

11. Nuclear Chemistry

Chemical reactions occur as a result of losing/gaining and sharing electrons in the valence shell which is far away from the atomic nucleus as we described in previous chapters in chemical bonding. In chemical reactions identity of the elements (**atomic**) and the makeup of the nuclei (mass due to protons and neutrons) is preserved which is reflected in the Law of Conservation of mass. This idea of atomic nucleus is always stable was shattered as **Henri Becquerel** discovered radioactivity in **uranium compound** where uranium nuclei changes or undergo **nuclear reactions** where nuclei of an element is transformed into nuclei of different element(s) while emitting ionization radiation. Marie Curie also began a study of radioactivity in a different form of uranium ore called **pitchblende** and she discovered the existence of two more highly radioactive new elements radium and polonium formed as the products during the decay of **unstable nuclide** of **uranium-235**. Curie measure that the radiation emanated was proportional to the amount (moles or number of nuclides) of radioactive element present, and she proposed that radiation was a property nucleus of an unstable atom. The area of chemistry that focuses on the nuclear changes is called **nuclear chemistry**.

What changes in a nuclide result from the loss of each of the following?

- a) An alpha particle. b) A gamma ray. c) An electron. d) A neutron.
- e) A proton. Answer: **a), c), d), e)**

11.1 Stable and Unstable Nuclides

There are **stable** and **unstable** radioactive nuclides. Unstable nuclides emit subatomic particles, with alpha $-\alpha$, beta $-\beta$, gamma $-\gamma$, proton-**p**, neutrons-**n** being the most common. Atomic nuclei are also called **nuclides** (nuclei of different **isotopes**) which is composed of **Z** protons and **N** neutrons with a mass **A** (mass number= $Z+N$), and held together by a strong nuclear force. As the atomic number increases number of protons increase and neutrons are added to the nucleus keep it stable. The stability is determined by number of protons as well as neutrons. For example, hydrogen has three isotopes: hydrogen-1(^1H), hydrogen-2(^2H) and hydrogen-3(^3H) which have separate isotope names, **hydrogen**, **deuterium** and **tritium**, respectively. Tritium nuclide has one proton and two neutrons and is radioactive/unstable. As the number of proton increases a nuclide also become unstable. Very large nuclei tend to be unstable because of the:

- a) repulsive forces between neutrons
- b) repulsive forces between electrons
- c) attraction of protons for neutrons

- d) attraction of electrons for the positively charged nucleus
- e) **repulsive forces between protons**

Stable Nuclides

Stable nuclides exist for an indefinite period of time, and they make up the bulk of ordinary materials. Roughly the ratio of number of protons to neutrons of a stable nucleus is equal to 1, i.e. there are equal number of proton and neutrons in stable nucleus. Most of the elements up to $Z = 83$ have stable nuclides. Most of nuclides (**isotopes**) of lighter elements ($Z < 83$) don't have unstable with two example: technetium-43 and promethium-61 do not have stable or unstable nuclide with long half-life and are not found naturally.

Unstable Nuclides

All unstable elements are radioactive contain large numbers of protons or higher or lower number of neutrons required for the nuclear stability. Any elements could have unstable nuclides and depends on the number of neutrons it has. E.g. **tritium-1** with mass number 3 is an isotope of hydrogen is a radioactive element. Carbon 14 is also radioactive. Elements are considered to be "naturally occurring" when they can be found in nature as stable or unstable nuclides. Unstable nuclides could be created by bombarding stable nuclides with neutrons of other particles in particles accelerators and are called **artificial elements**. Some naturally occurring elements have very unstable isotopes or short half-lives, so they do not exist in any significant quantities on Earth.

How many elements on the periodic table occur naturally? Answer: 91 elements. From hydrogen ($Z=1$) to neptunium-Np($Z=93$), except Tc and Pm.

Most of the heavier elements undergo **nuclear fission** (breaking up to smaller elements). However, some unstable nuclides with a long **half-life** ($t_{1/2}$) are found naturally since the age of earth is smaller compared to their half lives. Lighter stable elements only undergo **nuclear fusion** (smaller elements forming heavier elements) that occurs only at very high temperature as found in the sun: Hydrogen (H) is converted to helium (He) releasing enormous amount of nuclear energy.

Naturally occurring Nuclides

"Naturally occurring" only means existence not abundance. Many naturally occurring elements are in fact quite rare, although some were once more abundant but decayed with a faster rate. The first 93 elements, from element hydrogen-H ($Z=1$), to element neptunium-Np ($Z=93$) have nuclides that are naturally occurring except technetium-Tc, and but in fact some of these elements are highly unstable, and have only been observed when they have been created artificially.

is radioactive up to 94 (plutonium) should also be included on a list of naturally occurring elements.

Which of the following statements is true?

- a) None of the man-made isotopes are radioactive
- b) All man-made isotopes are radioactive**
- c) Some man-made isotopes are radioactive

Which of the following statements is true?

- a) No naturally occurring isotopes are radioactive
- b) Some naturally occurring isotopes are radioactive**
- c) All naturally occurring isotopes are radioactive

11.2 The Nature of Radioactivity

The nuclei of elements exhibiting radioactivity are unstable and are found to be undergoing continuous disintegration (i.e. gradual breakdown). The disintegration proceeds at a definite rate characteristic of the particular nucleus; that is, each radioactive isotope has a definite lifetime. However, the time of decay of an individual nucleus is unpredictable. The lifetime of a radioactive substance is not affected in any way by any physical or chemical conditions to which the substance may be subjected.

11.3 Radioactive Decay

Many unstable nuclei are radioactive and decay by emitting ionization radiation, transforming the nucleus into another nucleus, and releasing enormous amount of energy. A chain of decays takes place until a stable nucleus is reached. Mass of a nuclide is less than the mass of the individual neutrons and protons. This missing mass is known as the mass defect converted to energy binding energy according to Einstein's famous equation: $E = mc^2$.

Types of ionizing radiation:

Alpha particles- α : have a positive electrical charge and is essentially a helium nucleus. Because of their relatively large size, alpha particles collide readily with matter and lose their energy quickly. They therefore have little penetrating power and can be stopped by the first layer of skin or a sheet of paper.

Beta particles- β are fast-moving electrons ejected from the nuclei of atoms. These particles are much smaller than alpha particles and can penetrate up to 1 to 2 centimeters of water or human flesh. Beta particles are emitted from many radioactive elements. They can be stopped by a sheet of aluminum a few millimeters thick.

Gamma rays- γ and **X-rays**, like light, represent energy transmitted in a wave without the movement of material, just as heat and light from a fire or the sun travels through space.

X-rays and gamma rays are virtually identical except that X-rays do not come from the atomic nucleus. Unlike light, they both have great penetrating power and can pass through the human body. Thick barriers of concrete, lead or water are used as protection from them

Cosmic radiations consist of a variety of very energetic particles including protons which bombard the earth from outer space. They are more intense at higher altitudes than at sea level where the earth's atmosphere is most dense and gives the greatest protection.

Neutrons-n: are particles which are also very penetrating. On earth, they mostly come from the splitting, or fission, of certain atoms inside a nuclear reactor. Water and concrete are the most commonly used shields against neutron radiation from the core of the nuclear reactor.

Penetrating ability

Ionization radiation differs in penetrating ability increasing order: Alpha, beta, and gamma.

Which radioactive emanations have a charge of -1?

- a) Neutrons b) gamma rays c) alpha particles d) **beta particles**

Gamma (γ) rays are:

- a) **are very high energy, very short wavelength electromagnetic radiation**
b) are very low energy, very short wavelength electromagnetic radiation
c) are very low energy, very long wavelength electromagnetic radiation
d) are very high energy, very long wavelength electromagnetic radiation

For the most common types of radioactive decay, the order of least penetrating to human tissue, to most penetrating to human tissue is:

- a) beta, gamma, alpha
b) gamma, beta, alpha
c) gamma, alpha, beta
d) **alpha, beta, gamma**

For the most common types of radioactive decay, the order of mass from lightest to heaviest is:

- a) gamma, alpha, beta
b) **gamma, beta, alpha**
c) beta, gamma, alpha
d) beta, alpha, gamma

An alpha (α) particle is essentially a _____ nucleus.

- a) carbon-12
b) uranium
c) **helium**
d) hydrogen
e) plutonium

11.4 Rate of Radioactive Decay

The rate of disintegration of a radioactive substance is commonly designated by its **half-life**($t_{1/2}$), which is the time required for substance to decay one half of its original quantity. Depending on the element, a half-life can be as short as a fraction of a second or as long as several billion years.

Half life of some isotopes

Hydrogen (tritium)	Carbon	Oxygen
H-3 - 12.35 years	C-14 - 5730 years	O-15 - 122.24 seconds
Iodine	Radon	Strontium
I-123 - 13.2 hours I-125 - 60.14 days I-129 - 1.57E7 years I-130 - 12.36 hours I-131 - 8.04 days	Rn-219 - 3.96 seconds Rn-220 - 55.6 seconds Rn-222 - 3.824 days	Sr-85 - 64.84 days Sr-87m - 2.81 hours Sr-89 - 50.5 days Sr-90 - 29.12 years

Chemistry at a Glance: Radioactive Decay

11.5 Transmutation and Bombardment Reactions

11.6 Radioactive Decay Series

Radioactive Disintegration Series

The product of a radioactive decay may itself be unstable and undergo further decays, by either alpha or beta emission. Thus, a succession of unstable elements may be produced, the series continuing until a nucleus is produced that is stable. Such a series is known as a radioactive disintegration, or decay, series. The original nucleus in a decay series is called the **parent nucleus**, and the nuclei resulting from successive disintegrations are known as **daughter nuclei**.

Uranium, **radium**, and **thorium** occur in three **natural decay series**, that end up in stable nuclide of **lead-Pb**. These three series are headed by uranium-238, thorium-232, and uranium-235, respectively. In uranium-bearing rocks, the radioactive uranium decomposes through a series of steps. The final product of this decay is lead. In the process, eight alpha particles are given off for each atom of uranium converted to lead.

Radioactive decay occurs as unstable (radioactive) isotope transforms to a more stable isotope, generally by emitting a subatomic particle such as an **alpha** or **beta** particle. Radio-nuclides that give emit alpha and beta particles also emit significant gamma radiation. Gamma radiation is not a mode of radioactive decay (such as alpha and beta decay). Rather, it is a mechanism by which excess energy is emitted from certain radio-nuclides.

11.7 Chemical Effects of Radiation

Non-ionizing radiation: Radio, microwave Infrared and magnetic fields are considered non-ionizing but still can cause chemical changes though heat and energy transfer. Tanning is caused by infrared light exposure to infrared from the sun. Direct exposure cause more tanning. However the seriousness of exposure to non-ionizing radiation is much least to ionizing radiation. There is some evidence to suggest that non-ionizing radiation and magnetic fields also can cause chemical changes leading to brain tumor and cancer. It is still unproven that cell phone use can lead cancer but prolong exposure to non-ionization radiation could lead to some chemical changes.

Ionizing radiation: Alpha, beta, gamma, X-rays, cosmic rays and UV known as ionizing radiation can cause **ion-pair formation** trough knocking off electrons from atoms and molecules they pass through. The free electrons can cause more ionization and eventually rapped by some molecules as **free radicals**. Free radicals are associated with **faster aging** and **cancer**.

11.8 Biochemical Effects of Radiation

Ionization radiation can affect the body's cells. Passing through the body, they give up their energy over a relatively short distance; alpha particles can inflict more biological damage than other radiations.

Exposure very high doses of ionizing radiation causes injury to living tissue through the transfer of energy to atoms and molecules in the cellular structure. Ionizing radiation causes atoms and molecules to become ionized or excited. These excitations and ionizations can:

- Produce free radicals.
- Break chemical bonds.
- Produce new chemical bonds and cross-linkage between macromolecules.
- Damage molecules that regulate vital cell processes (e.g. DNA, RNA, proteins).
- Cell damage. The cell can repair certain levels of cell damage.
- At higher levels, cell death results. At extremely high doses, cells cannot be replaced quickly enough, and tissues fail to function.

X-rays and radiation therapy

Some of the harmful effects of ionizing radiation were apparent from the outset. Too much X-radiation caused recurrent reddening of the **skin or loss of hair**, hours or days later, often followed by painful radiation burns.

Cancer treatment using **radiation** therapy uses a focused beam of X-rays on a cancerous tumor and using lead to shield unwanted exposure. X-rays are now being used to treat cancer and to relieve arthritic pain.

Gamma rays for treating cancer

Becquerel carried a sealed tube of radium in his vest pocket without knowing the effects gamma radiation. As a result, he got a nasty burn on his chest which ulcerated and left a scar. Currently, radium-filled "needles" are being used to treat solid tumors. Such a needle, inserted into an unwanted growth, would deliver most of its harmful gamma energy to the diseased tissue, while minimizing the dose to healthy tissue.

Irradiated food: Is it safe?

The use of high energy irradiation to kill microbes in food was evaluated in this country since 1921. Ionizing radiation does not cause the food to become radioactive. Therefore, **irradiated food** should not process any danger from getting contaminated with radioactive materials. Pasteurization of food or milk is used to prevent foodborne diseases. Pasteurization involves heating and cause more denaturing milk proteins than using irradiation. Irradiation has become a standard process used to sterilize many consumer and medical products, from adhesive strips to surgical implants using gamma, x-ray and electron beams (beta). The shelf life of food is prolonged because organisms that cause spoilage are reduced along with pathogens.

Thyroid treatment

The iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses I-131 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 d and decays by e^- emission. Emission of a gamma ray accompanies the beta decay.

11.9 Detection of Radiation

The radiation from radioactive materials will ionize atoms by knocking off electrons. This property is useful in identifying radiation. A **radiation detecting device** such as **Geiger counter** can be made by taking a tube containing a gas, enclosing it in a sheet of metal foil,

and running a wire through the center of the tube. When a particle from a radioactive atom passes through the tube, it ionizes the gas, and the light shines. The detector can be connected to a number of different instruments other than a light, such as a buzzer or a meter. Using appropriate electronic attachments, a similar detector can be made which counts both the number and kinds of particles entering the tube

11.10 Sources of Radiation Exposure

11.11 Nuclear Medicine

Some medical uses for various radioisotopes

Carbon-14	Treating brain tumors.
Cobalt-60	Treating cancer, irradiating food, inducing mutations.
Iodine-131	Studying and treating the thyroid gland, finding leaks in water pipes.
Iron-59	Studying the blood.
Sodium-24	Diagnosing circulatory disease.
Strontium-90	Treating small lesions.

Thyroid treatment with I-131

The iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses I-131 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 d and decays by e^- emission. Emission of a gamma ray accompanies the beta decay.

11.12 Nuclear Fission and Nuclear Fusion

Nuclear Fission

If a very heavy nucleus becomes too unstable, it breaks into two approximately equal parts, with the release of a large amount of energy, by a process called FISSION. A nucleus can be made unstable by bombardment with a number of particles, including neutrons. The heaviest elements are the only ones which exhibit the phenomenon of fission. When a heavy nucleus breaks up, usually one or more neutrons are emitted, in addition to the production of the two heavy fragments. It is possible for the neutrons emitted to produce a chain reaction. In the process of splitting, the atom gives off a neutron, which in turn can cause a second atom to split. This continues until a very large number of the atoms present have reacted. Since a large energy change is involved in the fission process, a chain

reaction can serve as an energy source for various purposes. A nuclear reactor is a device for controlling nuclear fission.

Nuclear Fusion

Fusion is another kind of nuclear reaction, and is the reverse of the fission process. The energy of the sun comes from a continual fusion reaction. A great deal of energy is released when several small nuclei are fused into one larger nucleus. In the sun, the four hydrogen atoms fuse into one helium atom (Each second the sun produces 400 million tons of Helium). This is the same type of reaction employed in the hydrogen bomb, in which various isotopes of hydrogen react to produce helium. If such a reaction takes place among a very large number of hydrogen atoms in a very short time, the energy released is tremendous. For such a reaction to take place, it is necessary for the reactants to reach a very high temperature and pressure. These conditions are usually created by a fission reaction. A hydrogen bomb may use a fission bomb as a trigger.

Virtually all of the energy in the universe originates in the fusion of hydrogen nuclei into helium nuclei in stellar interiors, where hydrogen is the most abundant element. Two different reaction sequences are possible, with the likelihood of each depending upon the properties of the star involved. The proton-proton cycle is the predominant energy source of stars whose interiors are cooler than that of the sun, perhaps 2×10^6 oK. The proton-proton cycle proceeds by means of the following reactions:

Which reaction illustrates fusion?

1. ${}_1\text{H}^2 + {}_1\text{H}^2 \rightarrow {}_2\text{He}^4$
2. ${}_0\text{n}^1 + {}_{13}\text{Al}^{27} \rightarrow {}_{11}\text{Na}^{24} + {}_2\text{He}^4$
3. ${}_{13}\text{Al}^{27} + {}_2\text{He}^4 \rightarrow {}_{15}\text{P}^{30} + {}_0\text{n}^1$
4. ${}_7\text{N}^{14} + {}_2\text{He}^4 \rightarrow {}_1\text{H}^1 + {}_8\text{O}^{17}$

A process in which a very heavy nucleus splits into more-stable nuclei of intermediate mass is called:

- a) **nuclear fission**
- b) a chain reaction
- c) nuclear fusion
- d) radiocarbon dating
- e) radioactive decay

Chemistry at a Glance: Characteristics of Nuclear Reactions

11.13 Nuclear and Chemical Reactions Compared

Differences between nuclear reactions and chemical reactions are summarized below:

Nuclear Reactions	Chemical Reactions
1. Protons and neutrons react inside nucleus.	1. Electrons react outside nucleus.
2. Elements transmute into other elements. Elements change.	2. The same number of each kind of atom appears in the reactants and products.
3. Isotopes nuclides different stability.	3. Chemical reactions of isotopes are the same.
4. Independent of chemical combination.	4. Depend on chemical combination.
5. Energy changes equal 10^8 kJ. Large amount of energy released.	5. Energy changes equal $10 - 10^3$ kJ/mol. Small amount of energy released.
6. Mass changes are detectable. Law of conservation of mass not obeyed.	6. Mass reactants = mass products. Law of conservation of mass obeyed.

Compared to chemical reactions, nuclear reactions produce:

- a) proportionally far less energy
- b) proportionally far more energy**
- c) fewer changes in the nucleus
- d) more vegetables

In nuclear reactions:

- a) small amounts of mass are converted to large amount of energy**
- b) large amount of energy are converted to small amount of mass
- c) small amount of mass are converted to large amounts of mass
- d) mass and energy are destroyed

Nuclear changes differ from normal chemical changes in that all nuclear changes:

- a) absorb energy
- b) release energy**
- c) produce explosions
- d) involve the protons and/or neutrons (nucleus) of an atom

Chemical Connections: Tobacco Radioactivity and the Uranium-238 Decay Series; Preserving Food Through Food Irradiation; The Indoor Radon-222 Problem