process in which a nucleus spontaneously disintegrates, giving off radiation.*
 - Nuclei containing more than 83 protons are unstable. Putting it another way, no element beyond bismuth ($Z=83$) has a stable isotope. All the isotopes of such elements are radioactive.

- **Radioactive Decay Series** == a sequence in which one radioactive nucleus decays to a second, which then decays to a third, and so forth.
 - All nuclides with **atomic number (Z)** greater than $Z = 83$ are radioactive. Many of these nuclides decay by alpha emission. By emitting an alpha particle (loss of protons), the nucleus reduces its atomic number, becoming more stable; up to the point where it is stable and not radioactive any longer.

2. **Nuclear bombardment reaction** = a nuclear reaction in which a nucleus is bombarded or struck by another nucleus or by a nuclear particle.

Nuclear bombardment

- In 1919 Ernest Rutherford discovered it is possible to change the nucleus of one element into the nucleus of another element. This is called **transmutation**.
 - **Transmutation** = The change of 1 element to another by bombarding the nucleus of an element with nuclear particles.

Examples of transmutation experiments (nuclear bombardment) from Rutherford:

- Rutherford used a radioactive element as a source of alpha particles and allowed particles to collide with nitrogen nuclei.
- He discovered that protons are ejected in the process and a new element is formed.

3. Rate of Radioactive Decay and Half Life

Half-life (and rate of radioactive decay)

- Radioactive material is said to “**decay**” by emitting alpha, beta or gamma particles.
 - Therefore how can we figure out how long it will take for a radioactive substance to decay?
 - To answer this question we need to look at the rate of radioactive decay and most importantly the **half-life**.

Rate of radioactive decay = the number of nuclei disintegrating per unit time.

- This is found to be proportional to the number of radioactive nuclei in the sample.
- It can be expressed mathematically as:

$$\text{Rate} = kN_t$$

Where:

k = radioactive decay constant (This is unique to the radioactive substance in question.)

decay constant for Tritium = $1.79 \times 10^{-9}/s$

decay constant for Tellurium-123 = $1.7 \times 10^{-21}/s$

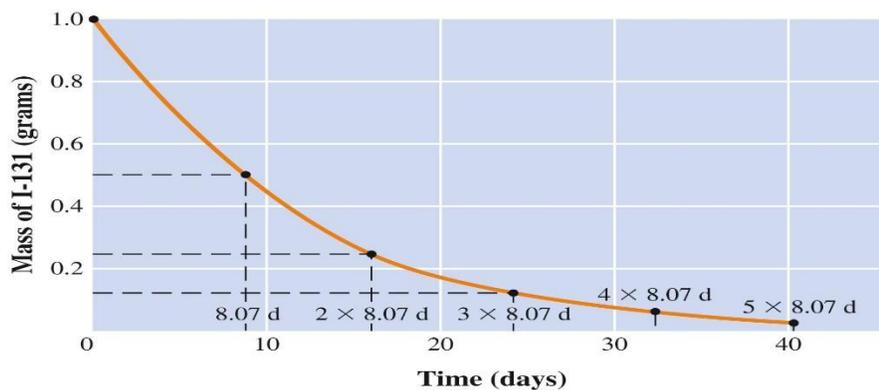
decay constant for Neptunium-237 = $1.03 \times 10^{-14}/s$

N = number of radioactive nuclei at time t

- **Half-life** = the time it takes for one half of the nuclei in a sample to decay.
 - It does not matter how much of the sample there is e.g., 5g or 500kg. ...

Example:

- 1) 1g of iodine-131 (an isotope used to calculate thyroid cancer), decays to 0.5g in 8.07 days. Therefore its half-life is 8.07 days.
 - 2) 1g of Uranium-238 decays to 0.5g in 4.5 billion years. Therefore its half-life is 4.51 billion years.
- Consequently, the half-life can be used to age various things?



Half-lives of Several Radioisotopes

Isotope:	${}^{60}_{27}\text{Co}$	${}^{32}_{15}\text{P}$	${}^{14}_6\text{C}$	${}^{131}_{53}\text{I}$	${}^{238}_{92}\text{U}$
Half-life:	5 years	14 days	5730 years	8 days	4.5 billion years
Use:	chemotherapy	detect tumors	archeological dating	hyperthyroidism	geological dating

How to calculate half-life

- Half-life is calculated from the decay constant.

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

where;

$t_{1/2}$ = half life

k = decay constant

Example:

Thallium-201 is used in the diagnosis of heart disease. This isotope decays by electron capture; the decay constant is $2.63 \times 10^{-6}/\text{s}$. What is the half-life of thallium-201 in days?

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

$$t_{1/2} = \frac{0.693}{2.63 \times 10^{-6} \text{ s}}$$

$$t_{1/2} = 2.63 \times 10^5 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ day}}{24 \text{ h}}$$

$t_{1/2} = 3.05 \text{ days}$

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Radiometric Dating

- Because the rate of radioactive decay is constant, this rate can serve as a sort of clock for dating objects.
- Carbon-14 is part of all living material. While a plant or animal is living, the fraction of carbon-14 in it remains constant due to exchange with the atmosphere. Once dead, the fraction of carbon-14 and, therefore, the rate of decay decrease. In this way, the fraction of carbon-14 present in the remains becomes a clock measuring the time since the plant's or animal's death.
- The half-life of carbon-14 is 5,730 years. Living organisms have a carbon-14 decay rate of 15.3 disintegrations per minute per gram of total carbon.
 - The ratio of disintegrations at time t to time 0 is equal to the ratio of nuclei at time t to time 0.

Applications of Radioisotopes: Medical Therapy and Diagnosis and for Commercial Purposes

- A **radioactive tracer** is a very small amount of radioactive isotope (Radioisotopes) that is added to a chemical, biological, or physical system so as to study the system.
 - **Radioisotopes** are used for diagnosis of many medical conditions. For example, they are used to develop images of internal body organs so those organs' functioning can be examined.
 - Radioactive isotopes are commonly used in cancer therapy, usually to eliminate any malignant cells left after surgery.
 - More than 100 different radioactive isotopes have been used in medicine.

Commercial uses:

- Using radiation to “irradiate” will help to kill insects, larvae, and parasites. Radiation can also inhibit the sprouting of onions and potatoes. For a commercial standpoint, irradiation can extend the shelf lives of many foods for weeks or even months. Consequently, radiation is commonly used to maintain food fresh for longer periods of time..

4. Energy of Nuclear Reactions (Nuclear Fission and Fusion)

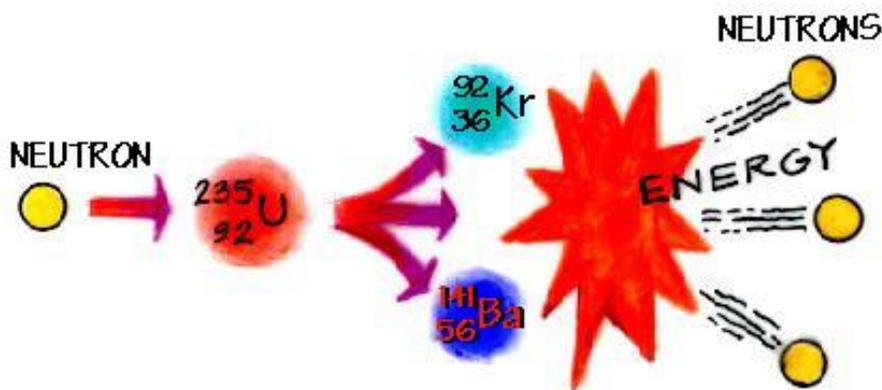
- **Nuclear reactions** involve changes of energy on a much larger scale than what occurs in chemical reactions. This energy is used in nuclear power reactors and to provide the energy for nuclear weapons.

(1) Nuclear fission (e.g. nuclear power stations – nuclear reactors)

- **Fission** = a nuclear reaction in which a heavy nucleus splits into a lighter nuclei and energy is released.
 - For example: The fission of Uranium-235 nuclei forms about 30 different elements!

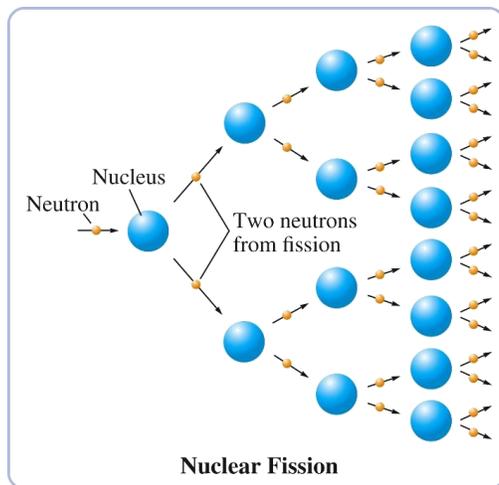
Fission of Uranium

- When Uranium-235 splits approximately 2-3 neutrons are released.
- If these neutrons are absorbed by another Uranium nuclei, these then split and release even more neutrons.
- This is called a **NUCLEAR CHAIN REACTION**.



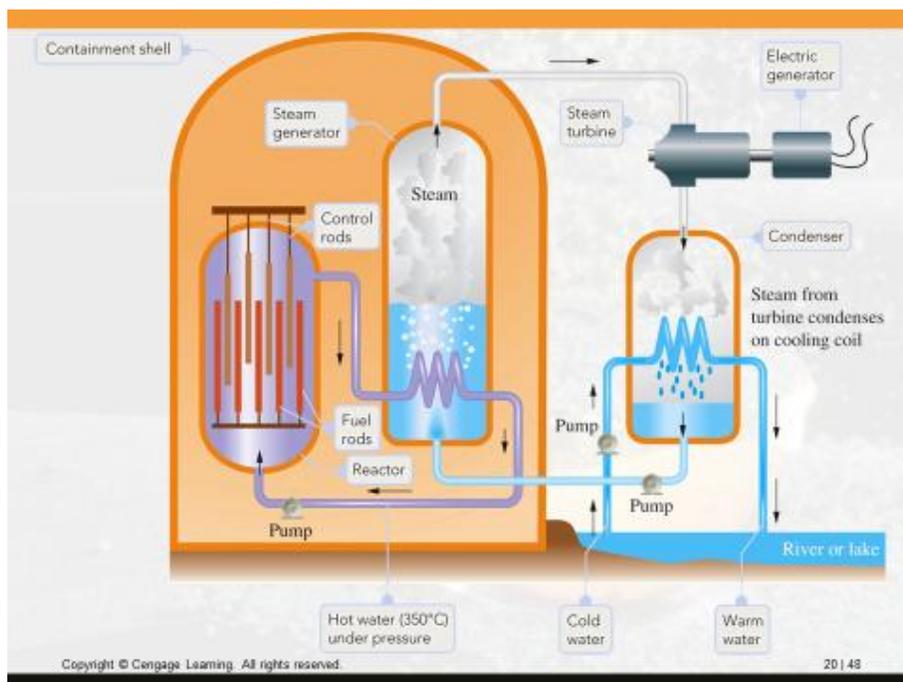
CHAIN REACTION = a self-sustaining series of nuclear fissions caused by the absorption of neutrons released from previous nuclear fission.

- The number of nuclei that split multiplies quickly as a result of absorption of neutrons released from previous nuclear fission.
- This chain reaction is the basis of nuclear power.
- To ensure fission continues, a nucleus that splits must produce at least 1 neutron that results in the fission of another nucleus and so on.
- If the sample is too small, many neutrons leave the sample before they have a chance to be absorbed. There is therefore a **CRITICAL MASS** for a particular fissionable material.
 - **Critical mass** = the smallest amount of a fissionable material in which a chain reaction can be sustained.
- If the mass is much larger than this (**subcritical mass**) then the numbers nuclei that split multiplies rapidly.



Nuclear Reactors:

- A **nuclear reactor** is a device that permits a controlled chain reaction of nuclear fission.
- A nuclear reactor consists of fuel rods alternating with control rods within some kind of vessel/container. (Figure below)
 - **Fuel rods** = cylinders that contain fissionable material like uranium dioxide (UO_2) pellets.
 - **Control rods** = cylinders composed of substances that absorb neutrons, such as boron and cadmium, and can therefore slow down the chain reaction.



- By varying the depth of the control rods within the fuel rods one can increase or decrease the absorption of neutron.
- If necessary, the control rods can be dropped all the way into the fuel rod assembly to stop the chain reaction.
- The heated water from the chain reaction passes through the steam generators. The water turns to steam and drives a turbo-generator that produces electricity.

Energy contained in the fission process:

- The fission of 1 gram of ²³⁵U (uranium-235) produces as much energy as the combustion of 2,700 kg of coal or the explosion of 30 metric tons of TNT.
- By the 1970s it was generally supposed that nuclear fission would replace fossil fuels (oil, natural gas, coal) as an energy source. That hasn't happened. The most evident reasons are:
 - Nuclear accidents (Three Mile Island; Chernobyl; Fukushima...) (see below)
 - Disposal of radioactive waste (NIMBY – Not In My Back Yard) – presently no permanent sites to store nuclear wastes – and there are hundreds of thousand tons of it
 - Decommissioning nuclear power plants (what do we do with the radioactive materials?)
 - Thermal pollution link to the water used as “coolant”.
 - Terrorism attacks or use --- production of “dirty bombs”

Case study: the Three Mile Island (March 1979)

- Three Mile Island, Pennsylvania, in March 1979, the main pump that supplied cooling water to the reactor broke down. The reactor temperature rose rapidly. The control rods eventually stopped fission in the reactor, but because of the loss of coolant, a partial core meltdown had occurred. Thus, the accident was caused by a combination of equipment failures, lack of appropriate information to the operator, and decisions by the operator. About 50 curries of radiation were released to the environment and there were no casualties.
- The crippled reactor was eventually defueled in 1990 at a cost of about \$1 Billion. It will be decommissioned when the companion reactor, reaches the end of its useful life.

Case study: the Chernobyl nuclear accident (April 1985)

- **Where is it?** Ukraine, north of Kiev.
- **Why did it happen?**
 - An experiment was undertaken to measure the amount of electricity that the still-spinning turbine would produce if the steam were shut off. During the experiment, operators violated six important safety rules. They shut off all automatic

warning systems, automatic shutdown systems, and the emergency core cooling system for the reactor. As the test continued, the power output of the reactor rose beyond its normal level and continued to rise. The operators activated the emergency system that was designed to put the control rods back into the reactor and stop the fission. But it was too late. The core had already been deformed, and the control rods would not fit properly; the reaction could not be stopped. In 4.5 seconds, the energy level of the reactor increased, 2,000 times. The cooling water in the reactor converted to steam and blew the 1,000 metric ton concrete roof from the reactor, and the graphite that was part of the reactor core caught fire.

- It took 10 days to bring the burning reactor under control.
- The explosion at Chernobyl occurred in April 1986. About 100 million curies were released, leading to at least 37 fatalities. Moreover, 135,000 people were permanently evacuated from the region surrounding the reactor. Since then, all the other reactors at Chernobyl, three, in addition to the one that exploded, have been permanently shut down.

Case study: the Fukushima Dai-ichi (Japan) (March 2011)

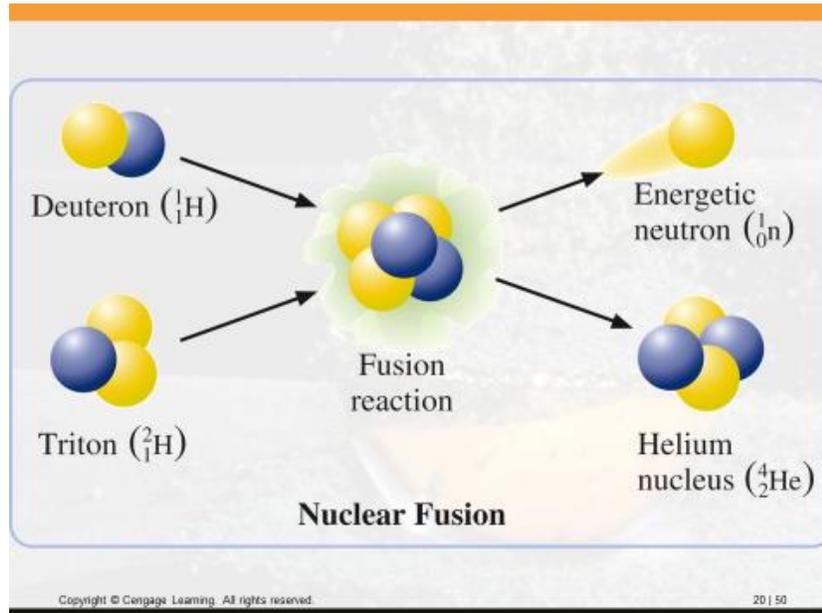
- On March 11, 2011, a magnitude 9 earthquake 130 km off the northeast coast of Japan triggered a tsunami which flooded the site at Fukushima nuclear power station. At the time of the earthquake and tsunami, there were six reactors in operation and three were shut down for refueling or maintenance. Each of the six reactors also had a spent fuel storage site adjacent to the reactor.
- The flooded water cut all electrical power to the pump cooling water system. The loss of the ability to cool the reactors and their adjacent spent fuel storage sites resulted in explosions and fires that were caused by the release of hydrogen from the overheated reactors and one of the spent fuel storage sites.
- The explosions, fires, and leak in the cooling system released radiation into the atmosphere and seawater. People living within 20 km of the plant were urged to evacuate and take iodine supplements to reduce the likelihood that radioactive iodine-131 would accumulate in the thyroid gland.

Fission as a way of producing – nuclear bombs

- The discovery of fission energy led to the idea harnessing this energy to produce the atomic bomb:
 - *Could the free neutrons created in fission start a chain reaction that would release an enormous amount of energy? If so, it might be possible to build a weapon of unimagined power.*

(2) NUCLEAR FUSION e.g., hydrogen bomb, thermonuclear bombs

- **Fusion** = a nuclear reaction in which light nuclei combine to give more stable, heavier nucleus, plus possible several neutrons, and energy is released.



- Fusion reactions have been observed in the laboratory by bombardment reactions using **particle accelerators**.
- A particle accelerator is needed because for a reaction to occur the particles that are bombarding the material must have enough kinetic energy to overcome repulsion by the electric charges of the nucleus.
- In other words, there has to be enough speed in the bombarding particles to not be effected by the charge of the nucleus.
- For now, this approach remains experimental.

Using fusion to produce bombs:

- Fission bombs worked, but they weren't very efficient.
- It didn't take scientists long to wonder if the opposite nuclear process -- fusion -- might work better.
- Fusion occurs when the nuclei of two atoms combine to form a single heavier atom.
- *For example: At extremely high temperatures, the nuclei of hydrogen isotopes deuterium and tritium can readily fuse, releasing enormous amounts of energy in the process.*
 - Weapons that take advantage of this process are known as **fusion bombs, thermonuclear bombs** or **hydrogen bombs**.
 - Fusion bombs have higher kiloton yields and greater efficiencies than fission bombs, but they present some problems that must be solved:
 - 1) Deuterium and tritium, the fuels for fusion, are both gases, which are hard to store.
 - 2) Tritium is in short supply and has a short half-life.
 - 3) Fuel in the bomb has to be continuously replenished.
 - 4) Deuterium or tritium has to be highly compressed at high temperature to initiate the fusion reaction.