Chapter 2 - NUCLEAR CHEMISTRY

1-Nuclear Stability and Radioactive Decay

Radioactivity is a decay process of the atomic nuclei, which produces high-energy radiation. The three common types of nuclear radiations are alpha- , beta- , and gamma- radiation. Alpha-particle is a helium nucleus ($^{4}_{2}$He), beta-particle ($^{0}_{-1}$e) is a nuclear electron, and gamma radiation is a high-energy electromagnetic radiation.

The term **nuclide** refers to atomic nuclei with specific number of protons and neutrons, both particles are referred to as **nucleons**. Nuclides are identified by the atomic number (Z) and mass number (A): $^{A}_{Z}X$ unstable nucleus is referred to as **radioactive nuclide.**

Radioactive materials was first discovered by Antoine-Henri Becquerel in 1896 when he discovered that minerals containing uranium wrapped in a paper and stored together in the dark with some photographic papers caused the latter to be exposed. He also found that the radiation from radioactive substances causes ionization of the air molecules. Later, more radioactive substances were discovered by Marie Curie. She also determined that the intensity of radiation is directly proportional to the concentration of the substance, but not to the nature of the compound in which the element occurs. Curie also showed that radioactive decay was not affected by temperature, pressure, or other physical and chemical conditions.

2-Nuclear Equations

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

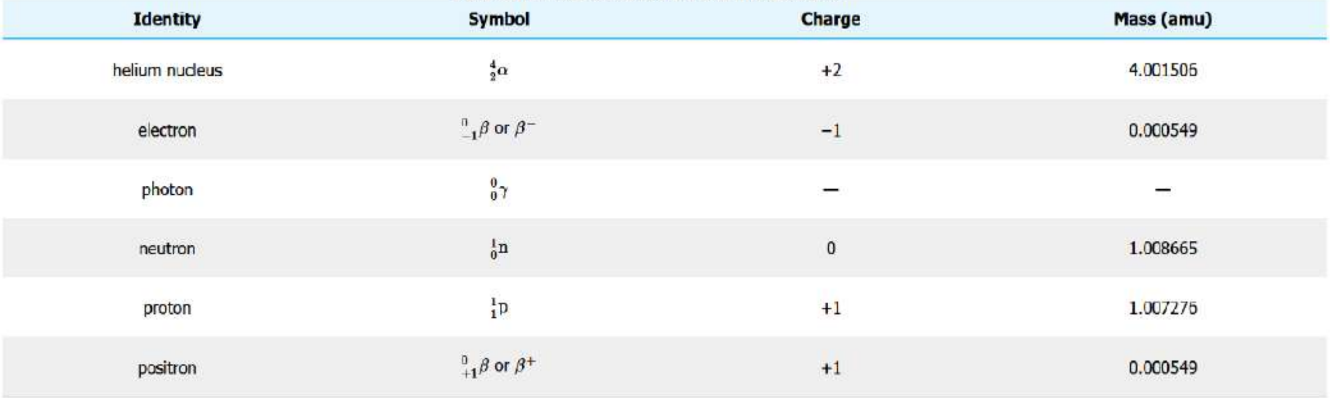
If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}O$ is a product of the nuclear reaction of $^{14}_{7}N$ and $^{4}_{2}He$ if we knew that a proton, $^{1}_{1}H$, was one of the two products. The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars.

Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.

3-Nuclear Decay Reactions

To describe nuclear decay reactions, chemists have extended the *A Z and* X notation for nuclides to include radioactive emissions. Table 1 lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table.1: Nuclear Decay Emissions and Their Symbols



Identity	Symbol	Charge	Mass (amu)
helium nucleus	$^{4}_{2}\alpha$	+2	4.001506
electron	$^{0}_{-1}\beta$ or β^-	−1	0.000549
photon	$^{0}_{0}\gamma$	—	—
neutron	$^{1}_{0}n$	0	1.008665
proton	$^{1}_{1}p$	+1	1.007276
positron	$^{0}_{+1}\beta$ or β^+	+1	0.000549

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy.

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3-1 Alpha α Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, $^4_2\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{^A_Z\mathrm{X}} \rightarrow \underset{\text{daughter}}{^{A-4}_{Z-2}\mathrm{X}'} + \underset{\substack{\text{alpha}\\\text{particle}}}{^4_2\alpha}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$$^{226}_{88}\mathrm{Ra} \rightarrow ^{222}_{86}\mathrm{Rn} + ^4_2\alpha$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

3-2 Beta β^- Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{^1_0\mathrm{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{^1_1\mathrm{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{^{0}_{-1}\beta}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{^A_Z\mathrm{X}} \rightarrow \underset{\text{daughter}}{^{A}_{Z+1}\mathrm{X}'} + \underset{\text{beta particle}}{^{0}_{-1}\beta}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$$^{14}_{6}\mathrm{C} \rightarrow ^{14}_{7}\mathrm{N} + ^{\ 0}_{-1}\beta$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

3-3 Positron *β*+Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$$^{1}_{1}\mathrm{p}^{+} \rightarrow ^{1}_{0}\mathrm{n} + ^{\ 0}_{+1}\beta^{+}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{^{A}_{Z}\mathrm{X}} \rightarrow \underset{\text{daughter}}{^{\ \ A}_{Z-1}\mathrm{X}'} + \underset{\text{positron}}{^{\ 0}_{+1}\beta^{+}}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

3-4 Electron Capture

A neutron-poor nucleus can decay by either positron emission or **electron capture (EC)**, in which an electron in an inner shell reacts with a proton to produce a neutron:

$$^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{1}_{0}\mathrm{n}$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$\underset{\text{parent}}{^{A}_{Z}\mathrm{X}} + \underset{\text{electron}}{^{0}_{-1}\mathrm{e}} \rightarrow \underset{\text{daughter}}{^{A}_{Z-1}\mathrm{X}'} + \text{x-ray}$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$^{55}_{26}\mathrm{Fe} \overset{\mathrm{EC}}{\rightarrow} {}^{55}_{25}\mathrm{Mn} + \text{x-ray}$$

The atomic numbers of the parent and daughter nuclides differ, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$^{55}_{26}\mathrm{Fe} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{55}_{25}\mathrm{Mn} + \text{x-ray}$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

3-5 Gamma γ Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** (γ) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\mathrm{U} \rightarrow \underset{\substack{\text{excited}\\\text{nuclear}\\\text{state}}}{^{234}_{90}\mathrm{Th}^{*}} +^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {^{234}_{90}\mathrm{Th}} + {^{0}_{0}\gamma}$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\mathrm{Th}^{*} \rightarrow {^{234}_{88}\mathrm{Th}} +^{0}_{0}\gamma$$

or more generally,

$$^{A}_{Z}\mathrm{X}^{*} \rightarrow {^{A}_{Z}\mathrm{X}} +^{0}_{0}\gamma$$

3-6 Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}{}_{98}\mathrm{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\mathrm{Cf} \rightarrow {^{118}_{46}\mathrm{Pd}} + {^{132}_{52}\mathrm{Te}} + 4^{1}_{0}\mathrm{n}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

4- The Kinetics of Radioactive Decay

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using N to represent the number of atoms of the radioactive isotope, we can define the **rate of decay** of the sample, which is also called its **activity (A)** as the decrease in the number of the radioisotope's nuclei per unit time:

$$A = -\frac{dN}{dt} \ldots \ldots \ldots . . (1)$$

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm). The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = \lambda N \ldots . . (2)$$

Here, the symbol λ is the radioactive decay constant, which has units of inverse time (e.g., s^{-1}, yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 1 and Equation 2, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{dN}{dt} = \lambda N \ldots (3)$$

Rearranging the equation (3) gives:

$$-\frac{dN}{N} = \lambda dt \ldots (4)$$

By integration of the equation (4) we obtain

$$N = N_0 e^{-\lambda t} \ldots.(5)$$

The SI unit of nuclear activity is called the *Becquerel* (Bq), where 1 Bq = 1 disintegration/s. More commonly used unit for activity is the Curie (Ci), where 1 Ci = 3.70 x 10^{10} Bq .

4-1 Half-life

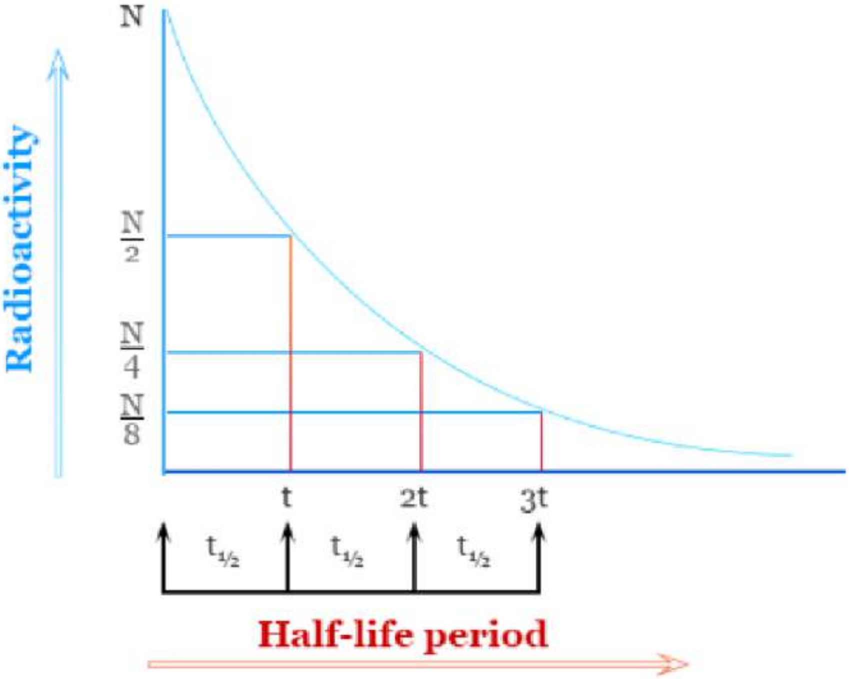
The half-life ($t_{½}$) is the amount of time necessary for one-half of the radioactive material to decay.

Consider the case where half of N0 has been consumed. The previous equation (5) gives

$$\boldsymbol{\frac{N_0}{2} = N_0 e^{-\lambda t_{1/2}} \ldots \ldots.(6)}$$

$$t_{\frac{1}{2}} = \frac{ln2}{\lambda} \ldots \ldots.(7)$$

Each successive half-life is the same length of time, as shown in Figure 1, and is *independent* of *N:*



If the radioactivity of an element is 100% and the half-life period of this element is 4 hours.

1. After four hours, it decomposes 50% and the remaining 50%.
2. After 8 hours it decomposes 75% and reaming 25% and the process continued.
3. Hence, after complete n half-lives, the amount of radioactive element reaming $(1/2)^n$.

5- Radioisotope Dating

Fixing the dates of relics or fossils is an application based on the rate of radioactive decay. The decay of carbon-14 is often used to date objects, which at one time contain living materials. Carbon-14 is continuously formed in the upper atmosphere by reaction of neutrons from cosmic radiation with nitrogen-14:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p}$$

Carbon-14 nuclide undergoes beta-decays with a half-life of 5730 yrs:

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$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$; $t_{½} = 5730$ yrs.

In nature, the rate of formation and decay of carbon-14 is equal, establishing a steady state concentration for carbon-14 in nature. The natural radioactivity of carbon-14 is about 14.9 dpm/g-C. In the atmosphere, carbon-14 is converted to $^{14}CO_2$, which is then absorbed by plants during photosynthesis and incorporated into the plant materials. Animals and human consumed plants and the carbon-14 become part of the body tissues, including bones. Carbon-14 is distributed throughout living matters (plants and animals), and the radioactivity of carbon-14 remains constant at about 14 dpm/g-C.

However, when the plant or an animal dies and metabolic processes stop and the level of carbon-14 decreases as it continues to decay but not get replaced. By comparing the radioactivity of isotope carbon-14 in the dead material with the steady state radioactivity, and the knowledge of its half-life, the age of the object can be calculated. The accuracy of carbon-14 dating is limited to periods between 500 to 30,000 years. Its accuracy also depends on the assumption that carbon-14 level in the atmosphere remains about constant.