⇒ **Radioactive decay or Disintegration law:**

All the radioactive isotopes/nuclei decay spontaneously following First order kinetics. The rate of disintegration or decay of a radioactive isotope/nucleus/element at a given instant of time is proportional to the amount/number of atoms present in it.

i.e; $-\frac{dN}{dt} \propto N$ or, $-\frac{dN}{dt} = \lambda N$ —(1) (where $\frac{dN}{dt}$ = rate of decay, N = amount/number of atoms, λ = decay or disintegration constant)

* **Mathematical deduction of decay law:** From disintegration law, $-\frac{dN}{dt} = \lambda N$ or, $-\frac{dN}{N} = \lambda dt$ —(2)

Integrating equation (2), we get $-\int \frac{dN}{N} = \lambda \int dt$ or, $-\log_e N = \lambda t + C$ —(3) (where C = Integration constant)

Now, at t = 0 (initial state), N = N_0 (No. of initial atoms)

Putting above values in equation (3), $\log_e N_0 = \lambda \times 0 + C$ or, $C = -\log_e N_0$

Putting the value of C in equation (3), we get $-\log_e N = \lambda t - \log_e N_0$ or, $\lambda t = \log_e N_0 - \log_e N$

Or, $\lambda t = \log_e N_0/N = 2.303 \log N_0/N$ ∴ $\boxed{\lambda = \frac{2.303}{t}\log\frac{N_0}{N}}$ —(4)

or, $\boxed{N = N_0 e^{-\lambda t}}$ —(5)

Equations (4) & (5) are required relationship between the number of atoms/amount at time 't' and initial number of atoms/amount.

⇒ **Half life Period:** Time for complete decay or disintegration of a radioactive substance is ∞ (undefine/infinity) by disintegration law/expression. So, half life period of a radioactive substance defined. The time during which half of the total radioactive element disintegrates is called half life period. It is defined as " the time taken for the number of atoms/amount/activity of a radioactive substance to fall half of its initial value is called half life period" It is denoted by $t_{1/2}$. It is characteristic of every radioactive substance. e.g. The half life of Ra is about 1600 years, means one half of Ra (1gm say) will disintegrate in 1600 years, half of the remainder one half (say 1/4 gm) will disintegrate in the same time, and so on:

$\underset{(1gm)}{Ra} \xrightarrow{1600yrs} \underset{(1/2gm)}{Ra} \xrightarrow{1600yrs} \underset{(1/4gm)}{Ra} \cdots$

* **Expression for $t_{1/2}$ or, Relation between $t_{1/2}$ & λ (decay constant):**

From disintegration law, $\lambda = \frac{2.303}{t}\log N_0/N$ —(1)

By definition of half life, $t = t_{1/2}$, $N = N_0/2$

Putting above values in equation (1), we get $\lambda = \frac{2.303}{t_{1/2}}\log\frac{N_0}{N_0/2} = \frac{2.303}{t_{1/2}}\log 2 = \frac{2.303 \times 0.301}{t_{1/2}}$

or, $\lambda = \frac{0.693}{t_{1/2}}$ ∴ $\boxed{t_{1/2} = \frac{0.693}{\lambda}}$ —(2)

Equation (2) is required expression of half life or, relation between half life & decay const.

From equation (2), i.e; expression of $t_{1/2}$ it is evident that half life period of a radioactive substance is independent of initial amount/no. of atoms/concentration.

⇒ **Average life period:** Since, the total decay period of any radioactive substant is infinity, it is meaningless to use life period, i.e; total decay period. Thus, the term average life period is used. It is defined as " the reciprocal of disintegration constant of the radioactive substance is known as average life period." It is denoted by T or E.

∴ Average life period (T or E) = $1/\lambda$ (Where λ = decay or disintegration constant)

* **Relation between average life period & half life period:** By definition of average life period, $T = \frac{1}{\lambda}$ —(1)

By half life period expression, $t_{1/2} = 0.693/\lambda$ or, $\lambda = \frac{0.693}{t_{1/2}}$ —(2)

From equation (1) & (2), $T = \frac{t_{1/2}}{0.693}$ or, $t_{1/2} = 0.693T$ ∴ $T = 1.443 t_{1/2}$ —(3) This is required relation between T & $t_{1/2}$.

⇒ **Mass defect**: It has been observed that the mass of the atom of an element is invariably less than the sum of the masses of the nucleons (i.e; protons & neutrons)." The difference between the calculated mass and actual or observed mass is called the mass defect." It is denoted by Δm.

∴ Mass defect (Δm) = Calculated mass (i.e, expected mass) − Actual mass (i.e; observed mass) = $[Z \cdot m_p + Z \cdot m_e + (A-Z) m_n] - A$ [Where A = observed or actual mass, Z = atomic no., m_p = mass of proton, m_e = mass of electrons, m_n = mass of neutron, m_H = mass of hydrogen atom]

∴ $\boxed{\Delta m = Z m_H + (A-Z) m_n - A}$

For example, Actual atomic mass of He (A) = 4.0039 amu. No. of protons = 2 = No. of electrons, Atomic no. of He (Z) = 2, No. of neutron = 2, m_p = 1.00758, m_n = 1.00893, m_e = 0.0005 amu

Calculated mass of He = 2×1.00758 + 2×1.00893 + 2×0.0005 = 4.0341 amu.

Hence, the mass defect (Δm) = 4.0341 − 4.0039 = 0.03021 amu.

Mass defect can be converted into binding energy in the nucleus, and hence decides its stability.

⇒ **Nuclear binding energy / Binding energy**: When a proton and neutron combine to form a nucleus, some mass is lost in the form of energy. Thus, the energy released, when neutron & proton combine to form nucleus is called nuclear binding energy or simply binding energy. It may also be defined as "the energy required to separate the proton and neutron from the nucleus of an atom".

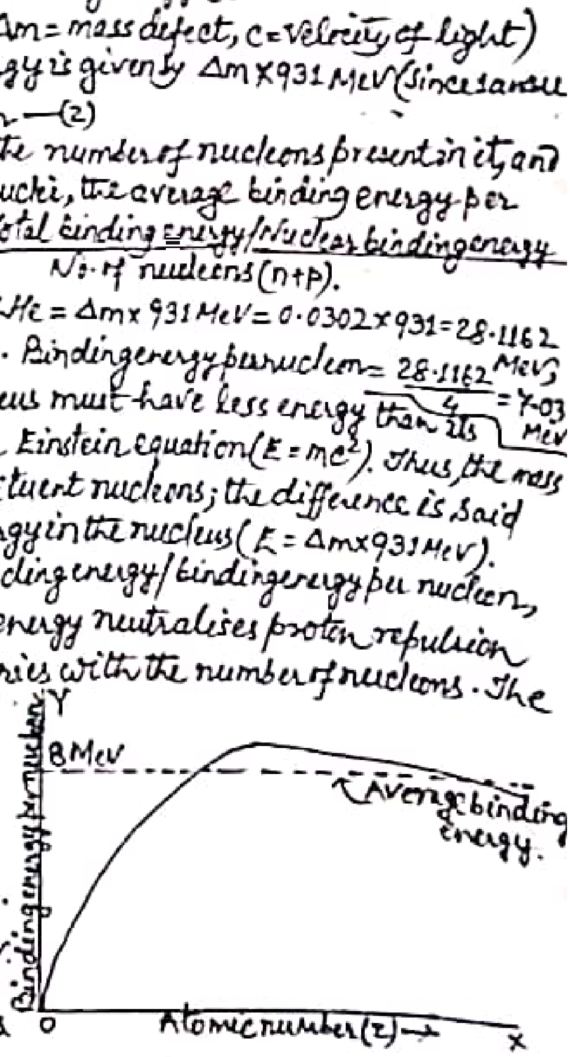
According to Einstein equation ($E = mc^2$), Nuclear binding energy (E) = $\Delta m \times c^2$ —(1)
(Where Δm = mass defect, c = Velocity of light)

If Δm is the mass defect in amu, then nuclear binding energy is given by $\Delta m \times 931$ MeV (Since 1 amu = 931 MeV), i.e, Nuclear binding energy (E) = $931 \times \Delta m$ —(2)

The binding energy of the nucleus varies with the number of nucleons present in it, and to compare the nuclear stability of different elements/nuclei, the average binding energy per nucleon is calculated. ∴ Binding energy per nucleon = $\frac{\text{Total binding energy / Nuclear binding energy}}{\text{No. of nucleons (n+p)}}$.

For example, Nuclear binding energy / Binding energy of He = $\Delta m \times 931$ MeV = 0.0302 × 931 = 28.1162 [Since mass defect (Δm) = 4.0341 − 4.0039 = 0.0302]. Binding energy per nucleon = $\frac{28.1162}{4}$ MeV = 7.03 MeV

* **Binding energy & stability of nucleus**: A stable nucleus must have less energy than its constituent particles. Energy and mass are related by the Einstein equation ($E = mc^2$). Thus, the mass of a stable nucleus must be less than that of the constituent nucleons; the difference is said mass defect. Mass defect converted to the binding energy in the nucleus ($E = \Delta m \times 931$ MeV). Clearly, the larger the mass defect, the larger the binding energy / binding energy per nucleon, and therefore the more stable the nucleus. Binding energy neutralises proton repulsion in the nucleus. The binding energy of the nucleus varies with the number of nucleons. The graph of binding energy per nucleon against atomic number for the different elements/nuclei shows that nucleons are held together with increasing force up to a mass no. of about 65. The binding energy for each additional nucleon decreases as the nuclei get larger. The average binding energy per nucleon is about 8 MeV for most nuclei. This amount of energy is needed to remove either a proton or a neutron from the nucleus.



⇒ Radioactive decay series:

The phenomenon of natural radioactivity continues till a stable isotope is reached. Nuclei from the parent or initial radioactive element (heavy) to the final (a stable isotope) constitute a series known as radioactive decay series. The common radioactive elements $^{232}Th_{90}$, $^{238}U_{92}$ & $^{227}Ac_{89}$ belong to three different series named after them. They decay by a series of α & β-particles emissions and finally reach a stable isotope (Pb_{82}). $^{237}Np_{93}$, an artificial element constitute fourth radioactive decay series which ends with $^{209}Bi_{83}$. There are four radioactive series: (i) Thorium (Th_{90}) Series or 4n series (ii) Uranium (U_{92}) Series or (4n+2) series (iii) Actinium (Ac_{89}) Series or (4n+3) series (iv) Neptunium (Np_{93}) Series or (4n+1) series. The number (n) indicate that the parent and all the members of a particular Series have mass numbers exactly divisible by 4 or, divisible by 4 with a remainder 1, 2 or 3. There are no natural cross-linking between the four radioactive series, although this can be performed artificially.

(i) <u>Thorium or 4n Series</u>: Radioactive series, whose starting nuclide is $^{232}Th_{90}$ and final nuclide is $^{208}Pb_{82}$, known as Thorium or 4n series ($n = \frac{232}{4} = 58$). In this series, 6α & 4β-particles are emitted and total number of steps are 10.

$$^{232}Th_{90} \xrightarrow[10\ steps]{(-6\alpha,\,-4\beta)} {}^{208}Pb_{82} \text{ (stable isotope of lead)}$$

(Here one α particle decreases atomic no. by 2 units and mass no. by 4 units while one β-particle increases atomic no. by 1 unit and mass no. remains unchanged.)

(ii) <u>Neptunium or (4n+1) series</u>: Radioactive Series, which starts from an artificial element $^{237}Np_{93}$ (obtained from $^{237}U_{92}$ by β-decay) and ends on $^{209}Bi_{83}$ (a stable isotope), known as (4n+1) or Np series, since mass no of parent element (^{237}Np) divisible by 4 with a remainder 1. In this Series, 7α & 4β particles are emitted and total number of steps is 11.

$$^{237}Np_{93} \xrightarrow[11\ steps]{(-7\alpha,\,-4\beta)} {}^{209}Bi_{83} \text{ (stable isotope)}$$

(iii) <u>Uranium or (4n+2) series</u>: Radioactive series which starts from $^{238}U_{92}$ and end on $^{206}Pb_{82}$ is known as uranium or (4n+2) series. Here mass no. of U-238 is divisible by 4 with a remainder 2, so called (4n+2) series. In this series, 8α & 6β particles are emitted in 14 different steps. This is longest radioactive series.

$$^{238}U_{92} \xrightarrow[14\ steps]{(-8\alpha,\,-6\beta)} {}^{206}Pb_{82}$$

(iv) <u>Actinium or (4n+3) series</u>: Radioactive series which starts from $^{235}U_{92}$ / $^{227}Ac_{89}$ and ends on a stable isotope of lead ($^{207}Pb_{82}$) is called actinium or (4n+3) series. The mass no. of U & Ac is divisible by 4 with a remainder 3, so called (4n+3) series. In this series 7α & 4β-particles are emitted and total numbers of steps is 11.

$$^{235}U_{92} \xrightarrow{(-\alpha)} {}^{231}Th_{90} \xrightarrow{(-\beta)} {}^{231}Pa_{91} \xrightarrow{(-\alpha)} {}^{227}Ac_{89} \xrightarrow[8\ steps]{(-5\alpha,\,-3\beta)} {}^{207}Pb_{82}.$$

(11 steps)

4n, (4n+2) & (4n+3) series are natural radioactive decay series while (4n+1) Series is artificial or manmade radioactive decay series.

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B.Sc-III Hons, Paper-06 (Inorganic Chemistry)

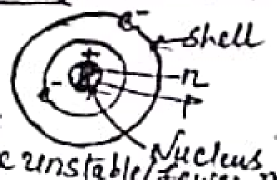
Unit-3, Nuclear Chemistry [By Dr. Birendra Kumar, Maharaja College]

Nuclear Chemistry is a branch of chemistry which dealing with radioactivity, nuclear processes and transformations in the nucleus of atom.

⇒ Constituents/structure of the Nucleus:

Atomic nuclei are made up of protons(p) and neutrons(n). The nuclear radius is very small($\simeq 10^{-14}$ cm). Numbers of protons is equal to atomic numbers(z). The total number of protons and neutrons (nucleons) is called mass number(A), responsible for most of the mass of an atom. It is possible to have two or more nuclei with the same numbers of protons but different numbers of neutrons. Such sets of nuclei are called isotopes. e.g. $^4He_2$(p=2, n=2) & $^3He_2$(p=2, n=1) are isotope nuclei. Density of nucleus is very high ($\simeq 10^{13}$ g cm^{-3}).

The nucleus is sometimes considered to resemble a 'liquid drop'. The repulsive forces between the like charges(+) on the protons tend to split the drop, and a surface tension effect opposes this. The density of different nuclei is almost constant and the range of nuclear attractive forces is very small. The nucleus may be regarded as 'shell structure' with the nucleons(n & p) arranged in shells rather like the orbital electrons(e).



Elements/nuclei of even atomic nos (n&p) are more stable and more abundant than elements of odd atomic nos. (n&p). Elements of even atomic nos (n&p) are stablest/richer in isotopes while with odd atomic nos (n&p) are unstable/fewer no. of isotopes. If two protons spins in opposite directions (in case even n&p), the magnetic field they produce will mutually cancel each other. The small amount of binding energy generated is sufficient to stabilize the nucleus. Nuclei with 2, 8, 20, 28, 50, 82 or 126 n/p are particularly stable and have a large no. of isotopes. These nos. are called Magic numbers.

⇒ Radioactivity:

Radioactivity is a phenomenon of spontaneous emission of radioactive rays (α, β, γ) from the substance containing unstable radio nuclides, and the substance is called radio active substance. It is a natural, spontaneous, continuous and stepwise process of disintegration. It was first observed by Henry Becquerel (1896) during study of fluorescence property of potassium uranyl sulphate. Later on, Madam Curie & Pierre Curie found that Pitch blende showed higher degree of radioactivity than that of Uranium deposits. Uranium(U), Radium(Ra), Thorium(Th), Polonium(Po) etc. are important radioactive elements.

⇒ Radioactive rays & Comparative properties:

The rays or radiations emitted from radioactive elements are known as radioactive rays. Radioactive rays are: α rays (He^{2+} particles stream), β-rays (e^-_1 stream) & γ-rays (electromagnetic radiations of high frequencies.

Properties	α-rays	β-rays	γ-rays
1. Nature	They are streams of He^{2+} particles, i.e. +vely charged.	They are streams of e^-_1, electrons, i.e. -vely charged.	They are electromagnetic radiations similar to X-ray (neutral)
2. Charge	+2 Unit, 3.2×10^{-19} coulomb	-1 Unit, -1.6×10^{-19} coulomb	Chargeless (0)
3. Mass	4 amu.	1/1840 amu	negligible
4. Velocity	Its velocity is one 10th of the velocity of light ($\simeq 3\times10^{9}$ cm/s)	Its velocity is near to velocity of light ($\simeq 2.36$-2.83×10^{10} cm/s)	Its velocity is same as the velocity of light (3×10^{10} cm/s).
5. Ionising power	Maximum ionising power (100 times of β-rays)	Less ionising power (100 times of γ-rays)	Least ionising power (1).
6. Penetration power	Least penetrating power	More (100 times of α) penetrating power	Highest penetrating power than α (10^3 times) & β (10 times)
7. Kinetic energy	High	Very less	zero