3 Atomic Structure

How are electrons organised around the nucleus?

All atoms would like to attain electron configurations like noble gases to form stable electron configurations by:

- Losing electrons
- sharing electrons
- Gaining electrons.

For a stable configuration each atom must fill its outer energy level. In the case of noble gases that means *eight electrons in the last shell* (with the exception of He which has two electrons).

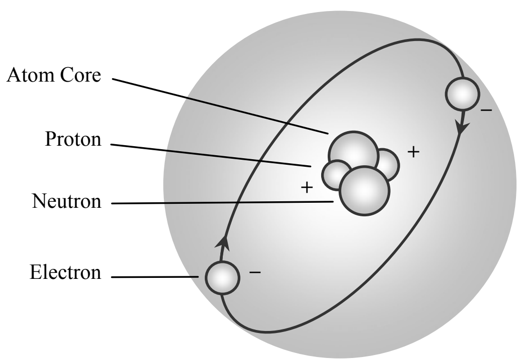

Figure: 3.1

The idea of tiniest unit of matter (Anu and Parmanu) was propounded by **maharishi Kanada** in Vedic period in our country. The word **"ATOM"** is given by **"John Dalton".** An element is a pure substance which cannot be subdivided into two or more new substances by any means. "The smallest indivisible particle or unit of an element is called an atom, which can take part in a chemical reaction and may or may not exist independently".

Later the works of **William Crookes (1878), J J Thomson** (1897) and **Goldstein** proved that atom of any element contains smaller particles which are either positively charged or negatively charged. Work of **Rutherford** and **Neil's Bohr** confirmed that an atom consists of three subatomic particles, which are electrons, protons and neutrons. It has been established that the central core of an atom consists of protons and neutrons and is commonly called **nucleus.** The electrons revolve around the nucleus.

The works of J J Thomson and Ernst Rutherford actually laid the foundation of the modern picture of the atom. It is now believed that the atom consists of several *sub-atomic particles* like electron, proton, neutron, positron, neutrino, meson, etc. Out of these particles, the electron, proton and the neutron are called fundamental subatomic particles and others are non-fundamental particles.

The atom as a whole is electrically neutral as the number of protons in it, is equal to the number of electrons.

Table: 3.1

Nucleus	Electrons
The nucleus is the centre of mass (1), but does not significantly contribute to volume.	The electronic cloud determines the **size,** or **volume** of the atom, but does not significantly contribute to mass.
It is made up of: **Protons:** Mass = 1 amu, charge = +1 **Neutrons:** 1amu, charge = 0	**Electron;** mass = 0.005 amu, charge = –1 Electrons are found outside the nucleus. They occupy **orbitals**. They are the unit of negative charge; determine the **atomic number (Z).**

Property	Electron	Proton	Neutron
1. Discovery	J J Thomson	E. Goldstein	James Chadwick
2. Symbol	e	p	n
3. Nature	Negatively charged	Positively charged	Neutral
4. Relative charge	–1	+1	0
5. Absolute charge	1.602×10^{-19} C	1.602×10^{-19} C	0
6. Relative mass	1/1837	1	1
7. Absolute mass	9.109×10^{-28} g	1.6725×10^{-24} g	1.6748×10^{-24} g

Discovery of Electrons

Faraday contributed significantly. He discovered that the amount of substance produced at the poles during electrolysis (the chemical change when electric current is passed through a solution of electrolytes) was proportional to the amount of electric current. He also found in 1833 that the amount of electricity required to produce 1 mole of substance at the electric poles is constant (96,500 C). These relations were summarised as **Faraday's law of electrolysis**.

Faraday himself had no intention to combine his law with the atomic theory. However, the Irish chemist George **Johnstone Stoney** (1826–1911) had the insight to notice the significance of Faraday's law for the structure of matter; he concluded that a fundamental unit of electricity exists, in other words, an atom of electricity.

He dared to give the name electron to that hypothetical unit. Then another interesting finding emerged due to vacuum discharge experiments.

When cations hit the anode upon application of high voltage at low pressure (lower than 10–12 to 10–14 Torr), the gas in the tube, although it was an insulator, became conductive and emitted light. When the vacuum was increased, the wall began to glitter, emitting fluorescent light.

The German physicist Julius Plücker (1801-1868) took interest in this phenomenon and interpreted it as follows: some particles are being emitted from the cathode. He gave the name cathode ray to these unidentified particles (1859).

Joseph John Thomson

The British physicist Joseph John Thomson (1856–1940) showed that the particle possessed negative charge. He further sought to determine the mass and the charge of the particle by estimating the effect of electric and magnetic fields on the motion of the particle. He obtained the ratio of the mass to the charge. To obtain their absolute values, one of the two had to be determined. The cathode ray generated in a vacuum tube when a high vacuum was applied provided very significant information on the structure of the atom.

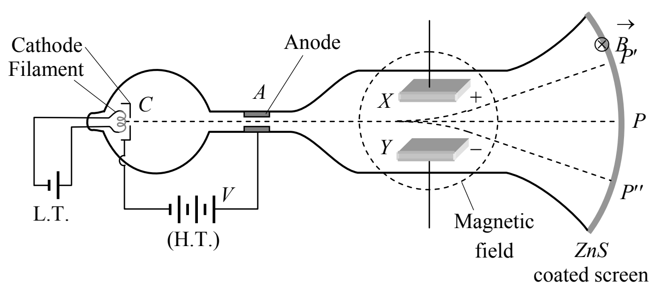

Figure: 3.2

This unidentified particle would, after being emitted from the *cathode*, fly straight toward the wall of the tube or to the *anode*. It was found that the particle was charged since its course of flight was curved when a magnetic field was applied. Furthermore, the properties of the ray did not depend on the type of metal used in the cathode tube, nor on the type of gas in the discharge tube. These facts suggested the possibility that the particle could be a fundamental constituent of matter.

Millikan's Oil Drop: The American physicist Robert Andrew Millikan (1868–1953) successfully proved by an ingenious experiment the particulate nature of electricity. The experiment is called Millikan's oil drop experiment.

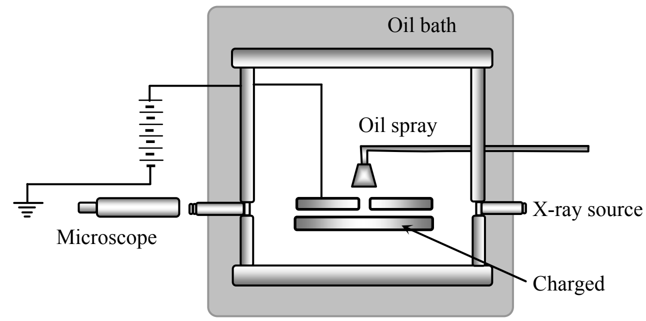

Figure: 3.3

Droplets of oil atomised in a chamber fall under the influence of gravity. If the oil droplet has an electric charge, its motion may be controlled by countering gravity with an electric attraction applied by an electric field.

- The combined motion can be analyzed by classical physics. Millikan demonstrated by these experiments that the charge of an oil drop is always an integral multiple of 1.6×10^{-19}C.
- This fact led to a neat explanation by attributing the charge of 1.6×10^{-19}C to the electron. The charge/mass ratio of the charged particle so far known was 1/1000 (C/g).
- The ratio Thomson obtained was much larger than that (the accurate value now accepted is as large as 1.76×10^8 C/g), and that finding was not in the framework of the knowledge at that time. The particle should not be a kind of ion or molecule, but should be regarded as a part or fragment of an atom.

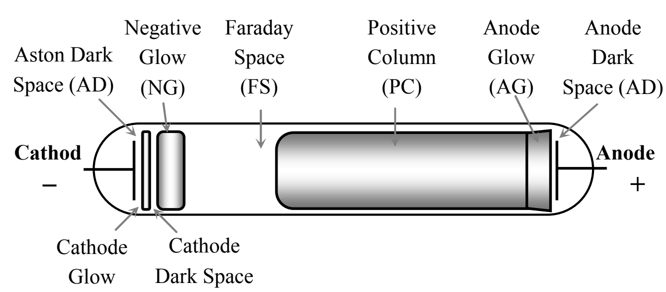

Figure: 3.4

In 1886, **Goldstein** using the discharge tube with perforated cathode discovered that in a discharge tube not only cathode rays, but also a stream of anode rays called canal rays or positive rays are present. The canal rays were found to be attracted towards the negative electrode showing that these are made up of positively charged particles.

X-rays: Wilhelm Röentgen (1845–1923) in 1895 showed that when electrons strike a material in the cathode ray tubes, produce rays which can cause fluorescence in the fluorescent materials placed outside the cathode ray tubes. Since **Röentgen** did not know the nature of the radiation, he named them X-rays and the name is still carried on. It was noticed that X-rays are produced effectively when electrons strike the dense metal anode, called targets. These are not deflected by the electric and magnetic fields and have a very high penetrating power through the matter and that is the reason that these rays are used to study the interior of the objects. These rays are of very short wavelengths (~0.1 nm) and possess electromagnetic character.

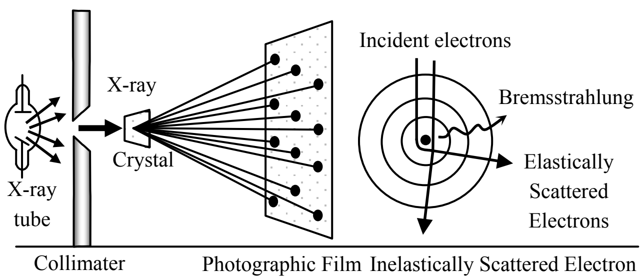

Figure: 3.5

Energy of X-ray photon $= h\nu = \dfrac{hc}{\lambda}$

Momentum of X-ray photon $= \dfrac{h\nu}{c} = \dfrac{h}{\lambda}$

- **Duane–Hunt Rule:** Minimum wavelength of continuous X-ray spectrum $\lambda_{min} = \dfrac{hc}{eV}$

Radioactivity: Henri Becquerel (1852–1908) observed that there are certain elements which emit radiation on their own and named this phenomenon as radioactivity and the elements known as radioactive elements.

This field was developed by **Marie Curie, Rutherford** and **Frederick Soddy**. It was observed that three kinds of rays i.e., α, β and γ-rays are emitted. Rutherford found that $\alpha -$ rays consist of high energy particles carrying two units of positive charge and four unit of atomic mass. He concluded that α-particles are helium nuclei as when $\alpha -$ particles combined with two electrons yielded helium gas. $\beta -$ rays are negatively charged particles similar to electrons. The γ – rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles. As regards penetrating power, $\alpha -$ particles are the least, followed by $\beta -$ rays (100 times that of α–particles) and γ – rays (1000 times of that $\alpha -$ particles).

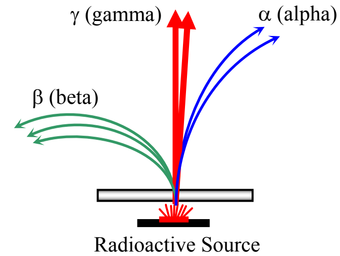

Figure: 3.6

Atomic Models

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, proposed by **J J Thomson** and **Ernest Rutherford** are discussed below.

Thomson Model of Atom

J J Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. "He proposed that an atom consists of a sphere of positive electricity in which electrons are embedded like plum in pudding or seeds evenly distributed in red spongy mass in watermelon." Although Thomson's model could explain the electrical neutrality of an atom but this model could not satisfy experimental facts proposed by Rutherford and hence was discarded.

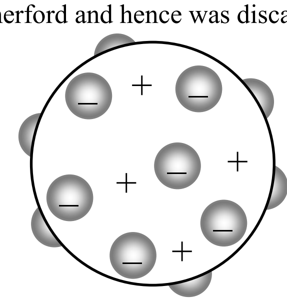

Figure: 3.7

Rutherford's Model of Atom

Ernest Rutherford and his co-workers performed numerous experiments in which $\alpha -$ particles emitted from a radioactive element such as polonium were allowed to strike thin sheets of metals such as gold and platinum. About 99% of the $\alpha -$ particles passed un-deflected through the gold foil and caused illumination of zinc sulphide screen. Very few $\alpha -$ particles underwent small and large deflections after passing through the gold foil. A very few (about 1 in 20,000) were deflected backward on their path at an angle of 180º as a result of their direct collisions with the heavy mass.

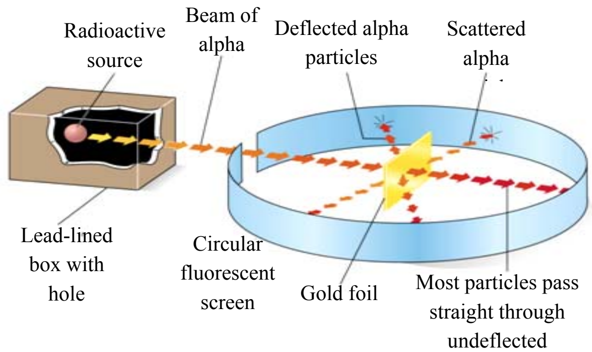

Figure: 3.8

Rutherford proposed the atom of an element consists of a small positively charged "Nucleus" which is situated at the centre of the atom and which carries almost the entire mss of the atom. The electrons are distributed in the empty space of the atom around the nucleus in different concentric circular paths (orbits).

The stability of such a system in which negatively charged electrons surround a positively charged nucleus was explained by proposing that the electrons revolve around the nucleus at very high speed in circular orbits. This arrangement is just like our solar system. The high sped of the moving electrons given them a centrifugal force acting away from the nucleus. The centrifugal force balances the electrostatic force of attraction acting between the nucleus and the electrons.

Defects in Rutherford's Model

Rutherford did not specify the number of electrons in each orbit. According to electromagnetic theory, if a charged particle (electron) is accelerated around another charged particle (nucleus) then there would be continuous radiation of energy. This loss of energy would slow down the speed of electron and eventually the electron would fall into the nucleus. But such a collapse does not occur. *Rutherford's* model of the atom was unable to explain certain observations with regard to the atom i.e. stability of the atom and the occurrence of the atomic spectra.

Valency of an element is the combining capacity of the atoms of the element with atoms of the same or different elements**.** The combining capacity of the atoms of other elements was explained in terms of their tendency to attain a fully-filled outermost shell (stable octet or duplet). Valency of an element is determined by the number of valence electrons in an atom of the element.

- **The valency of an element = number of valence electrons**
  (*when number of valence electrons are from 1 to 4***)**
- **The valency of an element = 8 – number of valence electrons.**
  (*when number of valence electrons are more than 4***)**

Example: Na has 1 valence electron, thus, its valency is 1. **Cl** has 7 valence electrons, thus, its valency is 8 – 7 = 1.

- Atoms that have 1, 2 or 3 electrons in their outer levels will tend to lose them in interactions with atoms that have 5, 6 or 7 electrons in their outer levels.
- Atoms that have 5, 6 or 7 electrons in their outer levels will tend to gain electrons from atoms with 1, 2 or 3 electrons in their outer levels.
- Atoms that have 4 electrons in the outer most energy level will tend neither totally lose nor totally gain electrons during interactions.

- **Bohr– Sommerfeld model**
  It is an extension of Bohr's model. The electrons in an atom revolve around the nuclei in elliptical orbit. The circular path is a special case of ellipse. Association of elliptical orbits with circular orbit explains the fine line spectrum of atoms.

Niels Bohr model: Bohr accepted Rutherford's idea that the positive charge and most of the mass of the atom is concentrated in its nucleus with the electrons present at some distance away. Electrons revolve around the nucleus in well defined orbits or shells, each shell having a definite amount of energy associated with the electrons in it. Therefore, these shells are also called energy levels.

- The energy associated with the electrons in an orbit increases as the radius of the orbit increases. These shells are known as K, L, M, N, etc. starting from the one closest to the nucleus.
- An electron in a shell can more to a higher or lower energy shell by absorbing or releasing a fixed amount of energy.
- The amount of energy absorbed or emitted is given by the difference of energies associated with the two energy levels.

Energy absorbed, $E = E_2 - E_1 = hv$

Energy emitted, $E = E_2 - E_1 = hv$

Where, h is Plank's constant $\left(h = 6.62\times10^{-34}\,Js\right)$ and ν is the frequency of the radiation.

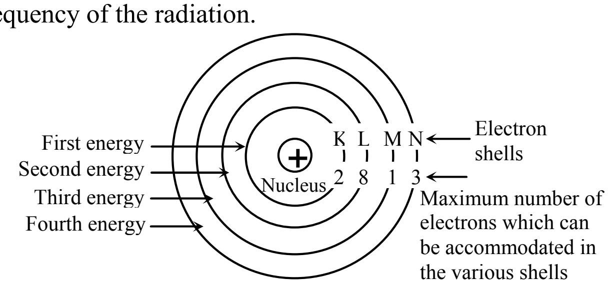

Figure: 3.9

The maximum number of electrons that can be accommodated in a shell is given by the formula $2n^2$ (where, n = number of shell i.e. 1, 2, 3.....)

Table: 3.2

Shell	n	$2n^2$	Max. no. of e^-
K	1	$2(1)^2$	2
L	2	$2(2)^2$	8
M	3	$2(3)^2$	18
N	4	$2(4)^2$	32

Each energy level is further divided into sub-shells designated as s, p, d, f.

- 1^{st} shell (K) contains 1 sub-shell (s)
- 2^{nd} shell (L) contains 2 sub-shells (s,p)
- 3^{rd} shell (M) contains 3 sub-shells (s,p,d)
- 4^{th} shell (N) contains 4 sub-shells (s,p,d,f).

Orbitals: Like shells are divided into sub-shells, subs-hells further contain orbitals. An orbital may be defined as a **"**Region in the three-dimensional space around the nucleus where the probability of finding an electron is maximum. The maximum capacity of each orbital is that of two electrons.**"**

Sub-shell	s	p	d	f
Orbital (s)	1	3	5	7
Max. no of electrons	2	6	10	14

The total number of nucleons is equal to the mass number (1) of the atom. Atomic number is the number of protons present in the atom of an element. It is denoted by "Z"

(In a Neutral atom): Atomic number = Number of protons = Number of electrons

(In an Ion): Atomic number = Number of protons **e.g.** $_{11}$**Na**

Different Types of Atomic Species

Mass number: Mass number (1) = Number of protons or Atomic number (*Z*) + Number of neutrons or Number of neutrons = $A - Z$. The atom of an element X having mass number (1) and atomic number (Z) may be represented by a symbol, $_ZX^A$.

Table: 3.3

Atomic species	Similarities	Differences	Examples
Isotopes (Soddy)	(i) Atomic no. (*Z*) (ii) No. of protons (iii) No. of electrons (iv) Electronic configuration (v) Chemical properties (vi) Position in the periodic table	(i) Mass no. (1) (ii) No. of neutrons (iii) Physical properties	(i) $^1_1H, ^2_1H, ^3_1H$ (ii) $^{16}_8O, ^{17}_8O, ^{18}_8O$ (iii) $^{35}_{17}Cl, ^{37}_{17}Cl$
Isobars	(i) Mass no. (1) (ii) No. of nucleons	(i) Atomic no. (*Z*) (ii) No. of protons, electrons and neutrons (iii) Electronic configuration (iv) Chemical properties (v) Position in the periodic table	(i) $^{40}_{18}Ar, ^{40}_{19}K, ^{40}_{20}Ca$ (ii) $^{130}_{52}Te, ^{130}_{54}Xe, ^{130}_{56}Ba$
Isotones	No. of neutrons	(i) Atomic No. (ii) Mass No., protons and electrons. (iii) Electronic configuration (iv) Physical and chemical properties (v) Position in the periodic table	(i) $^{30}_{14}Si, ^{31}_{15}P, ^{32}_{16}S$ (ii) $^{39}_{19}K, ^{40}_{20}Ca$ (iii) $^3_1H, ^4_2He$ (iv) $^{13}_6C, ^{14}_7N$
Isodiaphers	Isotopic no. (N – Z) or (A – 2Z)	(i) At no., mass no., electrons, protons, neutrons (ii) Physical and chemical properties	(i) $_{92}U^{235}, _{90}Th^{231}$ (ii) $_{19}K^{39}, _9F^{19}$ (iii) $_{29}Cu^{65}, _{24}Cr^{55}$
Isoelectronic species	(i) No. of electrons (ii) Electronic configuration	At. no., mass no.	(i) $N_2O, CO_2, CNO^-(22e^-)$ (ii) $CO, CN^-, N_2(14e^-)$ (iii) $H^-, He, Li^+, Be^{2+}(2e^-)$ (iv) $P^{3-}, S^{2-}, Cl^-, Ar, K^+$ and $Ca^{2+}(18e^-)$
Isosters	(i) No. of atoms (ii) No. of electrons (iii) Physical and chemical properties.		(i) N_2 and CO (ii) CO_2 and N_2O (iii) HCl and F_2 (iv) CaO and MgS (v) C_6H_6 and $B_3N_3H_6$

Multiple Choice Questions

1. Where are protons located in an atom?
a. Around the nucleus **b.** Inside the nucleus
b. Both (**a.**) & (**b.**) **d.** None of these

2. Which of the following statements is true?
a. A proton is 1837 times heavier than an electron
b. A proton is 1/1837 times heavier than an electron
c. A proton is 1/1837 times lighter than an electron
d. Proton has the same mass as an electron

3. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because
a. alpha particles are much heavier than electrons
b. alpha particles are positively charged
c. most part of the atom is empty
d. alpha particles move with high velocity

4. Rutherford's scattering experiment is related to the size of
a. nucleus **b.** atom **c.** electron **d.** neutron

5. The mass of a proton is
a. 1.00728 amu **b.** 1.673×10^{-24} gm
c. 1.673×10^{-27} kg **d.** All of these

6. Rutherford performed his alpha scattering experiment using
a. silver **b.** gold **c.** mercury **d.** diamond

7. A proton is usually represented as
a. ${}_{1}^{1}P$ **b.** ${}_{1}^{1}H$
c. ${}_{2}^{4}He$ **d.** both (**a.**) & (**b.**)

8. The protons and neutrons are collectively called
a. deuterons **b.** positrons **c.** mesons **d.** nucleons

9. Contains ${}_{11}^{23}Na^{-}$
a. 22 protons **b.** 22 neutrons
c. 12 neutrons **d.** None of these

10. The credit of discovering neutron goes to
a. Rutherford **b.** Thomson
c. Goldstein **d.** Chadwick

11. The formula that gives the maximum number of electrons in a particular shell is:
a. n^2 **b.** $2n^2$ **c.** $2n$ **d.** $n^2/2$

12. The radius of an atomic nucleus is of the order of
a. 10^{-10} cm **b.** 10^{-13} cm **c.** 10^{-15} cm **d.** 10^{-8} cm

13. The oil drop experiment by R.A. Mullikan was performed to find
a. Charge on the neutron **b.** Charge on the electron
c. Charge on the proton **d.** None of these

14. A p-orbital can accommodate up to
a. 4 electrons **b.** 2 electrons
c. 6 electron **d.** 3 electrons

15. Energy levels are designated as
a. K, L, M, N and so on **b.** k, l, m, n and so on
c. I, II, III, IV and so on **d.** All of these

16. A neutron is represented as
a. ${}_{0}^{0}n$ **b.** ${}_{1}^{1}n$ **c.** ${}_{0}^{1}n$ **d.** ${}_{-1}^{1}n$

17. The different sub-shells in an atom are represented as
a. s,p,d,f **b.** S,P,D,F
c. 1,2,3,4 **d.** All of these

18. The maximum number of electrons is N shell is
a. 2 **b.** 8 **c.** 18 **d.** 32

19. The maximum number of electrons is f–sub-shell is
a. 5 **b.** 6 **c.** 14 **d.** 10

20. The maximum number of electrons that can be accommodated in the valence shell of an atom is:
a. 5 **b.** 6 **c.** 7 **d.** 8

21. The maximum number of orbitals in f sub-shell are
a. 1 **b.** 3 **c.** 5 **d.** 7

22. The number of valence electrons in Na is:
a. 1 **b.** 2 **c.** 3 **d.** 4

23. The valency of ${}_{10}Ne = 2,8$ is
a. 10 **b.** 8 **c.** 2 **d.** 0

24. Which of the following has the same number of protons, electrons and neutrons?
a. ${}_{27}^{54}X$ **b.** ${}_{27}^{55}X^{+1}$ **c.** ${}_{26}^{54}X$ **d.** ${}_{28}^{55}X^{+}$

25. In an atom there are four orbits, the maximum number of electrons in this atom will be:
a. 30 **b.** 36 **c.** 32 **d.** 62

26. Isotones of an element have
a. same number of electrons
b. same number of protons
c. same number of neutrons
d. same number of neutrons and protons

27. An isotone of $^{76}_{32}Ge$ is:

a. $^{77}_{32}Ge$ **b.** $^{77}_{33}As$ **c.** $^{77}_{34}Se$ **d.** $^{79}_{34}Se$

28. A deuteron contains

a. a neutron and a positron. **b.** a neutron and a proton.

c. a neutron and 2 protons **d.** 2 neutrons and a proton.

29. Many elements have non-integral masses because

a. they have isobars

b. their isotopes have non - integral masses

c. they have isotopes

d. the constituents neutrons, protons and electrons combine to give fractional masses

30. The triad of nuclei that is isotonic is

a. $^{14}_{6}C$, $^{15}_{7}N$, $^{17}_{19}F$ ` **b.** $^{12}_{6}C$, $^{14}_{7}N$, $^{19}_{9}F$

c. $^{14}_{6}C$, $^{14}_{7}N$, $^{17}_{9}F$ **d.** $^{14}_{6}C$, $^{14}_{7}N$, $^{19}_{9}F$

31. Pick out the isoelectronic structures from the following

(I) CH_3^+ (II) H_3O^+ (III) NH_3 (IV) CH_3^-

a. I and II **b.** III and IV

c. I and III **d.** II, III, IV

32. Two atoms of the same element are found to have different number of neutrons in their nuclei. These two atoms are

a. isomers **b.** isotopes

c. isobars **d.** allotropes

33. Which of the following members have similar chemical properties?

a. Isotopes

b. Isobars

c. Allotropes

d. Both isotopes and allotropes

34. An atom which as a mass number of 14 and 8 neutrons is an

a. isotope of oxygen **b.** isobar of oxygen

c. isotope of carbon **d.** isobar of carbon

35. The electronic configuration of Mn^{+2} is:

a. 2, 8, 13 **b.** 2, 8, 11, 2

c. 2, 8, 13, 2 **d.** None of these

36. The number of electrons in the L-shell of phosphorus is not equal to that in the

a. L-shell of neon **b.** M-shell of potassium

c. M-shell of chromium **d.** M-shell of argon

37. How many electrons, protons and neutrons are present in X+, if atomic number of X is 19 and its mass number is 39?

a. E = 19, P = 19, N = 20 **b.** E = 18, P = 19, N = 20

c. E = 18, P = 19, N = 19 **d.** E = 19, P = 20, N = 20

38. Which of the following does not have 8 valence electrons?

a. He **b.** Ne **c.** Ar **d.** Cl^-

39. Which of the following does not have one electron in its valance shell?

a. Na **b.** Li **c.** H **d.** Ca

40. The electronic configuration of Cl^- ion is:

a. 2,8,7 **b.** 2,8,8 **c.** 2,8,6 **d.** 2,8,8,1

41. Which of the following are isotopes?

$1^1H, 1^2D, 1^3T, 1^1H^+$

a. $1^1H, 1^2D, 1^3$ **b.** $1^1H, 1^2D, 1^1H^+$

c. $1^1H, 1^1H^+$ **d.** $1^1H, 1^3T, 1^1H^+$

42. Which of the following are isobars?

$18Ar^{40}, {}_{19}K^{39}, {}_{20}Ca^{40}, {}_{19}[K^+]^{39}$

a. ${}_{19}K^{39}, {}_{19+}[K+]^{39}$ **b.** ${}_{18}Ar^{40}, {}_{19}K^{39}$

c. ${}_{18}Ar^{40}, {}_{20}Ca^{40}$ **d.** ${}_{18}Ar^{40}, {}_{19}K^{39}, Ca^{40}$

43. Cathode rays have

a. Charge only **b.** Mass only

c. Charge as well as mass **d.** Neither charge nor mass

44. The number of valence electrons determines

a. Physical properties of elements

b. Chemical properties of elements

c. Both physical and chemical properties of elements

d. Neither physical nor chemical properties of elements

45. C-14 has a half life of

a. 11520 yrs **b.** 2880 yrs **c.** 5760 yrs **d.** 17280 yrs

ANSWERS

1.	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**10.**
b	a	c	a	d	b	d	d	c	d
11.	**12.**	**13.**	**14.**	**15.**	**16.**	**17.**	**18.**	**19.**	**20.**
b	b	b	b	a	c	a	d	c	d
21.	**22.**	**23.**	**24.**	**25.**	**26.**	**27.**	**28.**	**29.**	**30.**
d	a	d	a	b	c	b	b	c	a
31.	**32.**	**33.**	**34.**	**35.**	**36.**	**37.**	**38.**	**39.**	**40.**
d	b	d	c	a	c	a	a	d	b
41.	**42.**	**43.**	**44.**	**45.**					
a	c	a	b	c					

□ □ □