PREFACE

In a bid to standardise higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, discipline specific, generic elective, ability* and *skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry acquired credits. I am happy to note that the University has been accredited by NAAC with grade 'A'.

UGC (Open and Distance Learning Programmes and Online Learning Programmes) Regulations, 2020 have mandated compliance with CBCS for U.G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the *six* semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

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Under Graduate Degree Programme
Choice Based Credit System (CBCS)
Subject: Honours in Chemistry (HCH)
Course Code : CC-CH-03
Course : Inorganic Chemistry–1 (Theory)

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UG : Chemistry
(HCH)

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(Theory)
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Unit-1 Extra nuclear Structure of atom

Structure

1.1 Objectives

After reading this unit, we will be able to:

- Know the detail of Bohr's atomic model.
- Energy calculation of an electron in Bohr's orbit.
- Dual characteristics of electrons and primary idea about quantum nature of atoms.
- Schrodinger equation and wave functions.
- Define classifications & significance of quantum numbers.
- The rules of electronic configuration of the atoms.

1.2 Introduction

Atomic structure refers to the structure of an atom containing nucleus (at the centre) in which there is protons (positively charged) and neutrons (neutral) and electrons (negatively charged) revolving around the nucleus. The history of atomic structure and quantum mechanics restates only one name who first proposed that matter is made up of atoms; the name is Democritus. The whole class of chemical reactions, bonds and their physical properties are profoundly related with the atomic structure. After Democritus, it is John Dalton who proposed the first scientific theory of atomic structure in 1800. The discovery of atomic structure led to many other inventions like subatomic particles. These are all the fundamental particles which compose the structure of a matter. The English Chemist John Dalton proposed the theory that every matter is composed of atoms which are indivisible and indestructible. The English chemist Sir Joseph John Thomson was better known for his discovery of electrons for which he got the Nobel Prize. After that Rutherford proposed the atomic model which was further modified by Bohr's Atomic theory.

1.3 Bohr's Model (1913)

Niels Bohr proposed a model for the hydrogen atom that explained the spectrum of the hydrogen atom. The Bohr model was based on the following assumptions.

1.4 Postulates

(A) In a Rurtherford type atomic model, electrons can circulate around the positively charged nucleus only along certain selected orbits. During its circular movement along the elected orbit electron neither absorbs nor emits any radiation.

Th angular momentum of the electron should be an integral multiple of $h/2\pi$ (h = Plank's constant, 6.626×10^{-34} Js)

Let us consider an electron having mass m moving with a velocity of v along an orbit of radius r.

The angular momentum will be mvr.

According to Bohr's theory.

$mvr = nh/2\pi$, n = any integer

1st orbit ($n = 1$): $mvr = 1h/2\pi$

2nd orbit ($n = 2$): $mvr = 2h/2\pi$

3rd orbit ($n = 3$): $mvr = 4h/2\pi$.............so on]

Thus the angular momentum of an electron is quantized.

(B) When one electron jumps form one selected orbit to another, the emitted or absorbed energy should be equal to the energy difference in between two states as per quantum theory of radiation.

When an electron jumps from an orbit having energy E_1 to another orbit energy E_2 ($E_1 > E_2$), the frequency of the emitted radiation will be,

$E_1 - E_2 = \triangle E = h\,v$

$\Rightarrow v = (E_1 - E_2) / h = \triangle E/h$

This shows that discrete line will appear depending on $\triangle E$ value.

1.5 Radii of a Bohr orbits

In Bohr's theory, the basic concept of Rutherford model has been maintained. The addition was the angular momentum.

Let us consider an electron of mass m, circulates around the nucleus of charge Z along an orbit of radius r with a velocity of v.

From Bohr's model we get that the centrifugal force will be equal to coulombic force,

$$\Rightarrow \frac{mv^2}{r} = \frac{ze^2}{4\pi\varepsilon_0 r^2} \qquad \text{...(i)}$$

ε_o = Permittivity of vacuum

$$\Rightarrow mv^2 = \frac{ze^2}{4\pi r\varepsilon_o} \qquad \text{...(ii)}$$

Applying Bohr angular momentum we get.

$$mvr = \frac{nh}{2\pi}$$

$$\Rightarrow m^2 v^2 r^2 = \frac{n^2h^2}{4\pi^2} \qquad \text{...(iii)}$$

$$\Rightarrow mv^2 = \frac{n^2h^2}{4mr^2\pi^2} \qquad \text{...(iv)}$$

Therefore we can write,

$$\Rightarrow \frac{ze^2}{4\pi r\varepsilon_o} = \frac{n^2h^2}{4r^2\pi^2 m} \qquad \text{...(v)}$$

$$\Rightarrow \mathrm{r} = \frac{\varepsilon_o n^2h^2}{\pi mze^2} \qquad \text{...(vi)}$$

Note : $\mathrm{r} \propto \mathrm{n}^2$

1.6 Energy of an electron in a Bohr orbit

An electron in an atom possesses both kinetic energy that arises due to its motion around the nucleus and potential energy due to its attachment to the nucleus. Therefore, the total energy acquire by an electron will be the sum of both energies.

i.e. Total energy (E_t) = Kinetic energy (E_k) + Potential energy (E_p)

Kinetic energy

Let us consider the mass of an electron is m, it circulates around the nucleus of charge Z along an orbit of radius r with a velocity of v.

$$E_k = \frac{1}{2}mv^2$$

From equation (iv) we get,

$$\frac{1}{2}mv^2 = \frac{ze^2}{8\pi\varepsilon_o r^2}$$

Therefore, $E_k = \dfrac{Ze^2}{8\pi\varepsilon_o r}$

Potential energy

Potential energy of an electron in an atom is given by the work to be done to bring an electron from infinity to its radius (r).

The total work done (W) will be then.

$$Ep = W = \int_{r=\infty}^{r=r} \frac{Ze^2}{4\pi\varepsilon_o r^2} = -\frac{Ze^2}{4\pi\varepsilon_o r} \qquad \text{...(vii)}$$

The negative sign implied that work has to be done to remove electron from the radius of the atom.

Total energy of the electron

Total energy (E_t) = Kinetic energy (E_k) + Potential energy (E_p)

$$E_t = E_k + Ep = \frac{Ze^2}{8\pi\varepsilon_o r} - \frac{Ze^2}{4\pi\varepsilon_o r} = -\frac{Ze^2}{8\pi\varepsilon_o r} \qquad \text{...(viii)}$$

1.7 Interpretation of atomic spectra of hydrogen atom by Bohr's Theory

Let us consider two orbits having quantum number n_1 and n_2, $n_2 > n_1$.

The energy corresponding to the orbits are, E_{n_1} and E_{n_2}, respectively.

Since, $n_2 > n_1$, $E_{n_2} > E_{n_1}$

Hence the difference in energy, ...(ix)

$$\triangle E = h\nu = E_{n_2} - E_{n_1}$$

$$E_{n_1} = \frac{me^4}{8\varepsilon_o^2 n_1^2 h^2} E_{n_2} = -\frac{me^4}{8\varepsilon_o^2 n_2^2 h^2}$$

($Z = 1$ for hydrogen atom)

$$\Rightarrow E_{n_2} - E_{n_1} = h\nu = \frac{me^4}{8\varepsilon_{\circ}^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad ...(x)$$

$$\Rightarrow \nu = \frac{me^4}{8\varepsilon_{\circ}^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Rightarrow \nu = \nu / c = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad ...(xi)$$

R=Rydberg constant =1.096776 ×$10^7\,m^{-1}$

Equation (*xi*) show that frequency varies with the initial and the final orbital quantum number.

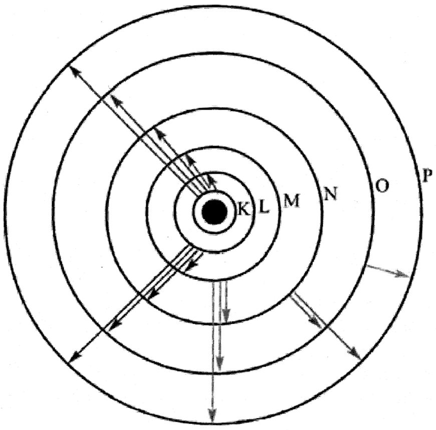


Figure 1.4 Bohr orbit of hydrogen and various series or spectral line. Lyman (rd), Balmer (blue), Paschen (green), Brackett (magna), Pfund (cyno).

Table 1.2.

Series name	**Region of scpectum**	**n1**
Lyman	UV	1
Balmer	UV-vis	2
Paschen	IR	3
Brackett	IR	4
Pfund	IR	5

According to the Bohr model, the wavelength of the light emitted by a hydrogen atom when the electron falls from a high energy (n = 4) orbit into a lower energy (n = 2) orbit.

Substituting the appropriate values of R_H, n_1, and n_2 into the equation shown above gives the following result.

$$\frac{1}{\lambda} = (1.09678 \times 10^{-2} nm^{-1}) \left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

Solving for the wavelenght of this light gives a value of 486.3mm, which agrees with the experimental value of 486.1nm for the blue line in the visible spectrum of the hydrogen atom.

1.8 Merits and demerits of Bohr Theory

Merits : (i) In this theory the stability of an atom has been explained by introducing angular momentum of electron.

(ii) The origin or discontinuous line spectrum by an atom can explained by this theory.

Demerits : (i) In this model the concept of integer (n) has been introduced in selecting stable orbits for electrons. This was merely to fit the experimental data. There is no theoretical justification for it.

(ii) Employing instruments of high resolving power, single line in the spectrum of atomic hydrogen can also be resolved in several fine lines, "fine structure". This Phenomenon cannot be explained by Bohr's theory.

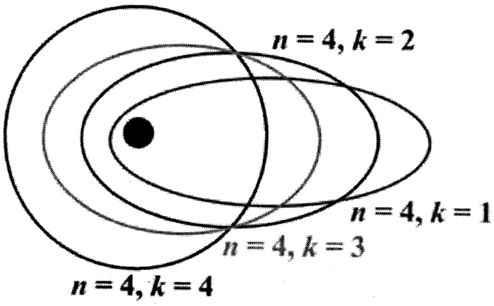
1.9 Improvement of Bohr's Atomic Model, Sommerfeld Model (1915)

Bohr atomic model cannot explain the appearance of "fine structure" To explain the phenomenon, Sommerfeld suggested that orbit of electron does not have to be circular out can also be elliptical. Electrons can move only on some allowed ellipses.

The motion of an electron along an elliptical orbit is described by (i) radial quantum number, n_r and (ii) an azimuthal quantum number, k. They are related to the principle quantum number (n) and the ellipticity of the orbit.

(A) $n = n_r + k$ and (B) n / k = major axis/minor axis

Example : $n = 4$, $n / k = 4/1, 4/2, 4/3$, and $4/4$. The first three will be elliptical. while the forth one (4/4) will be circular.



The presence of three extra orbits which are slightly different in energies from each other, accounts for extra lines in the spectrum revealed under high resolution. The original quantum number k has been replaced by a new quantum number l. where $l = k-1$.

Thus, for a given value of n, l may have values 0,1,2,....to $(n-1)$

This explained why some of the spectral lines splitted into two, three, four and more lines. In addition to this, some spectral lines further splitted into doublets. This can be explained by assuming that an electron spins on its axis in either clockwise or anti-clockwise direction. Energy is quantized, and the value of spin angular momentum was considered to be $m_s = \frac{h}{2\pi}$, where m_s = spin quantum number with values ± 1/2.

1.10 Zeeman effect

Zeeman showed that in the presence of strong magnetic field atom shows additional line in the spectrum. This is because elliptical orbits can only take up certain orientations with respect to the external magnetic field, rather than processing freely. The orientation is associated to a forth quantum number known as magnetic quantum number m and it can have $(2l + 1)$ value for a given l.

1.11 Dual natute of electrons (Particles or Wave)

1.11.1 de Bröglie postulation (1924)

de Bröglie suggested that some dual character exists with electrons. Sometimes they are considered as particles and other times it is convenient to consider them as waves. He assumed that each particle has its associated matter waves or *pilot wave* that guide the particle. The wavelength (λ) of such wave is given by,

$$\lambda = h/mv$$

Where m = mass of the particle, and v = velocity of the particle

1.11.2 Heisenberg uncertainty principle (1927)

It is impossible to determine simultaneously both the position amd the momentum of a body with any arbitrary desire accuracy. The product of uncertainty in position (Δx) and momentum (Δp) along a particular direction will be at least of the order of h.

$$\Delta x \,.\, \Delta p \geq h/4\pi$$

This principle can also hold for the uncertainties in energy and time.

$$\Delta E \,.\, \Delta t \geq h/4\pi$$

Where ΔE is difference in energy and Δt is time interval.

1.12 The Schrödinger Wave Equation

1.12.1 Standing waves

For a standing wave (such as a vibrating string) of wavelength λ. whose amplitude at any point along x may be described as a function of f (x), it can be show from the wave motion that,

$$\frac{d^2 f(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2} f(x) \qquad \text{...(xii)}$$

If an electron is considered as a wave which moves in only one dimension then,

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\Psi \qquad \text{...(xiii)}$$

An electron may move in three directions x, y, and z, therefore, we can write,

$$\frac{\partial^2\Psi}{dx^2} + \frac{\partial^2\Psi}{dy^2} + \frac{\partial^2\Psi}{dz^2} = -\frac{4\pi^2}{\lambda^2}\Psi \qquad \text{...(xiv)}$$

The symbol ∇^2 (del square) is used to represent differential operator in Cartesian coordinates,

$$\frac{\partial^2\Psi}{dx^2} + \frac{\partial^2\Psi}{dy^2} + \frac{\partial^2\Psi}{dz^2} = -\frac{4\pi^2}{\lambda^2}\Psi$$

Hence, equation (xiv) can be expressed as, ...(xv)

$$\nabla^2\Psi = -\frac{4\pi^2}{\lambda^2}\Psi$$

1.12.2 Matter Waves

According to de Broglie relationship, $\lambda = h / mv$

Putting the value to equation (xv) we get

$$\nabla^2\Psi = -\frac{4\pi^2 m^2 v^2}{h^2}\Psi \qquad \text{...(xvi)}$$

$$\Rightarrow \nabla^2\Psi + \frac{4\pi^2 m^2 v^2}{h^2}\Psi = 0 \qquad \text{...(xvii)}$$

The total energy (E) of the system must be equal to the kinetic energy (k) and potential energy (V)

E = K + V ...(xviii)

So, K = E – V.

We know that.

$$K = \frac{1}{2}mv^2$$

So, $$\frac{1}{2}mv^2 = E - V$$

So, $$v^2 = \frac{2}{m}(E - V)$$

Substituting this value to equation (xviii), we get,

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0 \qquad \text{...(xix)}$$

This is the time-independent Schrodinger equation.

Selection of the acceptable values of ψ is made according to the following conditions,

i. Ψ must be single valued, the probability of finding the electron at any point must have only one value.

ii. Ψ must be continuous.

iii. Ψ must be finite, an infinite value at a point mean that the electron is fixed there. This is contrary to wave representation.

iv. The probability of finding the electron over all the space from plus infinity to minus infinity must be equal to one.

The probability of finding the electron at a point *x, y, z* is Ψ^2.

$$\text{So, } \int_{-\infty}^{+\infty} \Psi^2 dx\, dy\, dz = 1$$

What is an orbital ?

Several wave functions called Ψ_1, Ψ_2, Ψ_3,....will satisfy the above stated condition to the wave equation and each of these has a corresponding energy, E_1, E_2, E_3,.... Three dimensional space around the nucleus where there is maximum probalility of finding the electron (wave) is known as orbital.

The hydrogen atom :

1.13 Schrödinger equation for hydrogen atom

Schrodinger equation can be solved completely for hydrogen atoms as well as hydrogen type atoms or ions, like, He^+, Li^{2+} (Z=1). For the other atoms only approximate solution can be achieved.

For most calculations. it is simpler to solve the wave equation if the Cartesian coordinates x, y and z are converted to polar coordinates. r, θ and φ.

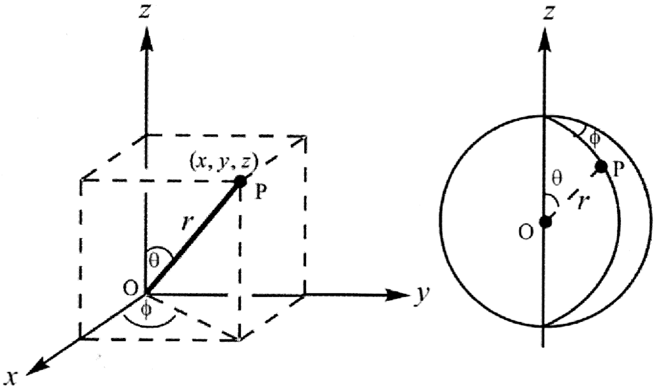


Figure 1.5. Cartesian and Polar coordinates.

It can be seen from Figure 1.5 that two of coordinates are related to each other by the following relation,

$$z = r \cos \theta$$

$$y = r \sin \theta \sin \Phi$$

$$x = r \sin \theta \cos \Phi$$

The Schordinger equation is written as,

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E-V)\Psi = 0 \qquad \text{...(xix)}$$

Where,

$$\nabla^2\Psi = \frac{\partial^2\Psi}{dx^2} + \frac{\partial^2\Psi}{dy^2} + \frac{\partial^2\Psi}{dz^2}$$

Changing to polar coordinates, $\nabla^2\Psi$ becomes,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial\Psi}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)$$

Now we can write equation (xix) as,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi^2} + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{8\pi^2 m}{h^2}(E-V)\Psi = 0 \quad \text{...(xx)}$$

$$\text{or, } \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

$$+\frac{8\pi^2 m}{h^2}\left(E + \frac{ze^2}{4\pi\varepsilon_o r}\right)\Psi = 0 \qquad \text{...(xxi)}$$

(Potential energy (E_k) = V, see equation vii)

The dependence of Ψ on r, θ and Φ can not be shown directly with equation (xxi). Becaues, it would require a four dimensional graph. However, the equation in this form can be expressed as follows,

$$\Psi = R(r).\Theta(\theta).\Phi(\phi) \qquad \text{...(xxii)}$$

- R (r) is a function that depends on the distance from the nucleus. It depends on the quantum numbers n and l.
- Θ (θ) is a function of θ and depends on the quantum numbers l and m.
- Φ (Φ) is a function of ϕ and depends on the quantum numbers m.
- Therefore, equation (xxii) can be expressed as.

$$\Psi = R(r)_{ni} A_{ml}$$

This splits wave function into two parts which can be solved separately,

- R (r) is a radial function that depends on the quantum numbers n and l.
- A_{ml} is the total angular wave function that depends on the quantum numbers m and l.

1.14 Radial part of wave functions, *R*

The radial function R has no physical meaning. R^2 dv gives the probability of finding the electron in a small volume dv near the point at which R is measured.

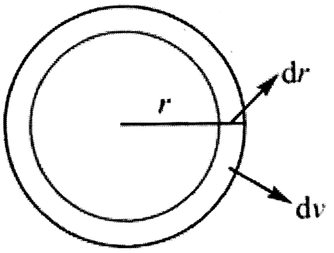


Figure 1.6. Showing volume difference

For a given value of r the total volume will be,

$$V = 4\pi r^3/3$$

We may consider that an atom is composed of thin layers of thickness d r. The volume dv for between r and $r + d\,r$ will be then (Figure 1.6),

$$dV = 4\pi r^2 dr$$

The probability of finding the electron in that volume will be,

$$R^2 dV = 4\pi r^2 R^2 dr$$

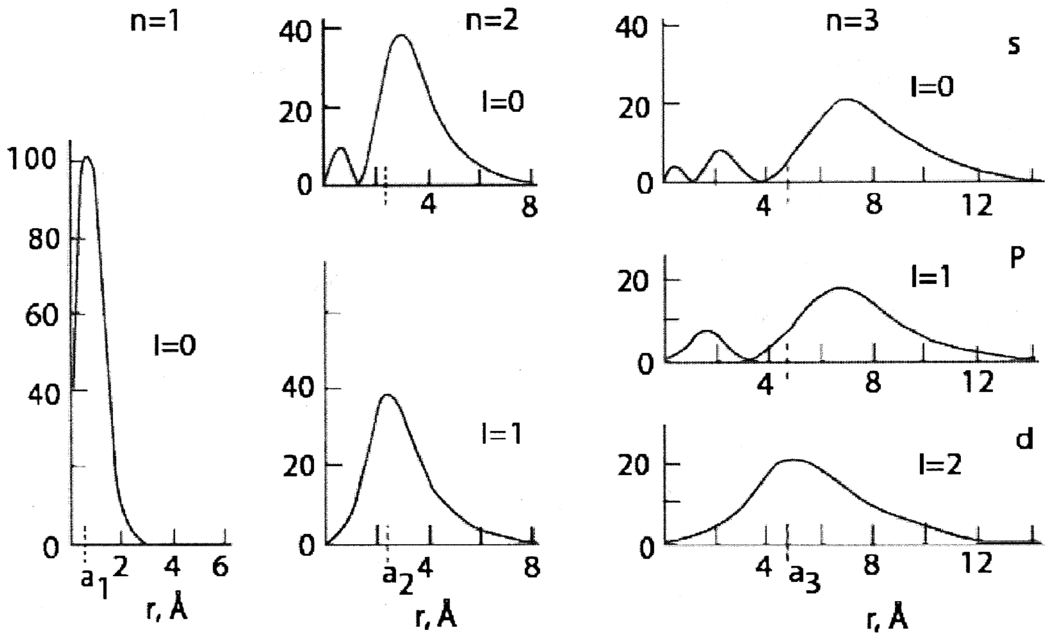


Figure 1.7 Radial Probability functions for n = 1,2,3 for the hydrogen atom. The radial density is along y axis.

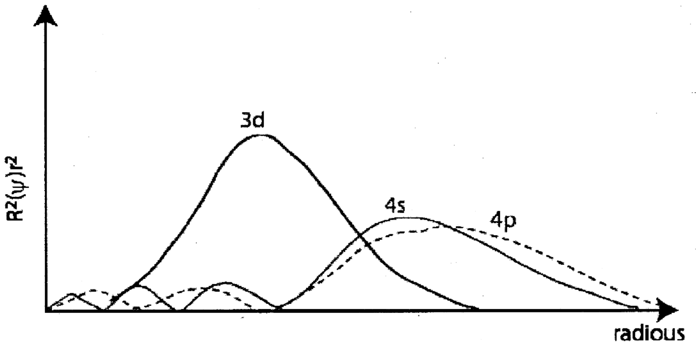


Figure 1.8.

Figure 1.8

Significance :

- The probability function is always positive as it involves the square of *R*.
- At r = 0, the porbability of finding electron is zero. This shows no existence of electron at the nucleus.
- *R* is a function of *n* and *l*. Therefore, with increase in value of either *n* or *l*, the distance of finding maximum electron density form the nucleus will also increase.
- At a large value of *r*, *R* approaches to zero. Therefore, the probability of finding electron will approach to zero.
- Most probable distance increases as the principle quantum number (*n*) increases.
- Most probable distance decreases slightly as the subsidiary quantum number (*l*) increases.

1.14.1 Penetration

Penetration of orbitals means their distribution into inner electronic core. For example, the radial density of 2*s* orbital spread into the curve for 1s orbital. Similarly, 3*s* orbital is spread into 1*s* and 2*s* orbital. Because of this spreading electrons in 2*s* orbital or in 3*s* orbital will not be fully screened by the inner 1s electrons from the nucleus. The extent of penetration decreases from *s* to *f* orbitals.

$$S > p > d > f$$

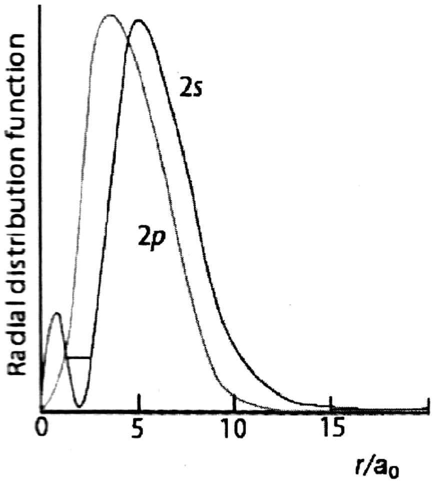


Figure : 1.9 Penetration decreases from *s* to *p* as radial distribution close to nucleus for s is more compared to *p*.

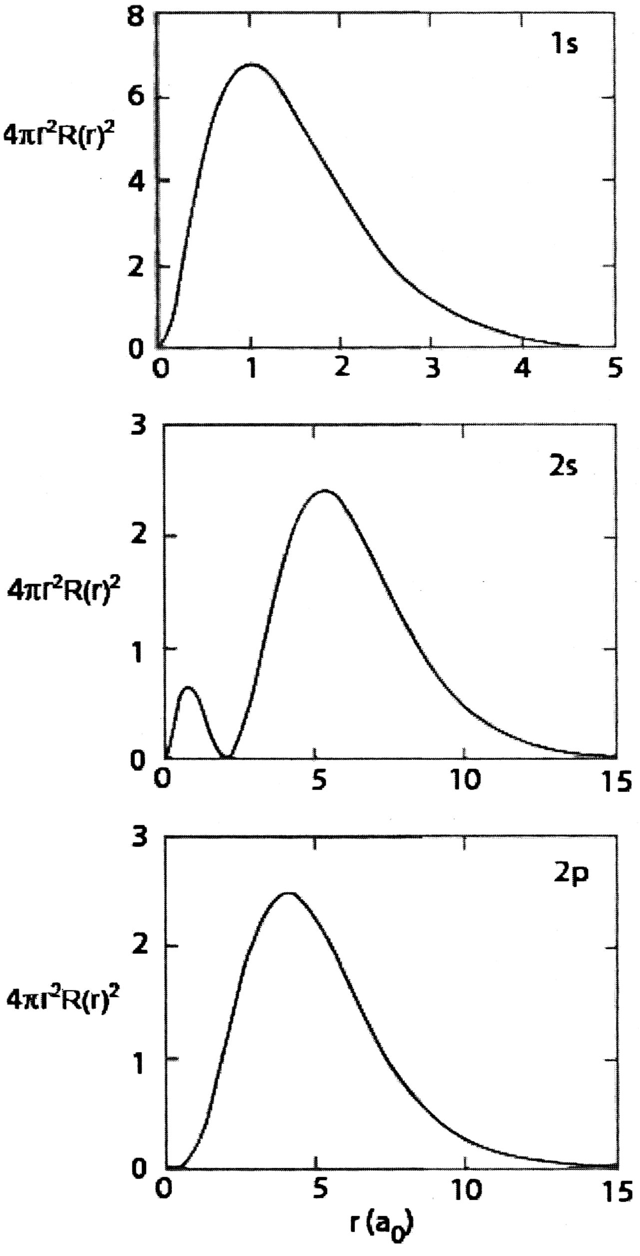


Figure : 1.10 Radial distribution of 1s, 2s, and 3s orbital.

1.14.2 Angular part of wave functions:

The angular parts of the wave function depend only on direction (Φ and Θ) are independent of the value of principle quantum number (n) and the distance from the radius (r). Thus, A^2 is the probability of finding an electron at a given direction Φ and Θ at any distance from the nucleus to infinity. They depend probably on the values of l. For $l = 0$, i.e. s orbitals, the angular wave function is constant and inependent of the angles θ and Φ. Therefore, this function will provide a sphere.

Angular function for some orbitals :

s orbital	p_z orbital	dz^2
$\Theta\Phi = (1/4\pi)^{1/2}$	$\Theta\Phi = (3/4\pi)^{1/2}\cos\theta$	$\Theta\Phi = (5/1\pi)^{1/2}(3\cos^2\theta\text{-}1)$

Here, z or z^2 refers the orientations of the orbitals along z axis. The angular wave function of the p_z orbital corresponds to two spheres whose center lies on z axis. The spheres touch each other tangentially at the origin. Since, $\cos\theta$ changes sign with θ, the wave function will have two different sign in two different lobes.

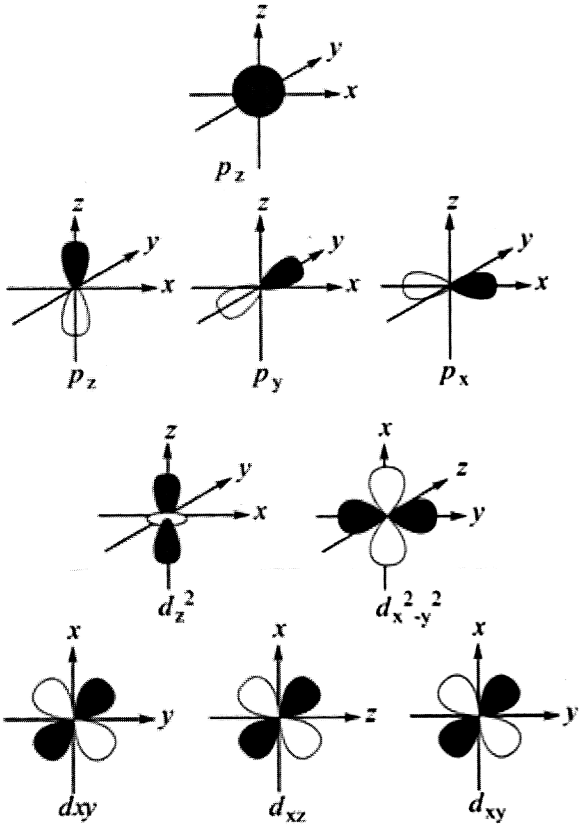


Figure 1.11. The angular part of the wave function A (θ,.Φ) for the 1*s*, 2*p*, and 3*d* orbitals for a hydrogen atom.

Similarly, there are set of five *d* orbitals ($l = 2$).

In case of *s* and *d* orbitals the wave functions have the same sign at the same distance in opposite directions from the center of symmetry. These orbitals are thus *centrosymmetric* and are said to be *gerade*. It means even and denoted as g . While, the wave functions for *P* orbitals have opposite signs on either side from the centre of symmetry. Therefore, they are known as *non-centrosymmetric* or ungerade orbitals. They are denoted as *u*.

1.14.3 Angular probability function :

The probability of finding an electron simultaneously at a distance *r* and in a given direction Φ, θ is $\Psi^2{}_{r,\Phi,\theta}$

$$\Psi^2{}_{r,\Phi,\theta} = R^2\,(\mathrm{r})\; A^2\,(\phi,\theta)$$

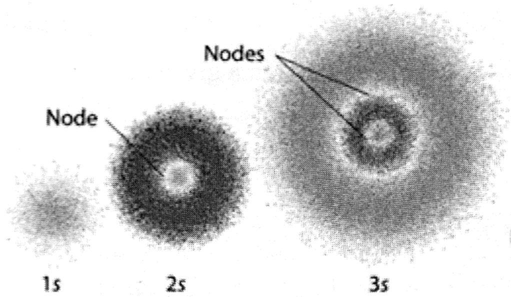
The probability of finding an electron in a given direction is then $A^2\,(\Phi,\theta)$.

s orbital is spherical so it remains unchanged on sqaring, while, for *p* and *d* orbitals sign factor vanished and lobes becomes more elongated.

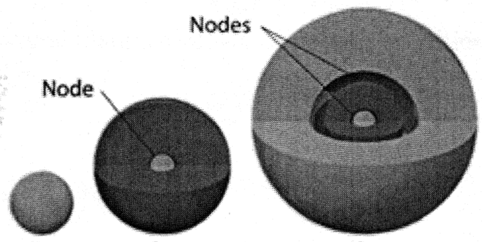
1.15 Difference between orbits and orbitals

Orbit represent discreate trajectories of electrons around the positively charged nucleus. The position, momentum and consequently, energy of an electron can be expressed precisely by using laws of newtonian mechanics assuming electron as particle.

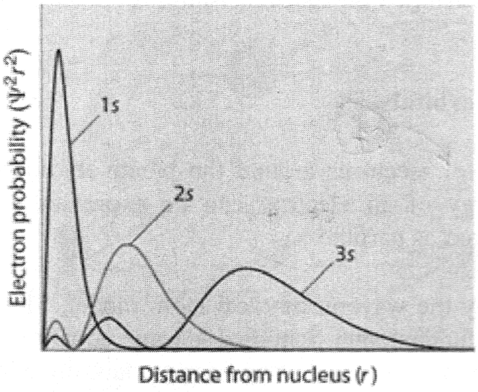
The idea of orbital was introduced by the wave mechanical atom model. The extranuclear part has been considered as wave and follows the fundamental Schrodinger wave equation. The orbital corresponds to the probability of finding an electron at a certain distance and certain direction. Hence, each orbital has definite energy, shape and described in terms of quantum numbers.



(a) Electron probability



(b) Contour probability



(c) Radial probability

1.16 Quantum numbers

Bohr-Sommerfeld atomic model and its later extensions, four quantum numbers (n, l, m, s) were introduced to explain the spectral features of atoms.

A. The principle quantum number, *n*.

This quantum number determines the energy level of an atom. The energy expressed as a function of n,

$$E_t = -\frac{Z^2 m e^4}{8\varepsilon_o^2 n^2 h^2}$$

According to the above equation energy should decrease with increase of n value. Due to negative sign energy also increases with increase in the value of n.

B. The Azimuthal or angular momentum quantum number, l :

The Azimuthal or angular momentum quantum number determines the orbital angular momentum of an electron through the following relation. This specifies the shape of an atomic orbital its bonding and bond angles.

$$L^2 = l(l+1)h^2$$

l may have any integral values between 0 to $(n-1)$. For $l = 0$, defines s orbit. $l = 1, 2, 3$ etc defines, *p, d, f* etc respectively.

C. The magnetic quantum number, m_l:

This quantum number determines the orientation of the angular momentum vector of an electron in the presence of external magnetic field along a specific axis (let us consider along *z* axis).

$$Lz = m_l h$$

For a given l value m_1 will be in between $+l$ to $-l$.

$$i.e.\ m_l = 2l + 1$$

Example : for *p* orbital, $l = 1$, therefore, $m_l = +1, 0, -1$. This indicates *p* orbital will have three different directions orientations in the presence of external magnetic field.

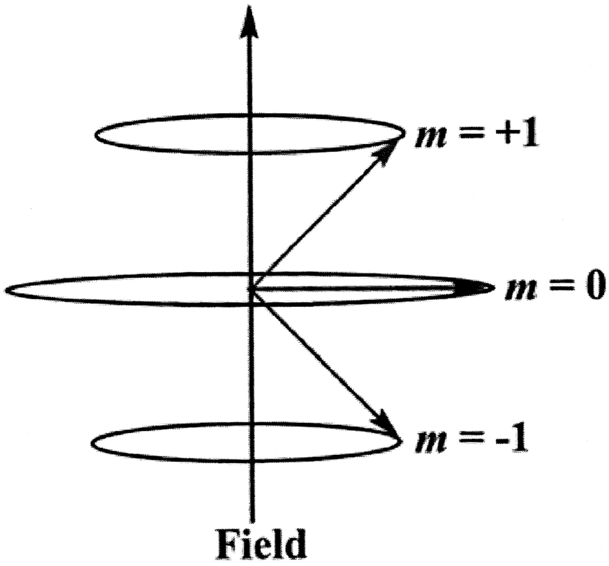


Figure 1.12. The orientation of orbital angular momentum vector in the presence of external magnetic field for $l = 1$.

(D) Spin projection quantum number, m_s :

An electron spins about its own axis. Because of this spinning an angular momentum is generated that is completely different from the orbital angular momentum. This angular momentum is expressed by spin projection quantum number (m_s).

$$L_z = m_s h$$

For a given s value m_s, will have value in the range of $+s$ to $-s$.

An electron has s = ½ spin. Hence, m_s, = +1/2, -1/2

Some other examples. S =3/2, m_s, = +3/2, +1/2, –1/2, -3/2

S = 3, m_s = +3/, +2, +1, 0, -1, -2, -3

This indicates. $m_s = 2s + 1$

Table 1.3

SL. No	l $0 \le l \le n - 1$	m_l $-l \le m_l \le l$	Type of Orbitals	Tabal no. of orbitals $2l + 1$	Maximum no of electrons $2(2l+1)$
1	0	0	*s*	1	2
2	0 1	0 +1, 0, –1	*s* *p*	1 3	2 6
3	0 1 2	0 +1, 0, –1 +2, +1, 0, –1, –2	*s* *p* *d*	1 3 5	2 6 10
4	0 1 2 3	0 +1, 0, –1 +2, +1, 0, –1, –2 +3, +2, +1, 0,–1,–2,–3	*s* *p* *d* *f*	1 3 5 7	2 6 10 14

Sequence of energy level :

Rules :

A. Orbital energies increases, a $(n + l)$ increases.

B. If there are two orbitals with the same value of $(n + l)$, the one with the smaller n has the lower energy.

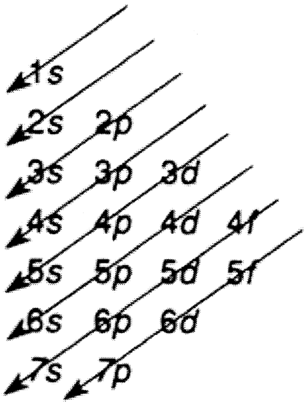


Figure 1.13. Energy Levels sequence.

1.17 Many electrons atom

Schrödinger wave equation stood good for the hydrogen atom. This wave equation become highly complicated as the number of electrons in a system increased. To avoid all the difficulties and to have the equation, a simpler form of a several approximations have been considered. It has been found that the radial 'part of the wave function changes appreciably with change in Z. The angular part of the wave function remains nearly unchanged. Therefore, the basic shape of the orbitals that depends on angular part of the wave function, are same.

1.18 Effective nuclear charge and Slater's rule

As the nuclear charge and the number of electrons in an atom increases, n, l also increase. It has been shown earlier that with increase of n value the probability of finding of electron at r also increases. But it does not mean that there is no electron density close to the nucleus. Electron density gradually decreases to the nucleus together with appearance of nodal plane. Nodal plane is the space where the probability of finding electron is zero and the number of nodal plane is governs by the formula, $n-l-1$.

Slater proposed that nuclear charge experienced by the electrons closer to the nucleus will be greater compared to the electrons far from the nucleus. This is because of the screening of nuclear charge by the inner electron core. This is called shielding effect. The screening or shielding efficiency decreases with decreasing to penetration properties of the orbitals. Hence, it follows the sequence,

$$s > p > d > f$$

Because of the screening effect, the actual nuclear charge (Z) may be replaced by Z^*_{eff} which is called effective nuclear charge. It is given by the equation,

$$Z^*_{eff} = Z - \sigma$$

σ is sum of the shielding contribution.

Estimation of σ is governs by the following rules,

(i) The electrons are arranged in sequences of group with increase of *n* and for equal n in order of *l*.

(1*s*), (2*s* ,2*p*), (3*s*, 3*p*), (3*d*), (4*s* ,4*p*), (4*d*), (4*f*), (5*s* ,5*p*), (5*d*), (5*f*)......

(ii) The contribution of the electrons right to the electron that is under consideration is zero.

(iii) The contribution of each electron from same group 0.35, except 0.3 for 1*s*.

(iv) If the considered electron is under (*ns, np*) group, all the other electrons present at *n*-1 will contribute 0.85 each and all the other at *n-2* or further left will contribute 1.00 each.

(v) If the considered electron is under (*nd*) or (*nf*) group, all the other electrons present further left will contribute 1.00 each.

Rules are in tabulated form

Electron group	**All group at right side**	***n* group**	**(*n*-1) Groups**	**≤ (n-2) Groups**
1*s*	0	0.3	0	0
(ns,np)	0	0.35	0.85	1.00
(nd) or (nf).	0	0.35	1.00@	1.00

@ this value will be same for *ns, np*.

Electron on consideration	**σ**	**Z*eff = Z – σ**
4*s*	(1×0.35) + (18×0.85)+(10×1.00)=25.65	30 – 25. 65 = 4.35
3*d*	(9×0.35) + (18 ×1.00)=21.15	28 – 21.15 = 6.85
3*s*, 3*p*	(7×0.35) + (8×0.85) + (2×1.00)=11.25	18 – 11.15 =6.85
2s, 2p	(7×0.35) + (2×0.85) =4.15	10 – 4.15 = 5.85
1s	0.30	2–0. 30 = 1.70

1.19 The Aufbau principle

This principle states that atoms are built up by successive addition of protons at nucleus and electron at the extra-nuclear part. The newly added electrons will occupy the available orbital of lowest energy before filling higher energy state.

1.20 The Pauli Exclusion Principle

According to this theory, no two electrons in an atom will pocess same set of four quantum numbers.

1.21 Hund's rules

This rule is applied for the determination of the electronic ground state.

(i) For a given electronic configuration the term with maximum multiplicity ($2S + 1$; S = spin angular momentum) will have the lowest energy.

(ii) For a given multiplicity the term with the largest L (angular momentum quantum number) value will occupy the lowest energy.

(iii) For a given term, in an atom with less than half- filled outer most electronic configuration, the lowest energy configuration will be with the lowest value of J (total angular momentum quantum number, $J = L \pm S$). For more than half- filled outer most electronic configuration, the lowest energy configuration will be with the highest value of J.

* Terms are in capital letter as they represent energy states of electronic configuration.

Example

$^{2s+1}L_J$

S = No. of unpaired electron (s) × 1/2. L stands as, $L = 0$ is S, $L = 1$is P, $L = 2$ is D, $L = 3$ is F, $L = 4$ is G, and so on. J is the vector sum of L and S. It varies as, $J = L + S, L + S - 1, L + S - 2, \ldots . L - S$

$p^2 \equiv l =$	+1	0	−1
	↑	↑	

S = 2 × 1/2 =1,

Hence, 2S + 1 = 2 ×1+1= 3

L = 1 + 0 = 1

Hence, symbol will be $^3P_2$, $^3P_1$, $^3P_0$ [*as* $J = L + S$ to $L - S$]

1.22 Summary

Atoms are the building blocks of elements. They are the smallest parts of an element that chemically react. The first atomic theory, proposed by John Dalton in 1808, regarded atom as the ultimate indivisible particle of matter. Towards the end of the nineteenth century, it was proved experimentally that atoms are divisible and consist of three fundamental particles: electrons, protons and neutrons. The discovery of Sub atomic particles led to the proposal of various atomic models to explain the structure of atom. Thomson in 1898 proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. This model in which mass of the atom is considered to be evenly spread over the atom was proved wrong by Rutherford's famous alpha-particle scattering experiment in 1909. Rutherford concluded that atom is made of a tiny positively charged nucleus, at its centre with electrons revolving around it in circular orbits. Rutherford model, which resembles the solar system, was no doubt an improvement over Thomson model but it could not account for the stability of the atom *i.e.*, why the electron does not fall into the nucleus. Further, it was also silent about the electronic structure of atoms *i.e.*, about the distribution and relative energies of electrons around the nucleus. The difficulties of the Rutherford model were overcome by Niels Bohr in 1913 in his model of the hydrogen atom. Bohr postulated that electron moves around the nucleus in circular orbits. Only certain orbits can exist and each orbit corresponds to a specific energy. Bohr calculated the energy of electron in various orbits and for each orbit predicted the distance between the electron and nucleus. Bohr model, though offering a satisfactory model for explaining the spectra of the hydrogen atom, could not explain the spectra of multi-electron atoms. The reason for this was soon discovered. In Bohr model, an electron is regarded as a charged particle moving in a well-defined circular orbit about the nucleus. The wave character of the electron is ignored in Bohr's theory. An orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behaviour of electron but also contradicts Heisenberg uncertainty principle. Erwin Schrodinger, in 1926, proposed an equation called Schrodinger equation to describe the electron distributions in space and the allowed energy levels in atoms. This equation incorporates de Broglie's concept of wave-particle duality and is consistent with Heisenberg uncertainty principle. When Schrödinger equation is solved for the electron in a hydrogen atom, the solution gives the possible energy states the electron can occupy [and the corresponding wave function (s) (Ψ) (which in fact are the mathematical functions) of the electron associated with each energy state]. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number m_e and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrodinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical model of the hydrogen atom successfully predicts all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model. According to the quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into shells. The shells, in turn, are thought to consist of one or more subshells and subshells are assumed to be composed of one or more orbitals, which the electrons occupy. While for hydrogen and hydrogen like systems (such as He^+ , Li^{2+} etc.) all the orbitals within a given shell have same energy, the energy of the orbitals in a multi-electron atom depends upon the values of n and 1. The lower the value of (n +1) for an orbital, the lower is its energy. If two orbitals have the same (n + 1) value, the orbital with lower value of n has the lower energy. In an atom many such orbitals are possible and electrons are filled in those orbitals in order of increasing energy in accordance with Pauli exclusion principle (no two electrons in an atom can have the same set of four quantum numbers) and Hund's rule of maximum multiplicity (pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied). This forms the basis of the electronic structure of atoms.

1.23 Questions

1. State Heisenberg's uncertainty principle and give it's Mathematical expression.
2. How will you account for the extra-stability of d^5 subshell?
3. Compare the Radial distribution plots for 2s and 2p orbitals and comment on their relative penetrating property. See Radial distribution section.
4. State the major postulates of Sommerfeld's modification of Bohr's theory.

5. What is radial wave function and what is radial probability function? How do they differ for 3s, 3p and 3d orbitals? See Radial distribution section.
6. Find the electronic configuration of Lead (Pb_{82}) and Chromium (Cr_{24}).
7. What is Pauli's exclusion principle?What are Aufbau and Madelung rules? See text.
8. What is wave-particle duality? Briefly explain the wavemechanical model of atomic structure.
9. Show that energy of an electron in hydrogen atom $E = -2\pi^2 me^4/n^2h^2 = -13.6/n^2$ e V. See energy expression section.
10. What is the value of azimuthal quantum number for 'g' sub shell?
11. Sketch the shapes of the s and p orbitals. State the relative energies of the s,p,d and f orbitals.See Radial distribution section.
12. What is Hund's rule of maximum multiplicity? Cite an example to explain this rule. See text.
13. An oxygen atom has a total of eight electrons. Write the four quantum numbers for each of the eight electrons in the groundstate.See Hund'srule.
14. Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14}. See energy expression section.
15. What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom? See text.
16. What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10m s^{-1} ? See de Broglie principle.
17. A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in they measurement of its velocity? See Heisenberg principle.
18. Calculate the wavelength, frequency and wavenumber of a light wave whose period is 2.0×10^{-10} s. See de Broglie principle.
19. The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

1.24 Further Reading

1. Boeyens JCA (2013) Chemistry in 4 dimensions, Struct Bond 148:25.
2. A. K. Das, Fundamental concepts of Inorganic Chemistry Vol.-1.
3. R. P. Sarkar, General & Inorganic Chemistry Part-I.

Unit-2 Radioactivity and nuclear chemistry

Contents

2.1 Objectives

After reading this unit, we will be able to:

- Discovery of radioactivity & types of radioactivity
- Nuclear stability & Radioactive decay
- Calculation of half life, average life periods of radioactive elements
- Knowledge about nuclear binding energy and mass defect
- Types of nuclear reactions.

2.2 Introduction

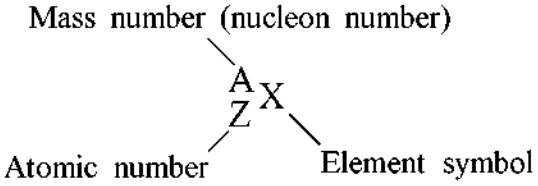
Nuclear chemistry is the sub discipline of chemistry that is concerned with changes in the nucleus of elements. That means nuclear chemistry is the sub-field of chemistry dealing with radioactivity, nuclear processes, and transformations in the nuclei of atoms, such as nuclear transmutation and nuclear properties. Since radioactivity is associated with nuclear power generation, the associated disposal of radioactive waste, and some medical procedures, everyone should have a fundamental understanding of radioactivity and nuclear transformations in order to evaluate and discuss these issues intelligently and objectively. In this unit the detail discussion on nuclear chemistry and radioactivity are presented.

2.3 Discovery of Radioactivity

The phenomenon of radioactivity was discovered by Antoine Henri Becquerel in 1896. He discovered that photographic plates develop bright spots when exposed to uranium minerals [potassium uranyl sulfate : $K_2UO_2(SO_4)_2.2H_2O$], and he concluded that the minerals give off some sort of radiation. Marie Sklodowska Curie (1867-1934), one of the first women in France to attempt doctoral work, pursued the study of uranic rays for her doctoral thesis. Curie discovered two new elements, both of which also emitted uranic rays. Curie named one of her newly discovered elements polonium after her home country of Poland. In 1903, Curie received the Nobel Prize in physics — which she shared with Becquerel and her husband, Pierre Curie — for the discovery of radioactivity. In 1911, Curie was awarded a second Nobel Prize, this time in chemistry, for her discovery of the two new elements polonium and radium. Element 96 (curium) is named in honor of Marie Curie and her contributions to our understanding of radioactivity.

2.4 Atomic nucleus & unclear stability

The protons and neutrons in each atom are found in a tiny, central nucleus that measures about 1/100,000 the diameter of the atom itself. The atoms of each element are not necessarily identical; they can differ with respect to the number of neutrons in their nuclei. When an element has two or more species of atoms, each with the same number of protons but a different number of neutrons, the different species are called isotopes. Different isotopes of the same element have the same atomic number, but they have a different mass number, which is the sum of the numbers of protons and neutrons in the nucleus. In the context of nuclear science, protons and neutrons are called nucleons, because they reside in the nucleus. The atom's mass number is often called the nucleon number, and a particular type of nucleus, characterized by a specific atomic number and nucleon number, is called a nuclide. Nuclides are represented in chemical notation by a subscript atomic number (Z) and superscript nucleon number (A) on the left side of the element's symbol (X) :



For example, the most abundant nuclide of uranium has 92 protons and 146 neutrons, so its atomic number is 92, its mass number is 238 (92 + 146), and its symbol is $^{238}_{92}U$. Nuclides can also be described with the name of the element followed by the nucleon number. Therefore, $^{238}_{92}U$. is commonly described as 238 U or uranium-238.

2.5 Nuclear stability

Two forces act upon the particles within the nucleus to produce the nuclear structure. One, called the electrostatic force (or electromagnetic force), is the force that causes opposite electrical charges to attract each other and like charges to repel each other. The positively charged protons in the nucleus of an atom have an electrostatic force pushing them apart. The other force within the nucleus, called the strong force, holds nucleons (protons and neutrons) together. If one proton were to encounter another, the electrostatic force pushing them apart would be greater than the strong force pulling them together, and the two protons would fly in separate directions. Therefore, nuclei that contain more than one proton and no neutrons do not exist. Neutrons can be described as the nuclear glue that allows protons to stay together in the nucleus. Because neutrons are uncharged, there are no electrostatic repulsions between them and other particles. At the same time, each neutron in the nucleus of an atom is attracted to other neutrons and to protons by the strong force. Therefore, adding neutrons to a nucleus increases the attractive forces holding the particles of the nucleus together without increasing the amount of repulsion between those particles. As a result, although a nucleus that consists of only two protons is unstable, a helium nucleus that consists of two protons and two neutrons is very stable. The increased stability is reflected in the significant amount of energy released when two protons and two neutrons combine to form a helium nucleus.

$$p + p + n + n \rightarrow {}^{4}_{2}He^{2+}$$

For many of the lighter elements, the possession of an equal number of protons and neutrons leads to stable atoms. For example, carbon-12 atoms, with six protons and six neutrons, and oxygen-16 atoms, with eight protons and eight neutrons, are both very stable. Larger atoms with more protons in their nuclei require a higher ratio of neutrons to protons to balance the increased electrostatic repulsion between protons. Table 2.1. shows the steady increase in the neutron-to-proton ratios of the most abundant isotopes of the elements in group 15 on the periodic table, n/p ratio and different modes of decay.

Table. 2.1

Neutron-to-Protan Ratio for the Most Abundant Isotopes of the Group 15 Elements

Element	Number of neutrons	Number of protons	Netron-to-proton ration
nitrogen, N	7	7	1 to 1
phosphorus, P	16	15	1.07 to 1
arsenic, As	42	33	1.27 to 1
antimony, Sb	70	51	1.37 to 1
bismuth, Bi	126	83	1.52 to 1

There are 264 stable nuclides found in nature. The graph in Figure 2. 1. shows the neutron-to-proton ratios of these stable nuclides. Collectively, these nuclides fall within what is known as the **band of stability**. A nuclide containing numbers of protons and neutrons that place it outside this band of stability will be unstable until it undergoes one or more nuclear reactions that take it into the band of stability. We call these unstable atoms **radioactive nuclides,** and the changes they undergo to reach stability are called **radioactive decay.**

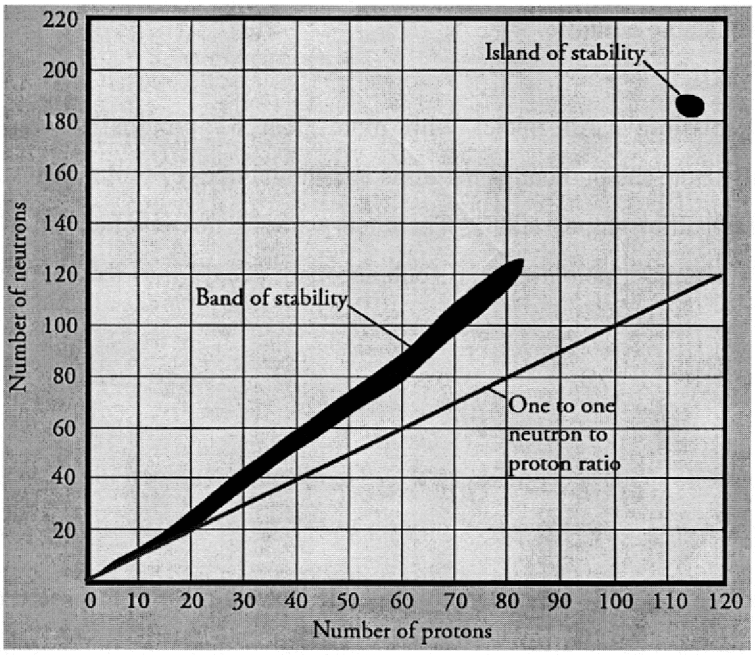


Figure 2.1 The Band of Stability

2.6 n/p ratio and different modes of decay

Since radioactivity is a nuclear phenomenon, it must be connected with the instability of the nucleus. This can be explained in the basis of relative number of protons and neutrons. The n/p ratio helps us to predict in which way an unstable nucleus will decay.

If for a stable isotope the number of proton in the nucleus is plotted against the number of neutrons in the nucleus, it is seen that the actual n/p plot of stable isotopes breaks from the hypothetical n/p (1:1) plot at around an atomic number '20' and raised rather steeply. This indicates that if the number of protons increases inside the nucleus, the more and more neutrons will be required to stabilise the nucleus. When an isotope is located above this actual n/p plot, it has too high n/p ratio and when located below the plot, it has too low n/p ratio. In either case the unstable nucleus should decay so as to approach actual n/p plot.

When n/p ratio is too low, i.e, the nucleus is neutron deficient: In this case the nucleus is proton riched, so it decays to reduce its +ve charge. When n/p ratio is very high, the neutron rich nucleus decay in such a way to attain the actual stable n/p ratio.

(i) **Alpha (α) emission :** All nuclei with more than 82 protons are radioactive and decay spontaneously. Both the number of neutrons and the number of protons must be reduced in order to make these radioisotopes stable. The very heavy nuclei often decay by emitting alpha particles. For example, polonium-210 spontaneously decays into lead-206 by emitting an alpha particle

$$^{210}_{84}Po \rightarrow {}^{206}_{82}Pb + {}^{4}_{2}He$$

(ii) **Beta emission (β or β) :** Some radioactive nuclides have a neutron-to-proton ratio that is too high, placing them above the band of stability. To reach a more stable state they undergo **beta emission** (β). In this process, a neutron becomes a proton and an electron. The proton stays in the nucleus, and the electron, which is called a **beta particle** in this context, is ejected from the atom.

$$n \rightarrow p + e^-$$

In nuclear equations for beta emission, the electron is written as either β, or β^- or ${}^{0}_{-1}e$. Iodine- 131, which has several medical uses, including the measurement of iodine uptake by the thyroid, is a beta emitter :

$$^{131}_{53}I \rightarrow {}^{131}_{54}Xe + {}^{0}_{-1}e$$

(ii) **Positron emission:** For nuclei with low neutron-to- proton ratios, two common radioactive decay processes occur: positron emission and electron capture. These two processes tend to increase the neutron-to-proton ratio of the neutron-poor atom, bringing the atom closer to, if not within, the band of stability. **Positron emission** is a radioactive decay process that involves the emission of a positron from a nucleus. A **Positron** is a particle with the same mass as an electron but opposite charge; thus, it is represented by the symbol ${}^{0}_{+1}e$ or e^+. During positron emission, a proton in the nucleus is converted into a neutron and a positron, and then the positron is emitted.

$$p \rightarrow n + e^+$$

Carbon- 11 undergoes positron emission to form boron-11. Positron emission decreases the number of protons from six to five, and increases the number of neutrons from five to six. The resulting atom, ${}^{11}B$ has a neutron-to-proton ratio of 1.2:1, which is within the band of stability.

$$ {}^{40}_{19}K \rightarrow {}^{40}_{18}Ar + {}^{0}_{+1}e $$

(iii) **Electron capture :**

Electron capture is the other common radioactive-decay process that decreases the number of protons in unstable nuclei lying below the band of stability. **Electron capture** occurs when the nucleus of an atom draws in a surrounding electron, usually one from the lowest energy level. This captured electron combines with a proton to form a neutron.

$P + e^- \rightarrow n$

The atomic number of the nucleus decreases by 1 as a consequence of electron capture. The formation of the neutron also results in an X-ray photon being emitted. These two characteristics of electron capture are shown in the electron capture of rubidium-81

$$ {}^{0}_{-1}e + {}^{125}_{53}I \rightarrow {}^{125}_{52}Te + \gamma $$

(iv) **Gamma (γ) rays :**

Because radioactive decay leads to more stable products, it always releases energy. Some of this energy is released in the form of kinetic energy, adding to the motion of the product particles, but often some of it is given off as the form of radiant energy called gamma rays. **Gamma rays** can be viewed as streams of high energy photons. For example, cesium-137 is a beta emitter that also releases gamma radiation. The energy released in the beta emission leaves the product element, barium-137, in an excited state. When the barium-137 descends to its ground state, it gives off photons in the gamma ray region of the radiant energy spectrum.

$$^{137}_{55}Cs \rightarrow {}^{137}_{56}Ba^{*} + {}^{0}_{-1}e \rightarrow {}^{137}_{56}Ba + \gamma - photon$$

2.7 Radioactive radiations

Radioactive radiations are of three types : Positively charged α-rays, negatively charged β-rays and uncharged γ-rays.

Type of radiation	Nuclear symbol	Nature of the radiation	Mass (amu)	charge	Ionizing power
Alpha	$^{4}_{2}He$	A helium nucleus of 2 Protons and 2 neutrons	4	+2	Very high ionizing power, Low Penetration
Beta	$^{0}_{-1}e$	High kinetic energy electrons	1/1850	–1	Moderate ionizing power, moderate penetration with a smaller mass and charge than the alpha particle
Gamma and X-rays	$^{0}_{0}\gamma$	High frequency electromagnetic radiation	0	0	Low ionizing power, highly penetrating, interact dominantly with the electron shell of the atom
Neutorn	$^{f}n_{0}$	Very high frequency	0	0	The lowest ionizing power of the four, very highly penetrating, interact primarily

2.8 Group Displacement Law

This law was given by Soddy, Russel and Fajans in 1913 to decide the position of element, obtained after radioactive disintegration, in the Peridic Table.

According to this law, 'In an α-emission, the daughter nuclei will occupy a position which is two places left to the position of parent nuclei and in a β-emission, the daughter nuclei will occupy a position one place right to the parent nuclei".

In alpha decay, an element is created with an atomic number less by 2 and a mass number less by four of that of the parent radioisotope, e.g.:

$$^{238}_{92}U \xrightarrow{\alpha} {}^{234}_{90}Th$$

In beta decay, the mass number remains unchanged while the atomic number becomes greater by 1 than that of the parent radioisotope, e, g.:

$$^{234}_{90}Th \xrightarrow{\beta} {}^{234}_{91}Pa \xrightarrow{\beta} {}^{234}_{92}U$$

2.9 Decay rate & chemical kinetics

2.9.1 Law of Radioactive Decay

When a radioactive material undergoes α, β or γ-decay, the number of nuclei undergoing the decay, per unit time, is proportional to the total number of nuclei in the sample material. So,

If N = total number of nuclei in the sample and ΔN = number of nuclei that undergo decay in time Δt then,

$$\Delta N/\Delta t \propto N$$

$$\text{Or, } \Delta N/\Delta t = \lambda N \ldots \ (2.1)$$

where λ, = radioactive decay constant or disintegration constant. Now, the change in the number of nuclei in the sample is, $dN = -\Delta N$ in time Δt. Hence, the rate of change of N (in the limit $\Delta t \to 0$) is,

$$dN/dt = \lambda N$$

$$\text{Or, } dN/N = -\lambda dt$$

Now, integrating both sides of the above equation. we get.

$$\int_{n_0}^{n} dN/N = \lambda \int_{t_0}^{t} dt \ldots (2.2)$$

$$\text{or, In } N - \text{In } N_0 = -\lambda(t - t_0) \ldots \ (2.3)$$

Where, N_0 is the number of radioactive nuclei in the sample at some arbitrary time t_0 and N is the number of radioactive nuclei at any subsequent time t. Next, we set $t_0 = 0$ and rearrange the above equation (3) to get,

$$\text{In } (N/N0) = -\lambda t$$

$$\text{Or, } N(t) = N_0 e^{-\lambda t} \ldots$$

Equation (2.4) is the Law of Radioactive Decay.

2.9.2. The Decay Rate

In radioactivity calculations, we are more interested in the decay rate R (= $-dN/dt$) than in N itself. This rate gives us the number of unclei decaying per unit time. Even if we don't know the number of nuclei in the sample, by simply measuring the number of emissions of α, β or γ particles in 10 or 20 seconds, we can calculate the decay rate Let's say that we consider a time interval dt and get a decay count ΔN (= $-dN$). The Decay rate is now defined as,

$$R = -dN/dt$$

Differenting equation (4) on both sides, we get,

$$R = \lambda N_0 e^{-\lambda t}$$

$$\text{Or, } R = R_0 e^{-\lambda t} \ldots (5)$$

Where, R_0 is the radioactive decay rate at time $t = 0$, and R is the rate at any subsequent time t. Equation (5) is the alternative form of the Law of Radioactive Decay. Now we can rewrite equation (1) as follows.

$$R = \lambda N \ldots (6)$$

where R and the numbers of radioactive nuclei that have not yet undergone decay must be evaluated at the same instant.

2.9.3 Half-Life and mean Life

The total decay rate of a sample is also Known as the *activity* of the sample. The S.I. unit for measurement of *activity* is *'becquerel'* and is defined as,

$$1 \text{ becquerel} = 1Bq = 1 \text{ decay per second}$$

An older unit, the curie, is still in common use :

$$1 \text{ curie} = 1\ Ci = 3.7 \times 10^{10}\ Bq \text{ (decays per second)}$$

There are two ways to measure the time for which a radionuclide can last.

Half-life $T_{1/2}$ – the time at which both R and N are reduced to half of their initial value

Mean life τ– the time at which both R and N have been reduced to, e^{-1} of their initial values.

2.9.4. Calculating half-Life

Let's find the relation between and the disintegration constant λ, For this, let's imput the following values in equation (5),

$$R = (1/2)\ R_0 \text{ and } t = T_{1/2}$$

$$\text{So, we get } T_{1/2} = (\text{In } 2)/\lambda$$

$$\text{Or, } T_{1/2} = 0.693/\lambda \ \ldots. \ (7)$$

2.9.5 Calculating mean life

Next, let's find the relation between the mean life τ and the disintegration constant λ, For this, let's consider equation (5),

- The number of nuclei which decay in the time interval : 't' to '$t + \Delta t$' is : $R(t)\ \Delta t = (\lambda N_0 e^{-\lambda t}\ \Delta t)$.
- Each of them lived for time 't'.
- Hence, the total life of all this nuclei is $t\lambda N_0 e^{-\lambda t}\ \Delta t$.

Hence, to obtain the mean life. we integrate this expession over all the times from 0 to ∞ and divide by the total number of nuclei at t = 0 (which is N_0)

$$\tau = \left(\lambda N_0 \int_{\infty}^{0} t e^{-\lambda t} dt\right) / N_0$$

$$= \lambda \int_{\infty}^{0} t e^{-\lambda t} dt.$$

On solving this integral, we get

$$\tau = 1/\lambda$$

Therefore, we can summarise the observations as follows :

$$T_{\frac{1}{2}} = (\text{In}2)/\lambda = \tau \text{ In } 2 \ldots (8)$$

2.10 Nuclear binding energy and mass defect

Nuclear binding energy is the energy required to split a nucleus of an atom into its component parts : protons and neutrons, or, collectively, the nucleons. The binding energy of nuclei is alway a positive number, since all nuclei require net energy to separate them into individual protons and neutrons.

2.10.1. Mass Defect

Nuclear binding energy accounts for a noticeable difference between the actual mass of an atom's nucleus and its expected mass based on the sum of the masses of its non-bound components.

Recall that energy (E) and mass (m) are related by the equation :

$$E = me^2$$

Here, c is the speed of light. In the case of nuclei, the binding energy is so great that it accounts for a significant amount of mass.

The actual mass is always less than the sum of the individual masses of the constituent protons and neutrons because energy is removed when the nucleus is formed. This energy has mass, which is removed from the total mass of the original particles. This mass, known as the mass defect, is missing in the resulting nucleus and represents the energy released when the nucleus is formed.

Mass defect (M_d) can be calculated as the difference between observed atomic mass (m_0) and that expected from the combined masses of its protons (m_p, each proton having a mass of 1.00728 amu) and neutrons (m_n, 1.00867 amu):

$$M_d = (m_n + m_p) - m_o$$

2.10.2. Nuclear binding Energy

Once mass defect is known, nuclear binding energy can be calculated by converting that mass to energy by using $E = mc^2$. Mass must be in units of kg.

Once this energy, which is a quantity of joules for one nucleus, is known, it can be scaled into per-nucleon and per-mole quantities. To convert to joules/mole, simply multiple by Avogadro's number. To convert to joules per nucleon, simply divide by the number of nucleons. Nuclear binding energy can also apply to situations when the nucleus splits into fragments composed of more than one nucleon; in these cases, the binding energies for the fragments, as compared to the whole, may be either positive or negative, depending on where the parent nucleus and the daughter fragments fall on the nuclear binding energy curve. If new binding energy is available when light nuclei fuse, or when heavy nuclei split, either of these processes result in the release of the binding energy. This energy—available as nuclear energy— can be used to produce nuclear power or build nuclear weapons. When a large nucleus splits into pieces, excess energy is emitted as photons, or gamma rays, and as kinetic energy, as a number of different particles are ejected.

Nuclear binding energy is also used to determine whether fission or fusion will be a favourable process. For elements, lighter than iron-56, fusion will release energy because the nuclear binding energy increases with increasing mass. Elements heavier than iron-56 will generally release energy upon fission, as the lighter elements produced contain greater nuclear binding energy. As such, there is a peak at iron-56 on the nuclear binding energy curve.

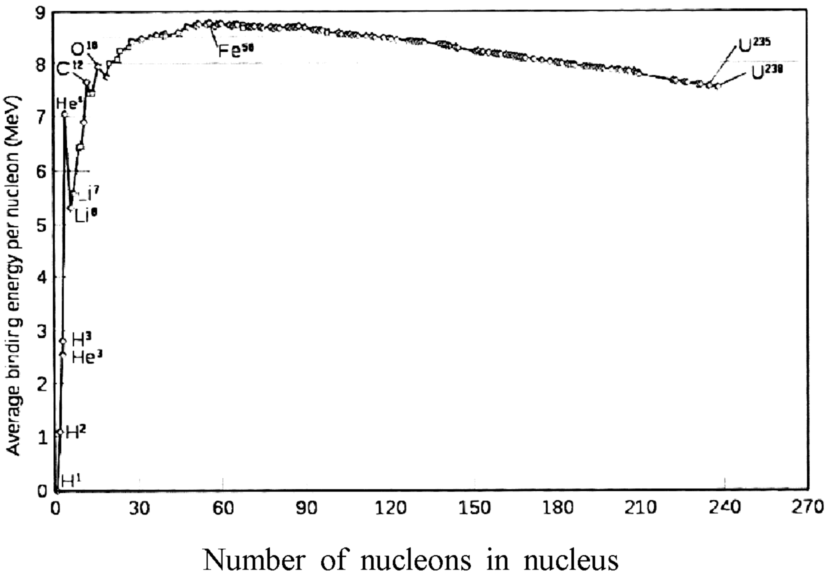


Figure.2.2 Nuclear binding energy curve. This graph shows the nuclear binding energy (in MeV) per nucleon as a function of the number of nucleons in the nucleus. Notice that iron-56 has the most binding energy per nucleon, making it the most stable nucleus.

The rationale for this peak in binding energy is the interplay between the coulombic repulsion of the protons in the nucleus, because like charges repel each other, and the strong nuclear force, or strong force. The strong force is what holds protons and neutrons together at short distances. As the size of the nucleus increases, the strong nuclear force is only felt between nucleons that are close together, while the coulombic repulsion continues to be felt throughout the nucleus; this leads to instability and hence the radioactivity and fissile nature of the heavier elements.

Ex : Let us calculate the mass defect (M_d) of **Helium** ($_2He^4$) atom

He^4 consists 2 protons and 2 neutrons in its nucleus.

Mass of proton (m_p) = 1.0078amu, Mass of neutron (m_n) = 1.0087amu

Total mass of 2 protons = 2 × 1.0078 = 2.0156 amu

Total mass of 2 neutrons = 2 × 1.0087 = 2.0174 amu

Total mass of 2 protons and 2 neutrons of Helium ($_2He^4$) atom is (2.0156 + 2.0174) amu =4.0330 amu

Observed mass of Helium is 4 amu.

Mass defect (m_d) = 4.0330 – 4 = 0.330 amu

The magnitude of mass defect is a measure of the stability of the nucleus. Thus the mass defect of Helium nucleus to be 0.0304 amu has been converted to energy; the energy is utilized to bind two protons and two neutrons together and is called Binding Energy (B.E).

B.E of nucleus = $m_d \times 931.5$ Mev.

2.11 Packing fraction

Aston defined Packing Fraction as
Packing Fraction =

$$\frac{\text{Isotopic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

Packing Fraction can have positive, negative or zero value.

i. Zero value of packing fraction is found in mono isotopic elements where the isotopic mass is equal to the mass number.

ii. Negative value of packing fraction indicates that there is mass defect, hence binding energy. Such nuclei are stable.

iii. Positive values of Packing fraction are unstable undergoing fission and fusion process, eg. ${}^{1}_{1}H$ (+ ve packing fraction) undergoes fusion.

${}^{235}U$ (+ve packing fraction) undergoes fission.

The stability of an atom appears to depend on the relative number of protons and neutrons present in the nucleus. Elements having mass number in the range of (40 – 120) have a high binding energy per nucleon and hence greater stability. On the other hand, heavy elements have very low binding energy per nucleon and have unstable nuclei.

The value of n/p ratio determines the nuclear stability. The nucleii of light isotopes have approximately an equal number of protons and neutrons. But for heavier nuclei, the number of neutrons is greater than the number of protons.

The figure given below shows the variation of the number of neutrons with the number of protons in the stable non-radioactive nuclei.

The stable nucleii lie within the shaded area which is called the region or zone of stability. A nucleus that lies outside the zone of stability will therefore be unstable. Nucleii that lie above the zone of stability will therefore be unstable. Nucleii that lie above the zone of stability have an excess of neutrons, while those lying below have excess of protons.

Nucleii are particularly stable and abundant when they have either Z or n equal to 2, 8, 20, 28, 50, 82 or 126. These are called magic numbers. A nucleus that possesses a higher n/p ratio would try to bring about reduction in number of neutrons and increase in number of protons. Similarly a nucleus that possesses a low n/p ratio would achieve stability by an increase of neutrons or decrease of protons. All such processes involving conversion of an unstable to a more stable nucleus result in radioactive emissions.

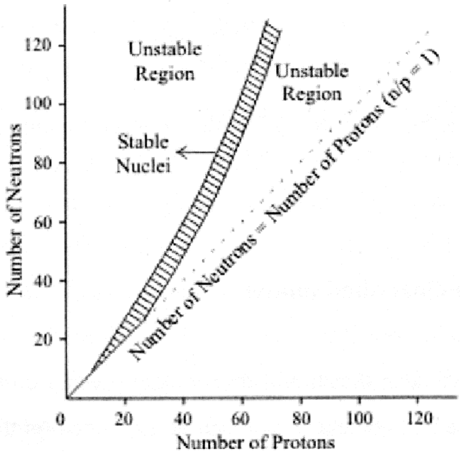


Figure 2.3. The variation of the number of neutron with the number of protons in the stable non radioactive nucleii

2.12 Nuclear forces : Meson exchange theory

Protons have positive charge. In any nucleus containing two or more protons there will be electrostatic repulsion between the like charges. In stable nucleus, attractive forces are greater than repulsive forces and in unstable nucleus, attractive forces are less than repulsive forces. In 1935 Japanese scientist H.Yukawa explained the mechanism of interaction of the elementary particles (Neutrons & Protons) in a nucleus. In order to explain his theory he considered a particle known as pions/ mesons (π°) and that came to be known as **Meson theory.** He postulated the existence of a nuclear particle π meson or pion which acts as a glue binding the protons and neutrons together in the nucleus.

A pion has two sub particles such as π^{-} , π^{+} and π° (neutral).

He explained, a neutron in a nucleus emits out a π^{-} particle and becomes a proton. Whereas a proton emits a π + and becomes a neutron, this exchange of particles continues repeatedly.

A Visualization of reaction-

neutron $+\pi^{-} \rightarrow$ • proton.

proton + $\pi^{+} \rightarrow$ • neutron

the binding force between like particles, *i.e.* exchange of n — n and p — p involves neutral π mesons.

$\mathrm{p} = \mathrm{p} + \pi^{0}$

$\mathrm{n} = \mathrm{n} + \pi^{0}$

Due to this exchange of particles there is a strong interactive force existing inside the nucleus.

2.13 Elementrary idea of nuclear shell model

In the previous chapter, we have seen that liquid drop model gives a quites clear picture on the nuclear stability and later on we will see that nuclear fission can be explained on the basis of the same. However, there are some other properties of nucleus which can't be explained on th basis of this model. It has been observed by nuclear physicists that nuclei with number of protons or neutrons equal to 2,4,8, 20, 50, 82 and 126, the B.E./A values are higher as compared to their neighbours, giving rise to discontinuities to the binding energy curves. This indicates stability of these nuclei as compared to their neighbouring nuclei of the B.E. curve, For example $^{140}Ce_{58}$ which has 82 neutrons has higher (almost 4 MeV) B.E. compared to its neighbours. The numbers 2,4,8,20,50,82 and 126 are known as magic numbers as they were not understood for quite a long time with existing models such as LDM.

Explanation of Magic numbers—Shell model of a nucleus

Whatever it may be, let me tell you that there is a resemblance between occurrence of magic numbers and higher ionization potential of the noble gases (element with specific atomic number, Z), which is basically a consequence of atomic shell structure. For these atoms the electron shells are completely filled. Therefore, naturally question arise whether nucleus too has a shell structure and if it is so, can it explain the magic numbers? It was not an easy job to shell model of a nucleus similar to atomic shell model as there is no obvious central attractive force in a nucleus. like Coulomb force in an atom. Secondly, the density of nucluear matter is extremly high ($\sim 10^{17}$kgm^{-3}) and hence free movement of nucleon in a nucleus like electrons in atom is difficult to imagine. However, Barlett Guggenheimer et al. proposed an independent particle model (shell model) for the nucleus in 1933 and could able to explain lower magic numbers (2,4,8) Later on, Maria G. Mayer in 1948 and independently Haxel et al. proposed shell structure of the nucleus and closed shell in nuclei having a corresponding to magic numbers. Their models were able to explain all magic numbers with a consideration of strong spin-orbit forces of nucleons and their coupling. Before discussing the shell structure of the nucleus given by Mayer, let us first discuss the concept of atomic shells and spin-orbit coupling. Atomic shell are basically some energy levels where electrons are allowed to stay following some quantum mechanical conditions. As electrons move in quantized orbits, it has orbital angular momentum associated with it. Apart from orbital angular momentum also spin angular momentum, arises due to its spin motion, which with much simplicity can be understood as a motion about its own axis. Not only electrons. but every elementary particle with such rotational condition has two types of angular momentum, *i.e.* spin angular momentum and orbital angular momentum. The first one is denoted by symbol s and the second one by symbol 1. The particles like electron, proton, neutron etc. have value of s as +1/2 or -1/2. There are several values of 1, corresponding to various orbitals where the particle is moving. In case of electron. the atomic orbitals are denoted by, s, p, d, f, g, h, i, etc. and corresponding 1 values are 0,1,2,3,4,5, 6 respectively. Now the 1 and s values of an electron (similarly, neucleons) can vectorially couple giving rise to a resultant angular momentum, j, where j = 1 s, i.e. 1 1/2. For example. if we consider spectroscopic term s, then, 1 = 0, s = 1/2 and j = 1/2. Now the next step is to consider the potential configuration within which the nucleons move inside the nucleus. The first assumption mode in nuclear shell model is single particle concept with an idea that the spin, parity and moments are determined by the unpaired nucleon alone and hence essentially reducing many nucleon problems to a single particle problem. It is also assumed that each nucleon experiences a central attractive force due to the average effect of the remaining nucleons (core) in the nucleus. This is something similar to the atom where nucleus acts as a central attractive force of the electons in the orbits. In this central field each nucleon is considered to move in a shell having specific energy and angular momentum. Another assumption of shell model is a weak inter nucleon interaction. The model of Mayer considers that the 1 and s values of a nucleon couples giving a distinct j value of a nucleon. Nucleon having different j values couple by a j-j coupling mode, which eventually explain the origin of magic numbers.

In order to describe shell model a detail quantum mechanical calculation is required by considering some standard potential. Various potential configutations have been chosen by various authors. M.Mayer and Haxel et al. independently showed that harmonic oscillator potential or square well potential can be used to obtain reasonable results. The forms of these potentials are :

(A) $V = -V_0 + 1/2\ M\omega^2 r^2$...... (m1.42) (linear harmonic oscillator). Where V_0 and ω are constants.

(B) $V = -V_0$ for $r < R$ .... (m1.43) = 0 for $r > R$.

Of late, more realistic potential configuration have been chosen by other Nuclear Physicists.

A detailed mathematical formulation is required to find the energy of the nlecleon in various shells. However, in this lecture we will just show the nucleons distribution in a closed shell and the associated magic numbers.

Shells are defined by principal quantum numbers n whose value runs from 0 to integer numbers. The sequence of nuclear spins with increasing n values as per standard spectroscopic notation is shown in table 2.2.

TABLE 2.2. Filling up of nuclear shells with nucleons corresponding to magic numbers.

Spectroscopic term	**n**	**I**	**J**	**Number of states (2J+1)**	**Number of Nucleons in a shell**	**Magic number**
${}^{1}s_{\frac{1}{2}}$	0	0	$\frac{1}{2}$	2	2	2
${}^{1}p_{\frac{3}{2}}$	1	1	$\frac{3}{2}$	4	6	8
${}^{1}p_{\frac{3}{2}}$	1	1	$\frac{1}{2}$	2		
${}^{1}d_{\frac{5}{2}}$	2	2	$\frac{5}{2}$	6	12	20
${}^{1}d_{\frac{3}{2}}$	2	2	$\frac{3}{2}$	4		
${}^{1}s_{\frac{1}{2}}$	2	0	$\frac{1}{2}$	2		
${}^{1}f_{\frac{7}{2}}$	3	3	$\frac{7}{2}$	8	20	40
${}^{1}f_{\frac{5}{2}}$	3	3	$\frac{5}{2}$	6		
${}^{2}p_{\frac{3}{2}}$	3	1	$\frac{3}{2}$	4		
${}^{2}p_{\frac{1}{2}}$	3	1	$\frac{1}{2}$	2		
${}^{1}g_{\frac{9}{2}}$	4	4	$\frac{9}{2}$	10	10	50

Spectroscopic term	n	I	J	Number of States (2J+1)	Number of Nucleons in a shell	Magic number
$^1g_{\frac{7}{2}}$	4	4	$\frac{7}{2}$	8	32	50
$^2d_{\frac{5}{2}}$	4	2	2	6		
$^2d_{\frac{3}{2}}$	4	2	$\frac{3}{2}$	4		
$^3s_{\frac{1}{2}}$	4	0	$\frac{1}{2}$	2		
$^1h_{\frac{11}{2}}$	5	5	$\frac{11}{2}$	12		82
$^1h_{\frac{9}{2}}$	5	5	$\frac{9}{2}$	10	44	
$^1f_{\frac{7}{2}}$	5	3	$\frac{7}{2}$	8		
$^2f_{\frac{5}{2}}$	5	3	$\frac{5}{2}$	6		
$^3p_{\frac{3}{2}}$	5	1	$\frac{3}{2}$	4		
$^3p_{\frac{1}{2}}$	5	1	$\frac{1}{2}$	2		
$^1i_{\frac{13}{2}}$	6	6	$\frac{13}{2}$	14		126

Now it is clear from the above table that in order to understand nuclear property like magic numbers concept of shell model is must. This model has great implication to understand nuclear structure and hence nuclear spectroscopic studies.

2.14 Radioactive series

The sequential decay of a given nuclei results in the production of a nuclei or element. This series of elements thus from is known as a radioactive decay series. There are 3 radioactive series depending on the original progenitor.

Disintegration Series	**Parent Element**	**Last element**	**Stable Total No.1. of α-an β-particles emitted**
1. Thorium Series or 4n series	$_{90}Th^{232}$	$_{82}Pb^{208}$	6α and 4 β
2. Neptunium Series or (4n + 1) series	$_{93}Np^{237}$	$_{83}Bi^{209}$	7α and 4 β
3. Uranium Series or (4n+2) series	$_{92}U^{238}$	$_{82}Pb^{206}$	8α and 6 β
4. Actinium Series or (4n+3) series	$_{92}U^{235}$	$_{82}Pb^{207}$	7α and 4 β

The important features of the radioactive series :

(1) In every one of these three series radioactivity finally ceases with a stable lead Isotope.

(2) Only Inert gas formed in these series are Radon (Rn) Z = 86

(3) In all the d series wherever there is a change in mass number, it alters by 4 only.

(4) Depending upon the masses of the element, the series are named as

Uranium (4n + 2)
Thorium (4n)
Actinium (4n + 3)

(5) There is another artificially produced radioactive series called as Neptunium or (4n +1) series.

2.15 Fission, fusion and spallation reactions

2.15.1 Nuclear fission

The heavy nucleus of radioactive atoms like uranium, plutonium or thorium is bombarded with low energy neutrons which split the nucleus into smaller nuclci. This process is called nuclear fission. For example when uranium-235 atoms are bombarded with neutrons then the heavy uranium nucleus splits to produce Barium-139 and krypton-94 with the emission of three neutrons. A lot of energy is also produced in this reaction because mass is converted into energy.

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{139}_{56}Ba + ^{94}_{36}Kr + 3\,^{1}_{0}n$$

In a typical nuclear fission reaction, more than one neutron is released by each dividing nucleus. When these neutrons collide with and induce fission in other neighboring nuclei, a self-sustaining series of nuclear fission reaction known as a **nuclear chain reaction** can result (figure 2.4). For example. the fission of ^{235}U releases two to three neutrons per fission event. If absorb by other ^{235}U nuclei, those neutrons induce additional fission events, and the rate of the fission reaction increases geometrically. Each series of events is called a generation. Experimentally. it is found that some minimum mass of a fissile isotope is required to sustain a nuclear chain reaction; if the mass is too low, too many neutrons are able to escape without being captured and inducing a fission reaction. The minimum mass capable of supporting sustained fission is called the **critical mass**. This amount depends on the purity of the material and the shape of the mass, which corresponds to the amount of surface area available form which neutrons can eseape, and on the identity of the isotope, if the mass of the fissile isotope is greater than the critical mass. Then under the right conditions. the resulting supercritical mass can release energy explosively. The enormous energy released from nuclear chain reactions is responsible for the massive destruction caused by the detonation of nuclear weapons such as fission bombs, but it also forms the basis of the nuclear power industry.

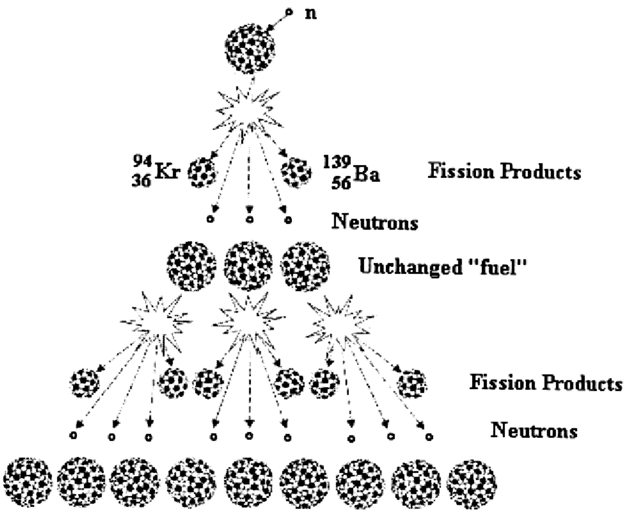


Figure 2.4. Schematic diagram of a nuclear chain reaction

The process is initiated by the collision of a single neutron with a ^{235}U nucleus, which undergoes fission. Because each neutron released can cause the fission of another ^{235}U nucleus, the rate of a fission reaction accelerates geometrically.

2.15.2 Nuclear fusion

The meaning of fusion is to join or to combine. Therefore, the process in which two nuclei of light elements are combined to form a heavy nucleus is nuclear fusion. In the process of nuclear fusion also tremendous amount of energy is released.

$$2\,{}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + \mathrm{Energy}$$

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + \mathrm{Energy}$$

The nuclei of atoms are positively charged and thus they repel each other. So in order to combine or fuse these two nuclei to form one heavy nucleus, a lot of heat energy and high pressure is requied. This shows that nuclear fusion is carried out by heating lighter atoms to an extremely high temperature at high pressure. Some mass is also lost in this process which gives tremendous amount of energy.

For example, when deuterium atoms are heated to an extremely high temperature under high pressure than two deuterium nuclei combine to form helium which has a heavy nucleus, a neutron is emitted and a lot of energy is liberated. Temperatures required for fusion reactions exist in stars where fusion reactions are the principle components of energy release. In the Sun, approsimately 90 percent of solar energy is a result of proton–proton interactions in several steps to form helium of mass number 4. These steps all involve binuclear collisions since multi nuclei collisions are very improbable events. Initially, two protons interact to form a deuterium nucleus (deuterium is an isotope of hydrogen with one proton and one neutron; the nucleus is a deuteron) that collides with another proton to form at He, tritrium nucleus. This nucleus collides with a neutron or another ^{3}He nucleus (with the emission of two protons) to form ^{4}He. The net reaction can be repesented as four protons fusing to form a ^{4}He nucleus releasing 26.7 MeV.

Nuclear fusion reaction is opposite of nuclear fission reaction. The energy produced in nuclear fusion reaction has not been controlled yet and is much more than nuclear fission reaction.

2.15.3 Hydrogen bomb

Nuclear reactions which occur at extremely high temperature are called thermonuclear reactions. This reaction is used in producing hydrogen bomb which causes mass destruction. Isotopes of hydrogen. deuterium (^{2}H) and tritium (^{3}H), along with an element lithium-6 is used in making a hydrogen bomb. This is because when atom bomb is exploded then its fission reaction produced a lot of heat which raises the temperature of deuterium and tritium in a few microseconds. Thus the fusion reaction takes place and hydrogen bomb is exploded producing enormous energy. Hydrogen bomb causes destruction of life.

2.15.4 Advantages of nuclear energy

- It produced tremendous energy from a small amount of fuel (Uranium-235)
- There is no need to put the fuel again and again in nuclear reactor. once the fuel (Uranium-235) is put in the reactor it can function for two to three years at a stretch.
- It does not produce gases like carbon dioxide or sulphur dioxide.

2.15.5 Disadvantages of nuclear energy

- The waste products of nuclear reactors are radioactive and keep on emitting harmful radiations.
- Risk of an accident in nuclear reactors which may cause leakage of radioactive material.
- The availability of fuel uranium is limited.
- High installation cost of nuclear power plant.

2.15.6 Spallation reactions

When an element of intermediate range of mass number and atomic number are bombarded with high energy α-particles, protons, deuterons; they do not undergo nuclear fission into two fragments of close mass; instead of this, these nuclei are split into a variety of nucleus of lower mass and atomic number. Such nuclear reactions are called nuclear spallation reaction.

$$^{75}_{33}\mathrm{As} + ^{2}_{1}\mathrm{H} \rightarrow ^{56}_{25}\mathrm{Mn} + 9^{1}_{1}\mathrm{H} + 12^{1}_{0}\mathrm{n}$$

2.16 Natural radioactivity

Nuclear reactions which occur spontaneously are said to be an example of natural radioactivity. There are three naturally occurring radioactive series among the elements in the periodic table. These are known as the uranium series, the actinium series and the thorium series, each named after the element at which the series start (except the actinium series which starts with a different uranium isotope). Each series decays through a number of unstable nuclei by means of alpha and beta emmission, until each series end on a different stable isotope of lead.

2.17 Artificial radioactivity

A nuclear process in which a stable element is converted into another element which is radioactive in nature is called artificial or induced radioactivity.

Not all nuclear reactions are spontaneous. These reactions occur when stable isotopes are bombarded with particles such as neutrons. This method of inducting a nuclear reaction to proceed is termed artificial radioactivity. These meant new nuclear reactions, which wouldn't have been viewed spontaneously, could now be observed. Since about 1940, a set of new elements with atomic numbers over 92 (the atomic number of the heaviest naturally occurring element, Uranium) have been artificially made. They are called the transuranium elements. It was first discovered by Curie in 1934. Their experiments is bombardment of aluminium with α particle.

$${}^{27}_{13}\text{Al} + {}^{4}_{2}\text{He}(\text{Alpha particle}) \rightarrow {}^{30}_{15}\text{P}^* + {}^{1}_{0}\text{n}(\text{neutron}) + \text{Q}(\text{energy})$$

$${}^{30}_{15}\text{P}^* \rightarrow {}^{30}_{14}\text{Si} + {}^{0}_{1}\text{e}(\text{Positron})$$

2.18 Super heavy elements and their IUPAC nomenclature

It is a generally accepted convention that the discoverer of an element has the honour of naming it. The inspiration often comes from origin, mythical characters, place, physical or chemical properties, and more recently to commemorate the names of eminent scientist. Of course, the suggestion has to be ractified by the International Union of Pure And Applied Chemistry (IUPAC).

Newly discovered or undiscovered superheavy elements are often referred to in the scientific literature but until they have received permanent names and symbols from IUPAC, temporary designators are required. In 1978, IUPAC Commission on the Nomenclature of Inorganic Chemistry decided that it is necessary to have a systematic naming for the elements with atomic number greater than 100 (Z >100).

even for those which had not been discovered. The Commission decided that these elements would be best named systematically and that names should accord with the following rules :

1. The name is derived directly from the atomic number of the element using the following Latin numerical roots :

Number	**Root**
0	nil
1	un
2	bi
3	tri
4	quad
5	pent
6	hex
7	sept
8	oct
9	enn

2. The roots are put together in the order of the digits which make up the atomic number and terminated by 'ium' to spell out the name. The final 'n' of 'enn' is elided when it occurs before 'nil', and the final 'i' of 'bi' and of 'tri' when it occurs before 'ium'.
3. The symbol of the element is composed of the initial letters of the numerical roots which make up the name.
4. The root 'un' is pronounced with a long 'u', to rhyme with 'moon'. In the element names each root is to be pronounced separately.

Here are a few examples of the names generated for elements with atomic numbers 101 to 900

Atomic Number	**Name**	**Symbol**
101	Unnilunium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uuu
112	Ununbium	Uub
113	Ununtrium	Unt
114	Ununquadium	Uuq
115	Ununpentium	Unp
116	Ununhexium	Unh
117	Ununseptium	Uus

118	Ununoctium	Uuo
119	Ununennium	Uue
120	Unbinilium	Ubn
121	Unbiunium	Ubn
130	Untrinilium	Utn
140	Unquadnilium	Uqn
150	Unpentinilium	Upn
160	Unhexnilium	Uhn
170	Unseptnilium	Usn
180	Unoctnilium	Uon
190	Unennilium	Uen
200	Binilnilium	Bnn
201	Binilunium	Bnu
202	Binilbium	Bnb
300	Trinilnilium	Tnn
400	Quadnilnilium	Qnn
500	Pentnilnilium	Pnn
900	Ennilnilium	Enn

So far, essentially all the transuranium elements have been discovered at four Berkeley National Laboratory in the United States (elements 93 – 101, 106, and joint credit for 103 – 105), the Joint Institute for Nuclear Research in Russia (elements

102 and 114 –118, and joint credit for 103 – 105), the GSI Helmholtz Centre for Heavy Ion Research in Germany (elements 107 – 112), and RIKEN in Japan (element 113)

- 93. neptunium, Np, named after the planet Neptune, as it follows uranium and Neptune follows Uranus in the planetary sequence (1940).
- 94. plutonium, Pu, named after the dwarf planet Pluto. following the same naming rule as it follows neptunium and Pluto follows Neptune in the pre -2006 Planetary sequence (1940).
- 95. americium, Am, named because it is an analog to europium, and so was named after the continent where it was first produced (1944).
- 96. curium, Cm, named after Pierre and Marie Curie, famous scientists who separated out the first radioactive elements (1944), as its lighter analog gadolinium was named after Johan Gadolin.
- 97. berkelium, Bk, named after the city of Berkeley, where the University of California, Berkeley is located (1949).
- 98. californium, Cf, named after the state of California, where the university is located (1950).
- 99. einsteinium. Es, named after the theoretical physicist Albert Einstein (1952).
- 100. fermium, Fm, named after Enrico Fermi, the physicist who produced the first controlled chain reaction (1952).
- 101. mendelevium, Md, named after the Russian chemist Dmitri Mendeleev, credited for being the primary creator of the periodic table of the chemical elements (1955).
- 102. nobelium. No, named after Alfred Nobel (1958).
- 103. lawrencium, Lr, named after Ernest O. Lawrence, a physicist best known for development of the cyclotron, and the person.
- 104. rutherfordium. Rf, named after Ernest Rutherford, who was responsible for the concept of the atomic nucleus (1968).
- 105. dubnium, Db, an element that is named after the city of Dubna.
- 106. seaborgium, Sg, named after Glenn T. Seaborg. This name caused controversy because Seaborg was still alive, but eventually became accepted by international chemists (1974). ;

- 107. bohrium, Bh, named after the Danish physicist Niels Bohr, important in the elucidation of the structure of the atom (1981)
- 108. hassium. Hs, named after the Latin form of the name of Hessen, the German *Bundesland* where this work was performed (1984).
- 109. meitnerium, Mt, named after Lise Meitner, an Austrian physicist who was one of the earliest scientists to study nuclear fission (1982).
- 110. darmstadtium. Ds, named after Darmstadt.
- 111. roentgenium. Rg, named after Wilhelm Conrad Rontgen, discoverer of X-rays (1994).
- 112. copernicium. Cn, named after astronomer Nicolaus Copernicus (1996).
- 113. nihonium. Nh, named after Japan (Nihon in Japanese) where the element was discovered. (2004).
- 114. flerovium, Fl, named after Soviet physicist Georgy Flvorov, founder of the JINR (2004).
- 115. moscovium, Mc, named after Moscow Oblast. Russia, where the element was discovered;
- 116. livermorium, Lv, named after the Lawrence Livermore National Laboratory, a collaborator with JINR in the discovery, (2004).
- 117. tennessine, Ts, named after the state of Tennessee, where the berkelium target needed for the synthesis of the element was manufactured;
- 118. oganesson. Og, named after Yuri Oganessian, who led the JINR team in its discovery of elements 114 to 118.

2.19 Introduction to reactor system

A nuclear reactor used for the purpose of power generation or for the production of radioisotopes is defined as a system wherein a nuclear fission is carried out as a controlled chain reaction. Nuclear reactors that utilize thermal neutrons to initiate and sustain fission are called thermal reactors and those that utilize fast neutrons are called fast reactors. The most important components of a nuclear reactor are (i) fuel (ii) moderator (iii) coolant and (iv) control materials.

2.19.1. Fuel

Analogous to the role of fuel in any heating application, the fuel in a nuclear reactor is the source of energy and hence it is the material containing a fissile nucleus. Materials that undergo nuclear fission when bombarded with thermal neutrons are called fissile material and their respective nuclei called fissile nuclei. U-235 is the only fissile nucleus that is available in nature, while Pu-239 and U-233 are produced in nuclear reactors. Hence most of the nuclear reactors for power generation use uranium as fuel. U-235 is not present in nature in pure form. It is present as a mixture with U-238, the major component present to the extent of 99.3 %. In other words the isotopic abundance of natural U-235 in a mixture of U-235 and U-238 is only 0.7 %. In most reactors the fuel is in oxide form as UO_2 Pu-239 is used as fuel in Fast Reactors while U-233 is proposed as fuel in Advanced Heavy Water Reactors.

2.19.2. Moderator

Moderation with respect to nuclear reactors implies slowing down of neutrons. In other terms, neutrons with higher kinetic energy (fast neutrons) are allowed to undergo elastic scattering with a light nucleus resulting in reduction in speed and change in direction of neutrons. As a result the neutron energy is brought down to thermal levels (0.025 eV). Comparing the fission cross sections of U-235 with fast neutrons and thermal neutrons, it is clear that the probability of fission in U-235 with thermal neutrons is more than with fast neutrons. Hence the neutron energies must be brought down. The most widely used moderators are the one that contain light nuclei like hydrogen, deuterium, carbon etc. Hence water (H_2O, also called light water), heavy water (D_2O) and graphite are used as moderators.

2.19.3. Coolant

The purpose of coolant is to remove the heat liberated during fission and to utilize the same for steam generation. The coolant supply to a nuclear reactor must be continued even if the chain reaction has ceased and reactor shut down. This is to ensure the removal of decay heat and to avoid the melting of reactor core. Water and heavy water are the most common liquid coolants in thermal reactors. Liquid sodium is used as coolant in fast reactors. Helium and CO_2 are used as gaseous coolants in Gas-cooled reactors.

2.19.4. Control materials

Substance of a controlled fission is the key for generating electricity from nuclear reactors. Control materials are essential for regulating the power of a reactor, apart from bringing about rapid shut down when required. These are the materials that have high tendency to absorb neutrons through neutron capture. Boron and Cadmium have high capture cross sections and hence are used as control materials in the form of rods or plates.

2.19.5. Other components

Apart the above four important components of a nuclear reactor, other components include structural components and control systems.

2.20 Slow and fast neutrons

Nuclear fission can occur when a nucleus is rendered sufficiently unstable by the capture of a passing neutron. The probability for a fission reaction to take place depends much on how energetic these neutrons are. The knowledge of their energies spectrum is vital for an understanding of how nuclear reactors work. One classifies these neutrons in groups according to their energy ranges, the most important being the **'fast'** and **'slow'** neutrons.

2.20.1. Slow neutrons

After a series of collisions with different nuclei, the energy of neutrons produced by fission reactions drops to the order of a few electron volts or a few fractions of an electron volt. Neutrons with energies in this range are collectively referred to as 'slow', and neutrons whose energies match those of the surrounding atoms are known as 'thermal'.

It is these slow neutrons that allow for nuclear reactors to run with fuel based on natural uranium or uranium lightly-enriched in fissile isotope 235. Without them, the most common pressurised (PWR) and boiling water (BWR) reactors would not operate. As a result, the neutrons emitted by nuclear fission have to be slowed down by collisions within a medium called a **moderator.** Reactors operating with natural uranium fuel, which contains only 0.7% of fissile uranium 235, require efficient moderators which absorb very few of the neutrons : such moderators are heavy water and pure graphite.

2.20.2. Fast neutrons

Before they are slowed down by a large number of nuclear collisions, neutrons produced by fission reactions are known as 'fast'. They usually have energies between 0.1 and 2 or 3 MeV.

The fact that they possess a substantial amount of kinetic energy allows fast neutrons to fission more easily nuclei once they get captured. They can therefore split not only nuclei reputed fissile by slow neutrons, but also minor actinides, the heavy nuclei which build up inside nuclear fuel as radioactive waste. Fast neutrons are needed to eliminate these waste products.

The use of fast neutrons in so-called 'fast reactors' allows for the production of more fissile nuclei than are destroyed, as the absorption of at least one neutron per fission by an uranium 238 nucleus transforms this uranium 238 into a fissile plutonium 239 nucleus. This process is known as breeding, leading to an almost inexhaustible supply of nuclear fuel.

One drawback of fast neutrons in reactors is that the probabilities of their capture by nuclei are comparatively small. Travelling in matter, neutrons see nuclei as targets. The apparent cross-section of these targets is much smaller for fast neutrons than it is for slower neutrons. As a result, an intense neutron flux and a fuel rich in fissile elements are both needed to compensate for this lower probability.

2.21 Applications of radio-isotopes in determination of structures, establishment of reaction mechanisms and radio-carbon dating

2.21.1. Applications of radio-isotopes in structures determination

When two or more atoms of same element are present is molecule, the question of their structural equivalence or otherwise arises which can be elegantly settled by the isotopic labeling technique. This can be illustrated with reference of two substances (1) phosphorus pentachloride and (2) the thiosulphate ion.

Phosphorus pentachloride

To know whether all the five chlorine atoms in PCl_5 occupy structurally equivalent position or not, the substance is synthesized using PCl_3 and Cl_2 labeled with its radio isotope ^{36}Cl.

$PCl_3 + {}^*Cl_2 \rightarrow P^*Cl_5$

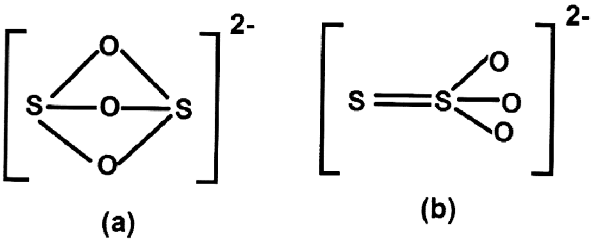
Subsequently, the product hydrolyzed when the following reaction takes place.

$P^*Cl_5 + H_2O \rightarrow POCl_3 + 2H^*Cl$

experimentally it was found that all the radioactivity remained with HCl and none with $POCl_3$. It is obvious that two Cl atoms in PCl_5 occupy positions different from the rest of three Cl atoms. This agree with the trigonal bipyramidal structure for PCl_5, with three Cl atoms in the equitorial plane and two along the vertices. Further, the equatorial P-Cl bond distance is known to be shorter than the apical P-Cl distance.

Thiosulphate ion

Two structures of thiosulphate ion can be envisaged.



The problem is to know which of the structures (a) or (b) is correct.

This has been solved by synthesizing sodium thiosulphate by boiling a solution of sodium sulphite with sulphur labelled with S-35.

$$Na_2SO_3 + {}^*S \rightarrow Na_2{}^*S_2O_3$$

The product is decomposed subsequently by adding to it a solution of silver nitrate in the presence of nitric acid. An examination of the final products, silver sulphide and sodium sulphate, showed the activity is exclusively on the former.

$$Na_2{}^*S_2O_3 + 2AgNO_3 + HNO_3 \rightarrow Ag_2{}^*S + Na_2SO_4 + \text{products}$$

This points to a non-equivalent structure (b) for the two sulphur atoms in the thiosulphate ion.

2.21.2. Applications of radio-isotopes in establishment of reaction mechanisms

(a) **Solubility of sparingly soluble salt:** The solubility of lead sulphate can be determined as follows. A lead salt containing known amount of radioactive lead is taken and is dissolved in water. Sulphuric acid is then added to the aqueous solution to precipitate lead as lead sulphate.

$$Pb{}^*(NO_3)_2 + H_2SO_4 \rightarrow Pb^*SO_4 + 2\,HNO_3$$

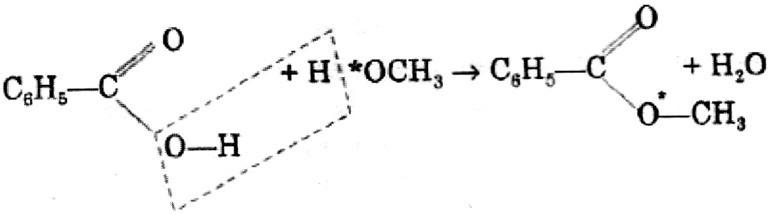
The precipitate is filtered. The radioactivity of filtrate is measured. From this the amount of lead still remaining solution is calculated.

(b) Tracer technique can be used to study the mechanisms or rates of chemical reactions. For example, consider the esterification of benzoic acid

$$C_6H_5COOH \quad + HO - CH_3$$

$$\rightarrow C_6H_5COOCH_3 + H_2O$$

In order to decide whether oxygen of ester comes from alcohol or from acid we use radioactive alcohol containing 18 isotope. The ester formed is found to contain O^{18} isotope but no radioactivity is detected in H_2O. This indicates that reaction follows the II path and not the I. This implies that during esterification oxygen comes from the alcohol and reaction involves replacement of OH part of acid with OCH_3 part of alcohol.



2.21.3. Applications of radio-isotopes in radio-carbon dating

It is a method of determining the ages of the archeological objects (wood, dead plants and animals). This technique was developed by Willard Libby. It helps in determining the date at which a particular plant or animal died. Libby was awarded Nobel Prize for his technique.

The principle of this technique lies in the fact that due to bombardment of cosmic rays, nitrogen atoms present in the upper atmosphere are converted into radioactive carbon, ^{14}C according to the reaction :

$$^{14}_{7}N + {}^{1}n_{0} \rightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

Carbon-14 is radioactive and has half-life period of 5770 years. It is oxidised in the air to give radioactive carbon dioxide. Thus, the atmospheric carbon dioxide contains a small proportion of ^{14}C carbon dioxide

($^{14}CO_2$) which is ascimilated by plants and animals. Living plants and animals have a definite and constant proportion of ^{12}C and ^{14}C. When plant or animal dies, no fresh L: C nuclei as $^{14}CO_2$ are received by the plant or animal. The C present in these, decays according to the reaction

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e; t_{\frac{1}{2}} = 5770\,\text{years.}$$

The amount of ^{14}C in a sample can be accurately determined by counting the number of 13-particles emitted per minute by one gram of the sample. By knowing ^{14}C content and half-life period, the age of the sample can be determined.

It may be noted that older the sample is, smaller is count rate. Ages of samples up to 50,000 years old can be determined accurately by this method.

2.22 Hazards of radiation and safety measures

Most people who grew up during the Cold War developed a strong fear of radiation. From fallout shelters to air raid drills, they faced constant reminders of nuclear war and its dangers.

While people feared the powerful blasts associated with nuclear weapons, the prospect of radiation was even more terrifying. Invisible and insidious, radiation could have devastating effects on humans. Those who were spared painful deaths would face highly increased chances of cancers and other problems. So when a tsunami crippled Japan's Fukushima nuclear power plant this spring, leading to the largest accidental release of radiation since the 1986 Chernobyl disaster, it came as no surprise that many people began to panic. For example, some Pacific coast residents began buying iodine pills to protect themselves from the effects of any radiation that would blow across the ocean.

What they didn't realize is that, on an average day, most of us are exposed to far more radiation than they could ever expect to receive from an accident halfway across the world. In addition, many of us are exposed to additional radiation through the nature of our jobs.

2.22.1. What exactly is radiation?

Simply put, radiation is energy that travels through the air. While there are many types of radiation, they are fall into one of two classes: ionizing or non-ionizing. The primary difference between the two is that ionizing radiation is able to change the atoms to which it is exposed by removing electrons. That's an important distinction, because human cells are made up of atoms, so they can be affected by ionizing radiation.

Although non-ionizing radiation can cause atoms to move or vibrate, it cannot remove electrons. Non-ionizing radiation is all around us — in forms as diverse as radio waves and visible light — and we use many of those forms in our daily life. When you put a sandwich in a microwave oven, non-ionizing radiation causes the atoms in the sandwich to vibrate and warm up. While the temperature and texture of the sandwich changes, its atoms remain the same, so it's safe to eat. Similarly, when you place a call with a cell phone, non-ionizing radio waves travel from the phone to the nearest tower to connect you with other towers and, eventually, the person you're calling.

When people talk about the hazards of radiation, they're generally referring to ionizing radiation. It's called that because when it removes electrons from atoms, it creates charged particles that are known as ions. If ions are used in a controlled manner, they can serve very useful purposes, whether that's generating electricity or wiping out cancer cells in the body. But when the body is exposed in other ways, those useful ions can become quite damaging. There are three basic types of ionizing radiation: alpha particles, beta particles, and a group that includes gamma rays and x-rays. Each operates at different frequencies and has different effects. For example, when used with special film, x-rays can be sent through an object such as person's arm or a welded pipe. Areas in the object that are denser will absorb the x-rays, so fewer of them will reach the film, which creates a lighter image. The resulting dark areas can pinpoint problems such as fractures, whether that's in a pipe or a human bone.

2.22.2. How does radiation affect people?

While all forms of ionizing radiation can have significant health effects, the potential impact depends upon the type of radiation and the amount to which a person is exposed. The different types of radiation affect different kinds of tissue in the body, primarily because of the amount of energy involved and the 'nature of each type of radiation. As an example, if a person is exposed to equal amounts of alpha and gamma radiation, the alpha particles will concentrate their energy in a much smaller area, and the gamma rays will spread out. ' Ionizing radiation can affect any type of living tissue in humans. The severity of the damage from radiation depends upon both the amount of radiation being received and the amount of time involved. What are known as stochastic health effects are those that result from long-term exposure to low levels of ionizing radiation. The most common of these is the various forms of cancer. A healthy body is able to regulate the growth of new cells and repair those that have been damaged. But when radiation causes damage that affects those regulation and repair processes, cells can grow at an uncontrolled rate. That uncontrolled growth is what we call cancer.

Another type of stochastic effect involves changes to DNA, which is the set of instructions that tells our cells how to form and behave. Changing DNA creates what are known as mutations. Some mutations affect only the individual who has been exposed to radiation, while others can be passed on through the womb to children.

Non-stochastic health effects are usually the result of exposure to significantly higher levels of radiation, often for a very short time. The effects include burns and what's known as radiation "poisoning," which can be fatal. High doses of radiation can destroy bone marrow, shut down the nervous and/or digestive system, and lead to the loss of limbs.

2.22.3. Radiation in the workplace

You're already aware that ionizing radiation in the form of x-ray machines is used in healthcare facilities and manufacturing settings. In healthcare, radiation is also used in a wide variety of diagnostic devices, such as CT scanners, and concentrated for the treatment of tumors and cancers.

In industrial settings, radiation can be used in testing devices, for sterilization of products, for determining the level of moisture in soils, in weapons production, and yes, in nuclear power plants. None of those uses is inherently dangerous, as long as all of the required safety devices and processes are in place and used properly. Those who work with radiation need to understand the safety procedures, the consequences of failing to follow them, and actions to take in the event of an incident.

Fortunately, the radiation levels encountered in the workplace tend to be very small. In fact, the levels that are high enough to cause non-stochastic health effects don't occur in workplaces. Even workers in towns close to the Fukushima plant received daily doses that were smaller than what most people receive with a dental x-ray. That's why radiation safety focuses on protecting workers from long-term exposure to lower doses.

2.22.4. Being safe around radiation

As with so many other facets of workplace safety, training plays a critical role in working around radiation. Effective safety training focuses on the three ways workers can limit their exposure to radiation: maintaining a safe distance from the source, limiting the time around the source, and using shielding to limit the exposure. Workers should also know what to do when something goes wrong.

Depending upon the work conditions and the type of radioactive material, other safety measures may also be needed. One example is the use of dosimeters that measure radiation on a cumulative basis and sound an alarm when specific thresholds are reached. If workers are around radioactive dust, respirators may be used to keep the dust from being inhaled. Gloves or other kinds of personal protective equipment may also be needed.

Like fire, radiation can be both a valuable tool and a serious danger. As with fire, there's no need to be afraid of radiation, but it's good to develop a healthy respect for its power and to follow practices that minimize the potential danger.

2.23 Uses for Radioactive Nuclides

Nuclide	**Nuclear Change**	**Application**
argon–41	beta emission	Measure flow of gases from smokestacks
barium–131	electron capture	Detect bone tumors
carbon–11	positron emission	PET brain scan
carbon–14	beta emission	Archaeological dating
cesium–133	beta emission	Radiation therapy
cobalt–60	beta emission	Cancer therapy
copper–64	beta emission, positron emission, electron capture	Lung and liver disease diagnosis
chromium–51	electron capture	Determine blood volume and red blood cell lifetime; diagnose gas trointestinal disorders
fluorine–18	beta emission, positorn emission, electron capture	Bone scanning; study of cerebral sugar metabolism
gallium–67	electron capture	Diagnosis of lymphoma and Hodgkin disease; whole body scan for tumors

Nuclide	**Nuclear Change**	**Application**
gold–198	beta emission	Assess kidney activity
hydrogen–3	beta emission	Biochemical tracer; measurement of the water content of the body
indium–111	gamma emission	Label blood platelets
iodine–125	electron capture	Determination of blood hormone levels
iodine–131	beta emission	Measure thyroid uptake of iodine
iron–59	beat emission	Assessment of blood iron metabolism and diagnosis of anemia
krypton–79	positron emission and electron capture	Assess cardiovascular function
nitrogen–13	positron emission	Brain, heart, and liver imaging
oxyge–15	positron emission	Lung function test
phosphorus–32	beta emission	Leukemia therapy, detection of eye tumors, radiation therapy, and detection breast carcinoma
polonium-210	alpha emission	Radiation therapy
potassium–40	beta emission	Geological dating
radium–226	alpha emission	Radiation therapy
selenium-75	beta emission and electron capture	Measure size and shape of pancreas
sodium-24	beta emission	Blood studies and detection of blood clots
technetium-99	gamma emission	Bone scans and detection of blood clots
xenon-133	beta emission	Lung capacity measurement

2.24 Summary

Radioactivity is the decay of unstable atoms by the emission of particles and electromagnetic radiation. A curie (Ci) is a unit of redioactivity equal to 3.7×10^{10} disintegrations per 10 second. A becquerel (Bq) is a unit of radioactivity equal to 1 disintegration per second. The radioactive half-life is the amount of time required for the activity to decrease to one-half its original value. The activity of a substance can be calculated from the number of atoms and the decay constant based on the equation stated above. The amount of activity remaining after a particular time can be calculated from the equation stated above. The relationship between the decay constant and the half-life is shown above. Plots of radioactive decay can be useful to describe the variation of activity overtime. Radioactive equilibrium exists when the production rate of a material is equal to the removal rate. Transient radioactive equilibrium exists when the parent nuclide and the daughter unclide decay at essentially the same rate. This occurs only when the parent has along half-life compared to the dauthter.

The radioactivity is explained then in terms of binding energy, nuclear binding energy, packing fraction and anomalies with magic number. The effect of radioactivity and hazardous radioactive materials on mankind is also described elaborately.

2.25 Questions

1. Cobalt-57 has a half-life of about 272 days. If a sample has an initial mass of 2.24 grams and undergoes decay until it has a mass of 0.140 grams, then how many half-lives passed? see Section-2.7.4
2. A sample of thalium-171 has a mass of 0.4055 grams. How much is left after 6 half-lives? see Section-2.7.4
3. How do you calculate half-life, mathematically? see Section-2.7.4
4. List three purposes of using radioactivity and how it is used? see Section-2.7.3
5. Which famous experiment, at the start of the twentieth century suggested the existence of the nucleus? see Section-2.11
6. What type of radioactive decay will emit particles with no overall charge? see Section-2.4
7. What type of radioactive decay is caused when there are too many neutrons in the nucleus? see Section-2.4
8. What is it called when two atomic nuclei are combined? Section see 2.13.2
9. ^{2}H is a loosely bound isotope of hydrogen. Called deuterium or heavy hydrogen, it is stable but relatively rare—it is 0.015% of natural hydrogen.

Note that deuterium has Z = N, which should tend to make it more tightly bound, but both are odd numbers. Calculate BE/A, the binding energy per nucleon for ^{2}H. see Section-2.8.2.

10. The half-life of carbon-14 is 5730 years. Rex the dog died in 1750. What percentage of his original carbon-14 remained in 1975 when he was found by scientists? see Section-2.19.3
11. A 5000-Ci ^{60}Co source used for cancer therapy is considered too weak to be useful when its activity falls to 3500 Ci. How long after itsmanufacture does this happen? see Section-2.7.2
12. The mass of a certain sample is found to decrease by 60% in 10 days. Find its half-life. see Section-2.7.2.
13. What is meant of 'packing fraction'? Explain the radioactivity in the light of 'packing fraction'. see Section-2.9.
14. Following n/p ratio principle exlain nuclear instability $^{14}C_{6}$, $^{13}N_{7}$ and $^{133}I_{53}$ see Section-2.4.
15. State group displancement law. Write radioactive disintegration series. see Section-2.6.
16. Write the short notes on (a) Spallation reaction, (b) Nuclear hazards, (c) Nuclear Medicine.
17. Gold-198 has a half-life of 2.7 days. How much of a 96 g sample of gold 198 will be left after 8.1 days? see Section-2.7.4
18. Write down the equation relating half-life, the number of halflives, and the decay time, and rearrange it to solve for the number of half-lives. see Section-2.7.4

2.26 Further Reading

1. R. N. Mahaling, Basics of Nuclear Chemistry.
2. A. K. Das, Fundamental concepts of Inorganic Chemistry Vol.-2.
3. R. P. Sarkar, General & Inorganic Chemistry Part-I.

Unit-3 Chemical Periodicity

Contents

3.1 Objectives

After reading this unit, we will be able to:

- Know the details of modern periodic table.
- Calculation of effective nuclear charge.
- Definition of atomic radii, ionic radii & lanthanide contraction etc.
- The concept and significance of electonegativity, electron affinity, ionisation energy, relativistic effect and inert pair effect.

3.2 Introduction

If there were a flag that represented the science of chemistry, it would be the periodic table. The periodic table is a concise organizational chart of the elements. The periodic table not only incorporates a theoretical framework for understanding the relationships between elements, but it also summarizes important facts about the elements. It is a dynamic blueprint for the basic building blocks of our universe. Inorganic chemistry covers the chemistry of over 100 elements. Though each element has its individual characteristics, there are patterns and trends that provide a framework of order.

It was the year of 1829, Johann Dobereiner noticed a repetitive pattern in the chemical properties of some of the elements, lumping them together in groups of three that he called *triads*. The elements chlorine, bromine, and iodine, for instance, formed a triad. A few years later, in 1865, the Englishman John Newlands stated that if the elements were listed in order of their increasing atomic weights, they could be arranged into what he called the *law of octaves* (orgroups of eight) according to their chemical properties. However, it was not until 1869, when the Russian teacher Dmitri Mendeleev gave a presentation to the Russian Chemical Society called "A Dependence between the Properties of the Atomic Weights of the Elements" that the idea of periodic trends among the various elements began to take hold. In Mendeleev's day, only a third of the elements known today had been discovered. The genius of Medeleev's work was that when he arranged the elements in order of increasing atomic mass and the next element did not fit the properties of the next group, he simply left a gap in his deck of cards, assuming that a new element would someday be discovered having the appropriate pattern of trends.

3.3 Modern IUPAC Periodic Table

In the modern periodic table elments are arranged sequentially by atomic number in rows and columns. In 1913, Henry Moseley's work established the concept of atomic number, the number of protons in the nucleus, as the key for determining an element's position in the periodic table. Rows in the periodic table are referred to as periods, and columns are called groups. The periods run left to right, and the groups from top to bottom. A goup may also comprise a chemical family. Groups are numbered across the top of the table. In recent years, scientists have suggested using the Arabic numerals 1–18 to number each group starting on the left. Fig. 1 represents the IUPAC periodic table of the elements.

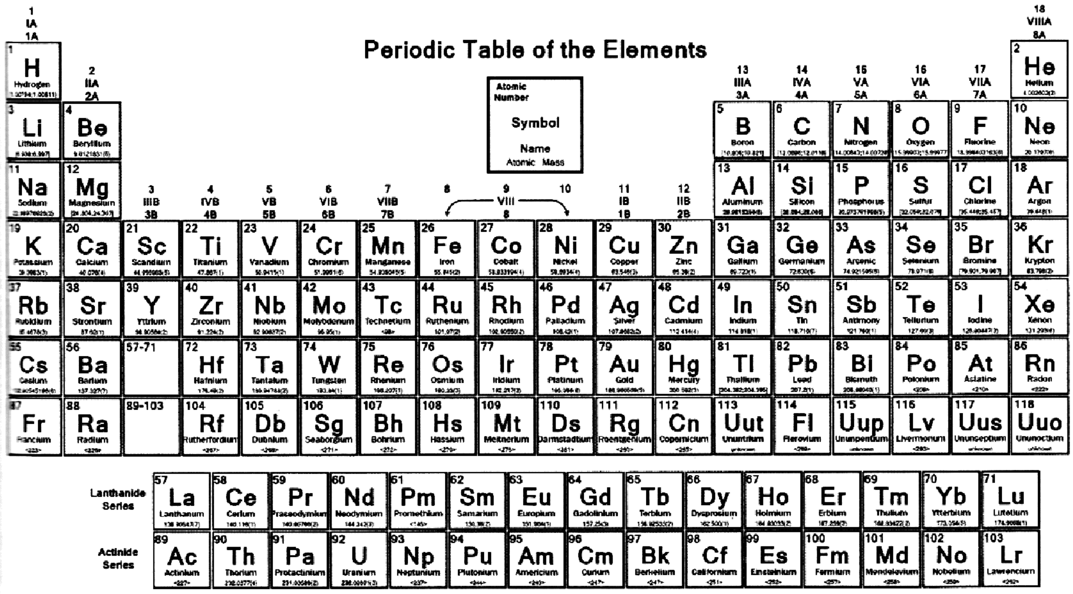


Fig.1 : IUPAC periodic table of the elements.

3.3.1. Classification of the elements :

The overall elements are classified in the following ways.

1. Alkali metals
2. Alkaline earth metals
3. Transition metals
4. Post-transition metals
5. Metalloids
6. Other non-metals
7. Halogens
8. Noble gases
9. Lanthanides
10. Actinides
11. Unknown chemical properities

3.3.1.1. ***Alkali metals :*** This “group I” of metals occupies the far-left column of the periodic table. They are all soft, but solid metals at room temperature, and are highly reactive *Elements Include* : Li, Na, K, Rb, Cs, and Fr.

3.3.1.2. ***Alkaline earth metals :*** The alkaline earth metals are silver-white metals at room temperature. The name is a term that refers to the naturally occurring oxides of these elements. For example, lime is the alkaline oxide of calcium. *Elements Include :* Be, Mg, Ca, Sr., Ba, and Ra.

3.3.1.3. ***Transition metals :*** The transition metals occupy a broad area in the centre of the periodic table. They are harder than the alkali metals less reactive and are generally good conductors of both heat and electrical current.

Elements Include : Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Rf, Db, Sg, Bh, Hs, and Cn.

3.3.1.4. ***Post-transition metals :*** Lying in a triangular region to the right of the transition metals, the post-transition metals are soft metals that mostly have low melting and boiling points. They also include mercury, which is liquid at room temperature. *Elements Include :* Al, Ga, In, Sn, Tl, Pb, and Bi.

3.3.1.5. ***Metalloids :*** The metalloid elements from a line between the metals and nonmetals in the periodic table. Their electrical conductivity in intermediate between the two grops, leading to their use in semiconductor electronics. *Elements Include :* B, Si, Ge, As, Sb, Te, and Po.

3.3.1.6. ***Other non-metals :*** In addition to halogens and noble gases, there are other elements that are simply classified as “other non-metals.” They display a wide range of chemical properities and reactivities. They have high ionization energies and electronegativities, and are generally poor conductors of heat and electricity. Most non-metals have the ability to gain electrons easily. They have lower melting points, boiling points and densities than the metal elemtns. *Elements Include :* H, C, N, O, P, S, and Se.

3.3.1.7. ***Halogens :*** The halogens, known as group 17, are the only group to contain all three principal states of matter at room temperature : gas (fluorine and chlorine), liquid (bromine) and solid (iodine and astatine)–all non-metals. *Elements Include :* F, Cl, Br., I, and At.

3.3.1.8. ***Noble gases :*** The noble gases are non-metals occupying group 18 of the table. They are all gaseous at room temperature and share the properties of being colourless, odourless and unreactive. Including neon, argon and xenon, they have applications in lighting and welding *Elements Include :* He, Ne, Ar, Kr, Xe, and Rn.

3.3.1.9. ***Lanthanides :*** The lanthanide elements occupy a horizontal strip normally appended at the foot of the periodic table. Named after lanthanum, the first element in the series, they are generally found in less common mineral rocks, such as monazite and bastnasite. *Elements Include :* La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

3.3.1.10. ***Actinides :*** The actinides fill the second horizontal strip at the foot of the table. Named after their first element, actinium, they are all highly radioactive. So much so, that natural reserves of many of these elements have decayed away to nothing. *Elements Include :* Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr.

3.3.1.11. ***Unknown chemical properties :*** This is a label reserved for elements that can only be manufactured in a laboratory. Very often, only minute quantities of such elements have been created—making it impossible to ascertain their exact chemical classification. *Elements Include :* Mt, Ds, Rg, Uut, Fl, Uup, Lv, Uus, and Uuo.

3.4 Effective nuclear charge and Slater's rule

The concept of the effective nuclear charge (often symbolized as Z_{eff} or Z^*) relates to the net positive charge experienced by an electron in a multi-electron atom. The term "effective" is used because the shielding effect of negatively charged inner electrons prevents higher orbital electrons from experiencing the full nuclear charge due to the repelling effect of the lower innerlayer electrons.

In an atom with one electron, that electron experiences the full charge of the prositive nucleus. In this case, the effective nuclear charge can be calculated from Coulomb's law. However, in an atom with many electrons the outer electrons are simultaneously attracted to the positive nucleus and repelled by the inner negatively charged electrons. The effective nuclear charge on such an electron is given by the following equation : $Z_{eff} = Z - S$; or $Z_{eff} = Z - \sigma$ where, Z is the number of protons in the nucleus (atomic number), and S or σ is the shielding constant/screening constant,.

A systematic method for determining this is given by **"Slater's rule"**. In 1930, J. C. Slater proposed a set of empirical rules to semiquantify the concept of effective nuclear charge.

Values of S may be estimated as follows

1. Write out the electronic configuration of the element in the following order and groupings : (Is), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p) etc.

2. Electrons in any group higher in this sequence than the electron under consideration contribute nothing to S.

3. Consider a particular electron in an ns or np orbital :

(i) Each of the other electrons in the (ns, np) group contributes S = $\boxed{0{\cdot}35}$.

(ii) Each of the electrons in the (n-1) shell contributes S = $\boxed{0{\cdot}85}$.

(iii) Each of the electrons in the (n-2) or lower shells contributes S = $\boxed{1{\cdot}00}$.

4. Consider a particular electron in an nd or nf orbital :

(i) Each of the other electrons in the (nd, nf) group contributes S = $\boxed{0{\cdot}35}$.

(ii) Each of the electrons in a lower group than the one being considered contributes S = $\boxed{1{\cdot}00}$.

■ ***Question : Confirm that the experimentally observed electronic configuration of K, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, is energetically more stable than the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$.***

Solution : For K, Z = 19; Applying Slater's rules, the effective nuclear charge experienced by the 4s electron for the configuration $Is^2 2s^2 2p^6 3s^2 3p^6 4s^1$"is :

$Z_{eff} = Z - S$

$= 19 - [(8 \times 0.85) + (10 \times 1)$

$= 2.20$

The effective nuclear charge experienced by the 3d electron for the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ is :

$Z_{eff} = Z - S$

$= 19 - (18 \times 1)$

$= 1.00$

Thus, an electron in the 4s (rather than the 3d) atomic orbital is under the influence of a greater effective nuclear charge and in the ground state of potassium, it is the 4s atomic orbital that is occupied.

Although the results of calculations using Slater's rules provide a more quantitative feel for the concept of effective nuclear charge, their simplicity makes them less than perfect. In particular. the rules assume that both *s* and *p* electrons in the same principal quantum number experience the same nuclear charge. Using calculations based on the atomic wave functions, E. Clementi and D. E. Raimondi derived more precise values for the values of effective nuclear charge. The Clementi and Raimondi values do indeed show a small but significant difference in effective nuclear charge for the more penetrating *s* electrons compared with the *p* electrons in the same principal quantum number. Note that the increasing Z_{eff} on the outermost electrons along the period correlates well with the trend of decreasing atomic radii.

3.5 Atomic radii

One of the most systematic periodic properties is atomic radius. Because the electrons can be defined only in terms of probability, there is no real boundary to an atom. We cannot directly measure the actual size of an atom. What we can do is to measure the inter nuclear distance between two atoms; this is obtained from spectroscopic or x-ray electron diffraction studies. The outer part of the atom is made up of diffuse "electron clouds" – the density of this cloud falls exponentially with the radius. So there cannot be any well-defined boundary of an atom and the radius of an isolated atom has no meaning. We can calculate the effective volume occupied by an atom in the solid and liquid state in an environment of other atoms. Even then, the situation is not simple because the nature of packing differs from one element to another. In a compound, the outer electrons of an atom are subject to the field of all the neighbouring atoms and so its "size" will depend on the chemical environment. Experimentally it is possible to measure the distances oetween atoms in a close-packed aggregate or in a compound. This gives us an idea of radius of an atom which will of course differ in different environments. Different sets of radii of atoms have been worked out depending on their environment like Vander Waals radii, covalent radii etc.

- ■ ***Group Trend**:-* Increases down a group (Caused by an increase in Shells)
- ■ ***Period Trend**:-* Decreases across a period(As nuclear strength increases the nucleus pulls the outer electrons closer)

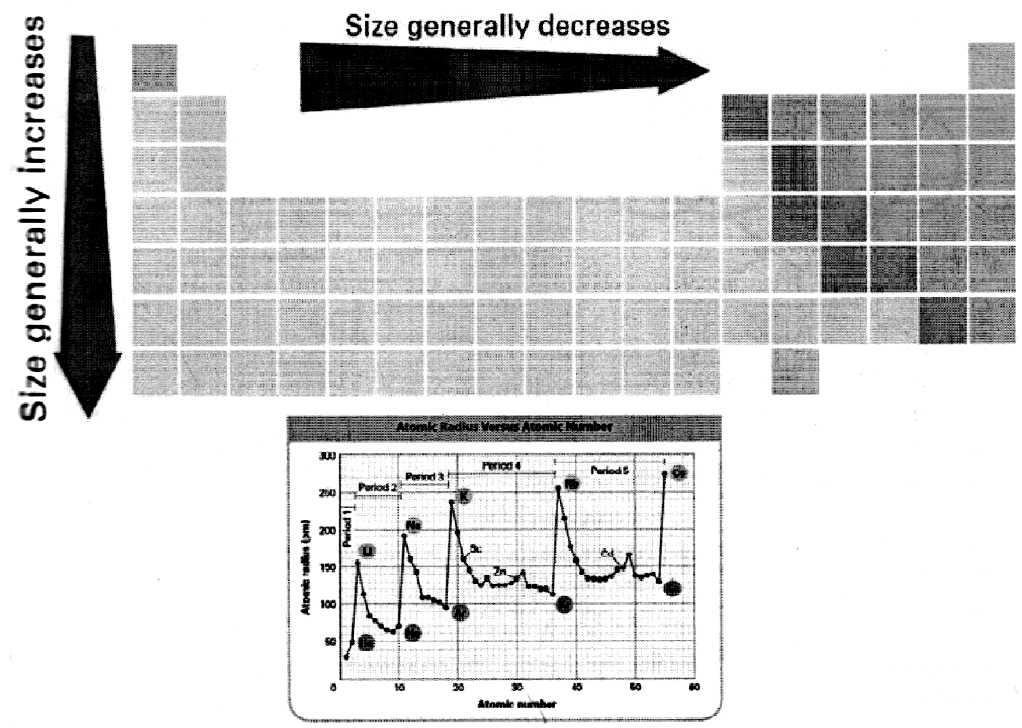


Fig. 2 : Periodic trend of atomic size

As a general rule, the radius of an atom will increase down and to the left in the periodic table. The radius of an atom depends on its electron probability. Across a period, the principal quantum number remains essentially the same, whereas the effective nuclear charge is increasing as more and more protons are added to the nucleus. This larger value of Z_{eff} exerts a stronger pull on the electrons, shrinking the atomic radius. Down a column or group in the periodic table, Z_{eff} varies only slightly, while *n* is increasing. As *n* increases, the outer-most electron will be added to an orbital having a larger average radial probability. Thus, the atomic radius increases down a column.

3.5.1. ***Vander Waals radii :*** The *vander Waals radius,* is defined as the half-distance between the nuclei of two atoms of neighboring molecules (Figure 3), more specifically, it is the shortest distance to which two non bonded atoms can approach before repulsion between their electron clouds comes into action. In solid xenon, for example, the measured inter atomic distance is 436 pm. The Vander Waals radius of xenon is thus estimated to be 218 pm. Steric effects between different parts of a molecule are governed mainly by this radius.

3.5.2. ***Covalent radii :*** The covalent radius of an element may by taken as half the inter nuclear distance between two atoms of the same element joined by a single bond. For elements forming single bonded units, the experimental inter nuclear distance may by halved to obtain the covalent radius (Fig.3).

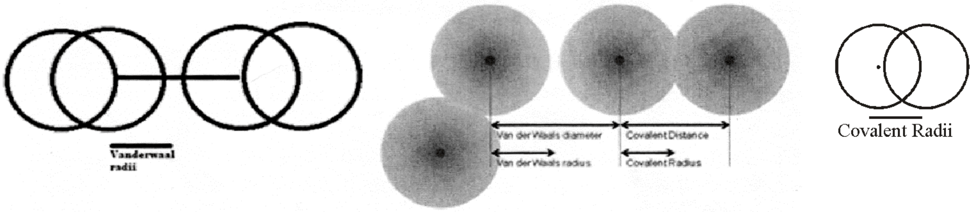


Fig.3: Atomic radii

3.6 Ionic radii

The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals. Although from a wave-mechanical viewpoint, the radius of an individual ion has no precise physical significance, for purposes of descriptive crystallography, it is convenient to have a compilation of values obtained by partitioning measured interatomic distances in 'ionic' compounds. Values of the ionic radius (r_{ion}) may be derived from X-ray diffraction data. However, experimental data only give the internuclear distance and we generally take this to be the sum of the ionic radii of the cation and anion Internuclear distance between a cation and the closest anion in a lattice = $r_{catlon} + r_{anion}$ A positive ion is always smaller than the corresponding atom, and the more electrons which are removed. Metallic radius of Na is 1.86A , whereas Ionic radius of Na^+ is 1.02A. When a negative ion is formed, one or more electrons are added to an atom, the effective nuclear charge is reduced and hence the electron cloud expands. Negative ions are bigger than the corresponding atom. Covalent radius of Cl is 0. 99 A, whereas, Ionic radius of Cl^- is 1.84A.

Trends in ionic radii :

Irrespective of which set of ionic radii are used, the following trends are observed :

1. In the main groups, radii increase on descending the group, e.g. Li^+ = 0.76A, Na^+ = 1.02A, K^+= 1.3 8 A, because extra shells of electrons are added.

2. The ionic radii decrease moving from left to right across any period in the periodic table, e.g. Na^+ = 1.02A, Mg^{2+} = 0.720Aand $A1^{3+}$ = 0.535 A. This is partly due to the increased number of charges on the nucleus, and also to the increasing charge on the ions.

3. The ionic radius decreases as more electrons are ionized off, that is as the valency increases, e.g. Cr^{2+} = 0.80 , Cr^{3+} = 0.615 A, Cr^{4+} = 0.55 A, and Cr^{6+} = 0.44A.

4. The *d* and *f* orbitals do not shield the nuclear charge very effectively. Thus there is a significant reduction in the size of ions just after *10d* or 14f electrons have been filled in. The latter is called the lanthanide contraction, and results in the sizes of the second and third row transition elements being almost the same.

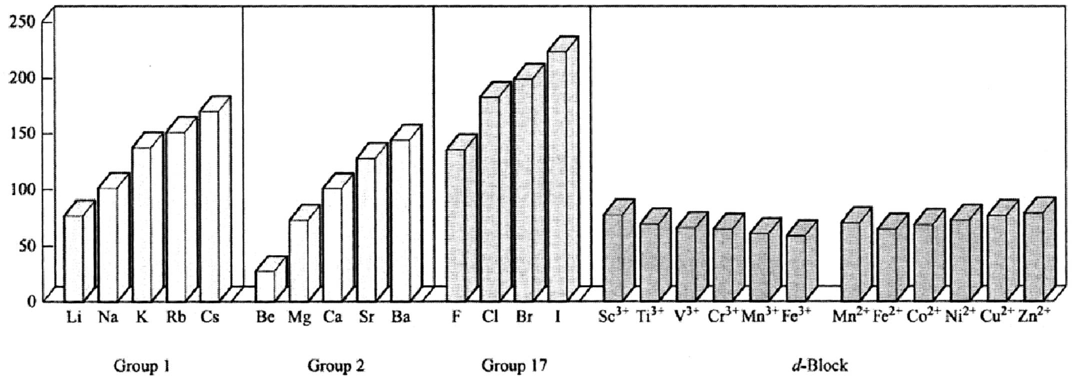


Fig.4 : Trends in ionic radii, r_{ion}, within the metal ions of groups 1 and 2, the anions of group 17, and metal ions from the first row of the d-block.

The right-hand side of Figure 4 illustrates the small variation in size for M^{3+} and M^{2+} ions of the d-block metals. As expected, the decrease in nuclear charge in going from Fe^{3+} to Fe^{2+}, and from Mn^{3+} to Mn^{2+}, causes an increase in r_{ion}. The cation size increases on descending groups 1 and 2, as does the anion size on descending group 17.

3.6.1. *Pauling's method for determining univalent ionic radii :*

Pauling used a theoretical model to calculate ionic radii. Recognizing that there is an inverse relationship between the radius and the effective nuclear charge, Pauling set up the ratio in Equations, where r_0 is the inter ionic distance between the cation and anion. r_+ and r_-. are radius of cation and anion respectively. Z_{eff}^+ and Z_{eff}^- are effective nuclear charge of cation and anion respectively.

$$^{r_+}\!/_{r_-} = Z_{eff} / Z_{eff}^+ \text{ and } r_0 = r_+ + r_-.$$

■ ***Question : calculate the univalent radii of Na^+ and F^- if the inter ionic distance in NaF is 231pm.***

Solution : Using Slater's rule we can find out $S_{Na^+} = S_{F^-} = 4.5$; Therefore $r_{Na^+} / r_{F.} = (9 - 4.5)/ (11 - 4.5) = 4.5/ 6.5$; $r_{Na^+} + r_{F^-} = 231$,

Solving above two equations, we get $r_{Na^+} = 194$ pm and $r_{F^-} = 136$ pm

3.7 Lanthanide contraction

The elements Cerium (Ce) to Lutetium (Lu) of atomic number 58 – 71 are called lanthanides. They are so similar in properties with Lanthanum (57) that they may be considered as a single element and so that they should be placed along with lanthanum in the same place of the periodic table.

On moving from left to right across a period the size of the atom of the element decreases due to increase in nuclear charge and introduction of electron in the same outer shell(4f) decrease in size also occurs among the 14 lanthanides. The contraction of size from one to another is fairly small, additive effect of 14 elements become about 0.2 angstrom unit and this contraction in size known as lanthanide contraction.

Cause of lanthanide contraction : In lanthanides the additional electron enters into 4f subshell not in the valence shell namely sixth shell. The shielding effect of 4f electrons are very little, because of the defused shape of the 4f subshell. The nuclear charge increases by unity at each step, while there is no comparable increase in the mutual shielding in 4f electrons. As a result, electrons in the outermost shell experience increasing nuclear attraction and hence atomic size go on decreasing as we move from La to Lu.

3.8 Electronegativity

Electronegativity is the ability of an atom in a molecule to attract the shared electrons closer to itself, as defined by Linus Pauling. Unlike most of the other periodic laws, such as radius, ionization energy, and E.A., electronegativity has no meaning outside the context of a chemical bond.

3.8.1. *Factors upon which Electronegativity depends* :

1. Valence state and oxidation state : Electronegativity increases with increasing + ve oxidation state and decreases with increasing -ve oxidation state.
2. Size of the atom : Electronegativity decreases with increasing the size of the atom and vice-versa.
3. Nature of hybridization : Electronegativity increases with increase the s character of the hybrid orbital i, e, sp > sp^2 > sp^3

3.8.2. *Variation of electronegativity in the periodic table* :

■ ***In a period :*** Electronegativity increases on moving a period in the periodic table from left to right. This is due to increase in nuclear charge as a result of which the added electrons can be held more tightly.

■ ***In a group :*** On moving down through a group of the periodic table, the size of the elements gradually increases. Since small atoms attract the electron more strongly than large ones and therefore more electronegative. Consequently a lower element of a group is less electronegative than upper elements.

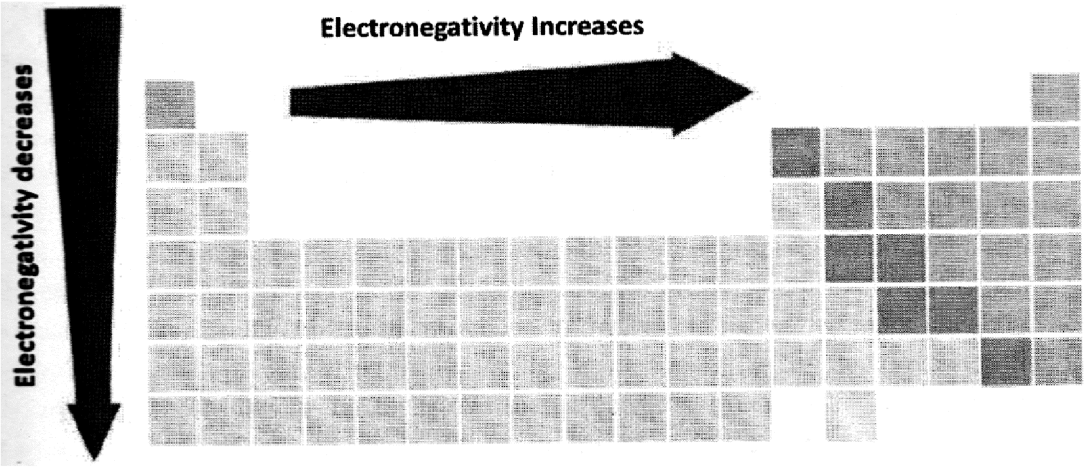


Fig. 5 : Periodic trend of electronegativity

The absolute magnitude of the electronegativity vales of an element is however not fixed , different values may be assigned to the same element from different theoretical approaches i,e different electronegativity scale.

3.8.3. *Pauling scale of Electronegativity* :

The Pauling scale of electronegativity was developed in 1932 and is still the most widely used. Let us consider two covalent molecules A-A & B-B. It is generally observed that rections of the type A-A + B-B - → A-B + A-B are almost always exothermic and bond A-B is thus more stable than A-A or B-B bonds. The extra stability was derived from unequal sharing of bonding electrons between A & B giving rise to some ionic character. Bond stabilities are measured in terms of bond energy so, we may express the extra stability of the bond A-B in the following way,

$\Delta = E_{A-B}$ – Energy of 100% covalent bond; where E_{A-B} is the observed bond energy of A–B. Pauling suggested that Δ is related to the difference of electronegativity between A & B $(\chi_A - \chi_B)$ by the relation $\chi_A - \chi_B = 0.208\sqrt{\Delta}$; where Δ is expressed in Kcal/mol. The energy of 100% covalent bond is $E_{100\%covalent} = \sqrt{(E_{A-A}\ E_{B-B})}$

Finally we have = $0.208\sqrt{\{E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}\}}$............1

(Converting the equation to SI units gives $0.1017\sqrt{\Delta}$, where Δ is measured in kJ/mol)........(2)

Pauling next arbitrarily assumed $\chi_H = 2.1$ as a standard and framed his electronegativity scale. In this scale F is the most electronegative with a value of 4.0

■ ***Question : Calculate the electronegativity of Cl given that the bond dissociation energies for Cl_2, F_2, and ClFare 242, 158, and 255 kJ/mol, respectively.***

Solution. according to Pauling scale, $\Delta = 255 - \sqrt{(242 \times 158)}$

$$= 59.45 \text{ kJ/mol}$$

The difference in electronegativity between F and Cl can be calculated from Equation 2 :

$$\chi_F - \chi_{Cl} = 0.101\sqrt{59.45} = 0.77 \text{ kJ/mol}$$

3.8.4. *Mulliken's scale of electronegativity* (χ_M) :

The Mulliken-Jaffe scale defines electronegativity on the basis of atomic parameters, namely the average of the valence ionization energy and E.A., as shown in Equation 3. The *v* subscripts indicate that the valence configuration must be used. Thus, for example, boron forms three equivalent bonds by hybridizing its valence 2*s* and 2p orbitals to make *sp*^{2} hybrid orbitals. The theoretical ionization energy and

E.A. for the sp^2 hybrid orbitals must be used in Equation 2 in place of those for an unhybridized $2p$ orbital. Hence, the original Pauling definition of electronegativity as a property of an atom within a molecule still rings true. Mulliken-Jaffe electronegativities are typically expressed in units of electron volts. However, the Pauling scale has been so firmly entrenched that more often than not the Mulliken-Jaffe scale is converted to the Pauling scale through a simple conversion factor. One advantage of the Mulliken-Jaffe scale is that it correctly predicts the periodic trend for electronegativity. Because the periodic trends for both first ionization energy and E.A. increase up and to the right in the periodic table, the average of these two values should also follow this trend. Indeed, the periodic trend for electronegativity is that it increases toward the upper right-hand corner of the periodic table. When comparing the electronegativities of the elements, there is a very clear demarcation line between the metals and the nonmetals. The metals have only a small difference in energy between their s and p orbitals, whereas the nonmetals have a much larger gap. Electronegativity in Mulliken scale (χ_M) can be extressed in the following way, $\chi_M = (I.E + E.A.)/2$; .....(3) hvhere IE & EA are the lonisation energy and Elcetron affinity respectively. χm may be related with Pauling electronegativity value (χ_P) through a relation, $\chi_P = 1.35\sqrt{\ } \chi_M -1.37$

3.8.5. *Allred-Rochow electronegativity values,* (χ_{AR}) :

Allred and Rochow chose as a measure of electronegativity of an atom the electrostatic force exerted by the effective nuclear charge Z_{eff} (estimated from Slater's rules) on the valence electrons. Allred-Rochow electronegativity can be calculated by the following way,

$\chi_{AR} = (0.359 \times Z_{eff})/\ r_{cov}^{\ 2} + 0.744$ (when r_{cov} is measured in Angstrom)

$xar = (3590 \times Z_{eff})/\ r_{cov}^{\ 2} + 0.744$ (when r_{cov} is measured in pm)

However, Slater's rules are partly empirical and covalent radii are unavailable for some elements, the Allred-Rochow scale is no more rigid or complete than the Pauling one. The Allred-Rochow scale is based on the electrostatic force exerted by the nucleus on the valence electrons, whereas the Sanderson scale represents a ratio of the experimental electron density to that predicted by interpolation of the electron densities of the two nearest noble gas atoms. Sanderson is also responsible for the concept of electronegativity equalization. When two or more atoms having different initial electronegativities combine to make a bond, they adjust to have the same intermediate electronegativity in the molecule. The electronegativities of ions and of groups of atoms, such as CF_3, NH_2, or COOH, have also been calculated using the principle of A electronegativity neutrality. For example, the group electronegativity of CF_3 (3.47) is greater than that of CH_3 (2.31) as a result of the inductive effect of the F atoms. Likewise, the calculated group electronegativity of the electron withdrawing group '-COOH' (3.04) is greater than that of the electron-donating group '-NH_2' (2.47)

Table-1

Element	x (Pauling)	Xmi (Mulliken)	Xspec (Allen)
H	2.20	2.25(*s*)	2.30
Li	0.98	0.97(*s*)	0.91
Be	1.57	1.54 (*sp*)	1.58
B	2.04	2.04 (sp^2)	2.05
C	2.55	2.48	2.54
N	3.04	3.04	3.07
O	3.44	3.68	3.61
F	3.98	3.91 (14% *s*)	4.19
Na	0.93	0.91 (*s*)	0.87
Mg	1.31	1.37 (*sp*)	1.29
Al	1.61	1.83 (sp^2)	1.61
Si	1.90	2.28	1.92
P	2.19	2.41	2.25
S	2.58	2.86	2.59
Cl	3.16	3.10 (14% *s*)	2.87
K	0.82	0.73 (s)	0.73
Ca	1.00	1.08 (*sp*)	1.03
Ga	1.81	2.01 (sp^2)	1.76
Ge	2.01	2.33	1.99
As	2.18	2.38	2.21
Se	2.55	2.79	2.42
Br	2.96	2.95 (14% *s*)	2.68
Kr	3.00	3.31	2.97
Rb	0.82	0.82 (*s*)	0.71
Sr	0.95	1.00 (*sp*)	0.96
In	1.78	1.76 (sp^2)	1.66
Sn	1.96	2.21	1.82
Sb	2.05	2.22	1.98
Te	2.10	2.57	2.16
I	2.66	2.95	2.36
Xe	2.60	3.01	2.58

Table 1 : Electronegativities of selected elements using the revised Pauling scale the Mulliken– Jaffe scale, and Allen's spectroscopic configuration energies. The

latter scales have been converted to the revised Pauling scale. The Mulliken–Jaffe values are listed for the *sp*3 valence hybridization, unless otherwise indicated.

■ ***Question : Calculate the electronegativity of bromine in the AR scale (**r_{cov} **= 114 pm)***

Solution : Z_{eff} *is calculated by taking into account the screening by all electrons* [Br = $(1s)^2(2s2p)^8(3s3p3d)^{18}(4s4p)^7$]; $Z_{eff} = 35-[0.35\times7+0.85\times18+1\times10]=7.25$; $\chi_{AR} = (3590\times7.25)/114^2+0.744 = 2.75$

3.8.6. *Grou Electronegativity :*

The overall effect of charge, substituents, hybridization of the bonding orbitals, etc. of a group on electronegativity may be summarily expressed in terms of its group electronegativity. The following table represents the electronegativity of some groups according to the Pauling scale.

Group	**Electronegativity**
$-CH_3$	2.34
$-CF_3$	3.35
$-CCl_3$	3.03
-COOH	2.8-3.5
$-NO_2$	3.4
C_6H_5	3

Table : 2 Group Electronegativity values of few groups

The values of Electronegativity of methyl group suggests that it should be slightly more electronegative than hydrogen. Yet the methyl group behaves as a better donor of Electron density presumably because of its larger size which makes it more easily polarizable.

3.8.7. *Electronegativity; final remarks :*

Despite the somewhat dubious scientific basis of these methods described above, the trends in electronegativities obtained by them are roughly in agreement as Figure 3 exemplifies. The most useful of the scales for application in inorganic chemistry is probably the Pauling scale which, being based empirically on thermochemical data, can reasobably be used to predict similar data. For example, if the electronegativities of two elements X and Y have been derived from the single covalent bond enthalpies of HX, HY, X_2, Y_2 and H_2, we can estimate the bond dissociation enthalpy of the bond in XY with a fair degree of reliability.

3.9 Ionization energy

The ionization energy is defined as the amount of energy required to remove an electron from an atom in the gas phase to a distance of infinity away from the uncleus. It is generally represented as I or IP (Ionization potential) or IE and is measured in electron volt or KJ/mole.

$$M(g) + E_1 \rightarrow M^+(g) + e$$

The first ionization energy for an atom is represented by E_1 and it is the one that removes the outer-most (or valence) electron from the electrostatic attraction of the uncleus. The second ionization energy is the additional amount of energy required to remove the second electron, and so on. Because it will always take energy to remove an electron, ionization energies are always positive.

3.9.1. *Factors upon which IE depends :*

1. **Charge of the nucleus** : The greater the charge on the nucleus of an atom it will be more difficult to remove an electron from the atom and hence greater would be the value of ionization potential. Thus the value of ionization potential generally increases from left to right in a period and decreases along a group from top to bottom.
2. **Completely filled and half filled orbitals** : According to Hund's rule, atoms having half filled or completely filled orbitals, are comparatively more stable hence more energy required to remove an electron from the atom. The ionisation potential of such atoms is therefore relatively higher than expected normal value from their position in the periodic table.
3. **Atomic radius :** With increasing the atomic radius, IE decreases. This is because of the fact that in case of larger atoms the attraction between the nucleus and outermost electron is less an hence it is easier to remove.
4. **Principal quantum number :** Principal quantum number(n) determine the location of an electron from the nucleus. Higher the value of n the lower will be the IE.

3.9.2. Variation of Ionisation Energy in the periodic table :

In general Ionisatin energy increases along a period and reaches a maximum value in the noble gas with minor fluctuation. On moving across a group from top to bottom IE of the elements decreases.

3.9.3. Variation of IE along transition elements :

Variation of IE along a transition series is not so much because with increase in atomic number, elements enters successfully into the inner d orbital with little penetrating ability. The first IE involves the removal of the outermost s orbital electrons. So the first IE of the transition elements increases very slightly due to increase in the effective nuclear charge. As the variation is not so much prominent, so it may be considered that 1st IE of the elements of a transition series remain almost constant. But on desending a group of transitin elements, there will be normal decrease in 1st IE from 1st to 2nd elements, but increase of the third elements. The value increases due to the effect of lanthanide contraction.

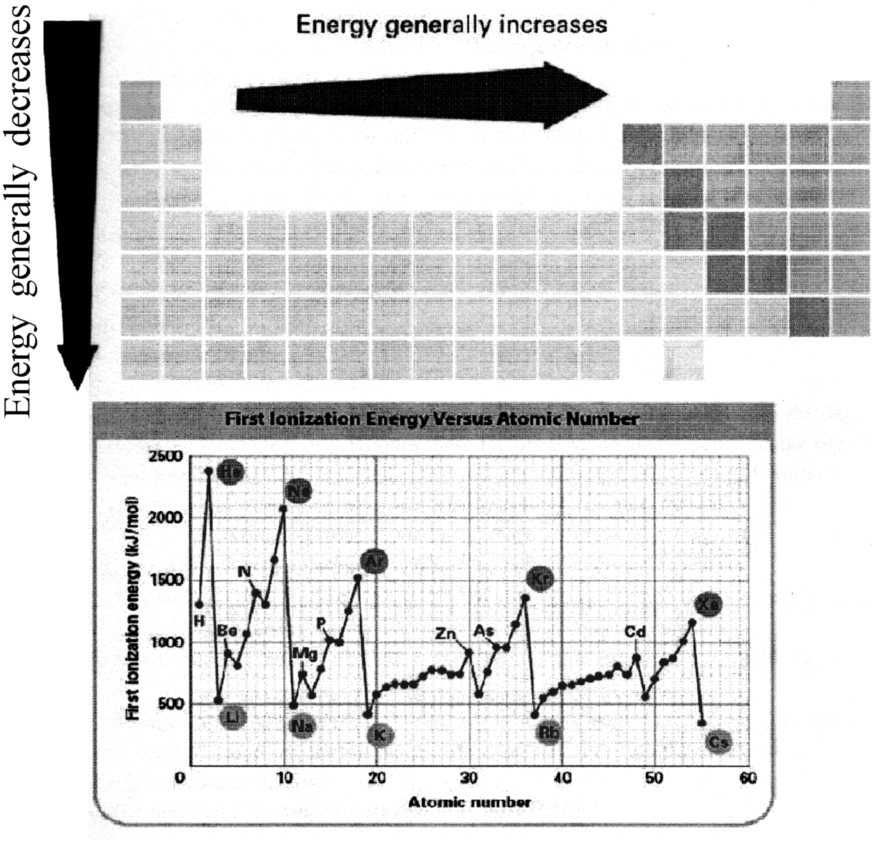


Fig.6 : Variation of Ionisation energies in the periodic table.

3.10. Electron affinity

The amount of energy released when an electron is added to an isolated neutral gaseous atom in its lowest energy state (ground state) to produce an anion ia called its electron affinity. It is generally representd by EA or E and is measured in electron volt (ev) or K. Cal per gm atom. Thus the electron affinity can be defined by the following equation.

$A(g) + e \rightarrow A^{-}(g) +$ Energy relased (EA)

Neutral gaseous atom Anion

Since EA represents the energy released, it is represented with a negative sign. First EA represented by E_1 and it corresponds to the addition of one electron only. In the case of 2nd EA, electron is added to an anion against the electrostatic repulsion between the electron being added and the negative charge ion $A^{-}(g)$. Hence, the energy instead of being relased is supplied to A^{-} (g) to form $A^{2-}(g)$

3.10.1. Factors upon which EA depends :

1. Atomic Size
2. Effective nuclear charge
3. Screening effect by inner electrons.

In general E value decreases with the increasing atomic radius and increases with decreased screening effect by the inner electrons. Besides these factors E value also depends on the type of the orbitals into which the electron is added. When other factors remain constant, E value is the greatest for an electron entering an s orbital and decreases for p, d, and f orbitals.

3.10.2. Variation of EA in the Periodic Table :

♦ **In a group :** In moving down a group EA values generally decrease due to the steady increase in the atomic radius of the elements.

♦ **In a period :** EA values generally increase on moving from left to right in a period in the periodic table.

Exceptions : Nitrogen and Phosphorus have unexpected lower values of EA. This is because of the presence of the half-filled 2p orbitals which are relatively more stable and hence it is very difficult to add an additional electron.

3.10.3. Difference between Electronegativity and Electron affinity

Sl.No.	Electronegativity	Electron affinity
1.	It refer to the attraction of the bonding electrons.	It refers to the attractin of the free electrons by an isolated gaseous atom.
2.	Only shifting of the bonding electrons towards the more electronegative atom occurs	Outright gain of the electrons occur
3.	The covalent bond becomes polar	Anion is formed
4.	It is the relative property of the atom	It is the inherent property of the atom

3.11 Relativistic effects

For most applications of chemistry the effect of relativity on electronic motion can largely be ignored. Einstein's theory of relativity states that the mass of a particle becomes infinite as its velocity approaches the speed of light. For the smaller elements, Schrodinger's nonrelativistic model is perfectly appropriate, as the velocities of the electrons in the lighter elements rarely approach the speed of light. However, the larger mass of the heavier elements exerts a stronger electrostatic pull on the inner-most electrons, sometimes accelerating them to speeds in excess of 10^8 m/s. According to Einstein's theory of relatively, particles that are traveling at velocities approaching the speed of light are more massive than they are at rest, as showm by the following equations, where m_{rel} is the relativistic mass of the electron and m_0 is its rest mass. As a result of their relativistic heavier mass, the accelerated electrons have a smaller average radius, which results from the derivation of the Bohr model of the atom :

$$m_{rel} = \frac{m_0}{\sqrt{1-(v/c)^2}}$$

$$r = \frac{4\pi\varepsilon_0 n^2 h^2}{m_e Z e^2}$$

Because the s and p electrons penetrate the nucleus better than the d or f electrons do, the s and p electrons are accelerated to a greater extent. Thus, the s and p orbitals effectively contract as relativistic effects become more prominent. Furthermore, as the s and p electrons migrate closer to the nucleus, this enhances their ability to shield the *d* and *f* electrons from experiencing the full attraction of the nucleus. Thus, the *d* and *f* orbitals expand as a result of relativity. The combined effect is to lower the energies of the *s* and *p* electrons, while raising the energy of the *d* and *f* electrons. The magnitude of the effect increases roughly as the squre of the atomic number. Thus, the heavier elements experience considerably larger relativistic effects than do the lighter ones. For a number of elements heavier than Pt, the magnitude of the effect is even comparable to the strength of a chemical bond! The relativistic effect enhances the inert-pair effect montioned in the preceding section. The smaller redius of the 6*s* orbital in Tl, for instance, causes the 6*s* electrons to be held more tightly than they would have been in the absence of relativity and raises their ionizatin energies. Hence, Tl, will commonly prefer the lower 1+ oxidation number over its 3+ state. However, unlike the inert-pair effect, any of the heavier elements can experience the relativistic effect. As an example, gold is the least reactive of the coinage metals. This explains why it was one of the first elements to be discovered by ancient civilizations (about 10,000 years ago). Gold exists in nature in its elemental from and is only rarely found in minerals, such as calverite, $AuTe_2$, and sylvanite, $AuAgTe_4$. The electron configuration of Au is [Xe] $4f^{14}5d^{10}6s^1$. As a result of the relativistic effect, the 6*s* electron has an unusually large ionization energy (890 kJ/mol, compared with 746 kJ/mol for Cu and 741 kJ/mol for Ag) and is extremely difficult to oxidize. Hence, gold will not rust in air, nor will it react with the oxidizing acid HNO_3. In fact, in order to dissolve gold, a combination of one part nitric acid with three parts conc. HCl must be employed. Nitric acid-acts as the oxidizer, while the Cl^- ion helps to solubilize the gold as the complex ion $AuCl_4^-$.

3.12 The Inert-Pair effect

One of the more unusual periodic trends is known as the inert-pair effect. The elements that immediately follow the 4d and 5d transition series are considerably less reactive than their group properties might have predicted and they also prefer oxidation states that are two lower than the usual group valence. Consider, for example, the Group IIIA elements. The lighter elements, B, Al, and Ga take only the 3+ oxidation state predicted by their group valence. However, the heavier elements, In and Tl, take both the 3+ and 1+ oxidation states. The same trend is observed for the Group IVA elements. Again, the lighter elements C, Si, and Ge take the 4+ valence predicted by their period. However, Sn and Pb can exist in either the 4+ or the 2+ oxidation state. The relative stability of the lower oxidation states for the fifth and sixth series post-transition elements (In, Sn, Sb, Tl, Pb, Bi, and Po) has been attributed to the higher-than-expected ionization energies for these seven elements. Consequently, it costs these elements relatively more energy to achieve a higher oxidation state than their lighter group congeners. At the same time, less energy is gained as a result of bond formation because they also exhibit lower-than-predicted bond dissociation enthalpies.Weaker bond enthalpies are expected for the heavier elements as a result of the diffuse nature of orbital overlap with increasing orbital size. The larger-than-expected ionization energies for the post-transition series Group IIIA elements result from the fact that the valence s electrons are not shielded from the nucleus very effectively by the intervening d electrons. As the two s electrons are both held tighter by the nucleus in the post-transition series elements, the ionization energies for these two electrons are unusually large. The end result is that these elements prefer oxidation states that are two lower than their typical group valence. Relativistic effects, which are discussed in the above section, also contribute to the higher-than-expected ionization energies of the valence s electrons.

3.13 Summary

- Elements are arranged in periods and groups on the periodic table. The elements are arranged according to increasing **atomic number**.
- The groups on the periodic table are labeled from 1 to 18. Group 1 is known as the **alkali metals**, group 2 is known as the **alkali earth metals**, group 17 is known as the **halogens** and the group 18 is known as the **noble gases**. The elements in a group have similar properties.
- The most fundamental property leading to periodic variation is "**Effective nuclear Charge**" (Z_{eff}). Where screening constant (a) is determined by Slater's rule.
- ***Van der Waals radius*** is defined as the half-distance between the nuclei of two atoms of neighboring molecules
- The ***Covalent radius*** of an element may by taken as half the inter nuclear distance between two atoms of the same element joined by a single bond.
- The ***Ionic radii*** can be estimated by measuring the distances between cations and anions in ionic crystals.
- Pauling set up the ratio in Equations, where r_0 is the inter ionic distance between the cation and anion. r^+ and r^- are radius of cation and anion respectively. Z^+_{eff} and Z^-_{eff} are effective nuclear charge of cation and anion respectively.

  $r_+ / r_- = Z_{eff}^- / Z_{eff}^+$ and $r_0 = r_+ + r_-$

- The contraction in size in the lanthanide series is known as **lanthanide contraction.**
- Electronegativity is the tendency of atoms to attract electrons.
- According to **Pauling scale** of Electronegativity, difference in Electronegativity between the two atom A and B = $0.208\sqrt{\{ E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}\}}$;
- According to **Allred and Rochow** Scale Electronegativity = $\chi_{AR} = (0.359 \times Z_{eff}) / r^2_{cov} + 0.744$ (when r_{cov} is measured in Angstrom).
- According to **Mulliken's scale** Electronegativity = = (I.E + E.A.)/2
- The overall effect of charge , substituents, hybridization of the bonding orbitals, etc. of a group on electronegativity may be summarily expressed in terms of its **group Electronegativity.**
- The first **ionisation energy** is the energy needed to remove one electron from an atom in the gas phase.
- The amount of energy released when an electron is added to an isolated neutral gaseous atom in its lowest energy state (ground state) to produce an anion is called its **electron affinity**
- **Inert pair effect** is often used in relation to the increasing stability of oxidation states that are two less than the group valency for the heavier elements of groups 13, 14, 15 and 16
- The change of different properties of element in the periodic table can be shown by the following picture.

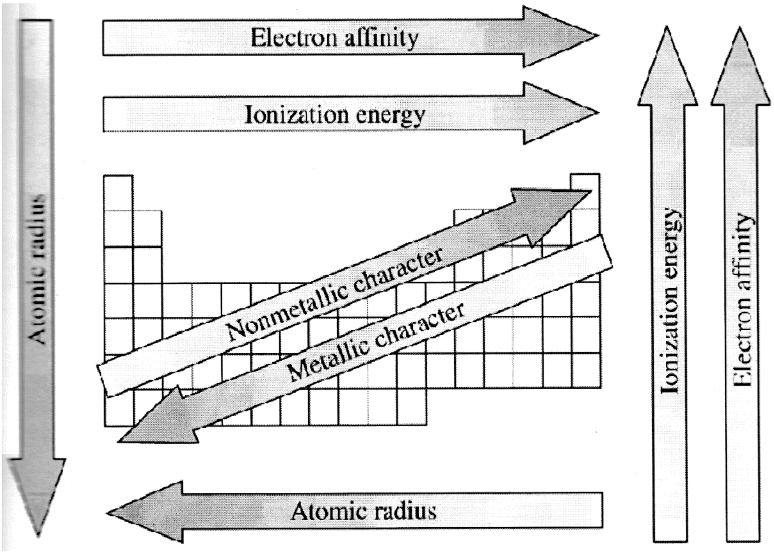
3.14 Questions

1. For each pair, circle the species with the larger radius and provide reasoning for your choice: (a) Mg or Mg^2+, (b) O or O^{2-}, (c) K^+ or Cl^-, (d) P^{3-} or S^2, (e) N or P, (f) Na or Mg, and (g) Na^+ or Mg^{2+}. (see section 4 & 5)
2. Why is Lu^{3+} smaller than Y^{3+}? (see section 6)
3. Arrange the following in increasing order of first ionization energy: F, Na, Al, P, S, and Cl. (see section 8)
4. Given the following bond dissociation energies, calculate the Pauling electronegativity of Br: C1-C1 (242 kJ/mol), Br-Br (183 kJ/mol), and Br-Cl (219 kJ/mol). The Pauling electronegativity of Cl is 3.16.(see section 5.1)

5. What is screening effect ? How it controls the atomic size ? (see section 3 & 4)
6. Show the difference between Vanderwaal radii and covalent radii (see section 4.1 & 4.2)
7. Write a short note on the lanthanide contraction (see section 6)
8. Compare the ionization energies (KJ/mol) of and comment on any irregularity, if present.

   (a) I_1 : Ca (590); Sr (550); Ba (503); Ra (509) (see section 8)

   (b) I_2 : Ti (1310); V (1365); Cr (1592); Mn (1509) (see section 8)
9. What is meant by ionic radius ? Discuss Pauling's method for the determination of univalent radii.(see section 5)
10. Calculate the A-R electronegativity of Zn taking its covalent radius as 125 pm (see section 7.5)



3.15 Further Reading

1. "General Inorganic Chemistry : Part-1" by "Ramaprasad Sarkar [New central book agency Ltd.]
2. "Concise Inorganic Chemistry" by J.D.Lee [Willey-India]
3. "Inorganic Chemistry" by R.I. Dutta [The New Book Stall]

Unit-4 Chemistry of s and p-block elements

Content

4.1 Objectives

After reading this unit, we will be able to :

- Know the diagonal relationship and anomalous behaviours of first member of each groups.
- About alltropy and catenation properties.
- Detail chemistry of s & p block elements.
- Noble gas chemistry.
- Synthesis, structural aspects and applications of silicones phosphazines.
- Structural properties of various silicates.

4.2 Introduction

The elements of groups 1 (1*A*), 2 (11 *A*), 13 (111 *A*), 14 (*IVA*), 15 (*VA*), 16 (*VIA*), 17 (*VIIA*) and 18 (zero) are called main group elements. Out of these the elements of groups 1, 2, 13, 14, 15, 16 and 17 are called normal or representative elements and those of 18 group are called noble gases or inert gases. On the basis of the orbital into which the last electron goes, main group elements have grouped into the following categories : (a) s-block elements. In the atoms of these elements the last electron to ns orbital. Thus the elements of groups 1 and 2 are s-block elements, (b) p-block elements. In the atoms of these elements the last electron enters np orbital.

4.3 Diagonal relationships

Although chemists usually think of periodic trends vertically (down groups) or horizontally (across periods), there are, in fact, other patterns to be found in the periodic table. One of these is the *diagonal relationship:* There are similarities in chemical properties between an element and that to the lower right of it. This relationship is found for elements in the upper-left corner of the periodic table. The diagonal relationship is only chemically significant for three pairs of elements: lithium and magnesium, beryllium and aluminum, and boron and silicon.

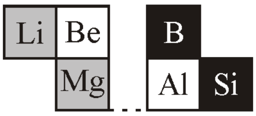


Fig. 1. Elements commonly considered linked by the diagonal relationship.

❑ Similarities of Lithium and Magnesium:

- The hardness of lithium metal is greater than that of the other alkali metals but similar to that of the alkaline earth metals.

- Lithium forms a normal oxide, Li_2O, like the alkaline earth metals but unlike the other alkali metals. (Sodium forms Na_2O_2, containing the O_2^{2-} ion, while the heavier alkali metals form compounds containing the O^{2-} ion, such as KO_2.)

- Lithium is the only alkali metal to form a nitride, Li_3N, whereas the alkaline earth metals all form nitrides.

- Three lithium salts — carbonate, phosphate, and fluoride — have very low solubility. These anions form insoluble salts with the alkaline earth metals.

- Lithium forms organometallic compounds similar to those of magnesium (the Grignard reagents used in organic chemistry).

- Many lithium salts exhibit a high degree of covalence in their bonding. This bonding is similar to that of magnesium.

❑ Similarities of Beryllium and Aluminum :

- In air, both metals form tenacious oxide coatings that protect the interior of the metal sample from attack.
- Both elements are amphoteric, forming parallel anions i, e, tetrahydroxoberyllates, $[Be(OH)_4]^{2-}$, and tetrahydroxoaluminates, $[Al(OH)_4]^{-}$ in reactions with concentrated hydroxide ion.
- Both form carbides (Be_2C and Al_4C_3) containing the C^{4-} ion that react with water to form methane.

❑ **Similarities of Boron and Silicon;**

■ Boron forms a solid acidic oxide, B_2O_3, like that of silicon, SiO_2, but unlike that of either aluminum, whose oxide is amphoteric, or carbon, whose oxide, CO_2, is acidic but gaseous.

■ Boric acid, H_3BO_3, is a very weak acid that is similar to silicic acid, H_4SiO_4 in some respects. It bears no resemblance to the amphoteric aluminum hydroxide, $Al\ (OH)_3$.

■ There are numerous polymeric borates and silicates that are constructed in similar ways, using shared oxygen atoms.

■ Boron forms a range of flammable, gaseous hydrides, just as silicon does. There is only one aluminum hydride—a solid.

4.4 Anomalous behavior of first element in each group of the main group elements

First member of each group of s- and p-block elements shows anomalous behavior due to the following reasons :

(i) Small size

(ii) High ionization enthalpy

(iii) High electronegativity

(iv) Absence of d-orbitals

Examples : Li in the first group shows different properties from the rest of elements like covalent nature of its compounds, formation of nitrides.

Similarly, beryllium, the first element of second group differs from its own group in the following ways:

■ Beryllium carbide reacts With water to produce methane gas while carbides of other elements give acetylene.

■ Beryllium shows a coordination number of four while other elements show a coordination number of six.

4.5 Allotropy and catination

4.5.1. *Allotropy*

■ Excepting Pb, all other elements of group 14 show allotropy, i.e., these elements exist in different allotropic forms. For example : (i) Carbon exists in the following two allotropic forms. (a) Crystalline forms : diamond and graphite, (b) Amorphous forms which are microcrystalline forms, e.g., coal, coke, charcoal etc. (ii) Silicon exists in two forms, (a) Crystalline form, (b) Amorphous form. It is the common variety of silicon, (iii) Germanium exists in two crystalline forms, (iv) Tin exists in three allotropic forms, (a) White tin (b) Grey tin (c) Rhombic tin.

- Excepting Bi, all the remaining elements of group 15 show allotropy. Nitrogen shows α-nitrogen with cubic crystalline structure and β-nitrogen having hexagonal crystalline structure.. Both these forms are solid allotropic forms. Phosphorus shows White, red, scarlet, metallic or α-black, β-black and violet. Arsenic shows Grey, yellow and black. Antimony shows Metallic, yellow or α-antimony and explosive
- All the elements of group 16 exist in different allotropic forms. Oxygen exists in two metallic forms which are oxygen and ozone . Sulphur exists in two allotropic forms i,e, yellow rhombic sulphur (α- sulphur) and the monoclinic (β-sulphur). Se has two forms: red (nonmetallic) and grey (metallic). Te exists in two forms nonmetallic and metallic (more stable). Po also exists in two forms α and β (both metallic).

4.5.2. *Catenation*

Chemical linkage into chains of atoms of the same element, occurring only among the atoms of an element that has a valence of at least two and that forms relatively strong bonds with itself. The property is predominant among **carbon** atoms. It can form long hydrocarbon chains and rings like benzene. Catenation is also significant among **sulfur** and **silicon** atoms, and slightly present among germanium, nitrogen, selenium, and tellurium atoms.

4.6 Berylium hydrides and halides

Berylium (*Be*) gives polymeric hydrides namely $(BeH_2)_n$

4.6.1. Preparation

BeH_2 is produced by reducing $BeCl_2$ with $LiAlH_4$ or LiH.

$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$

$$BeCl_2 + 2LiH \xrightarrow{\text{Ether}} BeH_2 + 2LiCi$$

4.6.2. Properties

- BeH_2 is covalent in nature.
- BeH_2 reacts with ethanol solution of B_2H_6 and form borohydride, $[BH_4]^-$

$$BeH_2 + B_2H_6 \rightarrow Be\,[\,BH_4\,]_2$$

- BeH_2 is a nonvolatile white solid which is stable at room temperature but dissociates into its elements at 125°C

- BeH_2 reacts with water and H_2 is liberated. Thus these hydrides are used as reducing agents.

$$BeH_2 + 2H_2O \rightarrow Be(OH)_2 + 2H_2$$

Anhydrous beryllium halides are covalent. The fluoride, BeF_2, is obtained as a glass (sublimation point 1073 K)

from the thermal decomposition of $[NH_4]_2[BeF4]$.

$$2BeO + CCl_4 \rightarrow 2BeCl_2 + CO_2$$

$$[Be(H_2O)_4]Cl_2 \xrightarrow{\Delta} Be(OH)_2 + 2H_2O + 2HCl$$

$BeCl_2$ is monomeric and has a linear structure. At lower temperature, the vapour also contains planar dimers. The coordination environment of each Be centre is tetrahedral. In the polymer, each Be atom can be considered to be sp^3 hybridized and a localized σ-bonding scheme is appropriate in which each Cl donates a lone pair of electrons into an empty hybrid orbital on an adjacent Be atom. The formation of this chain demonstrates the Lewis acidity of beryllium dihalides; $BeCl_2$ acts as a Friedel-Crafts catalyst (i.e. like $Alcl_3$, and the formation of adducts is illustrated by $[BeF_4]^{2-}$, $[BeCl_4]^{2-}$ and $BeCl_2 . 2L$ (L = ether, aldehyde, or ketone).

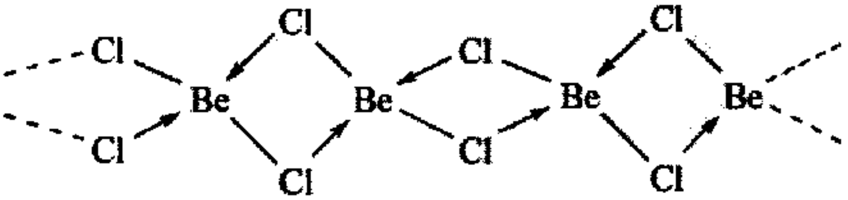


Fig.2 Structure of $BeCl_2$

4.7 Boranes

Boron is second (only after carbon) in the number of hydrides that it forms. Over 50 neutral boranes, (B_nH_m) and an even larger number of borane anions, ($B_nH_m^{x-}$), are known. There are three reasons why the chemistry of boranes is important.

i. The shapes of borane molecules are different from those of other hydrides.
ii. The bonding in boranes has required the expansion of molecular orbital theory.
iii. The reaction chemistry of the boranes has interesting and parallels to organic chemistry.

❑ *Structures of Boranes* :

The simplest borane is B_2H_6 (Figure 3). As can be seen from the figure, one of the most unique aspects of borane chemistry is that hydrogen atoms often act as bridges between neighboring boron atoms. Also, the boron atoms often form triangular units. Any polyhedron containing triangular faces (such as an octahedron) is generically known as a deltahedron. There are three common classes of boranes and borane anions:

i. The *closo*-cluster, where the boron atoms form a closed deltahedral cage. The generic formula is $[B_nH_n]^{2-}$, for example, $[B_6H_6]^{2-}$ (Figure 3).

ii. The *nido*-cluster, an open cage cluster derived from a closed deltahedron with one boron atom missing. The common generic formulas are B_nH_{n+4} or $[B_nH_{n+3}]^-$, for example, B_2H_6, B_5H_9 (Figure 3). and $[B_5H_8]^-$

iii. The *arachno*-cluster, an open cage cluster derived from a closed deltahedron with two boron atoms missing. The common generic formulas are for example B_nH_{n+6} or $[B_nH_{n+5}]^-$, B_4H_{10} (Figure 3) and. $[B_4H_9]^-$.

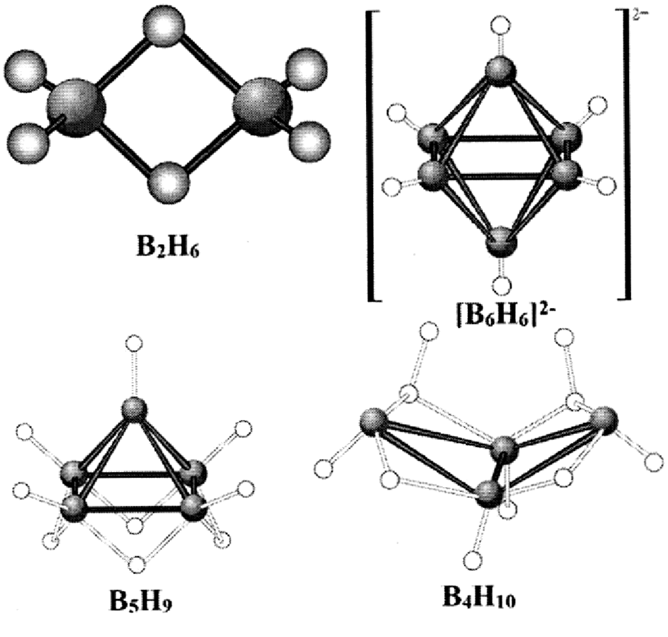


Fig. 3. Structure of different Borames

All of the Boranes are thermodynamically unstable with respect to decomposition into their constituent elements. To name a borane, the numbers of boron atoms are indicated by the normal prefixes, while the numbers of hydrogen atoms are denoted by Arabic numbers in parentheses. Hence, B_4H_{10} is called tetraborane and B_5H_9 is pentaborane. The discovery that the simplest borane had the molecular formula B_2H_6 (not BH_3) proved to be a major headache for inorganic chemists. Traditionally, a hydrogen atom was believed to form only one covalent bond. In fact, as can be seen from the structure in Figure 3, two hydrogen atoms link, or bridge, the pair of boron atoms. The utilization of hydrogen atoms as bridges means that one electron pair can satisfy the bonding requirements of two boron atoms. Each terminal hydrogen atom forms a normal two-electron bond with a boron atom. Each boron atom then has one electron left, and this is paired with the electron of one of the bridging hydrogen atoms (Figure 4A). The shape of the molecule can be described as approximately tetrahedral around each boron atom, with the bridging hydrogen atoms in what are sometimes called "banana bonds." The hydridic bonds behave like weak covalent bonds (Figure 4B). The bonding in a diborane molecule can be described in terms of hybridization concepts. According to these concepts, the four bonds, separated by almost equal angles, would correspond to sp^3 hybridization. Three of the four hybrid orbitals will contain single electrons from the boron atom. Two of these half-filled orbitals would then be involved in bonding with the terminal hydrogen atoms. This arrangement would leave one empty and one half-filled hybrid orbital. To explain how we make up the eight electrons in the sp^3 orbital set, we consider that the single half-filled hybrid sp^3 orbitals of the two borons overlap with each other and with the Is orbital of a bridging hydrogen atom at the same time. This arrangement will result in a single orbital that encompasses all three atoms (a *three-center bond*). This orbital is capable of containing two electrons (Figure 4C). An identical arrangement forms the other B-H-B bridge. The bonding electron distribution of diborane is shown in Figure 4D. Alternatively, we can consider the molecular orbital explanation. The detailed molecular orbital diagram for this eight-atom molecule is complex. Although molecular orbitals relate to the molecule as a whole, it is sometimes possible to identify molecular orbitals that are involved primarily in one particular bond. In this case, we find that the mixing of the orbital wave functions of the atoms in each bridge bond results in the formation of three molecular orbitals. When we compare the energies of the atomic orbitals with those of the molecular orbitals, we find that one molecular orbital is lower in energy (s bonding), one is higher in energy (s antibonding), and the third has an energy level equivalent to the mean energy of the three component atomic orbitals (s nonbonding). The bridging hydrogen atom contributes one electron, and each boron atom contributes one-half electron. This arrangement fills the bonding orbital between the three atoms (Figure 4E). Because there is one bonding orbital shared between two pairs of atoms, the bond order for each *B-H* component must be 1/2. The same arguments apply to the other bridge. From bond energy measurements, we do indeed find each *B-H* bridging bond to be about half the strength of a terminal *B-H* bond, although it is still in the energy range of a true covalent bond, unlike the much weaker protonic bridges in hydrogen bonded molecules. Of equal importance, the set of molecular orbitals shows that the structure makes maximum use of the few boron electrons. The presence of more electrons would not strengthen the bond because these electrons would enter nonbonding molecular orbitals.

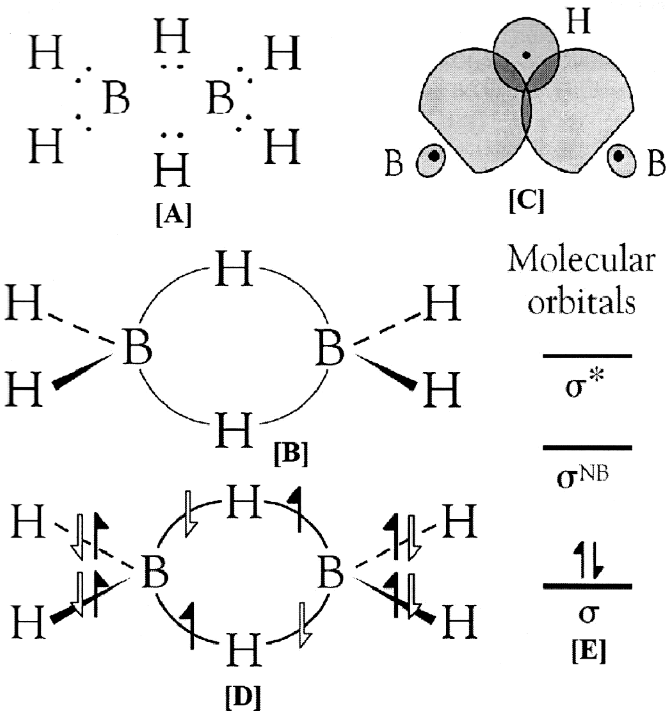


Fig. 4 [A] : Electron-pair arrangement in diborane, B_2H_6[*B*] : Geometry of the diborane molecule. [*C*]: Overlap of the sp^3 hybrid orbitals of the two boron atoms with Is orbital of the bridging hydrogen atom. [*D*]: The electron pairing that is consistent with sp^3 hybridization for each boron atom and with the two-electron, three-atom *B-H-B* bridging bonds. The electrons contributed by the hydrogen atoms are the open half-headed arrows.[*E*]: The molecular orbitals that are involved in the hydride bridge.

❑ *Synthesis and Reactions of Boranes* :

About 200 tonnes of diborane are produced each year. The industrial synthesis is accomplished by the reaction of boron trifluoride with sodium hydride to produce toxic, colorless diborane :

$$2\,BF_3\,(g) + 6NaH\,(s) \rightarrow B_2H_6\,(g) + 6NaF\,(s)$$

The boranes possess partially negatively charged hydrogen atoms because of the low electronegativity of boron. This reversed polarity of the bond results in a high chemical reactivity for these compounds. For example, diborane, like most of the neutral boranes, catches fire in air and explodes when mixed with pure dioxygen. The extremely exothermic reaction produces diboron trioxide and steam :

$$B_2H_6(g) + 30_2(g) \rightarrow \mathrm{B_20_3} + 3H_20(g)$$

Reaction with water to give boric acid (sometimes written as $[B(OH)_3]$ and hydrogen is also very exothermic :

$$B_2H_6\,(g) + 6\,H_2\mathrm{O}\,(l) \rightarrow 2\,H_3BO_3\,(aq) + 3\,\mathrm{H_2O}\,(l).$$

Most of the other boranes are synthesized from diborane. For example, tetraborane is formed from the condensation of two diborane molecules, then pentaborane is formed by reaction with another molecule of diborane :

$$2B_2H_6(g) \xrightarrow{high\ pressure} B_4H_{10}(g) + H_2(g)$$

$$B_4H_{10}(g) + B_2H_6(g) \rightarrow B_5H_{11}(g) + 2H_2(g)$$

Diborane is an important reagent in organic chemistry. The gas reacts with unsaturated hydrocarbons (those containing double or triple carbon-carbon bonds) to form alkylboranes. For example, diborane reacts with propene :

$$\mathrm{B_2H_6}\,(g) + 6\,\mathrm{CH_2{=}\,CHCH_3}\,(g) \rightarrow 2\,\mathrm{B\,(CH_2\,CH_2\,CH_3)_3\,(1)}$$

The product of this *hydrobomtion* reaction can be reacted with a carboxylic acid to give a saturated hydrocarbon, with hydrogen peroxide to give an alcohol, or with chromic acid to give a ketone or a carboxylic acid. Hydroboration is a favored route of organic synthesis for two reasons: the initial hydride addition is accomplished under very mild conditions, and a wide variety of final products is possible (depending on the other reagent used).

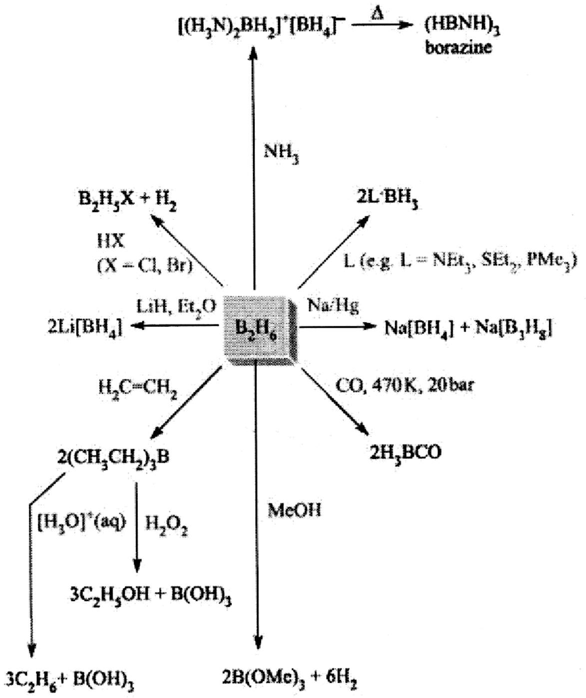


Fig. 5 Selected reactions of B_2H_6

4.8 Borazine

BH_3 forms adducts with a wide range of donor ligands, such as $Me_3N.BH_3$. When the donor is also a hydride, loss of hydrogen can also occur. For example, B_2H_6 and NH_3 initially form the expected $H_3N.BH_3$ which gives the compound borazine, $B_3N_3H_6$ '(Fig.6)' on warming to room temperature. Borazine is isoelectronic with benzene (C_6H_6) and also has a delocalized structure, with all *B-N* bond lengths identical (144 pm). However, in borazine the electronegative N atoms are polarized δ- and the electropositive B atoms δ +, so the reactivity of borazine is rather different to that of benzene, and the sometimes-used term 'inorganic benzene' is not a good description of borazine.

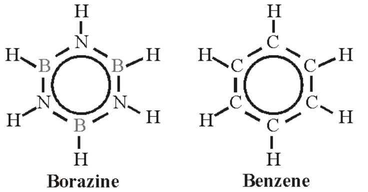


Fig. 6 : Borazene & Benzene

The reaction between diborane, B_2H_6, and ammonia gives borazine, $B_3N_3H_6$,

$$3B_2H_6(g) + 6NH_3\,(g) \rightarrow 2B_3N_3H_6\,(l) + 12\,H_2\,(g).$$

There are many other derivatives of this type, involving different substituents on B and/or N. The eaction of NH_4Cl with BCl_3 gives B,B,B trichloroborazine, $B_3N_3H_3Cl_3$

$$3NH_4Cl + 3BCl_3 \rightarrow B_3N_3H_3Cl_3 + 9HCl$$

Despite similarities in boiling points, densities, and surface tensions, the polarity of the boron nitrogen bond means that borazine exhibits less aromaticity than benzene. Hence, borazine is much more prone to chemical attack than is the homogeneous ring of carbon atoms in benzene. For example, hydrogen chloride reacts with borazine to give $B_3N_3H_9Cl_3$, in which the chlorine atoms bond to the more electropositive boron atoms :

$$B_3N_3H_6\,(l) + 3\,HCl\,(g) \rightarrow B_3N_3H_9Cl_3(s)$$

Chemical reactions wit Borazine

$$B_3H_6N_3 = 3BN + 3H_2(300^\circ C\, or in the light).$$

$$B_3H_6N_3 + 9H_2O(hot) = 3B(OH)_3 \downarrow + 3NH_3 \uparrow + 3H_2 \uparrow.$$

$$B_3H_6N_3 + 3NaOH(cone.) + 12H_2O(cold) = 3Na[B(OH)_4] + 3H_2 \uparrow + 3(NH_3.H_20)$$

$$4B_3H_6N_3 + 21O_2 = 6B_2O_3 + 12NO + 12H_2O(electrie\ discharge).$$

4.9 Boron nitride

Just as, borazine is isoelectronic with benzene, the material boron nitride (BN) is isoelectronic with carbon. Both carbon and BN form diamond and graphite-like structures. The graphite-like structure of BN (Figure 7) has layers consisting of planar, hexagonal B_3N_3 rings (with BN distances similar to those in borazine). These layers stack on top of each other such that the $B^{\delta+}$ and $N^{\delta-}$ atoms lie on top of each other.

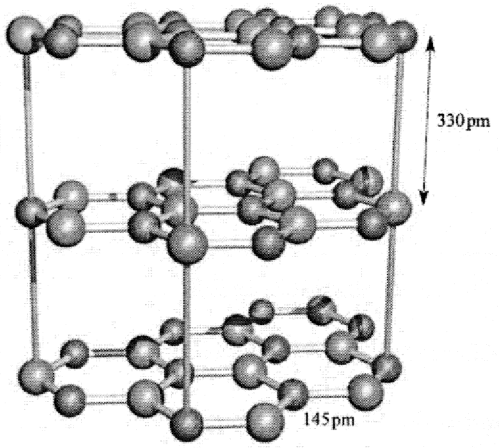
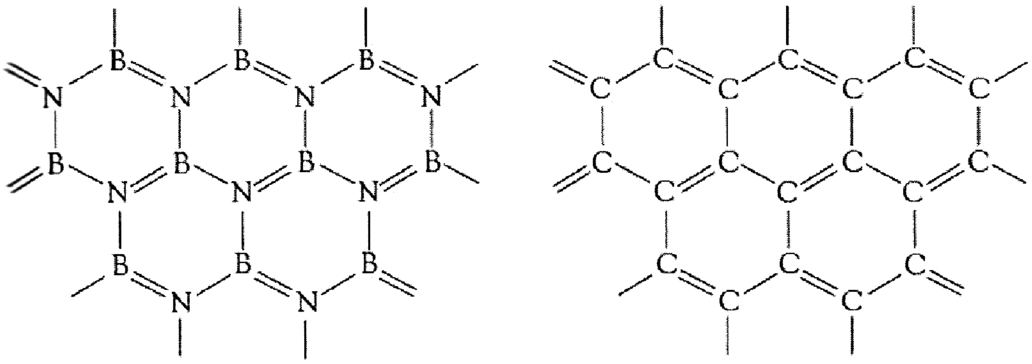


Fig.7: Part of the layer structure of the common polymorph of boron nitride, *BN*. Hexagonal rings in adjacent layers lie over one another so that *B* and *N* atoms are eclipsed.

Unfortunately, both carbon allotropes burn when heated to give carbon dioxide gas, thus precluding the use of either of these substances in high temperature applications. Boron nitride, BN, however, is the ideal substitute. The simplest method of synthesis involves heating diboron uioxide with ammonia at about 1000°C:

$$B_2O_3(s) + 2\ NH_3(g) \rightarrow 2BN(s) + 3H_2O\ (g)$$

The product has a graphite-like structure (Figure 8) and is an excellent high temperature, chemically resistant lubricant. Unlike graphite, boron nitride is a white solid that does not conduct electricity. This difference is possibly due to differences in the way the layers in the two crystals are stacked. The layers in the graphite-like form of boron nitride are almost exactly the same distance apart as those in graphite, but the boron nitride layers are organized so that the nitrogen atoms in one layer are situated directly over boron atoms in the layers above and below, and vice versa. This arrangement is logical, because the partially positive boron atoms and partially negative nitrogen atoms are likely to be electrostatically attracted to each other. By contrast, the carbon atoms in one layer of graphite are directly over the center of the carbon rings in the layers above and below. An alternative reason for the lack of electrical conductivity is the weaker aomaticity in the layers due to the differing electronegativities of boron an nitrogen.



Boron nitride Graphite

Fig. 8. Comparative layer structures of boron nitride and araphite.

Chemical reactions with boron nitride :

$2BN + 3H_2\ O\ (vapor) = B_2O_3 + 2NH_3\ (800^\circ\ C).$

$4BN + 3O_2 = 2B_2O_3 + 2N_2\ (above\ 700^\circ\ C).$

$2BN + 3F_2 = 2BF_3 + N_2\ (normal\ temp.).$

$BN + 4HF\ (cone.) = NH_4\ [\ BF_4\ ]\ (normal\ temp.).$

$BN + NaOH\ (come.) + 3H_2O = Na\ [B\ (OH)_4] + NH_3\ (boiling).$

4.10 Boric acid

The chemica formula of boric acid is H_3BO_3 [or $B(OH)_3$]. The chemical structure of boric acid is shown below :

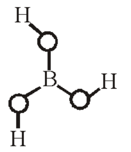


Fig. 9. Structure of Boric acid.

The central boron atom is connected to three hydroxyl (-OH) groups, which are capable of strong hydrogen bonding. Its solid crystalline structure consists of parallel layers of boric acid held together in place by hydrogen bonds. Boric acid is prepared by reacting minerals such as borax ($Na_2B_4O_7$.10 H_2O), with strong acids like *HCl*:

$$Na_2B_4O_7{-}10H_2O + 2\ HCl \rightarrow 4\ H_3BO_3 + 2\ NaCl + 5\ H_2O$$

It can also be prepared by the hydrolysis of boron trihalides (such as BBr_3) or diborane (B_2H_6) :

$$BBr_3 + 3\ H_2O \rightarrow B\ (OH)_3 + 3\ HBr$$

$$B_2H_6 + 6\ H_2O \rightarrow 2\ B\ (OH)_3 + 6H_2$$

Boric acid is a weak monobasic acid, and is considered a Lewis acid. It dissolves in boiling water and in anhydrous sulfuric acid. When heated to high temperatures (over 170°C), it undergoes dehydration to form metaboric acid (HBO_2) :

$$H_3BO_3 \rightarrow HBO_2 + H_2O$$

Boric acid is non-toxic with antibacterial properties, and it is mainly used as an antiseptic agent, acne treatment, preservative, insecticide, pH buffer, swimming pool chemical, flame retardant, and a precursor to many useful chemicals. It is used industrially for the manufacture of fiberglass, household glass products and the glass used in LCD displays.

Chemical reaction with boric acid:

$$B\ (OH)_3 = HBO_2 + H_2O\ (70 - 160°\ C),$$

$$2B\ (OH)_3 = B_2O_3 + 3H_2O\ (235°\ C).$$

$$B\ (OH)_3\ (diluted) + H_2O = [B\ (H_2O)\ (OH)_3\ ],$$

$$[B(H_2O)(OH)_3] + H_2O = [B(OH)_4]^{(-)} + H_3O^{(+)}$$

$$4B(OH)_3 + 2NaOH(\text{diluted}) = Na_2B_4O_7 + 7H_2O,$$

$$B(OH)_3 + NaOH(\text{saturated}) = Na[B(OH)_4].$$

$$B(OH)_3 + NaOH = NaBO_2 + 2H_2O(350 - 400°C).$$

$$2B(OH)_3 + Na_2CO_3 = 2NaBO_2 + CO_2 + 3H_2O(\text{above } 850°C).$$

$$B(OH)_3 + 4HF(\text{conc.}) = H[BF_4] + 3H_2O.$$

4.11 Borax

Sodium tetraborate decahydrate ($Na_2B_4O_7$, $10H_2O$)

Salts of boric acids are called borates, Borax is sodium salt of tetraboric acid and is an important borate. Borax is obtained when boric acid is boiled with soda ash(Na_2CO_3)

$$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2 + 6H_2O$$

It is also obtained by boiling finely powdered colemanite [$Ca_2B_6O_{11}$, $5H_2O$] with measured amount of Na_2CO_3 solution. On cooling it crystallizes out from the solution.

$$2Ca_2B_6O_{11} + 3Na_2CO_3 + H_2O = 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$$

Borax is now represented as $Na_2[B_4O_5(OH)_4], 8H_2O$

Th aqueous solution of borax is alkaline

$$Na_2[B_4O_5(OH)_4] + H_2O \rightarrow 2NaBO_2 + 2H_3BO_3$$

On heating it first swells losing water molecules. On further heating gives $NaBO_2$ and B_2O_3. A glossy bead is formed. When this glossy bead is heated strongly with coloured metal salts, specific colour beads are obtained. This offers a means of identifying certain metal ions like Cu, Co, Cr, Ni, Fe, etc.

$CuSO_4$ (with heat) $\rightarrow$ CuO + SO_3

CuO + B_2O_3 $\rightarrow$ $Cu(BO_2)_2$ (green in oxidisisng flame)

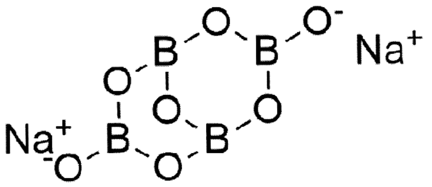


Fig. 10. structure of Borax

Chemical reactions with sodium tetraborate :

$$Na_2B_4O_7 \bullet 10H_2O = Na_2B_4O_7 + 10H_2O(380°C).$$

$$Na_2B_4O_7(diluted) + 8H_2O = 2[Na(H_2O)_4]^{(+)} + B_4O_7^{2-}$$

$$B_4O_7^{2-} + 11H_2O = 4[B(H_2O)(OH)_3] + 2OH^-$$

$$Na_2B_4O_7 + 2HCl(diluted) + 9H_2O = 2NaCl + 4[B(H_2O)(OH)_3],$$

$$Na_2B_4O_7 + 2H_2SO_4(conc.) + 5H_2O = 4B(OH)_3 \downarrow + 2NaHSO_4(40-50°C).$$

$$Na_2B_4O_7 + 7H_2O + 2NaoH(saturated) = 4Na[B(OH)_4],$$

$$Na\ B_4O_7 + 2NaOH = 4NaBO_2 + H_2O(700-750°C).$$

$$Na_2B_4O_7 + 3B_2O_3 = 2NaB_5O_8(650-700°C).$$

$$Na_2B_4O_7 + CoO = 2NaBO_2 + Co(BO_2)_2(blue)[750-800°C].$$

$$Na\ B_4O_7 + 2H_2SO_4(conc.) + 12C_2H_5OH = 4B(C_2H_5O)_3 \uparrow$$

$$+2NaHSO_4 + 7H_2O \text{ (normal temp.),}$$

4.12 Fluorocarbons

Fluoroarbons, sometimes refer to as perfluoracarbons or PFC, are strictly speaking, organofluorine compounds with the formula C_xF_y, i.e. they contain only carbon and fluorine though the terminology is not strictly followed. Compounds with the prefix perfluoro-are hydrocarbons, including those with heteroatoms, where all C-H bonds have been replaced by C-F bonds. Fluorocarbons can be perfluoroalkanes, fluoroalkenes and fluoroalkynes and perfluoroaromatic compounds. Fluorocarbons and their derivatives are used as fluoropolymers, refrigerants, solvents, and anesthetics.

❑ Chemical properties :

Due to high strength of the carbon-fluorine bond, one of the strongest in organic chemistry, Perfluoroalkanes are very stable. Its strength is a result of the electronegativity of fluorine imparting partial ionic character through partial charges on the carbon and fluorine atoms, which shorten and strengthen the bond through favorable covalent interactions and also multiple carbon-fluorine bonds increase the strength and stability of other nearby carbon-fluorine bonds on the same geminal carbon, as the carbon has a higher positive partial charge. Therefore, saturated fluorocarbons are more chemically and thermally stable than their corresponding hydrocarbon counterparts, and indeed any other organic compound. They are susceptible to attack by very strong reductants, e.g. Birch reduction and very specialized organometallic complexes. Fluorocarbons are colorless and have high density, up to over twice that of water. They are not miscible with most organic solvents (e.g., ethanol, acetone, ethyl acetate, and chloroform), but are miscible with some hydrocarbons (e.g., hexane in some cases).

❑ Preparation :

$$C_6H_{14} + 28CoF_3 \rightarrow C_6F_{14} + 14HF + 28CoF_2$$

$$2CoF_2 + F_2 \rightarrow 2CoF_3$$

Industrially, both steps are combined, fo the preparation of perfluorohexane. Synthesis is also possible by Electrochemical fluorination.

$$N(C_6H_{13})_3 + 45HF \rightarrow 3C_6F_{14} + NF_3 + 42H_2$$

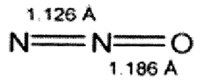
$$N(C_6H_{13})_3 + 39HF \rightarrow N(C_6F_{13})_3 + 39H_2$$

❑ Environmental and health concerns :

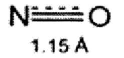
Fluoroalkanes are generally inert and non-toxic. Fluoroalkanes are not ozone depleting, as they contain no chlorine or bromine atoms, and they are sometimes used as replacements for ozonedepleting chemicals. The term fluorocarbon is used rather loosely to include any chemical containing fluorine and carbon, including chlorofluorocarbons, which are ozone depleting. Perfluoroalkanes do not bioaccumulate those used in medical procedures are rapidly excreted from the body. Low-boiling perfluoroalkanes are potent greenhouse gases, in part due to their very long atmospheric lifetime. The aluminium smelting industry has been a major source of atmospheric perfluorocarbons (tetrafluoromethane and hexafluoroethane especially), produced as by-product of the electrolysis process.

4.13 Oxides of nitrogen

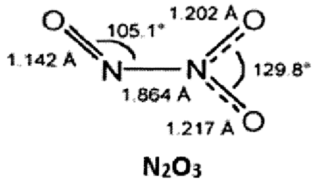
Here we shall consider the structure of N_2O, NO, NO_2, N_2O_4, N_2O_3 and N_2O_5 molecules.



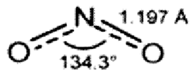
N_2O
Colourless gas



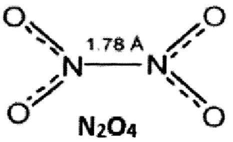
NO
Colourless gas,
Colourless liquid and
solid when pure



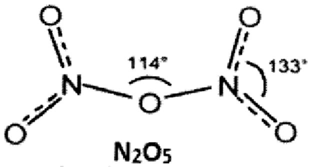
N_2O_3
Blue Solid



NO_2
Brown Gas



N_2O_4
Colourless liquid



N_2O_5
Colourless ionic solid

❑ Structure and shape of nitrous oxide molecule, N_2O :

Molecular spectroscopic study of this molecule has shown that the three atoms in this molecule are arranged in such a way that two N-atoms are directly linked together, i.e., the three atmos are arranged in the order

N—N—O and not as N–O–N. It has been suggested that the true structure of N_2O molecule is a resonance hybrid of the following structures. All these structures obey octet rule. N_2O molecule has a small value of its dipole moment equal to 0.16D.

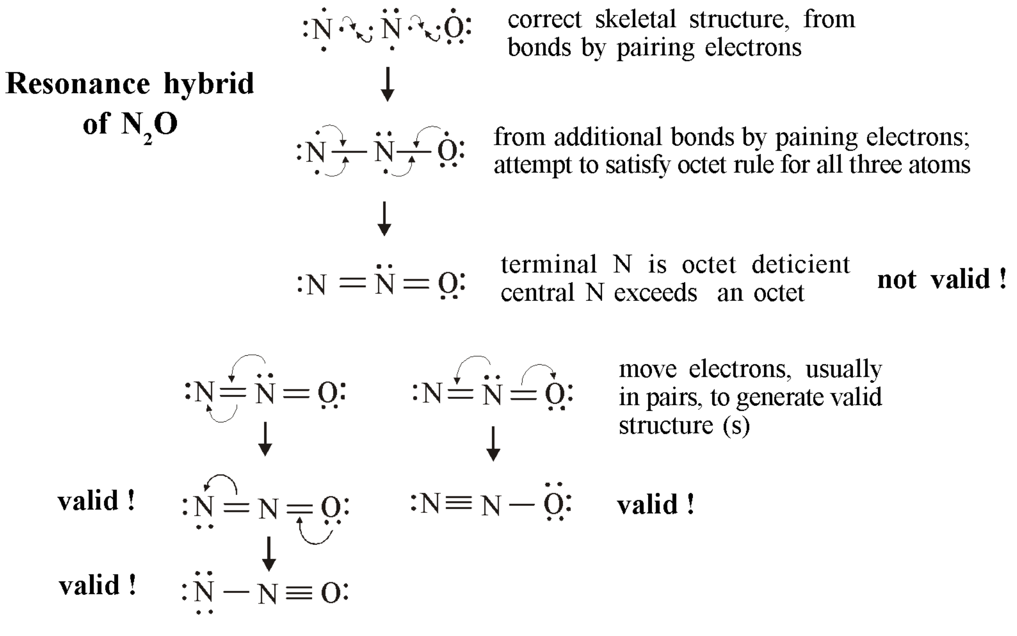


Fig. 12. Resonance hybrid of N_2O

The sweet-smelling, gaseous dinitrogen oxide is also known as nitrous oxide or, more commonly, laughing gas. This name results from the intoxicating effect of low concentrations. It is sometimes used as an anesthetic, although the high concentrations needed to cause unconsciousness make it unsuitable for more than brief operations such as tooth extraction. anesthetists have been known to become addicted to the narcotic gas. Because the gas is very soluble in fats, tasteless, and nontoxic, its major use is as a propellant in pressurized cans of whipped cream. Dinitrogen oxide is a fairly unreactive, neutral gas, although it is the only common gas other than oxygen to support combustion. For example, magnesium burns in dinitrogen oxide to give magnesium oxide and nitrogen gas :

$$N_2O(g) + Mg(s) = MgO(s) + N_2(g)$$

The standard method of preparation of dinitrogen oxide involves the thermal decomposition of ammonium nitrate. This reaction can be accomplished by heating the molten solid to about 280°C. An explosion can ensue from strong heating, however, so a safer route is to gently warm an ammonium nitrate solution that has been acidified with hydrochloric acid :

$$NH_4NO_3(aq)(H^+) \rightarrow N_2O(g) + 2\ H_2O(l)$$

❑ Nitrogen Monoxide :

One of the most curious simple molecules is nitrogen monoxide, also called nitric oxide. It is a colorless, neutral, paramagnetic gas. Its molecular orbital diagram resembles that of carbon monoxide but with one additional electron that occupies an antibonding orbital (Figure 13). Hence, the predicted net bond order is 2.5. Chemists expect molecules containing unpaired electrons to be very reactive. Yet nitrogen monoxide in a sealed container is quite stable. Only when it is cooled to form the colorless liquid or solid does it show a tendency to form a dimer, N_2O_2, in which the two nitrogen atoms are joined by a single bond. Consistent with the molecular orbital representation, nitrogen monoxide readily loses its electron from the antibonding orbital to form the nitrosyl ion, NO^+, which is diamagnetic and has a shorter $N—O$ bond length (106 pm) than that of the parent molecule (115 pm). This triple-bonded ion is isoelectronic with carbon monoxide, and it forms many analogous metal complexes.

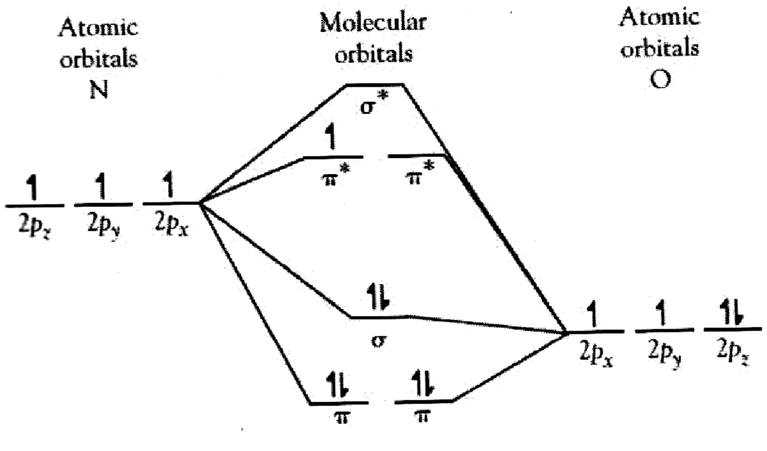


Fig. 13.Molecular orbital-energy-level diagram for the $2p$ atomic orbitals of the nitrogen monoxide molecule.

Nitrogen monoxide does show a high reactivity toward dioxygen, and once a sample of colorless nitrogen monoxide is opened to the air, brown clouds of nitrogen dioxide form :

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The molecule is an atmospheric pollutant, commonly formed as a side reaction in high compression internal combustion engines when dinitrogen adn dioxygen are compressed and spearked :

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

The easiest method for preparing the gas in the laboratory involves the reaction between copper and 50 percent nitric acid :

$$3Cu(s) + 8\ HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

However, the product is always contaminated by nitrogen dioxide. This contaminant can be removed by bubbling the gas through water, because the nitrogen dioxide reacts rapidly with water. A lack of nitrogen monoxide is implicated as a cause of high blood pressure, whereas septic shock, a leading cause of death in intensive care wards, is ascribed to an excess of nitrogen monoxide. The gas appears to have a function in memory and in the stomach. Male erections have been proved to depend on production of nitrogen monoxide, and there are claims of important roles for nitrogen monoxide in female uterne contractions. One questions still to be answered concerns the life span of these molecules, considering the ease with which they react with oxygen gas.

❑ Dinitrogen Trioxide :

Dinitrogen trioxide, the least stable of the common oxides of nitrogen, is a dark blue liquid that decomposes above 230°C. It is prepared by cooling a stoichiometic mixture of nitrogen monoxide and nitrogen dioxide :

$$NO(g) + NO_2(g) \rightarrow N_2O_3(l)$$

Dinitrogen trioxide is the first of the acidic oxides of nitrogen. In fact, it is the acid anhydride of nitrous acid. Thus, when dinitrogen trioxide is mixed with water, nitrous acid is formed, and when it is mixed with hydroxide ion, the nitrite ion is produced :

$$N_2O_3(l) + H_2O(l) \rightarrow 2HNO_2(aq)$$

$$N_2O_3(l) + 2OH^-(aq) \rightarrow 2NO_2^-(aq) + H_2O(l)$$

❑ Nitrogen Dioxide and Dinitrogen Tetroxide :

These two toxic oxides coesist in a state of dynamic equilibrium. Low temperatures favor the formation of the colorless dinitrogen tetroxide, whereas high temperatures favor the formation of the dark red-brown nitrogen dioxide :

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

colorless red-brown

At the normal boiling point of 218C, the mixture contains 16 percent nitrogen dioxide, but the proportion of nitrogen dioxide rises to 99 percent at 1358C. Nitrogen dioxide is prepared by reacting copper metal with concentrated nitric acid :

$$Cu(s) + 4HNO_3(l) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

It is also formed by heating havy metal nitrates, a reaction that produces a mixture of nitrogen dioxide and oxygen gases :

$$Cu(NO_3)_2(s)(\text{with heat}) \rightarrow CuO(s) + 2NO_2(g) + 1/2O_2(g)$$

And, of course, it is formed when nitrogen monoxide reacts with dioxygen :

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Nitrogen dioxide is an acid oxide, dissolving in water to give nitric acid and nitrous acid :

$$2NO_2(g) + H_2O(l) \xrightarrow{\Delta} HNO_3(aq) + HNO_2(aq)$$

This potent mixture of corrosive, oxidizing acids is produced when nitrogen dioxide, formed from automobile pollution, reacts with rain. It is a major damaging component of urban precipitation. Nitrogen dioxide is a V-shaped molecule with an O—N—O angle of 134°, an angle slightly larger than the true trigonal planar angle of 120°. Because the third bonding site is occupied by a single electron rather than by a lone pair, it is not unreasonable for the bond angle to be opened up (Figure 14A). The oxygen-nitrogen bond length indicates a 1.12 bond order, like that in the NO_2 half of dinitrogen trioxide. It is useful to compare the p bonding in nitrogen dioxide to that in carbon dioxide. The linear structure of carbon dioxide allows both sets of *p* orbitals that are at right angles to the bonding direction to overlap and participate in p bonding. In the bent nitrogen dioxide molecule, the *p* orbitals are still at right angles to the bonding direction, but in the plane of the molecule, they are skewed with respect to one another and cannot overlap to form a p system. As a result, the only p bond that can form is at right angles to the plane of the molecule

(Figure 15.13). However, this single p bond is shared between two bonded pairs; hence, each pair has one-half a p bond. The O—N—O bond angle in the dinitrogen tetroxide molecule is almost identical to tht in the nitrogen dioxide molecule (Figure 14.C). Though dinitrogen tetroxide has an abnormally long (and hence weak) nitrogen notrogen bond at 175 pm, it is not as weak as the N—N bond in dinitrogen trioxide. The N—N bond is formed by the combination of the weakly antibonding s orbitals of the two NO_2 units (overlap of the sp^2 hybrid orbitals containing the "odd" electrons, in hybridization terminology). The resulting N—N bonding molecular orbital will have correspondingly weak bonding character. In fact, the N—N bond energy is only about 60 kj/mol.

❑ Dinitrogen Pentoxide :

This colorless, solid, deliquescent oxide is the most strongly oxidizing of the nitrogen oxides. It is also strongly acidic, reacting with water to form nitric acid :

$$N_2O_5(s) + H_2O(l) \rightarrow 2HNO_3(aq)$$

In the liquid and gas phases, the molecule has a structure related to those of the other dinitrogen oxides, N_2O_3 and N_2O_4, except that an oxygen atom links the two NO_2 units (Figure 14.D). The two pairs of *p* electrons provide a half π bond to each oxygen-nitrogen pair. Of more interest, however, is the bonding in the solid phase. In fact, the crystal structure consists of alternating nitryl cations, NO_2^+ and nitrate anions NO_3^- (Figure 14.E & F).

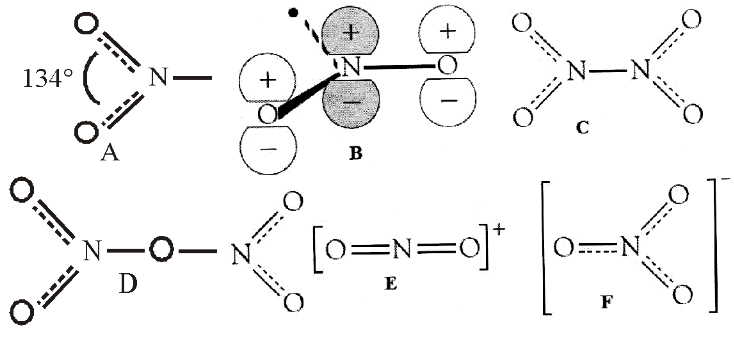


Fig. 14. A : The nitrogen dioxide molecule; B : Overlap of the *p* orbitals at right angles to the molecular plane of nitrogen Dioxide; C : The dinitrogen tetroxide molecule; D : The dinitrogen pentoxide molecule; E : Nitryl cation; F : Nitrate anion

4.14 Oxyacids of nitrogen :

❑ Nitrous Acid and Nitrites :

Nitrous acid is a weak acid that is unstable except in solution. It can be prepared by mixing a metal nitrite and a solution of a dilute acid at 0°C in a double replacement reaction. Barium nitrite and sulfuric acid give a pure solution of nitrous acid, because the barium sulfate that is formed has a very low solubility :

$$Ba(NO)_2(aq) + H_2SO_4(aq) \rightarrow 2HNO_2(aq) + BaSO_4(s)$$

The shape of the nitrous acid molecule is shown in Fig. 15(A). Even at room temperature, disproportionation of aqueous nitrous acid occurs to give nitric acid and bubbles of nitrogen monoxide. The latter reacts rapidly with the oxygen gas in the air to produce brown fumes of nitrogen dioxide :

$$3HNO_2(aq) \rightarrow HNO_3(aq) + 2NO(g) + H_2O(l)$$
$$2NO(g) + O_2(g) + 2NO_2(g)$$

Nitrous acid is used as a reagent in organic chemistry; for example, diazonium salts are produced when nitrous acid mixed with an organic amine (in this case, aniline, $C_6H_5NH_2$) :

$$C_6H_5NH_2(aq) + HNO_2(aq) + HCl(aq) \rightarrow [C_6H_5N_2]^+Cl^-(s) + 2H_2O(l)$$

The diazonium salts are used, in turn, to synthesize a wide range of organic compounds. The nitrite ion is a weak oxidizing agent; hence, nitrites of metals in their lower oxidation states cannot be prepared. For example, nitrite will oxidize iron(II) ion to iron (III) ion and is simultaneously reduced to lower oxides of nitrogen.

The ion is V shaped as a result of the lone pair on the central nitrogen, the bond angle being 115° compared with 134° for nitrogen dioxide. The N—O bond length is 124 pm, longer than that in nitrogen dioxide (120 pm) but still much shorter than the N—O single bond (143 pm). Sodium nitrite is a commonly used meat preservative, particularly in cured meats such as ham, hot dogs, sausages, and bacon. The nitrite ion inhibits the growth of bacteria, particularly *Clostridium botulinum*, an organism that produces the deadly botulism toxin. Sodium nitrite is also used to treat packages of red meat, such as beef. Blood exposed to the air rapidly produces a brown color, but shoppers much prefer their meat purchases to look bright red. Thus, the meat is treated with sodium nitrite; the nitrite ion is reduced to nitrogen monoxide, which then reacts with the hemoglobin to form a very stable bright red compound. It is true that the nitrite will prevent bacterial growth in this circumstance as well, but these days, the meat is kept at temperatures low enough to inhibit bacteria. To persuade shoppers to prefer brownish rateher than red meat will require a lot of re-education. Now that all meats are treated with sodium nitrite, there is concern that the cooking process will cause the nitrite ion to react with amines in the meat to produce nitrosamines, compounds containing the—NNO functional group. These compounds are known to be carcinogenic. However, as long as preserved meats are consumed in moderation, it is generally believed that the cancer risk is minimal.

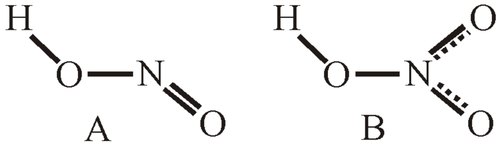


Fig. 15(A) Nitrous & (B) Nitric Acid

❑ Nitric Acid and Nitrates :

A colorless, oily liquid when pure, nitric acid is extremely hazardous. It is obviously dangerous as an acid, but very strong oidizing agent, making it a potential danger in the presence of any oxidizable material. The acid, which boils at 183°C, is usually slightly yellow as a result of a light-induced decomposition reaction :

$$4HNO_3(aq) \rightarrow 4NO_2(g) + O_2(g) + 2H_2O(l)$$

When pure, liquid nitric acid is almost completely nonconducting. A small proportion ionizes as follows (all species exist in nitric acid solvent) :

$$2HNO_3(l) \rightarrow H_2NO_3^+ + NO_3^-$$
$$H_2NO_3^+ \rightarrow H_2O + NO_2$$
$$H_2O + HNO_3 \rightarrow H_3O^+ + NO_3^-$$

giving an overall reaction of $3HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2NO_3^-$

The nitryl cation is important in the nitration of organic molecules; for example, the conversion of benzene, C_6H_6, to nitrobenzene, $C_6H_5NO_2$, an important step in numerous organic industrial processes. Concentrated nitric acid is actually a 70 percent solution in water (corresponding to a concentration of about 16 mol/L), whereas "fuming nitric acid," an extremely powerful oxidant. It is a red solution of nitrogen dioxide in pure nitric acid. Even when dilute, it is such a strong oxidizing agent that the acid rarely evolves hydrogen when mixed with metals; instead, a mixture of nitrogen oxides is produced and the metal is oxidized to its cation The terminal

O—N bonds are much shorter (121 pm) than the O—N bond attached to the hydrogen atom (141 pm). This bond length indicates multiple bonding between the nitrogen and the two terminal oxygen atoms. In addition to the electrons in the s system, there are four electrons involved in the O—N—O π system, two in a bonding orbital and two in a nonbonding orbital, a system giving a bond order of 1.5 for each of those nitrogen-oxygen bonds.

4.15. Oxides of phosphorus

Phosphorus (III) oxide P_4O_6, is obtained by burning white phosphorus in a restricted supply of O_2. It is a colorless, volatile solid (mp 297 K, bp 447 K)(Fig. 16) the P-O bond distances (165 pm) are consistent with single bonds, and the angles P-O-P and O-P-O are 128° and 99° respectively. The oxide is soluble in diethyl ether or benzene, but reacts with cold water.

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

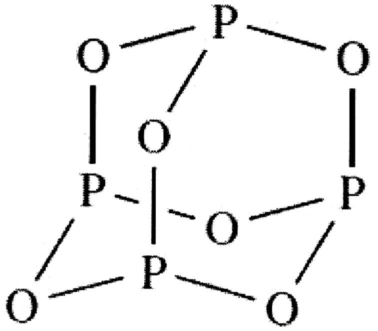


Fig. 16. Molecular structure of P_4O_6

Each P atom in P_4O_6 carries a lone pair of electrons and P_4O_6 can therefore act as a Lewis base. Adducts with one and two equivalents of BH_3 have been reported, but the reaction of P_4O_6 with one equivalent of Me_2SBH_3 followed by slow crystallization from toluene solution at 244K gives $P_8O_{12}(BH_3)_2$ rather than an adduct of P_4O_6. The solid state structure confirms that dimerization of P_4O_6 has occurred through P-O bond cleavage and reformation of P-O bonds between monomeic units. Free P_8O_{12} has not, to date, been isolated.

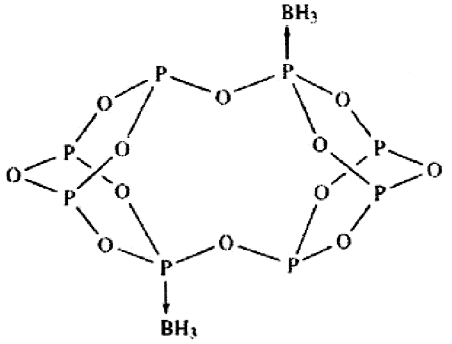


Fig. 17. Dimer of P_4O_6

The most important oxide of phosphorus is P_4O_{10} [phosphorus (*V*) oxide], commonly called phosphorus pentoxide. It can be made directly from P_4 or by oxidizing P_4O_6. In the vapour phase, phosphorus (*V*) oxide contains P_4O_{10} molecules. The *P-O* bridge and *P-O* terminal bond distances are 160 and 140 pm. When the vapour is condensed rapidly, a volatile and extremely hygroscopic solid is obtained which also contains P_4O_{10} molecules. If this solid is heated in a closed vessel for several hours and the melt maintained at a high temperature before being allowed to cool, the solid obtained is macromolecular. Three polymorphic forms exist at ordinary pressure and temperature, with the basic building block being unit 14.59; only three of the four *O* atoms are available for interconnecting the PO_4 units via *P-O-P* bridges. Phosphorus (*V*) oxide has a great affinity for water, and is the anhydride of the wide range of oxoacids. It is used as a drying agent.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

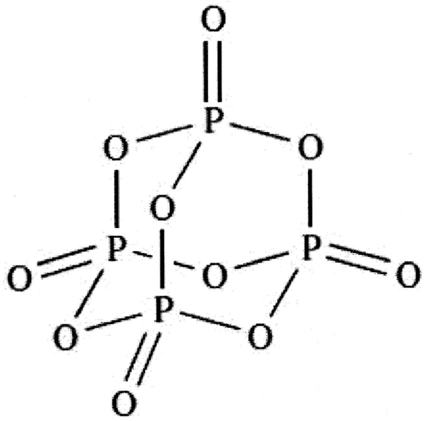
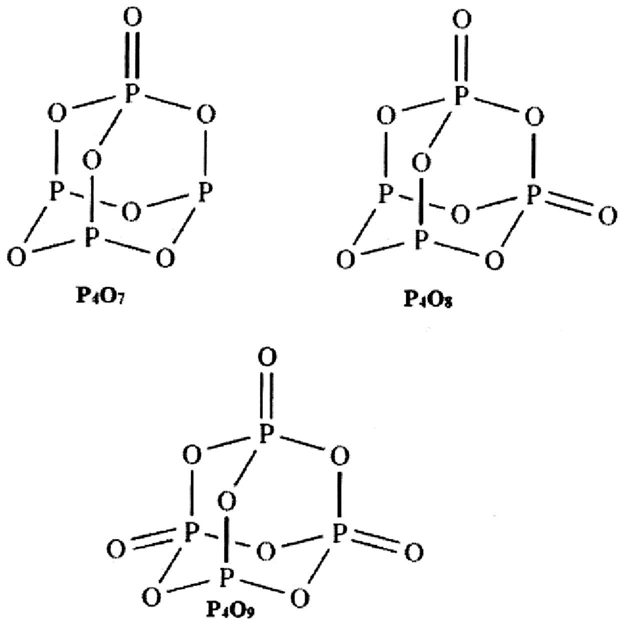


Fig. 18. Molecular structure of P_4O_{10}

Three other oxides of phosphorus, P_4O_7, P_4O_8 and P_4O_9 have structures that are related to those of P_4O_6 and P_4O_{10}.



P_4O_7 P_4O_8 P_4O_9

Fig. 19. Structures of P_4O_7, P_4O_8 and P_4O_9

These oxides are mixed *P*(III) & *P*(V) species, each centre bearing a terminal oxo group being oxidized to *P*(V). For example, P_4O_8 is made by heating P_4O_6 in a sealed tube at 710 *K*, the other product being red phosphorus.

4.16 Phosphorus oxo-acids and phosphates

Table 1 lists selected oxoacids of phosphorus. This is an important group of compounds, but the acids are difficult to classify in a straightforward manner. It should be remembered that the basicity of each acid corresponds to the number of OH-groups, and not smimly to the total number of hydrogen atoms, e.g. H_3PO_3 and H_3PO_2 are dibasic and monobasic respectively. Diagnostic absorptions in the IR spectra of H_3PO_3 and H_3PO_2 confirm the presence of P-H bonds; the P-attached hydrogens do not ionize in aqueous solution.

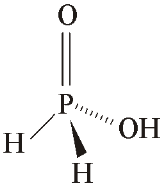
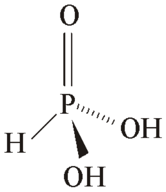
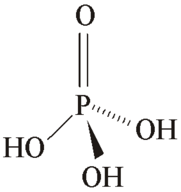
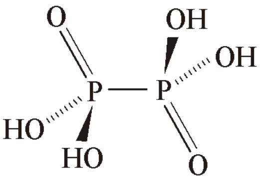
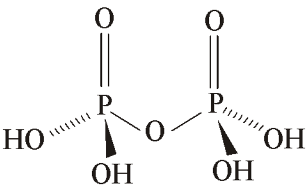
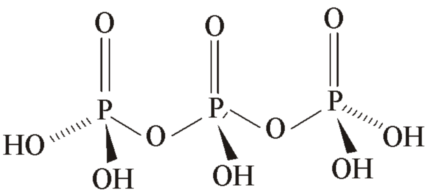
Formula	Name	Structure	pK_a values
H_3PO_2	Phosphinic acid (hypophosphorous acid)		$pK_a = 1.24$
H_3PO_3	Phosphonic acid (phosphorous acid)		$pK_a(1) = 2.00$; $pK_a(2) = 6.59$
H_3PO_4	Phosphinic acid (orthophosphoric acid)		$pK_a(1) = 2.21$; $pK_a(2) = 7.21$; $pK_a(3) = 12.67$
$H_4P_2O_6$	Hypophosphoric acid		$pK_a(1) = 2.2$; $pK_a(2) = 2.8$; $pK_a(3) = 7.3$; $pK_a(4) = 10.0$
$H_4P_2O_7$	Diphosphoric acid (pyrophosphoric acid)		$pK_a(1) = 0.85$; $pK_a(2) = 1.49$; $pK_a(3) = 5.77$; $pK_a(4) = 8.22$
$H_5P_3O_{10}$	Triphosphoric acid		$pK_a(1) \leq 0$ $pK_a(2) = 0.89$; $pK_a(3) = 4.09$; $pK_a(4) = 6.98$; $pK_a(5) = 9.93$

Table : 1 Oxoacids of Phosphorus.

❑ Phosphinic acid (H_3PO_2) :

The reaction of white phosphorus with aqueous alkali produces the phosphinate (or hypophosphite) ion, $[H_2PO_2]^-$. By using $Ba(OH)_2$ as alkali, preciptating the Ba^{2+} ions as $BaSO_4$, and evaporating the aqueous solution, white deliquescent crystals of H_3PO_2 can be obtained. In aqueous solution, H_3PO_2 is a fairly strong monobasic acid

$$H_3PO_2 + H_2O = [H_3O]^+ + [H_2PO_2]^-$$

Phosphinic acid and its salts are reducing agents, and $NaH_2PO_2.H_2O$ is used industrially in a non-electrochemical reductive process which plates nickel onto, for example, steel. When heated, H_3PO_2 disproportionates according to the products being determined by reaction temperature.

$$3H_3PO_2 \rightarrow PH_3 + 2H_3PO_3 \text{ or } 2H_3PO_2 \rightarrow PH_3 + H_3PO_4$$

❑ Phosphonic acid (H_3PO_3) :

Phosphonic acid (commonly called phosphorous acid) may be crystallized from the solution obtained by adding ice-cold water to P_4O_6 or PCl_3. Pure H_3PO_3 forms colourless, deliquescent crystals (mp 343 K) and in the solid state, molecules of the acid (Table 1) are linked by hydrogen bonds to form a three dimensional network. In aqueous solution, it is dibasic.

$$H_3PO_3(aq) + H_2O = [H_3O]^+ + [H_2PO_3]^-$$
$$[H_2PO_3]^- + H_2O = [H_3O]^+ + [HPO_3]^{2-}$$

Salts containing the $[HPO_3]^{2-}$ ion are called phosphonates. Although the name 'phosphite' remains in common use, it is a possible source of confusion since esters of type $P(OR)_3$ are also called phosphites, e.g. $P(OEt)_3$ is triethlphosphite. Phosphonic acid is a reducing agent, but disproportionate when heated.

$$4H_3PO_3(470K) \rightarrow PH_3 + 3H_3PO_4$$

❑ Hypophosphoric acid ($H_4P_2O_6$) :

The reaction between red phosphorus and $NaCl$ or $NaClO_2$ yields $Na_2H_2P_2O_6$, which can be converted in aqueous solution into the dihydrate of the free acid which is best formulated as $[H_3O]_2[H_4P_2O_6]$. Dehydration using P_4O_{10} gives $H_4P_2O_6$. All four terminal P-O bonds are of equal length (157 pm), and the bonding description shown in Fig. 20.

$$H_4P_2O_6 + H_2O \rightarrow H_3PO_3 + H_3PO_4$$

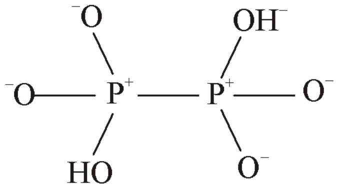


Fig. 20. Structure of $H_4P_2O_6$

❑ Phosphoric acid, H_3PO_4 and its derivatives :

Phosphoric acid is made from phosphate rock or by hydration of P_4O_{10}

$$Ca_3(PO_4)_2 + 3H_2SO_4(conc.) \rightarrow 2H_3PO_4 + 3CaSO_4$$

The qure acid forms deliquescent, colourless crystals (mp 315*K*). It has a molecular structure with *P-OH* and *P-O* bond distances of 157 and 152 pm; this difference is significantly less than in P_4O_{10} and is the result of extensive hydrogen bonding in the crystalline state which links H_3PO_4 molecules into a layered network. On standing, crystalline H_3PO_4 rapidly forms a viscous liquid. In this and in the commercially available 85% (by weight with water) acid, extensive hydrogen bonding is responsble for the syrupy nature of the acid. In dilute aqueous solutions, acid molecules are hydrogen-bonded to water molecules rather than to each other. When H_3PO_4 is heated at 510*K*, it is dehydrated to diphosphoric acid. Comparison of the structures of these acids (Table 1) shows that water is eliminated with concomitant *P-O-P* bridge formation. Further heating yields triphosphoric acid.

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

$$H_3PO_4 + H_4P_2O_7 \rightarrow H_5P_3O_{10} + H_2O$$

RESOURCES, ENVIRONMENTAL AND BLOLOGICAL

Phosphate fertilizers : essential to crops but are they damaging our lakes ?

Worldwide demand for fertilizers is enormous and world consumption is increasing at a rate of between 2% and 3% per year. Phosphorus is an esential plant nutrient and up to 90% (depending on country) of phosphate rock that is mixed is consumed in the manufacture of phosphorus containing fertilizers. Insoluble phosphate rock is treated with concentrated H_2SO_4 to generate soluble super phosphate fertilizers containing $Ca(H_2PO_4)_2$ mixed with $CaSO_4$ an other sulfates; reaction between phosphate rock and H_3PO_4 gives triple superphosphate, mainly $Ca(H_2PO_4)_2$. Ammonium phosphate fertilizers are valuable sources of both N and P. Environmentalists are concerned about the effects of phosphates and polyphosphates from fertilizers and detergents have on the natural balance of populations. Phosphates in run-off water which flows into lakes contribute to the ecessive growth of algae (eutrophication), the presence of which depletes the lakes of O_2, thereby affecting fish and other water-life. However, the issue of phosphates in lakes is not clear-cut: recent field studies indicate adding phosphates to acid lakes (the result of acid rain pollution) stimulates plant growth, which in leads to production of $[OH]^-$, which neutralizes excess acid.

4.17 Oxides of sulphur

The most important oxides of sulfur are SO_2 and SO_3, but there are also a number of unstable oxides. Among these S_2O and S_8O can be made by the following reactions.

$$SOCl_2 + Ag_2S \xrightarrow{430K} S_2O + 2AgCl$$

$$HS_7H + SOCl_2 \rightarrow S_8O + 2HCl$$

$$S_8[\text{with } CF_3C(O)OOH] \rightarrow S_8O$$

Sulfur dioxide is manufactured on a large scale by burning sulfur (the most important process) or H_2S, by roasting sulfide ores, or reducing $CaSO_4$. Desulfurization processes to limit SO_2 emissions and reduce acid rain are now in use.

$$FeS_2 + 11O_2 \xrightarrow{\Delta} Fe_2O_3 + 8SO_2$$

$$CaSO_4 + C \xrightarrow{\Delta} SO_2 + CO$$

$$Na_2SO_3 + 2HCl(conc.) \longrightarrow SO_2 + 2NaCl + H_2O$$

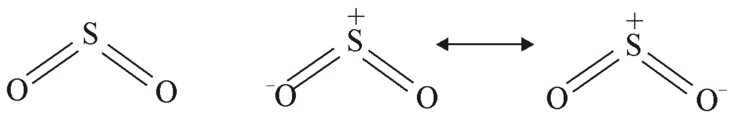


Fig. 1. Resonance structure of SO_2

Properties	**SO_2**	**SO_3**
Physical appearance and general characteristics	Colourless, dense gas: pungent smell	Volatile white solid, or a liquid
Melting point / K	198	290
Boiling point / K	263	318
$\Delta_{vap}H°(bp)$ /kJ mol^{-1}	24.9	40.7
$\Delta_f H°(298\ K)$ / kJ mol^{-1}	$-296.8(SO_2, g)$	$-441.0(SO_3, 1)$
Dipole momentn / D	1.63	0
S–O bond distance / pm	143	142
$\angle O$–S–O / deg	119.5	120

Table. 2.Properties of SO_2 and SO_3

$$SO_2 + X_2 \rightarrow SO_2X_2\ [X = F, Cl]$$

$$SO_2 + MF \xrightarrow{258K} M^+(SO_2F)^-\ \ [M = K, Rb, Cs]$$

The oxidation of SO_2 by atmospheric O_2 is very slow, but is catalysed by V_2O_5. This is the first step in the Contact process for the manufacture of sulfuric acid; operating conditions are crucial since equilibrium shifts further towards the left-hand side as the temperature is raised, although the yield can be increased somewhat by use of high pressures of air. In practice, the industrial catalytic proces operates at 750K and achieves conversion factors > 98%.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

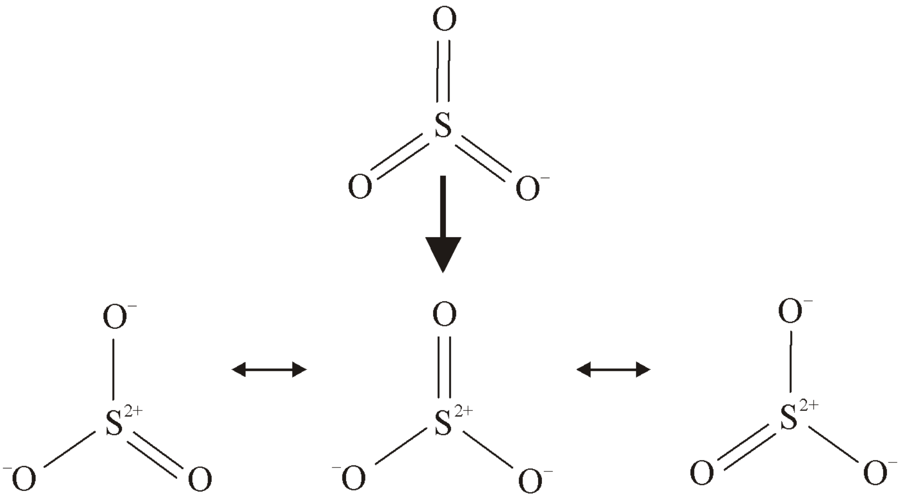
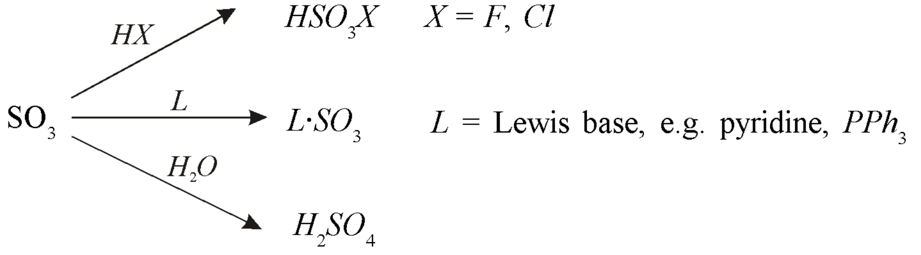


Fig. 22. Resonance structure of SO_3

Sulfur trioxide is very reactive and representative reactions are given in scheme.



4.18 Oxoacids of sulphur

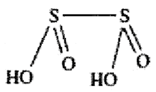
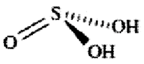
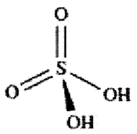
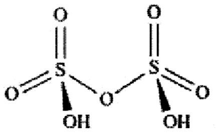
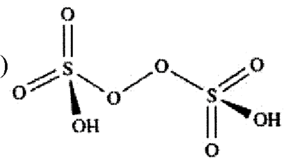
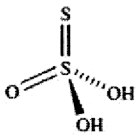
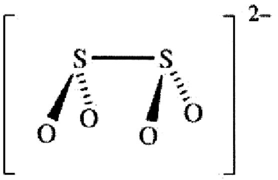
Formula	Name	Structure	pK$_a$ values (298*K*)
$H_2S_2O_4$	Dithionous acid (tetraoxodisulfuric acid)		$pK_a(1) = 0.35; pK_a(2) = 2.45$
H_2SO_3	Sulfurous acid (trioxodisulfuric acid)		$pK_a(1) = 1.82; pK_a(2) = 6.9$
H_2SO_4	Sulfuric acid (tetraoxosulfuric acid)		$pK_a(2) = 1.92$
$H_2S_2O_7$	Disulfuric acid (μ-oxo-hexaoxodisulfuric acid)		$pK_a(1) = 3.1$
$H_2S_2O_8$	Peroxodisulfuric acid (μ-peroxo-hexaoxodisulfuric acid)		$pK_a(1) = 0.6; pK_a(2) = 1.74$
$H_2S_2O_3$	Thiosulfuric acid (trioxothiosulfuric acid)		

Fig. 23. Oxacids of sulphur

❑ Dithionous acid ($H_2S_2O_4$) :

Dithionite is prepared by reduction of sulfite in aqueous solution by *Zn* or *Na* amalgam and possesses eclipsed structure



$$2[SO_3]^{-2} + 2H_2O + 2e^- \rightleftharpoons 4[OH]^- + [S_2O_4]^{2-}$$

$$E^o = -1.12V$$

In aqueous solutions, $[S_2O_4]^{2-}$ is oxidized by air but in the absence of air, it undergoes according to the following reaction.

$$[S_2O_4]^{2-} + H_2O \rightarrow [S_2O_3]^{2-} + 2[HSO_3]^-$$

❑ Sulfurous and disulfurous acids (H_2SO_3 and $H_2S_2O_5$) :

Neither 'sulfurous acid' nor 'disulfurous acid' has been isolated as a free acid. Salts containing the sulfite ion, $[SO_3]^{2-}$ are well established (e.g. Na_2SO_3 and K_2SO_3 are comercially available) and are quite good reducing agents. Applications of sulfites include those as food preservatives, e.g. an additive in wines. The $[SO_3]^{2-}$ ion has a trigonal pyramidal structure with delocalized bonding ($S–O$ = 151 pm, $\angle OSO$ = 106°). Although the $[HSO_3]^-$ ion exists in solution, and slts such as $NaHSO_3$ (used as a bleaching agent) may be isolated. Evaporation of a solution of $NaHSO_3$ which has been saturated with SO_2 results in the formation of $Na_2S_2O_5$. The $[S_2O_5]^{2-}$ ion is the only known derived anion of disulfurous acid.

❑ Dithionic acid, $H_2S_2O_6$:

Dithionic acid is another sulfur oxoacid that is only known in aquous solution (in which it behaves as a strong acid) or in the form of salts containing the dithionate, $[S_2O_6]^{2-}$ ion. Such salts can be isolated as crystalline solids. The dithonate ion can be prepared by controlled oxidation of $[SO_3]^{2-}$

$$MnO_2 + 2[SO_3]^{2-} + 4H^+ \rightarrow Mn^{2+} + [S_2O_6]^{2-} + 2H_2O$$

❑ Sulfuric Acid (H_2SO_4)

Hydrogen sulfate is an oily, dense liquid that freezes at 10°C. Concentrated sulfuric acid is a water mixture with an acid concentration of 18 mol/*L*. Hydrogen sulfate mixes with water very exothermically. For this reason, it should be slowly added to water, not the reverse process, and the mixture should be stirred continuously. The molecule contains a tetrahedral arrangement of oxygen atoms around the central sulfur atom (Figure 16.18). The short bond lengths and the high bond energies suggest that there must be double bond character in the sulfur bonds to each terminal oxygen atom.

❑ Reactions of Sulfuric Acid :

We usually think of sulfuric acid as just an acid, but infact it can react in five different ways :

☐ Dilute sulfuric acid is used most often as an acid. It is a strong, diprotic acid, forming two ions, the hydrogen sulfate ion and the sulfate ion :

$$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

The first equilibrium lies far to the right, but the second one, less so. Thus, the predominant species in a solution of sulfuric acid are the hydronium ion and the hydrogen sulfate ion.

☐ Sulfuric acid can also act as a dehydrating agent. The concentrated acid will remove the elements of water from a number of compounds. For example sugar is converted to carbon and water. This exothermic reactions is spectacular :

$$C_{12}H_{22}O_{11}(s) + H_2SO_4(l) \rightarrow 12C(s) + 11H_2O(g) + H_2SO_4(aq)$$

The acid serves this function in a number of important organic reactions. For example, addition of concentrated sulfuric acid to ethanol produces ethene, C_2H_4, or ethoxyethane, $(C_2H_5)_2O$, depending on the reaction conditions :

$$C_2H_5OH(l) + H_2SO_4(l) \rightarrow C_2H_5OSO_3H(aq) + H_2O(l)$$

$$C_2H_5OSO_3H(aq) \rightarrow H_2SO_4(aq)[\text{excess acid}] + C_2H_4(g)$$

$$C_2H_5OSO_3H(aq) \rightarrow C_2H_5OH(l) \rightarrow (C_2H_5)_2O(l) + H_2SO_4(aq)[\text{excess ethanol}]$$

☐ Although sulfuric acid is not as strongly oxidizing as nitrie acid, if it is hot and concentrated, it will function as an oxidizing agent. For example, hot concentrated sulfuric acid reacts with copper metal to give the copper(II) ion, and the sulfuric acid itself is reduced to sulfur dioxide and water :

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e$$

$$2H_2SO_4(l) + 2e \rightarrow SO_2(g) + 2H_2O(l) + SO_4^{2-}(aq)$$

☐ Sulfuric acid can act as a sulfonating agent. The concentrated acid is used in organic chemistry to replace a hydrogen atom by the sulfonic acid group ($-SO_3H$) :

$$H_2SO_4(l) + CH_3C_6H_5(l) \rightarrow CH_3C_6H_4SO_3H(s) + H_2O(l)$$

☐ The Industrial Synthesis of Sulfuric Acid :

Sulfuric acid is synthesized in larger quantities than any other chemical. All synthetic routes use sulfur dioxide, and in some plants this reactant is obtained directly from the flue gases of smelting processes. However, in North America most of the sulfur dioxide is produced by burning molten sulfur in dry air :

$$S(l) + O_2(g) \rightarrow SO_2(g)$$

It is more difficult to oxidize sulfur dioxide further. There is a kinetic barrier to the formation of sulfur trioxide. Thus, an effective catalyst must be uded to obtain commercially useful rates of reaction. We also need to ensure that the position of equilibrium is to the right side of the equation. To accomplish this, we invoke the Le Chatelier principle, which predicts that an increase in pressure will favor the side of the equation with the fewer moles of gas—in this case, the product side. This reaction is also exothermic; thus, the choice of temperature must be high enough to produce a reasonable rate of reaction, even though these conditions will result in a decreased yield. In the *contact process*, pure, dry dulfur dioxide and dry air are passed through a catalyst of vanadium (*V*) oxide on an inert support. The gas mixture is heated to between 400° and 500°c, which is the optimum temperature for conversion to sulfur trioxide with a reasonable yield at an acceptable rate :

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5, \Delta} 2SO_3(g)$$

Sulfur trioxide reacts violently with water. However, it does react more controllably with concentrated sulfuric acid itself to give pyrosulfuric acid, $H_2S_2O_7$:

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

The pyrosulfuric acid is then diluted with water to produce an additional mole of sulfuric acid :

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

All steps in the process are exothermic. In fact, the entire process of converting elemental sulfur to sulfuric acid produces 535 kJ/mol of heat. An essential feature of any sulfuric acid plant is effective utilization of this waste heat, either as direct heating for some other industrial process or in the production of electricity. This process is associated with two potentil pollution problems. First, some of the sulfur dioxide escapes. Legislation in most pollution-conscious countries limits emissions to less than 0.5 percent of the processed gas. Second, despite use of the pyrosulfate route, some of the sulfuric acid escapes as a fine mist. Newer plants have mist eliminators to reduce this problem. Use of the sulfuric acid varies from country to country. In the United States, the vast majority of acid is employed in the manufacture of fertilizers, such as the conversion of the insoluble calcium phosphate to the more soluble calcium dihydrogen phosphate :

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(aq) \rightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4(s)$$

or the production of ammonium sulfate fertilizer :

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

In Europe, however, a higher proportion of the acid is used for manufcturing other products such as paints, pigments, and sulfonate detergents. There is an increasing interest in trying to reclaim waste sulfuric acid. At present, the cost of removing contaminants and concentrating the dilute acid is greater than the cost of preparing the acid from sulfur. However, recovery is now preferred over dumping. If the acid is pure but too dilute, then pyrosulfuric acid is added to increase the concentration of acid to usable levels. For contaminated acid, high-temperature decomposition produces gaseous sulfur dioxide, which can be removed and used to synthesize fresh acid :

$$2H_2SO_4(aq) \xrightarrow{\Delta} 2SO_2(g) + 2H_2O(l) + O_2(g)$$

❑ Peroxosulfuric acids, $H_2S_2O_8$ and H_2SO_5

The reaction between cold, anhydrous H_2O_2 and chlorosulfonic acid yields peroxomonosulfuric acid, H_2SO_5, and peroxodisulfuric acid, $H_2S_2O_8$.

$$H_2O_2 \xrightarrow[-HCl]{ClSO_3H} H_2SO_5 \xrightarrow[-HCl]{ClSO_3H} H_2S_2O_8$$

$$H_2S_2O_8 + H_2O \xrightarrow{273K} H_2SO_5 + H_2SO_4$$

Both acids are crystalline solids at 298 K. Few salts of H_2SO_5 are known, but those of $H_2S_2O_8$ are easily made by anodic oxidation of the corresponding sulfates in acidic solution at low temperatures and high current densities. Peroxodisulfates are strong oxidizing agents, and oxidations are often catalysed by Ag^+, with $Ag(II)$ species being formed as intermediates. In acidic solutions, $[S_2O_8]^{2-}$ oxidizes Mn^{2+} to $[MnO_4]^-$, and Cr^{3+} to $[Cr_2O_7]^{2-}$

$$[S_2O_8]^{2-} + 2e \rightleftharpoons 2[SO_4]^{2-} \quad E^0 = +2.01V$$

4.19 Sulphur-nitrogen compounds

There are several sulfur-nitrogen compounds. Some of these are of interest because their shapes and bond lengths cannot be explained in terms of simple bonding theory. The classic example is tetrasulfur tetranitride, S_4N_4. Unlike the crown structure of octasulfur, tetrasulfur tetranitride has a closed, basket-like shape, with multiple bonding around the ring and weak bonds cross-linking the pairs of sulfur atoms. Of much more interest, however, is the polymer $(SN)x$, commonly called polythizyl. This bronze-colored, metallic-looking compound was first synthesized in 1910, yet it was not until 50 years later that an investigation of its properties showed it to be an excellent electrical conductor. In fact, at very low temperatures (0.26 K), it becomes a superconductor. There is an intense interest in making related nonmetallic compounds that have metallic properties, both because of their potential for use in our everyday lives and because they may help us develop the theory of metals and superconductivity.

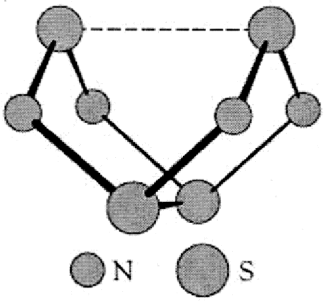


Fig. 24. The tetrasulfur tetranitride molecule.

$$6S_2Cl_2 + 16NH_3 \xrightarrow{CCl_4;\ 320K} S_4N_4 + 12NH_4Cl + S_8$$

$$2[(Me_3Si)_2N]_2S + 2SCl_2 + 2SO_2Cl_2 \rightarrow S_4N_4 + 8Me_3SiCl + 2SO_2$$

$$S_4N_4 + 6[OH]^- + 3H_2O \rightarrow [S_2O_3]^{2-} + 2[SO_3]^{2-} + 4NH_3$$

4.20 Chlorine oxides

Like nitrogen, there are chlorine oxides in which chlorine has every possible odd oxidation state. All of these oxides are thermodynamically unstable but kinetically stable. As a result of this and a low activation energy of decomposition, they are very unstable and have a tendency to explode. However, there are two oxides of importance, both of which have unpaired electrons; that is, they are free radicals. The first of these is chlorine monoxide, which is environmentally important even though it exists only in the upper atmosphere. The second is chlorine dioxide. Chlorine dioxide is a strong oxidizing agent, and it is becoming increasingly important as a disinfectant.

❑ Chlorine Monoxide :

Many species that are too unstabl to exist in significant concentrations at ambient temperature and pressure play important roles in atmospheric chemistry. Another important atmospheric molecule is chlorine monoxide, *ClO*. Chlorine monoxide is a key stratospheric species responsible for causing the "ozone hole," a decrease in *UV*-filtering ozone concentration over the south and, to a lesser extent, north polar regions during their respective spring seasons. The saga is believed to begin with the buildup of chlorine molecules, predominantly from the breakdown of *CFCs* during the dark winter in the isolated air mass over the Antarctic. With the arrival of spring, sunlight causes the weakly bonded chlorine molecules (bond energy 242 *Kj/mol*) to dissociate into chlorine atoms :

$$Cl_2(g) \xrightarrow{h\upsilon} 2Cl(g)$$

The chlorine atoms react with ozone (trioxygen) to give chlorine monoxide and dioxygen :

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$$

If the reaction terminated here, the damage to the oxone layer would be minimal. However, the chlorine monoxide takes part in a reaction cycle that regenerates the chlorine atoms, causing this process to be catalytic. That is, the chlorine atom acts as a catalyst for the conversion of ozone to dioxygen. The first step in this process is the combination of two chlorine monoxide radicals to form the *ClOOCl* dimer molecule. However, dissociation would immediately occur unless the to radicals simultaneously collide with a third body, *M*. It is the role of the species *M* to remove the excess energy. The identity of *M* is any molecule that can remove the energy—usually dinitrogen, N_2, or dixygen, O_2, as these are the most common atmospheric molecules.

$$2ClO(g) + M(g) \rightarrow Cl_2O_2(g) + M^*(g)$$

Sunlight again becomes involved, this time to fission the Cl_2O_2 molecule asymmetrically :

$$Cl_2O_2(g) \xrightarrow{h\upsilon} ClOO(g) + Cl(g)$$

The *ClOO* species is very unstable and rapidly breaks down to give a chlorine atom and a dioxygen molecule :

$$ClOO(g) \rightarrow Cl(g) + O_2(g)$$

Then the chlorine atmos are again available to react with ozone molecules. It is this catalytic cycle that results in the severe polar ozone depletion.

❑ Chlorine Dioxide

Chlorine dioxide, ClO_2, is a yellow gas that condnses to a deep red liquid at 11°C. The compound is quite soluble in water, giving a fairly stable, green solution. Being a free radical species, chlorine dioxide is paramagnetic, like nitrogen dioxide. Yet unlike nitrogen dioxide, it shows no tendency to dimerize. The chlorine-oxygen bond length is only 140 pm, much shorter than the 170 pm that is typical for a single bond length, and it is very close to that of a typical chlorine-oxygen double bond. Chlorine dioxide, usually diluted with dinitrogen or carbon dioxide for safety, is a very powerful oxidizing agent. For example, to bleach flour to make white bread, chlorine dioxide is 30 times more effective than dichlorine. Large quantities of chlorine dioxide also are used as dilute aqueous solutions for bleaching wood pulp to make white paper. In this role, it is preferred over dichlorine, because chlorine dioxide bleaches without significant formation of hazardous chlorinated wastes. Another advantage of chlorine dioxide is that, unlike dichlorine, it does not attack the cellulose structure, so it preserves the mechanical strength of paper. Similarly, chlorine dioxide is being used increasingly for domestic water treatment, because, in this context too, it does not chlorinate hydrocarbon pollutants that are present in the water to any measurable extent. Chlorine dioxide was used to destroy any anthrax spores contaminating congressional offices during the anthrax-letter scare in 2001. Thus, even though pure chlorine dioxide is explosive, it is of major industrial importance. About 106 tonnes are produced every year worldwide. It is difficult to determine the exact production total, because the gas is so hazardous that it is generally produced in comparatively small quantities at the sites where it is to be used. The synthetic reaction involves the reduction of chlorine in the +5 (ClO_3^-) oxidation state by chlorine in the –1(Cl^-) oxidatin state in very acid conditions to give chlorine in the +4(ClO_2) and 0(Cl_2) oxidation states :

$$2ClO_3^{2-}(aq) + 4H^+(aq) + 2Cl^-(aq) \rightarrow 2ClO_2(g) + Cl_2(g) + 2H_2O(l)$$

Sulfur dioxide is added to reduce (and remove) the dichlorine gas to chloride ion, the sulfur dioxide being simultaneously oxidized to sulfate :

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$

$$SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

4.21 Chlorine oxyacids

Chlorine forms a series of oxyacids and oxyanions for each of its positive odd oxidation states from 11 to 17. The shapes of the ions (and related acids) are based on a tetrahedral arrangement around the chlorine atom (Figure 25). The short chlorine-oxygen bonds in each of the ions indicate that multiple bonding must be present, possibly involving some contribution to the π bonding by the full *p* orbitals on the oxygen atoms and empty *d* orbitals on the chlorine atom.

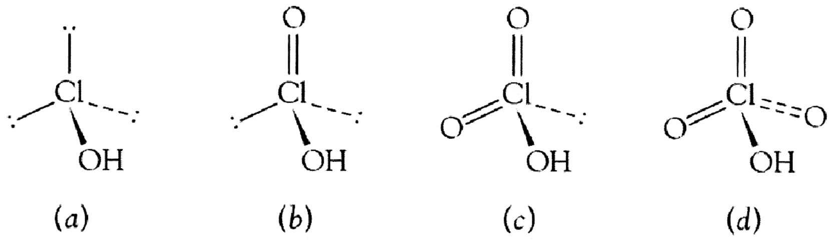


Fig. 25. A possible representation of the bonding in (*a*) hypochlorous acid, (*b*) chlorous acid, (*c*) chloric acid, and (*d*) perchloric acid.

Acid strength increases as the numebr of oxygen atoms increases. Thus, hypochlorous acid is very weak; chlorous acid, weak; chloric acid, strong; and perhloric acid, very strong.

❑ Hypochlorous acid and the hypochlorite ion :

Hypochlorous acid and hydrochloric acid are formed when dichlorine is dissolved in cold water :

$$Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl_2(aq) + HClO(aq)$$

Hypochlorous acid is a very weak acid; thus, solutions of hypochlorites are very basic as a result of the hydrolysis reaction :

$$ClO_2(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$$

Hypochlorous acid is a strong oxidizing agent and, in the process, is reduced to chlorine gas ;

$$2HClO(aq) + 2H^+(aq) + 2e \rightarrow Cl_2(g) + 2H_2O(l) \qquad E^\circ = +1.64V$$

The hypochlorite ion, however, is a weaker oxidizing agent that is usually reduced to the chloride ion :

$$ClO^-(aq) + H_2O(l) + 2e \rightarrow Cl^-(aq) + 2OH^-(aq) \quad E^\circ = +0.89V$$

It is this oxidizing (bleaching and bactericidal) power that renders the hypochlorite ion useful. The two compounds of industrial importance are sodium hypochlorite and calcium hypochlorite. Sodium hypochlorite is only stable in solution, not in the solid phase; thus, calcium hypochlorite is used as a solid source of hypochlorite ion. Sodium hypochlorite solution is used in commercial bleach solutions, and for bleaching and decolorization of wood pulp and textiles. Both sodium and calcium hypochlorites are used in disinfection. Calcium hypochlorite is also used as a disinfectant in dairies, breweries, food processing, and bottling plants and in domestic mildew removers.

☐ **Perchloric Acid :**

The strongest simple acid of all is perchloric acid. The pure acid is a colorless liquid that can explode unpredictably. As a result of its oxidizing nature and high oxygen content, contact with organic materials such as wood or paper causes an immediate fire. Concentrated perchloric acid, usually a 60 percent aqueous solution, is rarely used as an acid but is far more often used as a very powerful oxidizing agent, for example, to oxidize metal alloys to the metal ions so that they can be analyzed. Special perchloric acid fume hoods should be used when these oxidations are performed. Cold dilute solutions of perchloric acid are reasobably safe.

4.22 Interhalogen compounds and polyhalide ions

There is an enormous number of combinations of pairs of halogens forming interhalogen compounds and polyhalide ions. The neutral compounds fit the formulas XY, XY_3, XY_5, and XY_7, where X is the halogen of higher atomic mass and Y, that of lower atomic mass. All permutations are known for XY and XY_3, but XY_5 is only known where Y is fluorine. Thus, once again, it is only with fluorine that the highest oxidaton states are obtained. The formula XY_7, in which X would have the oxidation state of +7, is found only in IF_7. The common argument for the lack of chlorine and bromine analogs is simply that of size : only the iodine atom is large enough to accommodate seven fluorine atoms. The interhalogen compounds are of particular interest to inorganic chemists because of their geometries. The shapes of the compounds all follow the VSEPR rules, even iodine heptafluoride, IF_7, which has the rare pentagonal bipyramidal shape of a seven-coordinate species. All of the interhalogens can be prepared by combination reactions of th constituent elements. For example, heating iodine and fluorine in a 1:7 ratio gives iodine heptafluoride, IF_7 :

$$I_2(g) + 7F_2(g) \rightarrow 2IF_7(g)$$

Bubbling chlorine gas through an aqueous solution of iodide ion gives a brown-black solution of iodine, then dark brown iodine monochloride, and finally pale yellow iodine trichloride :

$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$

$$Cl_2(aq) + I_2(aq) \rightarrow 2ICl(aq)$$

$$Cl_2(aq) + ICl(aq) \rightarrow ICl_3(aq)$$

The simple interhalogens such as iodine monochloride have colors intermediate between those of the constituents. However, the melting points and boiling points of the interhalogens are slightly higher than the mean values of the constituents because the interhalogen molecules are polar. More important, the chemical reactivity of an interhalogen compound is usually similar to that of the more reactive parent halogen. To chlorinate an element or compound, it is often more convenient to use solid iodine monochloride than chlorine gas, although sometimes the nonhalogen atom in the two products has different oxidation states. This outcome can be illustrated for the chlorination of vanadium :

$$V(s) + 2Cl_2(g) \rightarrow VCl_4(l)$$

$$V(s) + 3ICl(s) \rightarrow VCl_3(s) + 3/2I_2(s)$$

When we add the brown solution of the interhalogen to the unsaturated fat, decolorization occurs as the halogens add across the double bond :

$$-CH = CH - +ICl \rightarrow -CH(I) - CH(Cl) -$$

When a permanent brown color remains, the reaction has been completed. The only interhalogen compound produced on an industrial scale is chlorine trifluoride, a liquid that boils at 11°C. It is a convenient and extremely powerful fluorinating agent as a result of its high fluorine content and highbond polarity. It is particularly useful in the separatin of uranium from most of the fission products in used unclear fuel. In aqueous solution, interhalogen molecules are hydrolyzed to the hydrohalic acid of the more electronegative halogen and the hypohalous acid of the less electronegative halogen. For example :

$$BrCl(g) + H_2O(l) \rightarrow HCl(aq) + HBrO(aq)$$

The halogens also form polyatomic ions. Iodine is the only halogen to readily form polyhalide anions by itself. The triiodide ion, (I_3^-) is important becuase its formation provides a means of "dissolving" molecular iodine in water by using a solution of the iodide ion :

$$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

The ion is linear and has equal iodine-iodine bond lengths of about 293 pm; these bonds are slightly longer than the single bond in the diiodine molecule (272 pm). There are many other polyiodide ions, including I_5^- and I_7^- but these are less stable than the triiodide ion. There also are a wide variety of interhalogen cations and anions, for example, the dichloroiodine ion, ICl_2^+ and the tetrachloroiodate ion, ICl_4^- .

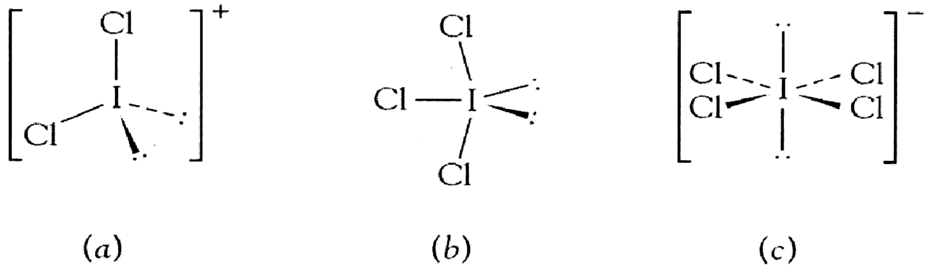


Fig. 26. (*a*) The dichloroidine ion, ICl_2^+ (*b*) the iodine trichloride olecule, ICl_3; and (*c*) the tetrachloroiodate ion, ICl_4^-

4.23. Cyanide ion as a pseudo-halide ion

The best example of a pseudo-halide ion is cyanide. Not only does it behave very much like a halide ion but also the parent pseudo-halogen, cyanogen, $(CN)_2$, exists. The cyande ion resembles a halide ion in a remarkable number of ways :

☐ Salts of cyanide ion with silver, lead(II), and mercury(I) are insoluble, as are those of chloride, bromide, and iodide ions. For example :

$$CN^-(aq) + Ag^+(aq) \rightarrow AgCN(s)$$

$$[\text{compared to } Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)]$$

☐ Like silver chloride, silver cyanide reacts with ammonia to give the diamminesilver(I) cation.

$$AgCN(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + CN^-(aq)$$

$$[\text{compared to } AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)]$$

☐ The cyanide ion is the conjugate base of the weak acid hydrocyanic acid, *HCN*, parallel to fluoride ion and hydrofluoric acid :

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$[\text{compared to } HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

☐ The cyanide ion forms numerous complex ions with transition metals, such as $[Cu(CN)_4]^{2-}$, which is similar to its chloride analog, $[CuCl_4]^{2-}$.

☐ Cyanide ion can be oxidized to the parent pseudo-halogen, cyanogen, similar to teh oxidation of halides to halogens. The parallel is particularly close with iodide ion since they can both be oxidized by very weak oxidizing agents such as the copper(II) ion :

$$2Cu^{2+}(aq) + 4CN^-(aq) \rightarrow 2CuCN(s) + (CN)_2(g)$$

$$[\text{compared to } 2Cu^{2+}(aq) + 41^-(aq) \rightarrow 2CuI(s) + I_2(S)]$$

☐ Cyanogen reacts with base to give the cyanide and cyanate ions :

$$(CN)_2(aq) + 2OH^-(aq) \rightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$$

$$[\text{compared to } Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)]$$

☐ Cyanogen forms pseudo-interhalogen compounds such as ICN in the same way that halogens form interhalogen compounds such as iodine monochloride, ICl.

4.24 Basic properties of iodine

Iodine is a non-metallic, dark-gray/purple-black, lusturous, solid element. Iodine is the most electropositive halogen and the least reactive of the halogens even if it can still form compounds with many elements. Iodine sublime easily on heating to give a purple vapour. Iodin dissolves in some solvents, such as carbon tetrachloride and it is only slightly soluble in water.

☐ Environmental effects of iodine :

Iodine in ar can combine with water particles and precipitate into water or soils. Iodine in soils will combine with organic matter and remain in the same place for a long time. Plants that grow on these soils may absorb iodine. Cattle and other animals will absorb iodine when they eat these plants.

Iodine in surface water will vaporize and re-enter the air as a result. Humans also add iodine gas to the air, by burning coal or fuel oil for energy. But the amount of iodine that enters the air through human activity is fairly small compared to the amount that vaporize from the oceans. Iodine may be radioactive. The radioactive isotopes are formed naturally during chemical reaction in the atmosphere. Most radioactive isotopes of iodine have very short half-lives and will reshape into stable iodine compounds quickly. However, there is one radioactive form of iodine that has a half-live of millions of years and that is seriously harmful to the environment. This isotope enters the air from nuclear power plants, where it is formed during uranium and plutonium processing. Accidents in nuclear power plants have caused the release of large amounts of radioactive iodine into air.

4.25 Xenon fluorides

Xenon forms three fluorides :

$$Xe(g) + F_2(g) \rightarrow XeF_2(s)$$
$$Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$$
$$Xe(g) + 3F_2(g) \rightarrow XeF_6(s)$$

The product depends on the mole ratios of teh reactants and on the exact reaction conditions of temperature and pressure, although very high partial pressures of difluorine are needed to form the xenon hexafluoride. All three xenon fluorides are white solids and are stable with respect to dissociation into elements at ordinary temperatures; that is, they have negative free energies of formation at 25°C. As noted earlier, it is not necessary to invoke any novel concepts to explain the bonding; in fact, the three compounds are isoelectronic with well-established iodine polyfluoride anions. All the fluorides hydrolyze in water; for example, xenon difluoride is reduced to xenon gas :

$$2XeF_2(s) + 2H_2O(l) \rightarrow 2Xe(g) + O_2(g) + 4HF(l)$$

Xenon hexafluoride is first hydrolyzed to xenon oxide tetrafluoride, $XeOF_4$, which in turn is hydrolyzed to xenon trioxide :

$$XeF_6(s) + H_2O(l) \rightarrow XeOF_4(l) + 2HF(l)$$

$$XeOF_4(l) + 2H_2O(l) \rightarrow XeO_3(s) + 4HF(l)$$

The fluorides are strong fluorinating agents, For example, xenon difluoride can be used to fluorinate double bonds in organic compounds. It is a very "clean" fluorinating agent, in that the inert xenon gas can be easily separated from the required product :

$$XeF_2(s) + CH_2 = CH_2(g) \rightarrow CH_2F - CH_2F(g) + Xe(g)$$

Furthermore, a fluoride in which the other element is in its highest possible oxidation state can be produced by using xenon fluorides as reagents. Thus, xenon tetrafluoride will oxidize sulfur tetrafluoride to sulfur hexafluoride :

$$XeF_4(s) + 2SF_4(g) \rightarrow 2SF_6(g) + Xe(g)$$

4.26 Xenon oxides

Xenon forms two common oxides : xenon trioxide and xenon tetraoxide. Xenon trioxide is a colorless, deliquescent silid that is quite explosive. The oxide is an extremely strong oxidizing agent, although its rections are often kinetically slow. Because of its lone pair, it is a trigonal pyramidal molecule. Xenon trioxide reacts with dilute base to give the hydrogen xenate ion, $HXeO_4^-$. However, this ion is not stable, and disproportionation to xenon gas and the perxenate ion, XeO_6^{4-} occurs.

$$XeO_3(s) + OH^-(aq) \rightarrow HXeO_4^-(aq)$$

$$2HXeO_4^-(aq) + 2OH^-(aq) \rightarrow XeO_6^{4-}(aq) + Xe(g) + O_2(g) + 2H_2O(l)$$

Perxenates are among the most powerful oxidizing agents known, which is not really surprising considering that the xenon is in the formal oxidation state of +8. For example, they rapidly oxidize manganese(II) ion to permanganate, themselves being reduced to the hydrogen xenate ion :

$$XeO_6^{4-}(aq) + 5H^+(aq) + 2e^- \rightarrow HXeO_4^-(aq) + 2H_2O(l)$$

$$4H_2O(l) + Mn^{2+}(aq) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^-$$

Xenon tetroxide is prepared by adding concentrated sulfuric acid to solid barium perxenate :

$$Ba_2XeO_6(s) + 2H_2SO_4(aq) \rightarrow 2BaSO_4(s) + XeO_4(g) + 2H_2O(l)$$

4.27 Clathrate compounds

The inert gases argon, krypton and xenon form solid compounds with certain organic such as phenol, hydroquionone, $C_6H_4(OH)_2$ under pressure. In these compounds the inert gases are enclosed into the crystal lattices of the organic molecules. These compounds are known as clathrates. (Latin : clathrote = enclosed or protected by cross bars or grating). These are also referred to as cage compounds. In clathrates the noble gases are trapped into the cavities of crystal lattices of certain organic and inorganic compounds. The organic or inorganic substance having the cavities of crystal lattices is called the 'host' while the atom of noble gases entrapped in it is called the 'guest'.

☐ Conditions for the formation of clathrates :

(i) The crystal lattice of the host component should contain cavities of appropriate size. (ii) Size of the guest component should be such that it should fit in the cavities of the host component without bringing any atoms closer together than which corresponds to the vander Wals radi of the atoms.

❑ Types and preparation of clathrates

(i) **Gas hydrates.** Clathrate of *Ar*, *Kr* and *Xe* in which water molecule is the host component are called gas hydrates. These have been prepared by solidifying water in presence of *Ar*, *Kr* and *Xe*. The general formula of these is 5.75 $H_2O.G$ where G = *Ar*, *Kr* or *Xe*. No gas hydrate of He and Ne has yet been prepared even under high pressure due to their small size and highly volatile nature. The stability of the gas hydrates increases as the atomic number of the 'guest' atom increases. In noble gas hydrates the water molecules are linked together by hydrogen bonds, leaving roughly spherical voids which are occupied by gas atoms.

(ii) **Quinol calthrates.** Clathrates of *Ar*, *Kr* and *Xe* have been obtained by dissolving any of these in aqueous saturated solution of quinol under a pressure of 10-40 atmospheres followed by slow cooling. These compounds are crystalline and can be stored for several years. However, when heatd or disolved in water, the gas atoms and quinol remains behind as such. Quinol molecules which form the cavities are held together by H-bonds.

(iii) **Phenol and β-hydroquionone clathrates :** Clathrates given by phenol and β-hydroquinone with *Ar*, *Kr* and *Xe* have been prepared by dissolving any of these gases in phenol or β-hydroquinone followed by show crystallisation. These clathrates are also quite stable.

❑ Reasons for the stability of clathrates

The stability of clathrates is due to the reasons (i) The guest molecules are tightly held in the cavities of the host molecules. (ii) Th guest within the cages are at minimum potential energy, The guest molecules can be made to leave the cavities in host lattices only when the forces holding the molecular cages together are overcome. The forces can be overcome either by heating the crystals, or by dissolving the crystals in a suitable solvent such as alcohol.

❑ Uses of clathrates

(i) In the separation of noble gases, e.g., *Ne* can be separated from *Ar*, *Kr* and *Xe*, since *Ne* is the only gas that does not form a clathrate with quinol. (ii) *Kr*-85 clathrate is used as a safe and useful source of beta radiations which are used for measuring thickness of gauges. (iii) *Xe*-133 clathrate provides a compact source for gamma radiations. (iv) Clathrates play an important role in some physiological actions.

4.28 Silicones

Silicones, more correctly called polysiloxanes, constitute an enormous family of polymers, and they all contain a chain of alternating silicon and oxygen atoms. Attached to the silicon atoms are pairs of organic goups, such as the methyl goup, $-CH_3$. The structure of this simplest silicone is shown in Fig. 27, where the number of repeating units, n, is very large. To synthesize this compound, chloromethane, CH_3Cl, is passed over a coper-silicon alloy at 300°C. A mixture of compounds is produced, including $(CH_3)_2SiCl_2$:

$$2CH_3Cl(g) + Si(s) \xrightarrow{\Delta} (CH_3)_2SiCl_2(l)$$

Water is added, causing hydrolysis :

$$(CH_3)_2SiCl_2(l) + 2H_2O(l) \rightarrow (CH_3)_2Si(OH)_2(l) + 2HCl(g)$$

The hydroxo compound then polymerizes, with loss of water :

$$n(CH_3)_2Si(OH)_2(l) \rightarrow [-O - Si(CH_3)_2-]n(l) + H_2O(l)$$

Silicones are used for a wide variety of purposes. The liquid silicones are more stable than hydrocarbon oils. In addition, their viscosity changes little with temperature, whereas the viscosity of hydrocarbon oils changes dramatically with temperature. Thus, silicones are used as lubricants and wherever inert fluids are needed, for example, in hydraulic braking systems. Silicones are very hydrophobic, hence, they are used in water-repellent sprays for shoes and other items. By the cross-linking of chains, silicone rubbers can be produced. Like the silicone oils, the rubbers show great stability to high temperature and to chemical attack. Their multitudious uses include the face-fitting edges for snorkel adn scuba masks. The rubbers also are very useful in medical applications, such as transfusion tubes. However, silicone gels have attained notoriety in their role as a breast implant material. While sealed in a polymer sack, they are believed to be harmless. The major problem arises when the container walls leak or break. The silicone gel can then diffuse into surrounding tisues. The chemical inertness of silicones turns from a benefit to problem, because the body has no mechanism for breaking down the polymer molecules. Many medical personnel believe that these alien gel fragments trigger the immune system, thereby causing a number of medical problems. The advantages of the silicone polymers over carbon-based polymers result from several factors. First, the silicon-oxygen bond in the backbone of the molecule is stronger than the carbon-carbon bond in the organic polymers (452 *kJ/mol*, compared to about 346 *kJ/mol*), making the silicon-based polymers more resistant to oxidation at high temperatures. It is for this reason that high-temperature oil baths always utilize silicone oils, not hydrocarbon oils. The absence of substituent on the oxygen atoms in the chain and the wider bond angle (*Si–O–Si* is 143° compared with 109° for *C–C–C*) results in the greater flexibility of a silicone polymer.

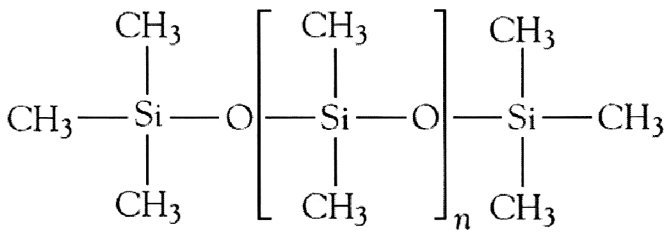


Fig. 27. Structure of the simplest silicone

It is interesting to note that Silicones are water repellent while alkyl substituent chlorisilanes readily undergo hydrolysis. It is believed that in silicones '*Si-O*' bonds have some double bond character. The π bonds are formed between filled *p* orbitals of '*O*' and empty d orbitals of Si. These π bonds make the *d* orbitals unavailable for nucleophilic attack by H_2O

4.29 Phosphazenes

Phosphazenes are a group of *P*(*V*)/*N*(*III*) compounds featuring chain or cyclic structures, and are oligomers of the hypothetical NPR_2. The reaction of PCl_5 with NH_4Cl in a chlorinated solvent (e.g. C_6H_5Cl) gives a mixture of colourless solids of formula $(NPCl_2)$n in which the predominant species have $n = 3$ or 4. The compounds $(NPCl_2)_3$ and $(NPCl_2)_4$ are readily separated by distillation under reduced pressure.

$$nPCl_5 + nNH_4Cl = (NPCl_2)_n + 4nHCl$$

Above reaction is the traditional method of preparing $(NPCl_2)_3$, but yields are typically 50%.

Improved yields can by obtained by using the following reaction. Yields of $(NPCl_2)_3$ can be optimized by ensuring a slow rate of addition of PCl_5 to $N(SiMe_3)_3$ in CH_2Cl_2.

$$3N(SiMe_3)_3 + 3PCl_5 \rightarrow (NPCl_2)_3 + 9Me_3SiCl$$

The bromo derivative is obtained by heating PBr_5 with NH_4Br and the fluoro derivative is obtained from chloride on treatment with NaF in acetonitrile.

$$(NPCl_2)_n + 2nNaF \rightarrow [PNF_2]_n + 2nNaCl$$

Alkoxy group can be introduced in the polymer by replacing Cl.

$$(NPCl_2)_n + 2nNaOR \rightarrow [NP(OR)_2]_n + 2nNaCl$$

The iodide derivative is not known yet.

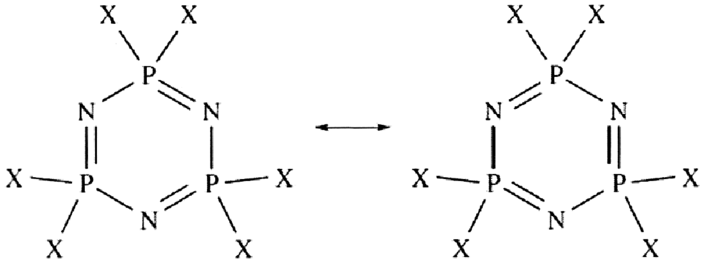


Fig. 28. Phosphazene structure

Traditional bonding descriptions for the 6-membered rings have involved N(2p)–P(3d) overlap, both in and perpendicular to the plane of the P_3N_3-ring. However, this model is not consistent with current opinion that phosphorus makes little or no use of its 3d orbitals. Fig. 29 provides another resonance form for a 6-membered cyclophosphazene, and is consistent with the observed P-N bond equivalence, as well as the observation that the N and P atoms are subject to attack by electrophiles and nucleophiles, respectively. Theoretical results support the highly polarized $P^{\delta+}$–$N^{\delta-}$ bonds and the absence of aromatic character in the P_3N_3-ring.

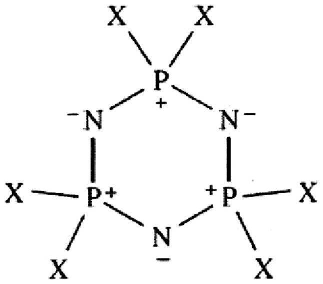


Fig. 29. Resonating structure of phosphazene.

When excess PCl_5 is refluxed with NH_4Cl, linear polymers are obtained They are rubbery in nature elastic and thermally stable. A long chain polymer $[PNCl_2]_n$ of molecular weight of 20,000 is obtained. These rubbery substance are called inorganic rubber.

Use : It is used as plasticiser and as catalysts in the manufacture of silicones.

4.30 Silicates

About 95 percent of the rocks of the Earth's crust are silicates, and there is a tremendous variety of silicate minerals. The simplest silicate ion has the formula SiO_4^{4-}; zirconium silicate, $SrSiO_4$, the gemstone zircon, being one of the few minerals to contain this ion. Silicates ar generally very insoluble, as one might expect of rocks that have resisted rain for millions of years. The one common exception is sodium silicate, which can be prepared by reacting solid silicon dioxide with molten sodium carbonate :

$$SiO_2(s) + 2Na_2CO_3(l) \xrightarrow{\Delta} Na_4SiO_4(s) + 2CO_2(g)$$

A concentrated solution of sodium (ortho) silicate is called water glass, and it is extermely basic as a result of hydrolysis reactions of the silicate antion. Before modern refrigeration became available, the water glass solution was used to preserve eggs, the soft porous shell of calcium carbonate being replaced by a tough, impervious layer of calcium silicate that seals in the egg contents :

$$2CaCO_3(s) + SiO_4^{4-}(aq) \rightarrow Ca_2SiO_4(s) + CO_3^{2-}(aq)$$

The silicates are classified on the basis of the way by which the $(SiO_4)^{4-}$ tetrahedral units are linked together.

❑ **Orthosilicates :** These contain discrete tetrahedral SiO_4^{4-} unit. Example : Phenacite $[Be_2SiO_4]$, Zircon $[ZrSiO_4]$

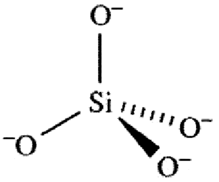


Fig. 30. Orthosilicate

❑ **Pyrosilicates :** These contain $(Si_2O_7)^{6-}$ units formed by joining two tetrahedral units through one oxygen atom. Ex. Thortveitite $(Sc_2Si_2O_7)$

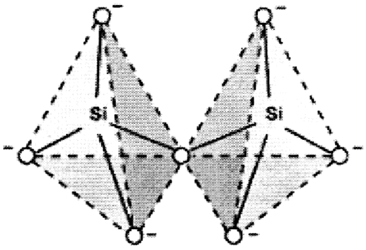


Fig. 31. Pyrosilicates

❑ **Cyclic Silicates :** Tetrahedra sharing two 'O' atoms to form a ring structures with either $[Si_3O_9]^{6-}$ or $[Si_6O_{18}]^{12-}$ anions. Ex. Wollastonite, $Ca_3[Si_3O_9]$

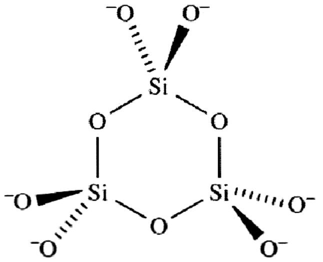


Fig. 32. Cyclic silicates

❑ **Chain Silicates :** An open chain linear polymeric structure is possible if the tetrahedra share two 'o' atoms. This contains $(SiO_3)_n^{2n-}$. Example : Pyroxenes ($MgSiO_3$)

❑ **Three dimensional Silicates :** Sharing all four corners of tetrahedral gives an infinite three dimensional frame work. Example : Silica $[(SiO_2)_n]$

❑ **Sheet Silicates :** An infinite two dimensional structure with empirical formula $(Si_2O_5)_n^{2n-}$ is obtained when SiO_4 tetrahydra share three cornrrs. Example : Mica Sheet.

4.31 Summary

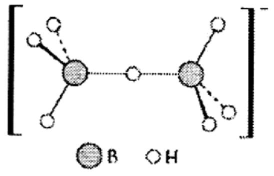
- The diagonal relationship is only chemically significant for three pairs of elements : lithium and magnesium, beryllium and aluminum, and boron and silicon.
- First member of each group of s– and p–block elements shows anomalous behavior.
- Allotropy is the property of some chemical elements to exist in two or more different forms.
- Catenation is the linkage of atoms of the same element into longe chains. Catenation occurs most readily in carbon.
- Over 50 neutral boranes, (B_nH_m) and an even larger number of borane anions, $(B_nH_m^{x-})$, are known.
- Borazine is called 'inorganic benzene' due to similarities with Benzene.
- Both carbon and boron nitride form diamond and graphite-like structures.

- Boric acid is prepared by reacting minerals such as borax ($Na_2B_4O_7.10H_2O$), with strong acids like HCl
- On heating it first swells losing water molecules. On further heating gives $NaBO_2$ and B_2O_3, a glossy bead is formed.
- Fluorocarbons (C_xF_y) and their derivatives are used as fluoropolymers, refrigerants, solvents, and anesthetics.
- Nitrous oxide is known as laughing gas.
- Dinitrogen trioxide is the least stable of the common oxides of nitrogen.
- "*Nitrogen Dioxide and Dinitrogen Tetroxide*"—These two toxic oxides coexist in a state of dynamic equilibrium.
- Phosphorus forms two common oxides, phosphorus(III) oxide (or tetraphosphorus hexoxide), P_4O_6, and phosphorus(V) oxide (or tetraphosphorus decaoxide), P_4O_{10}.
- Phosphorus oxoacids are oxoacids of phosphorus where Phosphorus exhibits oxidation states from + 1 to + 5
- The most important oxides of sulfur are SO_2 and SO_3, but there are also a number of unstable oxides.
- Dithionite is prepared by reduction of sulfite in aqueous solution by Zn or Na amalgam.
- Sulfuric acid can act as a dehydrating agent, sulfonating agent.
- The chlorine atoms react with ozone (trioxygen) to give chlorine monoxide and dioxygen.
- Hypochlorous acid and hydrochloric acid are formed when dichlorine is dissolved in cold water.
- An interhalogen compound is a molecule which contains two or more different halogen atoms (fluorine, chlorine, bromine, iodine, or astatine)
- The pseudohalogens are polyatomic analogues of halogens, whose chemistry, resembling that of the true halogens.
- Xenon forms two common oxides : xenon trioxide and xenon tetroxide.
- Inert gases enclosed crystal lattices of the organic molecules are known as clathrates.

- Silicone is a chain of alternating silicon atoms and oxygen atoms, combined with carbon, hydrogn, and sometimes other elements.
- Phosphazenes are a group of *P*(*V*)/*N*(*III*) compounds featuring chain or cyclic structures, and are oligomers of the hypothetical NPR_2
- Silicate is any member of a family of **anions** consisting of **silicon** and **oxygen.**

4.32 Questions

1. Why few properties of Li is very much related to Mg ? [See section 4.2]
2. The figure below shows the structure of the borane anion, $B_2H_7^-$ —. To which family does this borane belong ? [See section 4.6]



3. Explain different types of silicates with example. [See section 4.29]
4. What is Phosphazene ? How it can be synthesized ? [See section 4.28]
5. What is Inorganic Rubber ? [See section 4.28]
6. Why silicones are water repellent but not the alkyl substutuated chlorosilanes. [See section 4.27]
7. Why fluorocarbon do not attack the ozone layer [See section 4.11]
8. Explain the structure and bonding of Diborane. [See section 4.6]
9. How boric acid can be prepared [See section 4.9]
10. Write a short note on Borax [See section 4.10]
11. Why Borazine is called inorganic Benzene. [See section 4.7]
12. Why Boron Nitride is called inorganic Graphite [See section 4.8]
13. 'Cyanogen is called a pseudohalogen'-Explain [See section 4.22]
14. What si Clathrate ? [See section 4.26]

15. Explain why Clathrate compounds are stable ? [See section 4.26]
16. What are the environtal effects of Iodine ? [See section 4.23]
17. Show two methods by which tetrasulfur tetranitride can be prepared. [See section 4.19]
18. Show the structures of *Phosphinic acid, Phosphonic acid, & Hypophosphoric acid* [See section 4.15]
19. Show the structure and bonding of Nitrous oxide and Dinitrogen trioxide [See section 4.16]
20. Show the reaction of diborane with NH_3, *MeOH, CO, Na/Hg.* [See section 4.6]
21. Show the structures of P_4O_7, P_4O_8 and P_4O_9 [See section 4.14]
22. Show the Resonance hybrid of N_2O [See section 4.12]
23. Show the chemical reactions of Borazine with hot water, Conc. *NaOH* and O_2. [See section 4.7]
24. Why happens in the time of heating Borax ? [See section 4.10]
25. What is 'banana bond' ? [See section 4.7]

4.33. Further Reading

1. "Concise Inorganic Chemistry" by ***J.D.Lee*** [Willey-India]
2. "General Inorganic Chemistry; Part-2" by **"Ramaprasad Sarkar** [New central book agency Ltd.]
3. "Inorganic Chemistry" by **R. L. Dutta** [The New Book Stall]

Unit-5 Redox and precipitation reaction

Contents

5.1 Objectives

After reading this unit, we will be able to:

- The qualitative idea about various types of redox reactions
- Knowledge about redox potential, cell EMF and their calculations
- Various applications of electrochemical series
- Knowledge about pH and definition of related terms
- Knowledge about redox titration and redox indicators
- Idea about potential diagrams

5.2 Introduction

Oxidation-reduction reactions are some of the most important chemical reactions. Redox reactions, as they are called, are the energy-producing reactions in industry as well as in the body. The core of a redox reaction is the passing of one or more electrons from one species to another. The species that loses electrons is said to be oxidized, and the species gaining electrons is reduced. These are old terms, but they are still used today. Oxidation and reductin occur simultaneously.

Oxidation numbers are assigned to each element in a chemical reaction to help us learn which element is oxidized and which element is reduced. If, in a reaction, the oxidation number of an element increases (becomes more positive), the element is being oxidized. On the other hand, if the oxidation number of an element decreases, the element is being reduced. The changes in oxidation numbers are also used to balance redox equations. The goal is to keep the total number of electrons lost in the oxidation equal to the total number gained in the reduction. Clearly, the study of oxidation-reduction reactions should begin by learning about oxidation numbers.

In chemistry, the word precipitation has a different meaning : instead of something that falls out of the sky, a precipitate is something that falls out of a solution. One of the ways a prcipitate can be formed is when two soluble compounds interact. A soluble compound is one that will dissolve in water. Insoluble compounds do not dissolve in water.

5.3 Qualitative idea about complementary, noncomplementary, disproportionation and comproportionation redox reactios

❑ **Complementary reaction**

The change in oxidation state of the reducing agent is the same as the change in oxidation state of the oxidizing agent. Some examples are

$Cr^{+2} + Ag^{+} \rightarrow Ag^{0} + Cr^{+3}$

$Zn^{0} + Cu^{+2} \rightarrow Zn^{+2} + Cu^{0}$

❑ **Noncomplementary reaction**

The oxidizing agent and reducing agent undergo different net changes in oxidation state. Some examples are

$2Cr^{+2} + Tl^{+3} \rightarrow Cr^{+3} + Tl^{+}$

$Zn^{0} + 2Fe^{+3} \rightarrow Zn^{+2} + 2Fe^{+2}$

The complementary reactions are generally faster than the noncomplementary reactions. The noncomplementary and multiple electron transfer reactions cannot occur in a single step electron transfer and it takes place multistep. If any one step of such reaction is slow then the overall reaction becomes slow, or if any such step is thermodynamically disfavored then it leads to the low concentratin of an essential intermediate and consequently the overall reactions become slow.

☐ Disproportionation reaction

A particular species act as a reducing agent as well as oxidizing agent. Thus a fraction of the species is brought to higher oxidatin state and at the same time, an equivalent fraction is brought down to a lower oxidatin state.

$$3Au^{+} \rightleftharpoons Au^{+3} + 2Au$$

$$2Cu^{+} \rightleftharpoons Cu + Cu^{+2}$$

☐ Comproportionation reaction

The reverse of disproportionation reaction is called a comproportionatin reaction in which two species of a particular substance with different oxidation state combine to form a product having an intermediate oxidation state.

$$Ag^{+2} + Ag \rightleftharpoons 2Ag^{+}$$

5.4 Standard redox potential with sign convention

For the process, $Ox + ne \rightleftharpoons$ Red, the electrode potential (more correctly, the reductin potential) is given by the Nernst equation as follows :

$$E = E^{0} + RT/nFIn^{a}{}_{Ox}/^{a}{}_{Red} = E^{0} + 0.059/n\ In^{a}{}_{Ox}/^{a}{}_{Red.} \text{ at } 25°C$$

Where n is the number of electrons getting transferred, F = 96,500 coulombs per mole of electron, R = 8.3 joules/degree/mole, T = temperature in Kelvin scale, E = electrode potential in volt, E° = Standared potential in volt. Thus, it is evident that when both the oxidant and reductant are at unit activity, the electrode potential becomes the standard electrode potential.

There are two different sign conventions which are apparently confusing but each one is justified in its own argument. These are European convention and American convention.

According to European convention, sign of the electrode potential is the experimentally observed electrostatic potential with respect to the standard hydrogen electrode (*SHE*). It is obtained from the emf of a cell in which the negative electrode is *SHE* (for which a potential of 0 V has been arbitrarily assigned) and the positive electrode is made up of the electrode whose potential is to be determined. Thus, in this convention, the sign of the electrode potential is the same as that of the electrostatic charge of the electrode in forming the electrical double layer. On the other hand, the American convention takes care of the thermodynamic property of the electrode reaction.

In the European convention, the $Zn - Zn^{2+}$ electrode has the potential – 0.76 volt, because on dipping a *Zn*-rod in a solution containing Zn^{2+} ions, the *Zn*-rod becomes negatively charged electrostatically. It happens so due to the higher tendency (compared to the tendency of hydrogen in SHE, i.e. $H \rightarrow 2H^{+} + 2e$) of Zn-metal to pass into the solution as Zn^{2+} ions (i.e. $Zn \rightarrow Zn^{2+} + 2e$). According to the American convention, the electrode potential for the above process is + 0.76 volt. The reason is that, if the potential is taken as –ve then the corresponding Gibbs free energy change (i.e. $\Delta G = -nFE'$) becomes positive and the process cannot be spontaneous; but if it is taken as + *ve*, then ΔG becomes –ve which is in conformity with the thermodynamic criterion of spontaneity of the electrode process, $Zn + 2H^{+} \rightleftharpoons Zn^{2+} + H_2$, $\Delta G < 0$.

To overcome this aparent confusion, IUPAC has recommended the electrostatic potential as the electrode potential designated by V (a sign invariant quantity) and the thermodynamic quantity (i.e. *emf*) designated by E should be related as proper sign in the relation, $\Delta G = -nFE$. Thus, when a standard Zn/Zn^{2+} ($a = 1$) electrode is coupled with a *SHE*, the experimental potential is – 0.76 *V* and it is actually the standard electrode potential (*V*) of Zn/Zn^{2+}. When this electrode is used as negative electrode in some cell, the electrod potential will still be taken as – 0.76 *V* (i.e. a sign invariant). But, here we shall follow the thermodynamic convention. Thus – 0.76 volt is regarded as standard reduction potential of th couple, $Zn - Zn^{2+}$, while + 0.76 volt can be taken as the standard oxidation potential. Thus, so-called European convention refers to actually to the reduction potential.

5.5 Electrochemical series and its application to explore the feasibility of reactions and equilibrium constants

If the standard reduction potentials of the electrode process, $M^{n+}_{(aq)} + ne \rightleftharpoons M_{(s)}$ for different metals are placed in a series in order of increasing value, we get the table 1 which gives the electrochemical series.

Here the potential values are given as per the thermodynamic convention. The Gibbs free energy change for the reduction electrode process is given by, $\Delta G^\circ = -nFE^\circ_{red}$. Thus, for the system of higher positive value of $E^0_{red,}$ the reduction process gets more favoured. In fact for the systems having negative E^0_{red} value, the reverse process, i.e. oxidation is favoured. In the table 1, the metals residing at the top are highly electropositive. With the increase of $E^0_{red,}$ the oxidizing power increases and the reducing power runs in the opposite direction.

Table 1. The electrochemical series (standard reduction potentials, at 25°C)

Element	***Electrode couple***	***$E^0(V)$***
Li	Li^+/Li	– 3.05
K	K^+/K	– 2.93
Ca	Ca^{2+}/Ca	– 2.84
Na	Na^+/Na	– 2.71
Mg	Mg^{2+}/Mg	– 2.36
Al	Al^{3+}/Al	– 1.66
Mn	Mn^{2+}/Mn	– 1.08
Zn	Zn^{2+}/Zn	– 0.76
Fe	Fe^{3+}/Fe	– 0.44
Cd	Cd^{2+}/Cd	– 0.40
Co	Co^{2+}/Co	– 0.27
Ni	Ni^{2+}/Ni	–0.23
Sn	Sn^{2+}/Sn	– 0.14
Pb	Pb^{2+}/Pb	– 0.13
H_2	H^+/H_2	0.00*
Cu	Cu^{2+}/Cu	+ 0.35
Ag	Ag^+/Ag	+ 0.80
Au	Au^{3+}/Au	+ 1.38

*Standard Hydrogen Electrode (SHE)

This difference in the reduction tendencies of the two electrodes in a cell finds many applications in chemistry.

5.6 Applications of electrochemical series

The main applications of the electrochemical series are :

5.6.1 Oxidizing and Reducing Strengths

The electrochemical series helps to pick out substances that are good oxidizing agents and those which are good reducing agents. For example, a very high negative reduction potential of lithium electrode indicates that it is very difficult to reduce Li^+ions to Li atoms. Therefore, Li^+ cannot accept electrons easily and so loses electrons to behave as a reducing agent. As the reduction potential increases (negative value decreases), the tendency of the electrode to behave as reducing agent decreases. Thus, all the substances appearing on the top of the series behave as good reducing agents. For example Li and K are good reducing agents while Ag and Au are the poorest reducing agents.

Similarly, substances at the bottom of the table have high reductin potential and they can be easily reduced. Therefore, they act as strong oxidizing agents. From the table we ca conclude that H^+ is a better oxidizing agent than Zn^{2+} while Cu^{2+} is a better oxidizing agent than H^+; Fe^{3+} is a better oxidizing agent than Al^{3+} and so on. All the substances appearing at the bottom of the table are good oxidizing agents.

5.6.2 Comparison of Reactivities of Metals

The relative ease with which the various species of metals and ions may be oxidized or reduced is indicated by the reduction potential values. The metals with lower reduction potential are not reduced easily but are easily oxidized to their ions losing electrons. These electrons would reduce the other metals having higher reduction potentials. In other words, a metal having smaller reduction potential can displace metals having larger reduction potentials from the solution of their salt.

For example, copper lies above silver in the electrochemical series, therefore, if copper metal is added to $AgNO_3$ solution, silver is displaced from the solution. In general, a metal occupying higher position in the series can displace the metals lying below it from the solutions of their salts and so are more reactive in displacing the other metals. Thus, Li is the most electropositive element in solutions and fluorine is the most electronegative element.

5.6.3 Calculation of the EMF of the Cell

The following steps determine the reduction potential of the cathode and anode :

Step I

The two half-cell reactions are written in such a way that the reaction taking place at the left hand electrode is written as an oxidation reaction and that taking place at the right electrode is written as reduction reaction.

Step II

The number of electrons in the two equations are made equal by multiplying one of the equations if necessary, by a suitable number. However, electrode potential values (E°) are not multiplied.

Step III

The electrode potentials of both the electrodes are taken to be reduction potentials and so the EMF of the cell is equal to the difference between the standard potential of the right-hand side and the left-hand side electrode.

$$E_{\text{cell}} = E_R - E_L$$

Step IV

If the *EMF* of the cell is +ve, the reaction is feasible in the given direction and the cell is correctly represented, i.e., oxidation occurs at left electrode (anode) and reduction occurs at the right electrode (cathode). If it is –ve, the cell reaction is not fesible in the given direction and the cell is wrongly represented. Thus, to get positive value for the *EMF* the electrodes must be reversed.

5.6.4 Predicting the liberation of hydrogen gas from acids by metals

All metals having negative electrode potentials (negative E° values) show greater tendency of losing electrons as compared to hydrogen. So, when such a metal is placed in an acid solution, the metal gets oxidized, and H^+ (hydrogen) ions get reduced to form hydrogen gas. Thus, the metals heving negative E° values liberate hydrogen from acids.

$$M_{(s)} \rightleftharpoons M^{n+}(aq) + ne^-$$

metal having negative E° value

$$nH^+(aq) + ne^- \rightleftharpoons n/2\ H_2(g)$$

Thus, $M + nH^{+}(aq) \rightleftharpoons M^{n+}(aq) + n/2\ H_2(g)$

For example, metals such as Mg ($E°(Mg^{2+} + \rightarrow Mg) = -2.37\ V$),

Zn ($E°(Zn^{2+}/Zn) = -0.76V$), Iron ($E°(Fe^{2+}/Fe) = -0.44\ V$) etc., can displace hydrogen from acids such as HCl and H_2SO_4. But metals such as Copper, ($E°(Cu^{2+}/Cu) = +0.34V$), silver ($E°(Ag^{+}/Ag) = +0.80V$) and gold ($E°(Au^{3+}/Au) = +1.42V$) cannot displace hydrogen from acids because of their positive reduction potential value.

5.6.5 Predicting feasibility of a redox reaction

From the E° values of the two electrodes one can find out whether a given redox reaction is feasible or not. A redox reaction is feasible only if the species which has higher potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidized i.e., loses electrons.

The electrochemical series gives the increasing order of electrode potentials (reduction) of different electrodes on moving down the table. This means that the species, which accept the electrons (reduced) must be lower in the electrochemical series as compared to the other which is to lose electrons. (oxidized). For example,

$$2Ag(s) + Cu^{2+}(aq) \rightarrow 2Ag^{+}(aq) + Cu(s)$$

From the electrochemical series E° value of Cu = + 0.34V and that of Ag = + 0.80 V since the reduction potential of Ag is more than that of Cu, this means that silver has greater tendency to get reduced in comparison to copper. Thus, the reaction

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$

occurs more readily than the reaction

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

The reduction potential of copper is less than that of Ag, this means that copper will be oxidized or will go into solution as ions in comparison to Ag. Thus, the reaction,

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$$

occurs more readily than

$$Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$$

Therefore, silver will be reduced and copper will be oxidized and the above reaction is not feasible. Rather the reverse reaction,

$$2Ag^{+}(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

can occur. Thus a metal will displace, any other metal, which occurs below it in the electrochemical series from its salt solution. When a metal having lower E° value is placed in a solution, containing ions of another metal having higher E° value, then the metal having lower E° value gets dissolved and the ions of the metal having higher E° value get precipitated.

5.6.6 The Relationship between Cell Potential & the equilibrium constant

We can use the relationship between $\Delta G°$ and the equilibrium constant K, to obtain a relationship between $E°_{cell}$ and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation :

$$\Delta G° = -RT\ln K$$

Given the relationship between the standard free-energy change and the standard cell potential $-nFE°_{cell} = -RT\ln K$

Rearranging this equation,

$$E°_{cell} = (RT/nF)\ln K$$

For $T = 298\ K$,

$$E°_{cell} = [[8.314J/(\text{mol}\cdot K)(298K)]/n[96{,}486J/(V.\text{mol})]]2.303\log K = (0.0591\ V/n)\log K$$

$$\log K = nE°_{cell}/0.0591V$$

Thus $E°_{cell}$ is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of $E°_{cell}$ and vice versa.

5.7 Nernst equation, effect of pH, complexation and precipitation on redox potential, formal potential

5.7.1. Formal Potential

In the process, Ox + ne $\rightleftharpoons$ Red, the potential is given by :

$$E = E^{0} + RT/nF\ ln^{a}{}_{Ox}/^{a}{}_{Red} = E^{0} + 0.059/n\,ln^{a}{}_{Ox}/^{a}{}_{Red,}\ \text{at } 25°C$$

Where n is the number of moles of electrons getting transferred, F = 96,500 coulombs per mole of electron, R = 8.3 joules/degree/mole, T = temperature in Kelvin scale, E = electrode potential in volt, E^0 = Standard potential in volt.

$E = E^0 + 0.059/n \ ln \ [Ox]/[Red]$ (in dilute solution)

Here it is believed that all the involved species will remain in their simple forms and the activity equals the concentration. Such a situation may only exist n a very dilute condition. In practice, the solution is sufficiently concentrated to disallow the condition, activity = concentration. But in reality, we deal with the concentration terms instead of the activity term. Beside this, the ions may not exist as in simple forms in presence of other electrolytes. In such cases, the concept of standard potential is of no practical use and it requires another parameter called formal potential or conditional potential which takes care of the actual situation existing in solution.

The formal potential of a system is the experimentally observed potential of the system in solution where the formal concentration of the oxidized and reduced forms is same. The formal potentials cover the effect of the concentration of the species, pH of the solution, the possibility of complexation and other factors.

5.7.2. Formal potential depending on the pH of the medium

Nernst equation describes potential of electrochemical cell as a function of concentrations of ions taking part in the reaction :

$$E = E_0 - \frac{RT}{nF} In(Q)$$

Where Q is a **reaction quotient** and n is number of electrons exchanged. For constant temperature expression RT/F has constant value. To simplify the calculation, it is often combined with conversion factor between natural logarithm (denoted here by In) and decimal logarithm (denoted here by log) to form value of 0.0591 (for 25°C). Thus, for example for half reactin of MnO_4^- in acidic media :

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2OE^0_{MnO4^-/Mn^{2+}} = +1.51 \text{ volt}$$

potential is given by

$$E = 1.51 - \frac{0.0591}{5}\log\left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right)$$

To be precise we should use not concentrations, but thermodynamic activities of the ions present in the solution.

$$E = 1.51 - 8/5(0.059)pH + 0.059/5\log[MnO_4^-]/[Mn^{2+}]$$

$$E = E^0{}_f + 0.059/5\log[MnO_4^-]/[Mn^{2+}] \qquad [\text{Where } E^0{}_f = 1.51 - 8/5(0.059)pH]$$

To express $E^0{}_f$ the pH term is to be included with in the E^0 term. Thus, we can write :

$$E = E^0{}_f = E^0 - 8/5(0.059)pH = E^0 - 0.0944pH \text{ when} [MnO_4^-] = [Mn^{2+}] = 1M;$$

activity coefficients are taken to be unity.

Thus the Nernst equation in terms of $E^0{}_f$ (formal potential) of the couple is given by :

$$E = E^0{}_f + 0.0118 \log[MnO_4^-]/[Mn^{2+}]$$

5.7.3. Formal potential depending on the complexation of the medium

Potential (in aqueous solution) of the involved couples are : $E^0_{Cu^{2+}/Cu} = 0.34V > E^0_{Zn^{2+}/Zn} = -0.76V$. Hence, on the electrolysis of a solution containing both Cu^{2+} and Zn^{2+}, copper deposition should start earlier. But in presence of excess CN^-, Zn^{2+} forms $Zn(CN)_4{}^{2-}$ complex while Cu^{2+} oxidises CN^- to CN_2 gas and itself reduced to $Cu(\mathrm{CN})_4{}^{2-}$ which is more stable than zinc complex. In fact the stability constants are so widely different that the deposition potentials of the couples becomes comparable, i.e. $E^0{}_{Cu(CN)_4^{2-}/Cu} \approx E^0{}_{Zn(CN)_4^{2-}/Zn^-}$ Thus the simultaneous deposition of both Cu and Zn can be achieved by the complexation with excess cyanide in the medium.

$$Cu^+ + e \rightleftharpoons Cu \qquad\qquad E^0 = 0.52V$$

$$Cu^+ + 4CN^- \rightleftharpoons Cu(CN)_4^{3-}\ , \log K \approx 30.0$$

$$K = [Cu(CN)_4^{3-}]/[Cu^+][CN^-]^4$$

$$E = E^0 = 0.059 \log[Cu^+] = E^0 = 0.059 \log[Cu(CN)_4{}^{3-}]/[CN^-]^4$$

$$= (0.52 - 0.059 \times 30) + 0.059[Cu(CN)_4{}^{3-}]/[CN^-]^4 = -1.25 + [Cu(CN)_4{}^{3-}]/[CN^-]^4$$

$$E = -1.25 - 0.059 \times 4 \log[CN^-] + 0.059 \log[Cu(CN)_4{}^3]$$

$$E = -1.25 + 0.236 \log[CN^-] \text{ when } [Cu(CN)_4{}^{3-}] = 1M$$

Thus the standard potential of the following couple is

$$-1.25V (= E^0{}_f \text{ for} [CN^-] = 1M)$$

$$[Cu(CN)_4{}^{3-}] + e \rightleftharpoons Cu + 4CN^-,$$

We can calculate the change of potential of the system Zn^{2+}/Zn couple in the presence of CN^- in the same way.

$Zn^{2+} + 2e \rightleftharpoons Zn \qquad E^0 = -0.76V$

$Zn^{2+} + 4CN^- \leftrightarrow Zn(CN)_4^{2-}$, $\log K \approx 20.0$

$K = [Zn(CN)_4^{2-}]/[Zn^{2+}][CN^-]^4$

$E = E^0 + 0.059\log[Zn^{2+}] = E^0 + 0.059\log[Zn(CN)_4^{2-}]/K[CN^-]^4$

$E = E^0 + (0.059/2)\log(1/K) + (0.059/2)\log[Zn(CN)_4^{2-}]/[CN^-]^4$

$= -1.35 + (0.059/2)\log[Zn(CN)_4^{2-}]/[CN^-]^4$

i.e. for the couple, $Zn(CN)_4^{2-} + 2e \rightleftharpoons Zn + 4CN^-$ the standard potential is -1.35V.

5.7.4. Effects of precipitation on electrode potentials

Iodometric determination of copper is based on the oxidation of iodides to iodine by copper (II) ions, which get redced to Cu^+.

Comparison of standard potentials for both half reactions $(Cu^{2+}/Cu^+ E^0 = 0.15V$, $I_2/I^- E^0 = 0.54V)$ suggests that it is iodine that should be acting as oxidizer. However, that's not the case, as copper (I) iodide CuI is very weakly soluble $(K_{sp} = 10^{-12})$. That means concentration of Cu^+ in the solution is very low and the standard potential of the half reaction Cu^{2+}/Cu^+ in the presence of iodides is much higher (arround $0.85V$).

$Cu^2 + e \rightleftharpoons Cu^+ E^0 = 0.15V$; $E = E^0 + 0.059\log[Cu^{2+}]/[Cu^+]$, (in dilute solution)

In presence of I^-, Cu^+ is precipitated as CuI, having the solubility product 10^{-12}, i.e.

$Cu^+ + I^- \rightleftharpoons CuI(\downarrow)$, $K_{sp} = 10^{-12}$.

Now we get;

$E = E^0 + 0.059\log([Cu^{2+}][I^-]/K_{sp})$

$E = E^0 - 0.059\log K_{sp} + 0.059\log([Cu^{2+}][I^-]$

$E = 0.85 + 0.059\log([Cu^{2+}][I^-]$

$E = 0.85 + 0.059\log[I^-]$ when $[Cu^{2+}] = 1M$

We can express E^0_f as follows :

$E^0{}_f = E = E^0 - 0.059\log K_{sp} + 0.059\log[I^-] = 0.85 + 0.059\log[I^-]$

Thus formal potential of the system depends on the concentration of the iodide. Under the condition, $[I^-] >> [Cu^{2+}]$, the formal potential becomes : $E^0{}_f = 0.85 + 0.059\log[I^-]$

It explains the oxidation of iodide by Cu(II) in presence of excess iodide. The reaction is $2Cu^{2+} + 4I^- \rightarrow 2CuI(s) + I_2$

5.8 Basis of redox titration and redox indicators

All of us know that wine is made from the fermentation of grape juice using specific yeast cells. However, do you know wine requires a particular amount of fruit acid ? So how is this acid content measured in industries ? The determination of acid content is done by titration. Yes, the lab technique we all have done as well as read about.

Moreover, a specialized titration technique known as redox titration is used for analysis of wines for sulfur dioxide. This is just one example. similarly, many other industrial processes require titration with respect to redox reactions. So let us know more about redox reactions as the basis of titration.

5.8.1. Titration

It is a very common laboratory technique. Titration helps in the quantitative chemical analysis. It helps in the determination of an unknown concentration of an already known analyte. Moreover, titration also helps in volumetric analysis or measurement of volume. There are different types of titration techniques which is applicable according to the goals and methods.

Types of Methods

- Acid-base Titrations
- Redox Titrations
- Precipitation titrations
- Complexometric Titrations

The most common titration methods that are commonly in use for "quantitative chemical analysis" are Redox and Acid-Base Titration. In the acid-base system, a titration method helps in finding out the strength of one solution against another solution by the use of the pH-sensitive indicator.

Similarly, in redox system, a titration method helps in determination of the strength of a particular oxidant or a reductant with the help redox-sensitive indicator. We will now discuss the definition of redox titration and how to use indicators in this technique.

Redox Titrations

When the oxidation-reduction reactions happen in a titration method, it is known as a redox titration. In this technique, transfer of electrons occurs in the reacting ions present in the aqueous solutions during the chemical reaction. This is further classified on the basis of regent used in the redox titration.

Sub-Diisions of Redox Titrations

- Permanganate Titrations
- Dichromate Titrations
- Iodometric Titrations

Permanganate Titrations

Potassium Permanganate is the oxidizing agent in this type of redox titration method. Maintenance of the solution is done with the help of dilute sulphuric acid. Moreover, the addition of Sulphuric acid also helps to increase the hydrogen ions present in the solution.

In this technique, the reagent has intense colour due to the permanganate ion MnO^-_4. In the case, the permanganate ion acts as a self-indicator in this method. The solution remains colourless prior to the endpoint. The equation of redox reaction

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 3H_2 + 5[O]$$

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$$

The result of the end point is noticeable when oxidation of the last of the reductant such as Fe^{2+} or $C_2O_4^{2-}$ occurs. At this point, the solution retains the first lasting tinge of the MnO_4^- (pink colour) appears. The concentration can be minimum of 10^{-6} mol L^{-1}. This assures the minimal "overshoot" of the pink colour after the equivalence point.

The equivalence point is where reductant and oxidant are equal with respct to the mole stoichiomety or the total number of electrons lost and electron gained in oxidation and reduction reaction will be equal. The postassium permanganate titration helps in the estimation of oxalic acid, hydrogen peroxide, ferrous salts, oxalates and more. However, it is very important to always standardize the solution prior to use.

Dichromate Titrations

In this method, potassium dichromate acts as the oxidant in the acidic medium. It is necessary to maintain the acidity of the medium by addition of dilute sulphuric acid. The equation of the reaction is

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2Cr_2(SO_4) + 4H_2O + 3[O]$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$$

In this situation, there is no substantial auto colour change as seen in the MnO_4^- titration. $Cr_2O_7^{2-}$ is not a self-indicator, However, $Cr_2O_7^{2-}$ oxidizes the indicator substance diphenylamine soon after achieving the equivalence point thereby producing an intense blue colour. The change in signals the end point of the titration. We can use the potassium dichromate solution in titrations directly. This method helps in the estimation of ferrous salts and iodides.

Iodimetric Titrations

This is an interesting but common method. In this case, free iodine reduction to iodide ions occurs as well as iodide ion oxidation to free iodine occurs. The oxidation and reduction reactions are

$I_2 + 2e \rightarrow 2I^-$ Reduction

$2I^- \rightarrow I_2 + 2e$ Oxidation

The solution acts as an indicator. The use of this method is limited to the reagents capable of oxidizing I^- ions. One of the examples of such reaction is of $Cu(II)$

$$2Cu^{2+}(aq) + 4I^- (aq) \rightarrow Cu_2I_2 (S) + I_2(aq)$$

The ability of iodine to produce intense blue colour with starch as the substance and its capacity to react with thiosulphate ions ($S_2O_3^{2-}$) forms the basis of this method. The specific reaction with ($S_2O_3^{2-}$) is also a redox reaction.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

In this case, I_2 is insoluble in nature with water but it remains in the solution in the form of KI_3 that contains KI. After the addition of starch, the iodine in the reaction liberates as iodide ions producing intense blue colour. However, the colour disappears on the consumption of iodine by the thiosulphate ions. The end point of the reaction is easily noticeable. Thus, it is easy to determine the concentration of the unknown solution by stoichiometric calculation.

5.8.2. Redox indicator

Redox indicators are the chemicals used during the redox titration in order to detect the end point. In acid-base titrations, the indicators used were weak acids or bases which had two forms : dissociated (ionized) or non-ionized and both of these forms have a different color. Some common redox indicators with characteristic properties are listed in table 2.

Similarly, the redox indicators have two forms : oxidized form and reduced form. In both the forms, the color is different. Both the form has got a specific standard reduction potential.

$$In_{ox} + ne \rightarrow In_{red}$$

Here we apply the same concept.

Let us suppose an indicator (In), and represent its oxidized form as (In_{ox}) and reduced form as (In_{red}).

Applying Nernst equation,

Thus, the electrode potential of the indicator when the ratio of (In_{ox}) to (In_{red}) is 10:1 would be :

$$E = E^0_{In} - 0.059\log[In_{red}]/[In_{ox}]$$

n = transfer of electrons = 1.

$$E = E^0_{In} - 0.059\log(1/10)$$

$$E = E^0_{In} + 0.059$$

Thus, the electrode potential of the indicator when the ratio of (In_{ox}) to (In_{red}) is 1:10 would be :

$$E = E^0_{In} - 0.059\log 10$$

$$E = E^0_{In} - 0.059$$

$$E_{tp} = E^0_{In} \pm 0.059/n$$

The change in the potential of the indicator which is required during the redox titration for the indicator to impart a color change is called transition potential.

The transition potential should coincide with the potential of the solution at the equivalence point (E_{ep}) for getting a better end point. $E_{ep} = E_t$

Table 2 : Some common redox indicators with characteristic properties

Indicators	**colour**		$E^0_{Ind}[H+] = 1.0$
	Ind$_{ox}$	**Ind$_{Red}$**	**mol dm^{-3}**
Methylene blue	Blue	Colourless	0.53
Diphenylamine	Blue-violet	Colourless	0.76
Diphenylamine-sulphonic acid	Red-violet	Colourless	0.85
N-Phenylanthranilic acid	Red-violet	Colourless	1.08
Ferroin, (Fe(II)-phenanthroline complex)	Paleblue	Red	1.14

5.9 Potential diagrams

In addition to Pourbaix diagrams, there are two other kinds of redox stability diagrams known as Latimer and Frost diagrams. Each of these diagrams contains similar information, but one representation may be more useful in a given situation than the others. Latimer and Frost diagrams help predict stability relative to higher and lower oxidation states, usually at one fixed *pH*.

5.9.1. Latimer diagram

Latimer diagrams are the oldest and most compact way to represent electrochemical equilibria for substances that have multiple oxidation states. Electrochemical potential values are written for successive redox reactions (from highest to lowest oxidation state), typically under standard conditions in either strong acid ($[H^+] = 1\ M$, pH 0) or strong base ($[OH^-] = 1\ M$, pH 14). The oxidation states of successive substances in a Latimer diagram can differ by one or more electrons. Oxidation states for the element undergoing redox are typically determined by difference; we assign the oxygen atoms an oxidation state of -2 and the hydrogen atoms an oxidation state of $+1$.

The Latimer diagram for *Mn* illustrates its standard reduction potentials (in 1 *M* acid) in oxidation states from +7 to 0.

$$\underset{(+7)}{MnO_4^-} \xrightarrow{0.56} \underset{(+6)}{MnO_4^{2-}} \xrightarrow{+0.274} \underset{(+5)}{MnO_4^{3-}} \xrightarrow{4.27} \underset{(+4)}{MnO_2} \xrightarrow{0.95}$$

$$\underset{(+3)}{Mn^{3+}} \xrightarrow{1.51} \underset{(+2)}{Mn^{2+}} \xrightarrow{-1.18} \underset{(0)}{Mn}$$

The Latimer diagram compresses into shorthand notation all the standard potentials for redox reactions of the element *Mn*. For example, the entry that connects Mn^{2+} and Mn gives the potential for the half-cell reaction :

$Mn^{2+}(aq) + 2e \rightarrow Mn(s)E^0{}_{1/2} = -1.18V$

and the entry connecting Mn^{4+} and Mn^{3+} represents the reaction :

$MnO_2(s) + 4H^+(aq) + e \rightarrow Mn^{3+}(aq) + 2H_2O(l)E^0{}_{1/2} = +0.95V$

We can also calculate values for multi-electron reactions by first adding $\Delta G^0(= -nFE^0)$ values and then dividing by the total number of electrons

For example, for the 5-electrons reduction of MnO_4^- to Mn^{2+}, we write

$E^0 = [1(0.564) + 1(0.274) + 1(4.27) + 1(0.95) + 1(1.51)]/5 = +1.51V$

and for the three-electron reduction

$E^0 = [1(0.564) + 1(0.274) + 1(4.27)]/3 = +1.70V$

Remember to divide by the number of electrons involved in the oxidation number change (5 and 3 for the above equations).

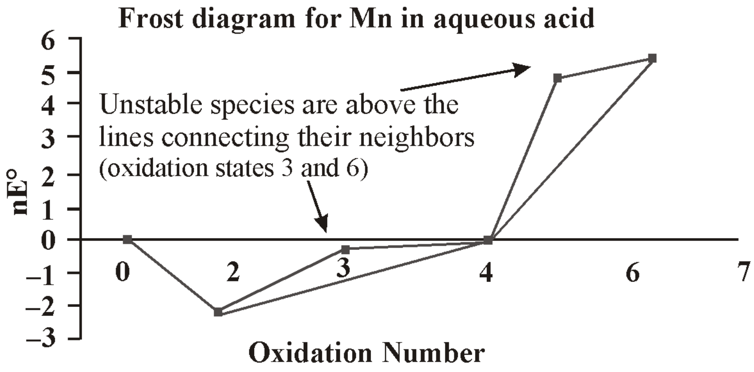
In general we can write :

$E^0 = (n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + ...)/(n_1 + n_2 + n_3 + ...)$

5.9.2. Frost diagrams

Frost diagram or Frost-Ebsworth diagram is a type of graph to illustrate the relative stability of a number of different oxidation states of a particular substance. The graph illustrates the oxidation state vs free energy of a chemical species. This effect is dependent on pH, so this parameter also must be included. The free energy is determined by the oxidation–reduction half-reactions. The Frost diagram allows easier comprehension of these reduction potentials than the Latimer diagram, because the "lack of additivity of potentials" was confusing. In a Frost diagram, we plot $\Delta G^0/$

F (= nE^0) *vs*. oxidation number. The zerooxidation state is assigned a nE^0 value of zero.



Stable and unstable oxidation states can be easily identified in the plot. Unstable compounds are higher on the plot than the line conecting their neighbors. Note that this is simply a graphical representation of what we did with the Latimer diagram to determine which oxidation states were stable and unstable.

The standard potential for any electrochemical reaction is given by the slope of the line connecting the two species on a Frost diagram. For example, the line connecting Mn^{3+} and MnO_2 on the Frost diaram has a slope of + 0.95, the standard potential of MnO_2 reduction to Mn^{3+}. This is the number that is written above the arrow in the Latimer diagram for *Mn*. Multielectron potentials can be calculated easily by connecting the dots in a Frost diagram.

- Thermodynamic stability is found at the bottom of the diagram. Thus, the lower a species is positioned on the diagram, the more thermodynamically stable it is (from a oxidationreduction perspective)
  Mn (II) is the most stable species.
- A species located on a convex curve can undergo disproportionation MnO_4^{2-} and *Mn* (III) tends to disproportionate.
- Those species on a concave curve do not typically disproportionate.
  MnO_2 does not disproportionate
- Any species located on the upper left side of the diagram will be a strong oxidizing agent.
  MnO_4^- is a strong oxidizer.
- Any species located on the upper right side of the diagram will be a reducing agent. Manganese metal is a moderate reducing agent

- These diagrams describe the termodynamic stability of the various species. Although a given species might be thermodynamically unstable toward reduction, the kinetics of such a reaction might be vey slow.

  Although it is thermodynamically favorable for permanganate ion to be reduced to Mn (II) ion, the reaction is slow except in the presence of a catalyst. Thus, solutions of permanganate can be stored and used in the laboratory
- The information obtained from a Frost diagram is for species under standard conditions ($pH = 0$ for acidic solution and $pH = 14$ for basic solution). Changes in pH may change the relative stabilities of the species. The potential of any process involving the hydrogen ion will change with pH because the concentration of this species is changing.

Under basic conditions aqueous Mn^{2+} does not exist. Instead Insoluble $Mn(OH)_2$ forms.

5.10 Solubility and solubility product principle

5.10.1. Solubility

When a sparingly soluble ionic substance is dissolved in any solvent, it dissociates into positively charged cations and negatively charged anions. The extent of solubility of the ionic substance depends on different factors like temperature, pressure, presence of common ions etc. The ability of an ionic substance to dissolve in any solvent is called solubility.

5.10.2. Solubility product principle

Solubility product of a sparingly soluble electrolyte is defined as the product of its ions in its saturated condition at 25°C. The value of solubility product of a sparingly soluble salt is always constant at given temperature. For example the solubility product of $AgCl$ at 25°C is 1.6×10^{-10}. It represents the level at which a solute dissolve in solution.

Let us consider a sparingly soluble electrolyte AB that dissolves very slightly in water. It dissociates into cations and anions.

$$AB \rightleftharpoons A^+ + B^-$$

At first, AB dissociates to give A^+ and B^-. As the concentration of A^+ and B^- is increased, the backward reaction initiates and the reaction comes under equilibrium. When the solution is saturated at 25°C, the concentration of AB, A^+ and B^- remains constant. Now, we can apply the law of mass action to this equilibrium system.

$K = [A^+][B^-]/[AB]$ or, $K \times [AB] = [A^+][B^-]$, At saturated condition in 25°C,

$K \times [AB] = K_{sp} \quad \therefore K_{sp} = [A^+][B^-]$

The above expression defines the solubility product principle.

5.10.3. Application of solubility product principle

1. It is used for the precipitatin of :
    - Group I cations [*Pb*, *Hg*(*I*), *Ag*] form precipitates as metal chloride with dilute hydrochloric acid.
    - Group II cations [*Hg*(*II*), *Cu*, *Bi*, *Cd*, *As*(*III*), *Sb*(*V*), *Sn*(*II*)] form precipitate as metal sulfide with hydrogen sulphide.
    - Group III cations [*Co*(*II*), *Ni*(*II*), *Fe*(*II*), *Fe*(*III*), *Cr*(*III*), *Al*(*III*), *Zn*(*II*), *Mg*(*II*)] form precipitate as metal hydroxide with treatment of ammonium chloride in neutral or ammoniacal media.
    - Group IV cations [*Ba*, *Sr*, *Ca*) forms precipitate as carbonates with treatment of ammonium chloride and in ammonium carbonate.
    - Group V cations [*Mg*, *Na*, *K*, NH_4^+] form precipitate as hydrogen phosphate salt by the treatment with NH_4OH, NH_4Cl and HPO_4^{2-}salt.
2. It has wide range of application in qualitative analysis.
3. This principle is usde for the purfication of common salt.

When the solubility product of given salt is less than its ionic product value, then precipitation occurs. This is called solubility product principle.

5.10.4. Ionic product

When the temperature of solubility is greater or less than 25°C, then the product of its ion is called ionic product.

$[A^+][B^-]$ = Ionic product

We know that if the product of concentration of ions present in any solution at a given temperature is less than K_{sp}, the solution is called unsaturated and more solute can be dissolved in the solution. Thus,

- When solubility product is greater than ionic product, the solution is unsaturated.
- When solubility product is equal to ionic product, the solution is saturated.
- When ionic product is greater than solubility product, the solution is unsaturated.

5.11 Common Ion effect

Let us consider the dissociation of equalibrium $HA \rightleftharpoons H^+ + A^-$. Dissociation constant $K_a = C_{H+.}C_{A-} / C_{HA}$ [assuming very dilut solution where $f\pm = 1$]. To this solution if we add common ion say H^+ or A^-, then in order to keep K_a constant some of the added ions will combine with opposite ion to produce *HA*. The net result is an increase in amount of undissociated part i.e. decrease in degree of dissociation. So, effect of common-ion is to depress degree of dissociation.

5.12 Summary

In this unit we discussed that in complementary reaction the oxidation state changes same in oxidizing and reducing agent whereas in noncomplementary reaction oxidation state changes are different. In disproportionation reaction a species acts as an oxidizing as well as reducing substance. The reverse of disproportionation reaction is called comproportionation reaction. In European convention reduction potential of a cell reaction is considered as negative sign whereas oxidation potential considered as positive sign. For a system, the higher positive value of E°red, the reduction process is more favoured, and having negative value of E°_{re}d, oxidation is favoured. In a cell reaction the cell potential is related with equilibrium constant as follows: E°_{ce}ii = (RT/nF)lnk

The Formal potential of a system is the experimentally observed potential of a system in solution where the formal concentration of the oxidized and reduced forms is same. Formal potential depends on pH, complexation of the medium and effect of precipitation.

Titration is a quantitative chemical analysis. It helps to determine the unknown concentration of a known analyte. There are mainly four types of titration methods. Acid-base titration method helps in finding out the strength of one solution against another solution by the use of pH sensitive indicator. In redox titration oxidation and reduction reactions happen. Redox titrations are mainly permanganate titration, dichromate titration and iodometric titration. There are two types of redox stability diagrams: Latimer and Frost diagrams.

Latimer diagram is the most oldest and compact way to represent electrochemical equilibria for substances that have multiple oxidation states. Frost diagram is a type of graph to illustrate the relative stability of a number of different oxidation states of a particular substance.

The ability of an ionic substance to dissolve in any solvent is called solubility. Solubility product of a sparingly soluble electrolyte is defined as the product of its ions saturated condition at 25°C.

When the temperature of solubility is greater or less than 25°C, then the product of its ion is called ionic product.

5.13 Questions

(1) What are the complementary, noncomplementary, disproportionation and comproportionation redox reactions ?

(2) What is standard oxidation and reductin potential ?

(3) What is electrochemical series ? How you can explain teh feasibility of the any reaction and reactivity of certain metal from electrochemical series ?

(4) How can you calculate the equilibrium constant in terms of standard electrode potential ?

(5) What is called formal potential ? Why it is more important than standard potential ?

(6) How formal potential varies with the change of pH of the reaction medium ?

(7) Why excess cyanide is used in the electrolysis of Cu and Zn for the simultaneous and equal deposition of both Cu and Zn for the preparation of brass.

(8) How copper is estimated in the iodometric titration of iodine ?

(9) What is called redox titration ? State the basic principles of permanganate and dichromate titrations.

(10) What is called redox indicator ? Derive the Nernst equation for the redox indicator at equivalence point ?

(11) What is Latimer diagram ? How standard electrod potential of Mn for different oxidation states can be calculated ?

(12) What is Frost diagram ? How can you explain the thermodynamic stability of certain oxidation state of any complex.

(13) What is called solubility product and ionic product ? How basic radicals are separated with the help of solubility product principle in the qualitative group separation ?

5.14 Answers

(1) See the section 5.2
(2) See the section 5.3
(3) See the section 5.5 and 5.5.5
(4) See the section 5.5.6
(5) See the section 5.6.1
(6) See the section 5.6.2
(7) See the section 5.6.3
(8) See the section 5.6.4
(9) See the section 1.7.1
(10) See the section 5.7.2
(11) See the section 5.8.1
(12) See the section 5.8.2
(13) See the section 5.9.1 to 5.9.4

5.15 Further Reading

1. *Inorganic Chemistry : Principles of Structure and Reactivity* James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi
2. *Advanced Inorganic Chemistry* F. A. Cotton and G. Willkinson
3. *Fundamental Concepts of Inorganic Chemistry* : Volume 3, A. K. Das
4. *General & Inorganic Chemistry,* Volume 1 & 2, R. Sarkar
5. *Concise Inorganic Chemistry,* J. D. Lee

Unit-6 Acids and Bases

Contents

6.1 Objectives

After reading this unit, we will be able to:

- Concepts of acid-base theories
- Drago-Wayland equation
- Definition of levelling and differentiating effect
- Concept of relative strength of acids and bases
- Details concept of HSAB theory and its applications
- Definition of super acid, buffer, pH and their significations
- Detail study on acid-base titrations

6.2 Introduction

Acids and bases play a central role in chemistry because, with th exception of redox reactions, every chemical reaction can be classified as an acid-base reaction. Our understanding of chemical reactions as acid-base interactions comes from the wide acceptance of the Lewis definition of acids and bases, which suppliment both the earlier Bronsted-Lowry concept and the first definition the Arrhenius model. Arrhenius first defined acids as proton (H^+) producers in aqueous solution and bases as hydroxide (OH^-) producers. Although this model is intuitively correct, it is limited to substances that include proton and hydroxide groups. Bronsted and Lowry proposed the more general definitions of acids and bases as proton donors and acceptors, respectively. Unlike the Arrhenius conception, the Bronsted-Lowry model accounts for acids in solvents other than water, where the proton transfers do not necessarily involve hydroxide ions. But the Bronsted-Lowry model fails to explain the observation that metal ions make water more acidic. Finally, Lewis gave us the more general definition of acids and bases that we use today. According to Lewis, acids are electron pair acceptors and bases are electron pair donors. Any chemical reaction that can be represented as a simple exchange of valence electron pairs to break and from bonds is therefore an acid-base reaction.

Acid-base chemistry is important to us on a practical level as well, outside of laboratory chemical reactions. Our bodily functions, ranging from the microscopic transport of ions across nerve cell membranes to the macrosopic acidic digestion of food in the stomach, are all ruled by the principles of acid-base chemistry. Homeostasis, the temperature and chemical balances in our bodies, is maintained by acid-base reactions. For example, fluctuations in the pH, or concentration of hydrogen ions, of our blood is moderated at a comfortable level through use of buffers. Learning how buffers work and what their limitations are can help us to better understand our physiology. We will start by introducing fundamentals of acid-base chemistry and the calculation of pH, and then we will cover techniques for measuring pH. We learn about buffers and see how they are applied to measure the acidic content of solutions through titration.

6.3. Different types of acid-base concepts and solvents

Various concepts of acids and bases were developed from time to time, though each concept has its limitation. Latter on, G. N. Lewis listed the following based upon which the definition are to be developed to avoid limitations.

(a) The process of neutralization is a rapid one.

(b) Acid and bases can be titrated one against the other in presence of indicator.

(c) A stonger acid or base can displace a weaker acid or base during reaction.

(d) Acid and bases act as a catalyst in various reaction.

In addition to these Faraday's recognization that the ions carry current and acids-bases are electrolytes, led much foundation for the development of semi-modern and modern concept of acids and bases.

there are six concepts regarding acids and bases, which are discussed below with their advantages and limitations.

6.3.1. Arrheniu concept or water ion concept

According to Arrhenius "acids are hydrogen containing substances which gives H^+ ions in aqueous solution whereas bases are substances which gives OH^- ions in aqueous solution."

The process of neutralization amounts to the combination of H^+ with OH^- to form water

ACID : $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

BASE : $NaOH + H_2O \rightleftharpoons Na^+ + OH^- + H_2O$

Neutralization : $H^+ + OH^- \rightleftharpoons H_2O$

Advantages : (i) This concept readily explains that the heat of neutralization of a strong acid by a strong base should be constant.

(ii) The comcept offered a means of co-relating catalytic behavior with the concentration of H^+ ion.

Limitation : (i) Acid base behavior is restricted to the presence of solvent water only. But acid-base behavior observed in other solvents as well as in absence of solvent.

(ii) The concept can not explain the acidic character of certain salt like $AlCl_3$ in aqueous solution.

6.3.2. Solvent system concept

In this model, the autoionization of the solvent is considered and any subtance capable of increasing the concentration of the cation (i.e. lyonium) produced by the autoionization of the solvent is regarded as an acid in that solvent. On the other hand, the species which can enhance the concentration of the anion (i.e. lyate) produced in the autoionization of the solvent is considered as a base in the solvent. Hence to characterize the substances as acid or base in a particular solvent, it is required to know the mode of autoionization of the solvent under consideration. Some common solvents with their autoionization modes are given below.

Solvent	Acid		Base
$H_2O + H_2O \rightleftharpoons$	H_3O^+	+	OH^-
$NH_3 + NH_3 \rightleftharpoons$	NH_4^+	+	NH_2^-
$SO_2 + SO_2 \rightleftharpoons$	SO^{2+}	+	SO_3^{2-}
$HF + HF \rightleftharpoons$	H_2F^+	+	F^-

In liquid H_2O, NH_3, SO_2, HF typical acid base reaction are :

$HCl(acid) + NaOH(base) \rightleftharpoons NaCl(salt) + H_2O(solvent)$

$NH_4Cl(acid) + NaNH_2(base) \rightleftharpoons NaCl(salt) + 2NH_3(solvent)$

$Na_2SO_3(base) + SOCl_2(acid) \rightleftharpoons NaCl(salt) + SOCl_2(solvent)$

$H_2NO_3^+(acid) + F^-(base) \rightleftharpoons HNO_3(salt) + HF(solvent)$

Advantage : It can extend the concept of acid-base interaction in both protic and aprotic solvents

Limitation : (i) It pays an excessive attention to the idea of autoionization of the solvents ignoring the other physical and chemical properties of the solvents. It even ignores the properties arising from the dielectric constant which is fact, determines the possibility of autoionization.

(ii) It cannot explain many acid-base reactions occuring in the absence of any solvent.

(iii) Many acid base reactions involving the neutral molecules cannot be explained in this model.

6.3.3. Bronsted-lowry concept or protonic concept

Bronsted and Lowry in 1923 independetly proposed a more fruitful concept for acid and bases. According to them "An acid is defined as any hydrogen containing molecule or ions that can release a proton (H^+) to any other substance and a base is any molecule or ion which can accept a proton." In short "An acid is a proton donor and base is a proton acceptor."

Following are some examples :

Protonic acids : $HCl \rightarrow H^+ + Cl^-$ $[Al(H_2O)_6]^{3+} \rightarrow H^+ + [Al(H_2O)_5OH]^{2+}$

Protonic bases : $NH_3 + H^+ \rightarrow NH_4^+$ $HCO_3^- + H^+ \rightarrow H_2CO_3$

An acid and a base that are related by the gain and loss of a proton are called a conjugate acidbase pair. For example, NH_4^+ is the conjugate acid of NH_3, and NH_3 is the conjugate baseof NH_4^+. Every acid has associated with it a conjugate base. Likewise, every base has associated with it a conjugate acid.

$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{Conj}\\\text{acid}}}{NH_4^+(aq)} + \underset{\substack{\text{Conj}\\\text{base}}}{OH^-(aq)}$$

AND

$$\underset{\text{Acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)} \rightleftharpoons \underset{\substack{\text{Conj}\\\text{base}}}{NH_3(aq)} + \underset{\substack{\text{Conj}\\\text{acid}}}{H_2O(l)}$$

Advantage : (i) According to this concept acid-base behavior is not made dependent upon the presence or absence of any particular solvent.

(ii) This concept is useful in according for the acidic or alkalin nature of aqueous solution of certain salts like $FeCl_3$ or Na_2CO_3. The acidic or alkalinity character develop due to hydrolysis.

$$FeCl_3 + 6H_2O \rightleftharpoons [Fe(H_2O)_6]^{3+} + 3Cl^-$$

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H^+$$

(iii) This concept gives idea regarding the relative strength of acids and bases (both qualitative and quantitative).

Limitation : (i) It gives too much emphasis on the proton although the common acids are protonic in nature, yet there are many acids which are not protonic e.g. $AlCl_3$, CO_2, SO_2, etc.

(ii) Although this concept gives a major of the relative strength from the determined K values with respect to a common base or acid. Yet it fails to compare the relative strength of the so called common strong acids like HCl, H_2SO_4, HNO_3 etc. due to the levelling effect of the solvent. In aqueous solution these acids behave equally stronger due to levelling effect of water.

6.3.4. Lux-flood concept

They put forward a concept for defining acid base character of oxides, according to them acids are oxide ion acceptor and bases are oxide ion donor.

$$\text{Acid} + O^{2-} \rightleftharpoons \text{Base}$$

$$CO_2 + O^{2-} \rightleftharpoons CO_3^{2-}$$

$$SO_3 + O^{2-} \rightleftharpoons SO_4^{2-}$$

This view is particularly-useful in high temperature chemistry, as in the field of ceramics and metallurgy :

$$CaO \rightleftharpoons Ca^{2+} + O^{2-}$$

$$\underline{SiO_2 + O^{2-} \leftrightarrow SiO_3^{2-}}$$

$$CaO + SiO_2 \rightleftharpoons CaSiO_3$$

Base + Acid Salt

Zinc oxides shows amphoterism as it can both donate or accept oxide ions.

$$\text{Base} : ZnO + S_2O_7^{2-} \rightleftharpoons Zn^{2+} + 2SO_4^{2-}$$

$$\text{Acid} : Na_2O + ZnO \rightleftharpoons Na_2ZnO_2$$

This concept is very much limited and it gained very little importance. This concept is unable even to explain the acidic and basic character of very common acids and bases such as HCl, H_2SO_4, HNO_3 etc.

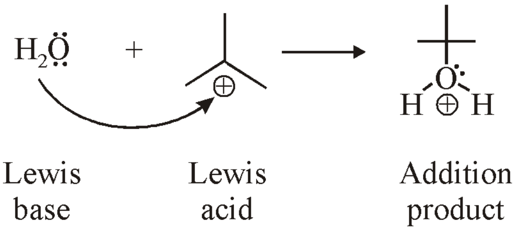
6.3.5. Lewis electronic concept

Lewis concept was proposed in 1923 by **Gilbert N. Lewis** which includes reactions with acid-base characteristics that do not involve a hydrogen transfer. A Lewis acid is a species that reacts with a Lewis base to form a Lewis adduct. The Lewis acid accepts a pair of electrons from another species; in other words, it is an electron pair acceptor. Bronsted acid-base reactions involve hydrogen transfer reactions while Lewis acid-base reactions involve electron pair transfers. All Bronsted acids are Lewis acids, but not all Lewis acids are Bronsted acids.

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

In the first example BF_3 is a Lewis acid since it accepts an electron pair from the fluoride ion. This reaction cannot be described in terms of the Bwonsted theory because there is no hydrogen transfer. The second reaction can be described using either theory. A hydrogen is transferred from an unspecified Bronsted acid to ammonia, a Bronsted base; alternatively, ammonia acts as a Lewis base and transfers a lone pair of electrons to form a bond with a hydrogen ion. Lewis acids and bases are defiened in terms of electron pair transfers. A Lewis base is an electron pair donor, and a Lewis acid is an electron pair acceptor. An organic transformtion (the creation of products from reactants) essentially results from a process of breaking bonds and forming new ones. This process basically amounts to electron pair transfers. Ionic mechanisms involve electron pair transfers and are therefor described by the Lewis acid-base theory. The Lewis definition implies the presence of high electron density centers in Lewis bases, and a Lewis base the electron pair donated by the base is used to form a new sigma bond to the electron deficient center in the acid. The identification of Lewis bases follows basically the same guidelines as the identification of Bronsted bases. They frequently contain atoms that have nonbonding electrons, or *lone pairs*. On the other hand, Lewis acids frequently contain atoms with an incomplete octet, a full positive charge, or a partial positive charge. Water is an example of a Lewis base. Carbocations are examples of Lewis acids. When water reacts with a carbocation as shown below, one of the electron pairs from oxygen is used to form a new sigma bond to the central carbon in the carbocation. As with Bronsted acid-base reactions, curved arrow is used to indicate the movement of electron pairs during the reaction process. The arrow always originates with the Lewis base and moves towards the area of electron deficiency in the Lewis acid. To avoid confusion between the Lewis and the Bronsted definitions of acids and bases, Lewis bases are sometimes called nucleophiles, and Lewis acids are called electrophiles. In the example above, water acts as a nucleophile (donates electrons), and the carbocation acts as an electrophile (receives electrons). Since Bronsted acids and bases are a sub category of the more encompassing Lewis definition, It can be said that most Bronsted bases are also nucleophiles, and that the proton ia a Lewis acid, or an electrophile, There are however some subtle differences to keep in mind.



Recognizingnucleophiles : For the most part, the same criteria used for identifying Bronsted bases can also be used to identify nucleophiles. Here is a summary.

1. The most common type of nucleophiles are those containing atoms with unshared electron pairs, such as the following. Notice that nonbonding electrons are frequently omitted from formulas. Always remember their presence on oxygen, nitrogen, and negatively charged carbon atoms. H_2O, OH^-, NH_3, RNH_2, CN^-

2. A negatively charged species is usually a stronger nucleophile or base than its neutral analog. Thus, hydroxide ion is stronger, both as a base and as a nucleophile, than water.

3. Carbon bonded to a metal has strong negative character, revealed when writing resonance structures. The carbon atom in such molecules is conidered a strong nucleophile. Recall the molecules is structures of *n*-butyllithium and Grignard (organo-magnesium) reagents from previous notes.

4. The pi bond is a region of high electron density. Pi bonds are not as strong as sigma bonds, which means that pi electrons are more available for reactions because pi bonds are more easily broken. Molecules containing pi bonds are considered weak nucleophiles or bases, because they can react with strong acids or electrophiles. See examples under Bronsted acid-base chemistry.

5. Periodic trends in nucleophilicity are such that, other factors being similar, nucleophilicity increases from right to left across the same row, and from top to bottom across the same period or group. Make a note that this trend is different from the basicity trend, which increases in the same way across a row, but from bottom to top within a period.

Nucleophilicity trends

Same row $OH^{\ominus} > F^{\ominus}$ and $NH_3 > H_2O$

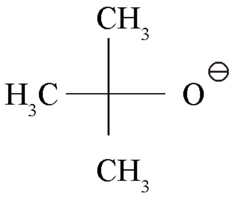
Same group $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ and $CH_3S^{\ominus} > CH_3O^{\ominus}$

6. Basic vs. nucleophilic behavior. There are some differences between Bronsted bases and nucleophiles. First, the term base is reserved for substances seeking acidic protons, whereas the term nucleophile is used for substances seeking electron-deficient centers, be they protons or other atmos (most commonly carbon).

Second, in acid-base reactions the size (or bulk) of the base seldom matters. In nucleophilic reactions, the size of the nucleophile can be an important (steric) factor. Smaller is more effective. Thus, although the nucleophilic atom in the two species below is the same (oxygen) and they have similar structures, methoxide ion is a more effective nucleophile than *t*-butoxide ion, even though they are about equally effective as bases. The larger *t*-butoxide ion has more difficulty reaching an electrophilic center, which is typically a carbon buried at the core of the molecular structure. That is not a problem when it acts as a base because acidic protons usually lie in the periphery of the molecule and are easily accessible.

$$CH_3O^{\ominus}$$

methoxide ion
smaller ion
better nucleophile



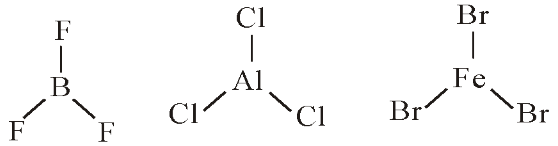
$$(CH_3)_3C-O^{\ominus}$$

t-butoxide ion
larger ion,
poorer nucleophile

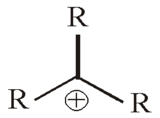
Recognizing electrophiles : There are two requirements for a molecule to be considered a good electrophile. First, it must contain an electrophilic center or atom. Second, the electrophilic atom must be able to accommodate a new sigma bond. Please keep in mind the difference between electrophile and electrophilic center. The term electrophile refers to the modlecule. The term electrophilic center refers to the particular part of the molecule susceptible to nucleophilic attack. To avoid confusion, the term *substrate* is frequently used in reference to electrophiles. This term denotes a molecule being acted upon by another agent. For example, an enzyme substrate is a molecule being modified by an enzyme. Likewise, an electrophile can be thought of as the substrate of a nucleophile when the latter "attacks" its electrophilic center. *Electrophilic centers are areas of low electron density.* Most often they are atoms which (a) *contain an incomplete octet,* and/or (b) *carry a full or a partial positive charge.* A partial positive charge can be revealed by writing resonance structures, or by identifying a polar bond.

1. The following are examples of electrophiles containing atoms with incomplete octets :

Proton

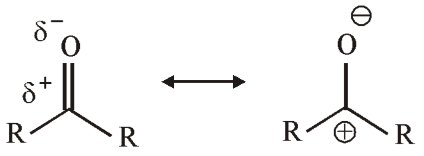


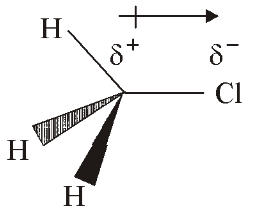
Molecules containing group III elements o transition metals



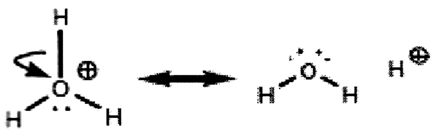
Carbocations

2. These are examples of electrophiles containing atoms with partial positive charges :

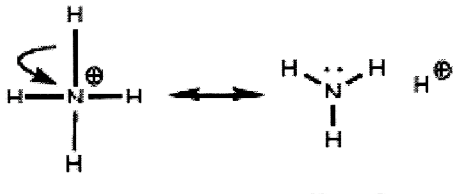




3. Atoms of the second row like oxygen and nitrogen, which are more electronegative than carbon, seldom act as electrophilic centers, even if they carry a positive charge. In that situation they seek to lessen their positive character by sharing the charge with adjacent atoms, causing them to become acidic (protons) or electrophilic (carbon for instance). Resonance structures can reveal this shift of positive charge.

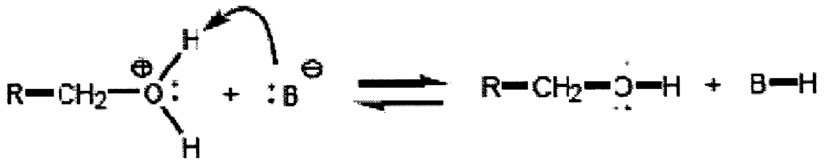


Hydronium ion, pK_a~ −1.7



Ammonium ion, pK_a ~ 9

The ammonium and hydronium are of moderate high acidity because the highly negative oxygen and nitrogen seek to transfer the positive charge to adjacent proton, to make acidic. In addition, those atoms cannot accommodate another bond without violating the octate rule.



The reaction with a base (B^-) is an equilibrium process that normally has low activation energy and is therefore relatively fast.

Advantage : (i) This concept is more general than the other concepts because the acid base behavior is not dependent upon the presence or absence of any solvent.

(ii) It explains the long accepted basic properties of metallic oxides and acidic properties of nonmetallic oxides.

(iii) This theory can explain those acid-base reaction which occur at the high temperature in the gas phase and in absence of solvent.

Limitation : (i) Since the strength of Lewis acids and bases depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

(ii) According to phenomenological criteria the process of neutralization is a rapid one. But those are many reaction Lewis acid-base reactions are slow.

6.3.6. Usanovich concept

Actually, this concept (1934) extents and generalizes the idea of Lewis acid-base concept. It does not get confined within the domain of electron pair donation and acceptance. It defines acids bases as follows.

An acid is a substance capable of accepting anions or electrons or giving up cations, and a base is a substance which can combine with the cations or give up anions or electrons. Thus the redox reactions (i.e. electron transfer reactions) are also regarded as acid-base reactions. Here it is worth mentioning that both the Lewis and Usanovich concepts are identical in terms of kind but they may differ on the degree of the process. In Lewis acid base interactions, the donated electron pair is commonly shared by the reactants in the adduct but in Usanovich concept, the electrons might be completely or partially transferred. There are some reactions which may be considered as redox reactions (i.e. Usanovich's acid base reactions) as well as Lewis acid base adduct formation. These are,

$$O + :SO_3^{2-} \rightleftharpoons SO_4^{2-}, \quad C_6H_5N: + O \rightleftharpoons C_6H_5N^+ \rightarrow O^-$$

Practically, Usanovich concept includes all the reactions as acid-base reactions. These are illustrated by considering some specific examples.

(i) $SiO_2 + CaO \rightleftharpoons Ca^{2+}SiO_3^{2-}$ Here SiO_2 takes up the anion, O^{2-} which is given up by CaO

(ii) $Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$ Here Fe^{2+} combines with the anion CN^-

(iii) $2Fe^{3+} + Sn^{2+} \rightleftharpoons Sn^{4+} + 2Fe^{2+}$ Here Sn^{2+} gives up electrons which are taken up by Fe^{3+}. Thus Sn^{2+} act as a base while Fe^{3+} act as an acid.

6.4 The Drago-wayland equation

Consider the gas phase reaction : $A(g) + \,:B(g) \rightarrow A\text{–}B(g)$

Drago and Wayland proposed the equation : $-\Delta H = E_A E_B + C_A C_B$

where ΔH is the standard enthalpy of the reaction, and E_A, E_B and C_A, C_B values represent the abilities of the acid and base to participate respectively in ionic and covalent interactions. Large enthalpies result from combinations of acids and bases with either large E or large C values.

Predictions using this equation typically agree with experimental values (for uncharged species) unless there is spacial interference of groups attached to the donor or acceptor atoms.

Drago-Wayland E and C Paramenters for Uncharged Lewis Acids and Bases

Acid	Acceptor atom	E_A	C_A	C/E
Iodine	I	1.00	1.00	1.00
Iodine monobromide	I	2.41	1.56	0.65
Iodine monochloride	I	5.10	0.830	0.16
Sulfur dioxide	S	0.92	0.808	0.88
Antimony pentachloride	Sb	7.38	5.13	0.70
Chlorotrimethylstanname	Sn	5.76	0.03	0.01
Boron trifluoride	B	9.88	1.62	0.16
Trimethylborane	B	6.14	1.70	0.28
Trimethylaluminium	Al	16.9	1.43	0.08
Trimethylgallium	Ga	13.3	0.881	0.07
Trimethylindium	In	15.3	0.654	0.04
Water	H	1.64	0.571	0.35

Base	Donor atom	E_B	C_B	C/E
Phenol	H	4.33	0.422	0.10
Thiophenol	H	0.99	0.198	0.20
Ethanol	H	3.88	0.451	0.12
(Tetraphenylporphyrinato)zinc(II)	Zn	5.15	0.620	0.12
Tetraphenylporphyrinato)cobalt(II)	Co	4.44	0.58	0.13
Dimethyl selenide	SE	0.217	8.33	38.4
Dimethyl sulfide	S	0.343	7.46	21.8
Diethyl sulfide	S	0.339	7.40	21.8
Diethyl ether	O	0.936	3.25	3.5
Acetone	O	0.937	2.33	2.5
Ethyl acetate	O	0.975	1.74	1.8
Telrahydrofuran	O	0.978	4.27	4.4
Trimethylphosphine	P	0.838	6.55	7.8
Trimethylamine	N	0.808	11.54	14.2
Pyridine	N	1.17	6.40	5.5
Dimethylamine	N	1.09	8.73	8.0
Methylamine	N	1.30	5.88	4.5
Ammonia	N	1.15	4.75	4.1
Acetonitrile	N	0.886	1.34	1.5
1-Azabicyclo [2.2.1] octanc	N	0.700	13.2	18.9

6.5 Leveling and differentiating effect of solvent

In water, no stronger than H_3O^+ can survive. Thus, water levels off all such stronger acids to the acidity of H_3O^+. The effective proton affinity of H_2O in water 1130 $kJ\ mol^{-1}$. Hence, all acids (HA) for which effective proton affinity of their conjugate bases (A^-) is smaller than 1130 $kJ\ mol^{-1}$ are levelled off in water (i.e. $HA + H_2O \rightarrow H_3O^+ + A^-$).

In water, any base stronger than OH^- cannot survive. The effective proton affinity of OH^- in water is 1188 $kJ\ mol^{-1}$. Thus any base (B) for which the effective proton affinity is greater than 1188 $kJ\ mol^{-1}$ will be completely converted into the conjugate acid (BH^+) with the release of OH^- in water ($B + H_2O \rightarrow BH^+ + OH^-$).

This is why, we cannot study NH_2^- or CH_3^- in water as these get completely protonated as follows : $LiCH_3 + H_2O \rightarrow Li^+ + OH^- + CH_4$

For liquid NH_3, the proton affinity of NH_3 is greater than that of H_2O and consequently the acids which are weaker and differentiated in water may be levelled off in liquid NH_3. The proton affinity of NH_2^- is greater than that of OH^- and consequently, the stronger bases which are levelled off in water may not be levelled off in liquid NH_3.

6.6. Relative strength of different acids and bases

To measure the proton donating strength of an acid, a reference must be taken into consideration, as the extent of proton transfer definitely depends on two factors : (i) the proton donating power of the acid and (ii) the proton accepting power of the reference base participated in proton transfer equilibrium. Generally, to measure the proton donating strength (i.e. acid strength) of an acid, the solvent is taken as the refence base. This is an aqueous solution the following proton transfer equilibrium is to be considered.

$\text{Acid}_1\ (A_1) + \text{Base}_2\ (H_2O) \rightleftharpoons \text{Base}_1\ (B_1) + H_3O^+\ (\text{Acid}_2)$

$K_{eq} = [H_3O^+][B_1]/[A_1][H_2O]$

The extent of proton transfer is measured by the equilibrium constant (in dilute solution), K. The conventional acid dissociation constant (K_a) is given by :

$K_a = K_{eq}[H_2O] = [H_3O^+][B_1]/[A_1]$

In dulute solution, $[H_2O]$ can be taken as 55.5 moles per litre. Thus, $K_a = K_{eq} x\ 55.5$. Thus in general, the acid dissociation constant can be defined as follows :

The acid dissociation constant is the product of the equilibrium constant of the proton transfer process and the concentration of the reference base (generally the pure solvent) with respect to which the extent of proton transfer is being measured.

Strongest acids are classified as $Ka > 1$ and usually $Ka >> 1$ (i.e. negative pKa values), while weak acids are classified as $Ka < 1$ (i.e. positivepKa values).

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression :

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H_3O^+ and A^- when the acid ionizes in water; Table 1 lists several strong acids. A weak acid gives small amounts of H_3O^+ and A^-.

Table 1 : *Some of the common strong acids and bases are listed here.*

Strong acid		Strong base	
$HClO_4$	perchloric acid	$LiOH$	lithium hydroxide
HCl	hydrochloric acid	$NaOH$	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a grater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA :

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

we write the equation for the ionization constant as :

$$K_a = \left[H_3O^+\right]\left[A^-\right]/\left[HA\right]$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include [H_2O] in the equation. The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength $CH_3CO_2H < HNO_2 < HSO_4^-$

$$CH_3CO_2H(aq)+H_2O(l) \rightleftharpoons H_3O^+(aq)+CH_3CO_2^-(aq)K_a=1.8\times10^{-5}$$

$$HNO_2(aq)+H_2O(l) \rightleftharpoons H_3O^+(aq)+NO^{-2}(aq)K_a=4.6\times10^{-4}$$

$$HSO_4^-(aq)+H_2O(aq) \rightleftharpoons H_3O^+(aq)+SO_4^{-2}(aq)K_a=1.2\times10^{-2}$$

Another measure of the strength of an acid is the percent ionization. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100 :

$$\%\text{ionization} = ([H_3O^+]_{eq}/[HA]_0)\times100$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Bronsted-Lowry base with water is given by :

$$B(aq)+H_2O(1) \rightleftharpoons HB^+(aq)+OH^-(aq)$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yield 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

Table 2 : Ionization Constants of Some Weak Acids

Ionization Reaction	**K_a at 25°C**
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}

$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}

As we did with acids, we can measure the relative strengths of bases by measuring their base ionization constant (K_b) in aqueous solutions. In solutions of the saem concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B :

$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq),$

We write the equation for the ionization constant as :

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Where the concentrations are those at equilibrium. Again, we do not include $[H_2O]$ in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are :

$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq) K_b = 2.17 \times 10^{-11}$

$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) K_b = 5.6 \times 10^{-10}$

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) K_b = 1.8 \times 10^{-5}$

A table of ionization constants of weak bases appears in TAble 3. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Tabl 3. : Ionization Constants of Some Weak Bases

Ionization Reaction	**K_b at 25°C**
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2 + +OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.3×10^{-10}

Consider the ionization reactions for a conjugate acid-base pair, HA, A^- :

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O + (aq) + A^-(aq), K_a = [H_3O^+][A^-]/[HA]$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + HO^-(aq)$$

As shown in the previous chapter on equilibrium, the *k* expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' *K* expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that :

$$K_a \times K_b = [H_3O^+][A^-]/[HA] \times [HA][OH^-]/[A^-] = [H_3O^+][OH^-] = K_w$$

For example the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = Kw$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+– the acid is strong. Stong acids from very weak conjugate bases, and weak acids from stronger conjugate bases (Figure 1)

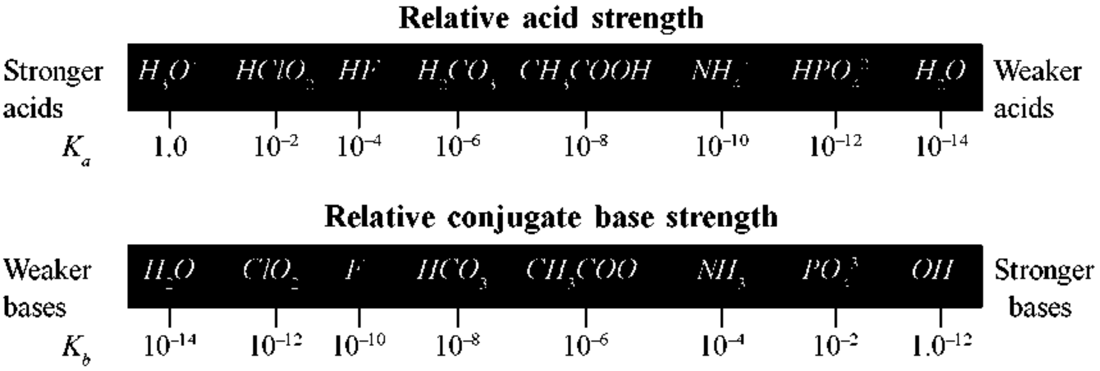


Figure 1 : This diagram shows the relative strengths of conjugate acid-base pairs, as inicated by their ionization constants in aqueous solution.

Figure 3. lists a series of acids an bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

	Acid				**Base**		
Increasing acid strength	Perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion	Increasing base strength
	sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion	
	hydrogen iodide	HI			I^-	iodide ion	
	hydrogen bromide	HBr			Br^-	bromide ion	
	hydrogen chloride	HCl			Cl^-	chloride ion	
	nitric acid	HNO_3			NO_3^-	nitrate ion	
	hydtonium ion	H_3O^+			H_2O	water	
	hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion	
	phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion	
	hydrogen fluoride	HF			F^-	fluoride ion	
	nitrous acid	HNO_2			NO_2^-	nitrite ion	
	acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion	
	carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion	
	hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion	
	ammonium ion	NH_4^+			NH_3	ammonia	
	hydrogen cyanide	HCN			CN^-	cyanide ion	
	hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion	
	water	H_2O			OH^-	hydroxide ion	
	hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion	
	ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion	
	ammonia	NH_3			NH_2^-	amide ion	
	hydrogen	H_2			H^-	hydride ion	
	methane	CH_4			CH_3^-	methide ion	

Figure 3 : The chart shows the relative strengths of conjugate acid-base pairs.

The first six acids in Table 1 are the most common strong acidss These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water form conjugate bases that can complete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Table 2 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in the Table. 3. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

6.7. Relative strength of mononuclear oxyacid : pauling rule

In H_nXO_m all the oxygen atoms are directly linked with the central atom X and ome of which are present as *OH* groups. Thus from the structural view point H_nXO_m can be represented as $O_{m-n}X(OH)_n$. Hence it is assumed that all *H-s* exist as *OH* groups. Each *X-OH* bond is formed by using one *X* electron and one *O* electron while in each $X \rightarrow O$ bond, there is a net loss of electron from *X*. In this way, the formal positive charge accumulated on the central atom is given by the number of $X \rightarrow O$ bonds and it becomes (*m-n*). With the increase of (*m-n*), the central atom becomes more and more electron deficient and it facilitate the removal of the proton from the *-O-H* bonds due to the enhanced electron withdrawing inductive effect towards the central atom. An empirical relationship between the values of (*m-n*) and acid strength measured by pK_1(i.e. first acid dissociation constant) has been proposed by Pauling as follows : $pk_1 \approx 8 - 5(m\text{-}n)$

(*m-n*)	0	1	2
pk_1 (observed)	~8.5	~2.8	<< 0
k_1 (observed)	$\sim10^{-8}–10^{-9}$	$\sim10^{-3} - 10^{-4}$	very strong

The successive pK values differ by 5 units. In many cases, the prediction has been supported experimentally.

(*m-n*)	Acid	pK_1	pK_2	pK_3
0	$HClO_4$	7.5	—	—
	$HBrO_4$	8.7	—	—
	H_3AsO_3	9.2	—	—
	H_6TeO_6	8.8	—	—

	H_3PO_3	1.8	6.15	—
1	H_3PO_4	2.1	7.2	12.0
	H_3PO_2	2	—	—
	H_3AsO_4	3.5	7.2	12.5
	H_5IO_6	3.3	6.7	—
	H_2SO_3	1.9	7.3	—
	H_2SeO_3	2.6	6.6	—
	HNO_2	3.3	—	—
	H_2CO_3	6.4	10.3	—
2	HNO_3	Highly negative	—	—
	H_2SO_4	do	1.9	—
	H_2SeO_4	do	2.0	—
3	$HClO_4$	do	—	—
	$HMnO_4$	do	—	—

6.8. Hammett acidity function and auper acid

The concept of pH measuring the acidity is only meaningful in aqueous dilute solutions of acid and bases. But in concentrated solutions of the so-called strong acids and bases and in nonaqueous media, a new parameter called the Hammett acidity function (H) has been defined to measure the acidity of the solution. To express the Hammett acidity function, protonation deprotonation equilibria of an indicator base (B) are to be considered. Depending on the charge of the indicator base, the Hammett acidity function are denoted by H_0, H_+, H_- for neutral (B), cationic (B^+) and anionic (B^-) indicator bases respectively. To measure the H_0, p-nitroanilline (a neutral base) is used. For particular solution, H_0, H_+ and H_- values differ but these run parallel.

Let us illustrate H_0 (i.e. reference base is neutral) by considering the following equilibrium :

$$BH^+ \rightleftharpoons B + H^+$$

$$K_{BH}{}^+ = a_B a_H{}^+ / a_{BH}{}^+ = (a_H{}^+[B]f_B)/([BH^+]f_{BH}{}^+)$$

$$H_0 = -\log(a_H{}^+ f_B)/(f_{BH}{}^+) = -\log h_0 = pK_{BH}{}^+ + \log[B]/[BH^+]$$

Here, a denotes the activity term and f denotes the corresponding activity coefficient. In dilute solutions, the ratio of activity coefficients (i.e. $f_B/f_{BH}{}^+$) becomes unity and it leads to :

$$H_0 = -\log a_H{}^+ = pH = pK_{BH}{}^+ + \log[B]/[BH^+]$$

Which is the Henderson's equation.

It is evident that the Hammett acidity function measures the effective pH of the solution and it is formally equivlent to

$H_O = -\log h_O = -\log(a_H + f_B)/(f_{BH}+)$

Similarly, H_+ and H_- may be defined as follows :

$$B^+ + H^+ \rightleftharpoons BH^{2+}$$

$$H_+ = -\log(a_H{}^+ f_B{}^+)/(f_{BH}{}^{2+}) = -\log h_+ = pK_{BH}{}^{2+} + \log[B^+]/[BH^{2+}]$$

$$B^- + H^+ \rightleftharpoons BH$$

$$H_- = -\log(a_H{}^+ f_B{}^-)/(f_{BH}) = -\log h_- = pK_{BH} + \log[B^-]/[BH]$$

In general, organic bases used as indicator bases posses different colours in their protonated and deprotonated forms. Thus the ratio $[B]/[BH^+]$ or $[B^+]/[BH^{2+}]$ or $[B^-]/[BH]$ can be determined spectrophotometrically. By using suitable organic bases, it is possible to determine the Hammett acidity functions of different solutions. Acidity functions of some solutions are given below in table.

In aqueous media, the strongest acid which can survive is H_3O^+. Hence, the idea of superacid only exists in nonaqueous media. Generally, the superacids are 10^6 to 10^{10} times more acidic than the fairly concentrated ($1M$) aqueous solution of strong acids like H_2SO_4, HNO_3, etc. The powerful proton donating property of superacids can protonate even very weak bases and stabilize the species susceptible to the base attack. Superacids are produced by concentrated solutions of very strong Bronsted acids, like $H_2S_2O_7$(i.e. $SO_3 + H_2SO_4$), FSO_3H or combination of a Bronsted acid and Lewis acid (e.g.SbF_5) acting as the acceptor of conjugate base of the Bronsted acid.

Hammett acidity function of some solutions

Solution/Pure acid	H_0	Solution	H_-
6M HNO_3(aq)	–1.5	5 M KOH (aq)	15.4
$HSO_3H + SbF_5$(14.1 mol %)	–26.5	10 M KOH (aq)	16.9
HSO_3H	–15.0	15 M KOH (aq)	18.2
HF + SbF_5(0.6 mol%)	–21.1		
HF	–11.0		
HF + NaF (1M)	–8.4		

7 M HCl (aq)	–2.0
8 M $HClO_4$ (aq)	–2.63
H_2SO_4 (63% in water)	–4.9
H_2SO_4	–12.0
Oleum	–15.0
F_3CSO_3H	–15.1
H_3PO_4	–5.0
HCO_2H	–2.2

(i) Bronsted acid + Lewis acid : It is noticed that the acidity of HF increases by the addition of Lewis acid SbF_5.

$$2HF \rightleftharpoons H_3F^+ + F-, SbF_5 + F- \rightleftharpoons SbF_6^-$$

(ii) Strong Bronsted acid + Lewis acid : SbF_5 also increases the acidity of fluorosulfonic acid (HSO_3F) and it produces superacid.

$$2HSO_3F + SbF_5 \rightleftharpoons H_2SO_3F^+ + FSO_2O - SbF_5^-$$

(iii) Triflic acid (F_3CSO_3H) can act as powerful strong acid (H_0 = – 15.1). It acts as like superacid.

6.9. Hard and soft acid-base (HSAB) principle and its application

According to Lewis concept acid base reaction involves the formation of coordination complex. A strong acid strong base will form a stable complex.

$$A + :B = A \leftarrow B$$

R. G. Person (1963) introduced the soft and hard or hard and soft concept of acids and bases for determining the strengths of Lewis acids and bases. According to this concept, "a hard acid prefers to combine with a hard base and a soft acid prefers to combine with a soft base to form a more stable adduct." This is known as SHAB or HSAB concept. Hardness and softness refer to firmly and loosely bound electron respectively.

For the determining the hardness and softness of bases R. G. Pearson measured the equilibrium constant of the following exchange reaction.

$$BH^+ + CH_3Hg(H_2O)^+ \rightleftharpoons [CH_3HgB]^+ + H_3O^+$$

It was found that bases having more electronegative donors (O, N, and F) prefer to bind to the proton but bases with less electronegative donors (P, S, I, Br, Cl) prefer to bind to CH_3Hg^+. The former bases are hard bases and the later are soft bases.

6.9.1. Classification of acids and bases

From the measured K values R. G. Person classified Lewis bases as hard and soft having the following criteria. Bases with intermediate character are said to be boarder line.

Hard base	Soft base
(i) High electronegatively	(i) Low electronegativity
(ii) Low polarisibility	(ii) High polarsibility
(iii) Presence of filled orbital, empty may exist at higher energy level	(iii) Parially filled orbitals, empty orbitals are low lying.
e.g., H_2O, OH^-, F^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, NH_3, $R\text{-}NH_2$, $R\text{-}OH$, R_2O, etc.	e.g, H^-, I^-, SCN^-, $S_2O_3^{2-}$, CO, C_2H_4, C_6H_6, R_2S, R_3P, etc,

Border line : $C_6H_5 - NH_2$, C_5H_5N, N_2, N_3^-, NO_2^-, Br^-, etc.

Lewis acids also classified as hard, soft and boarder line having the following characteristics :

Hard acid	Soft acid
(i) Small size	(i) Large size
(ii) High positive oxidation state	(ii) Zero or low positive oxidation stae
(iii) Absence of any outer electrons which easily excited to higher states.	(iii) Presence of several exicitable valency electrons.
e.g., H^+, Li^+, Na^+, K^+, Mg^{2+}, Fe^{3+}, CO_2, SO_3, BF_3, $AlCl_3$, etc.	e.g, Cu^+, Ag^+, Hg^+, Hg^{2+}, I^+, I_2, Cl, M^0, etc,

Border line : Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, SO_2 etc.

6.9.2. Usefulness of SHAB principle

Hard –hard and soft-soft principle can be used as guide lines for predicting various chemical reactions. Following are some examples.

(i) BF_3 being a hard acid prefer to combine with hard base F^- and BH_3 being a soft acid prefer to combine a soft base H⁻. So the following reactions proceeds to the right.

$BF_3H^- + BH_3F^- \rightarrow BF_4^- + BH_4^-$

For similar reason the following reaction proceeds to the right.

$CF_3H + CH_3F \rightarrow CF_4 + CH_4$

(ii) Hard-hard and soft-soft combination can be used to explain the 'Pearson-Pauling paradox' of chemistry. According to the Pauling concept of electronegativity, *Cs* and *Hg* should form more stable bond with *F* as their electronegativity difference is greater. So the following reaction should not proceed to the right.

$LiI + CsF \rightleftharpoons LiF + CsI$

$HgF_2 + BeI_2 \rightleftharpoons BeF_2 + HgI_2$

In fact both the reactions proceed to the right and this anomaly can be explained by SHAB principle. On the left hand side there hard-soft and soft-hard combination (Li^+ – hard acid, I^- –soft base, Cs^+ – soft acid, F^- – hard base). To attain more stable hard-hard and soft-soft combination these reactions proceeds to the right.

(iii) The concept can explain the existance and non-existance of certain ion like AgI_2^-, is known for soft-soft combination whereas AgF_2^- does not exist as it involves soft-hard combination.

(iv) SHAB principle can be used to explain the existance of certain type of compounds as metal ores and non-existance of others. Thus hard acid like Mg^{2+}, Ca^{2+} and Al^{3+} occur in nature as $MgCO_3$, $CaCO_3$, and Al_2O_3 i.e. combining with a hard bases (CO_3^{2-}, O^{2-}). But they do not occur as sulphides because S^{2-} is a soft base. Soft acids such as Cu^+, Ag^+ and Hg^{2+} occur as their sulphides for soft-soft combination. On the otherhand border line acids like Ni^{2+}, Cu^{2+}, Pb^{2+} occur in nature both as carbonates and sulfides.

6.10. Acid-Base equilibria in aqueous solution

We are going to be working with acid-base equilibria in aqueous solution, and we will use the Bronsted-Lowry definitions that an acid is a source of H^+ and a base is an acceptor of H^+.

Acid ionization constant *K*a

A convenient way to write the reaction of an acid HA in water is

$HA(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Here water is acting as a base, accepting the H^+; the result, H_3O^+, called the conjugate acid of H_2O, since H_3O^+ can donate H^+ to reform H_2O. In a similar way, A^- is called the conjugate base of the acid HA, since A^- can accept H^+ to reform HA. The equilibrium constant is known as the acid ionization constant Ka,

$$K_a = [H_3O^+][A^-]/[HA]$$

with the understanding that [....] stands for the numerical value—without units—of the concentrationin mol/L. As usual K_a is unit-less.

An example acid ionization is

$$CH_3COOH(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = [H_3O^+][CH_3COO^-]/[CH_3COOH]$$

If Ka is much greater than 1, the acid is mostly dissociated and so is said to be a *strong acid*. If Ka is much less than 1, the acid is dissociated only to a small extent and so is said to be a *weak acid*.

Base Ionization constant K_b

Similarly, we can write the reaction of a base B in water as

$$B(aq) + H_2O(1) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

Here water is acting as an acid, donating the H^+; the result, OH^-, is called the conjugate base of H_2O, since OH^- can accept H^+ to reform H_2O. Analogously, HB^+ is called the conjugate acid of the base B, since HB^+ can donate H^+ to reform B. The equilibrium constant is konwn as the base ionization constant K_b,

$$K_b = [HB^+][OH^-]/[B]$$

where we have used the abbreviated form. Here is an example of base ionization,

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = [NH_4^+][OH^-]/[NH_3]$$

If K_b is much greater than 1, the base reacts nearly completely with water and so is said to be a strong base. If K_b is much less than 1, the base reacts hardly at all with water and so is said to be a weak base.

Water Autoionization Constant K_w

In this analysis of acid and base ionizaton we see that water in one case plays the role of a base and the other plays the role of an acid. Indeed, the role that water plays in an aqueous equilibrium can be used as another definition of acid or base.

A consequence of this dual role of water is that its equilibrium with H_3O^+ and OH^- is the reference standard against which aqueous acidity and basicity are defined.

Here is how this works. A general base ionization reaction is

$$B(aq) + H_2O(1) \rightleftharpoons BH^+(aq) + OH^-(aq), \quad K_b$$

and the ionization reaction of its conjugate acid is

$$HB^+(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + B(aq), \quad K_a$$

The sum of these two reactions is $2H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq), \quad K_w$

This equation is called the autoionization of water and its equilibrium constant is known as the water autoionization constant *Kw*. At 25°C it is equal to

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Now, we have seen that the equilibrium constant of a sum of two reactions is the product of the equilibrium constants of the summed reactions. Therefore, we know that water autoionization constant can be expressed as $K_w = K_a K_b$.

This means we can compute the base ionization constant from the ionization constant of its conjugate acid,

$K_b = K_w / K_a = 10^{-14}/Ka$, where the last equality is for 25°C. It is for this reason that base ionization constants are generally not tabulated.

6.11 pH

Because K_w is so small, water is ionized only very slightly. We an compute the concentration of H_3O^+ and OH^- by solving the autoionization equilibrium.

	$[H_3O^+]/M$	$[OH^-]$/M
Initial	0	0
Equilibrium	x	x

Initial and equilibrium activities for the autoionization of liquid water. The equilibrium expression is then $K_w = 1.0 \times 10^{-14} = x^2$ and so the concentration of H_3O^+ and OH^- are each 1×10^{-7} *M* at 25°C.

Now, as we will see in a moment, strong acids can have H_3O^+ concentrations of 1 *M* or more. This means that H_3O^+ varies over many powers of 10 (orders of magnitude), and so it is convenient to measure $[H_3O^+]$ on a logarithmic scale. Also, for weak acids and bases, which is what we will be interested in primarily, concentrations of H_3O^+ and OH^- are generally much less than 1 *M*, which means their logarithms are negative, and so it is more convenient to work with the negative logarithms so that we have a positive quantity and in particular pH and pOH are defined as $pH = -\log_{10}H_3O^+$, and $pOH = -\log_{10}OH^-$ where in each case the second equality is written with undersanding that [...] stands for the numerical value—without units—of the concentration of mol/L.

Since acids produce additional H_3O^+, their pH is always less than 7. Similarly, since bases produce additional OH^-, their pOH is always less than 7. We can relate pH and pOH. By calculating pK_w

$$pK_w$$

$$= -\log_{10}K_w$$

$$= -\log_{10}(H_3O^+ + OH^-)$$

$$= -\log_{10}H_3O^+ - \log_{10}OH^-$$

$$= pH + pOH$$

This means that at 25°C

$$pH = 14 - pOH.$$

so that bases have pH greater than 7, at 25°C.

It is important always to be mindful of the temperature being used. The reason is that equilibrim constants in general, and the value of K_w in particular, are different at different tempratures. This means that the pH of pure water will be different at different temperatures. For this reason, saying a solution has $pH = 7$ does not, by itself, mean the solution is "neutral" (has equal concentrations of H_3O^+ and OH^-. More generally, the acidic or basic character of a solution is due to the relative concentrations of H_3O^+ and OH^-, rather than a particular numerical value of pH.

6.12 Buffer and buffer capacity

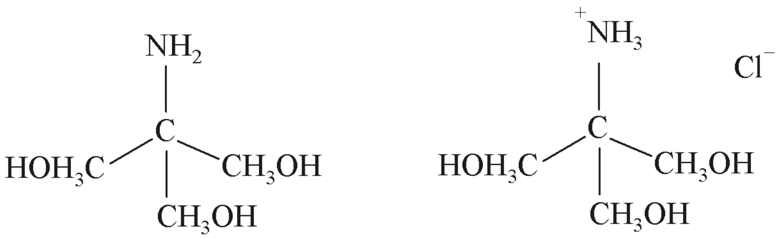
Before we get into what a buffer capacity is, we should first understand buffers. A buffer is a mixture that resists changes in pH when a limited amount of acid or base is added to it. The chemical composition of a buffer solution usually entails a weak acid or a weak base accompanied by its conjugate salt.

For example :

Acetate buffer : CH_3COOH (the weak acid) + CH_3COONa (the salt, conjugated base)

Phosphate buffer : NaH_2PO_4 (the weak acid) + Na_2HPO_4 (the salt, conjugated base)

Tris buffer :



Tris (free base) + TrisHCl (the salt, conjugated acid)

(Tris : Tris [2-amino-2-(hydroxymenthyl)-propan-1, 3-diol)1, an organic base)

Now, Buffer Capacity can be defined as the measure of the efficiency of a buffer in resisting its change in pH. This definition does present a bit of a problem as to 'what is the significant change?' Sometimes, a change of 1 unit does not bring about any significant change. At other times, even a 0.1-unit change can cause a significant difference. So, to give clear definition, buffer capacity may be defined as the quantity of a strong acid or strong base that must be added to one litre of a solution to change it by one pH unit. The buffer capacity equation is as follows :

$$\beta = dn/dpH$$

where n is some equivalents of added strong base (per 1 L of the solution). Note that the addition of n moles of acid will change the pH by the same value, but in the opposite direction. We will derive a formula connecting buffer capacity with pH, pK_a and buffer concentration.

It can be shown that the buffer capacity is maximum when the concentration of the weak acid and the base participating in the major proton transfer process in the buffer solution are same.

Let us have a buffer solution prepared by mixing a weak acid (HA) with a strong base (MOH) having their initial equivalent concentration a and b (where $a > b$) respectively. Thus in the buffer prepared, concentrations of the unconsumed weak acid and its conjugate base are : $[HA] = a - b$; $[A] = b$. From the Henderson's equation,

$$pH = pK_A + \log[A^-]/[HA] = pK_A + \log[b/(a-b)]$$

$$pH = pK_A + (1/2.303)\ \text{In}\ [b/(a-b)]$$

Therefore, $d(pH)/db = (1/2.303)[(a-b)/b][a/(a-b)^2]$

$d(pH)/db = (1/2.303)[a/(a-b)b]$

$db/d(pH) = 2.303[b(a-b)/a]$

$\beta = 2.303[b(a-b)/a]$

$d\beta/db = 2.303(a-2b)/a$

for maximum β, $d\beta/db = 0$, Then $b = a/2$

Hence, for $b = a/2$ (i.e., at half neutralization), β is maximum or minimum. Therefore, at half neutralization, the buffer capacity is maximum.

Importance of buffer solution

(1) In biological processes : The pH of our blood is maintained constant inspite of various acid and base producing reactions going on in our body. The buffer action is due to the presence of carbonic acid, bicarbonate ion and carbon dioxide in the blood.

(2) In industrial processes : The use of buffers is an important part of many industrial processes, e.g., in electroplating, in the manufacture of leather, dyes, photographic materials.

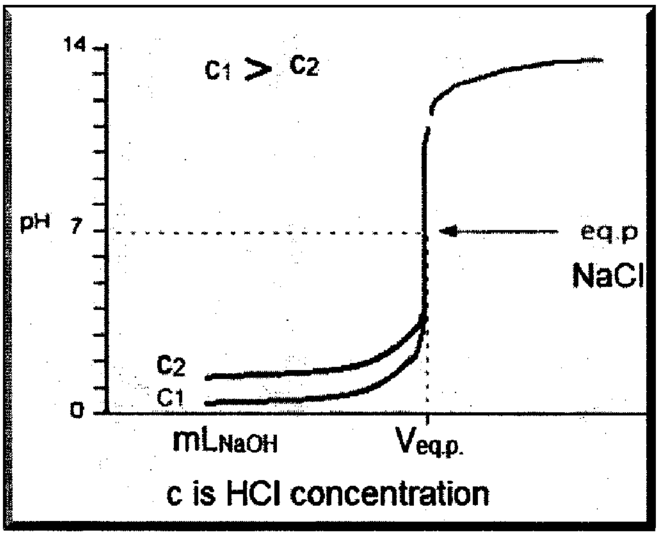
(3) In analytical chemistry : (i) in the removal of acid radicals such as phosphae, oxalate and borate which interfere in the precipitation of radicals of group 3.(ii) in complexometric titration(iii) to calibrate the pH metres

(4) In bacteriological research, culture media are generally buffered to maintain pH required for the growth of the bacteria being studied.

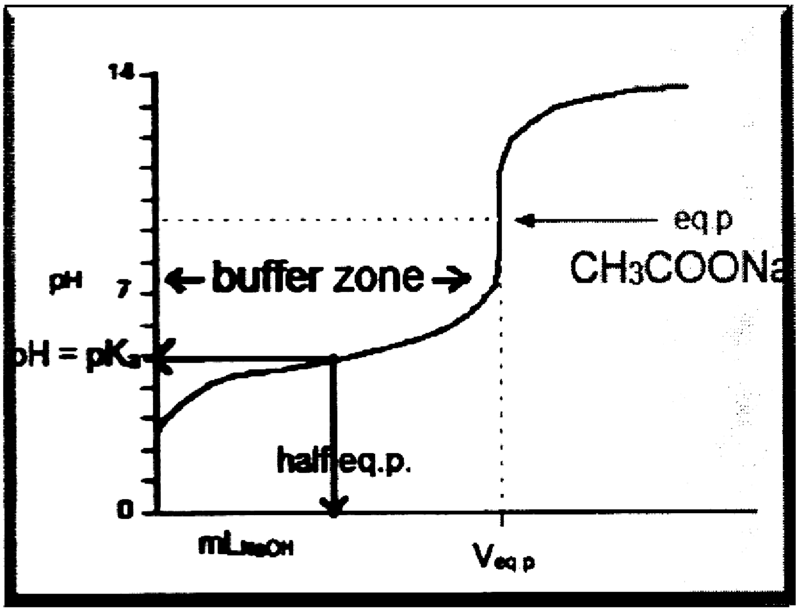
6.13 Acid–Base neutralization curves and choice of indicators

Acid – base titration, which is sometimes called neutralization titration is used to titrate any species having an acidic characteristic enough ($Ka > 1 \times 10^{-8}$) where it can be titrated with a standard solution of a strong base. Like wise any species that has basic property enough ($K_b > 1 \times 10^{-8}$) can be titrated with a standard solution of a strong acid. The most important characteristics of a neutralization titration can be ummarized in the titration curve (usually pH as a function of volume of the titrant). The titration curve can be calculated theoretically, whereupon conclusion can be drawn from it for the feasibility and the expected accuracy of a titration, and the selection of the proper indicator. The most common approach for the calculation of titration curves is based on approximations depending on the relative strength of the acid and base, the concentration levels, and the actual region of the titration curve relatively to the equivalence point.

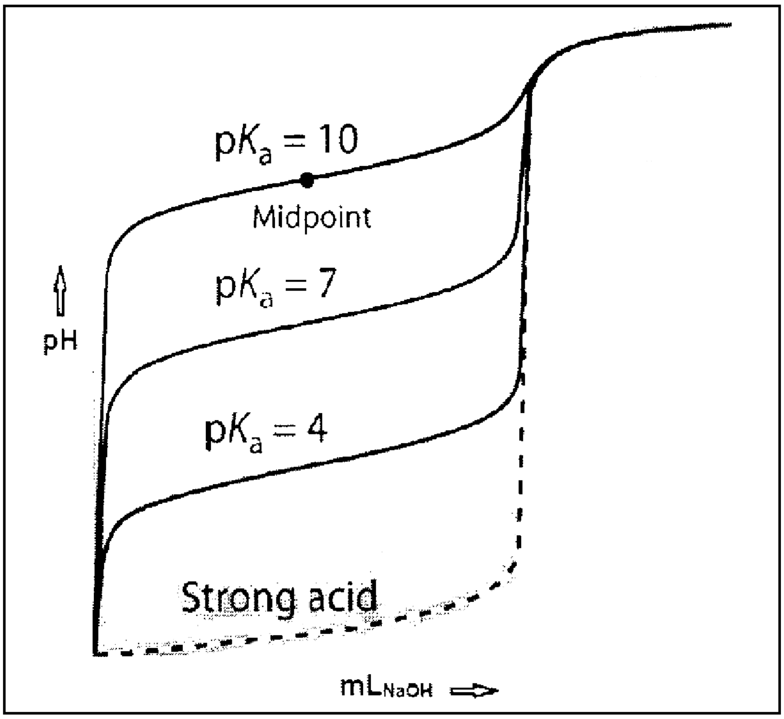
6.13.1. Strong acid and strong base titration curve



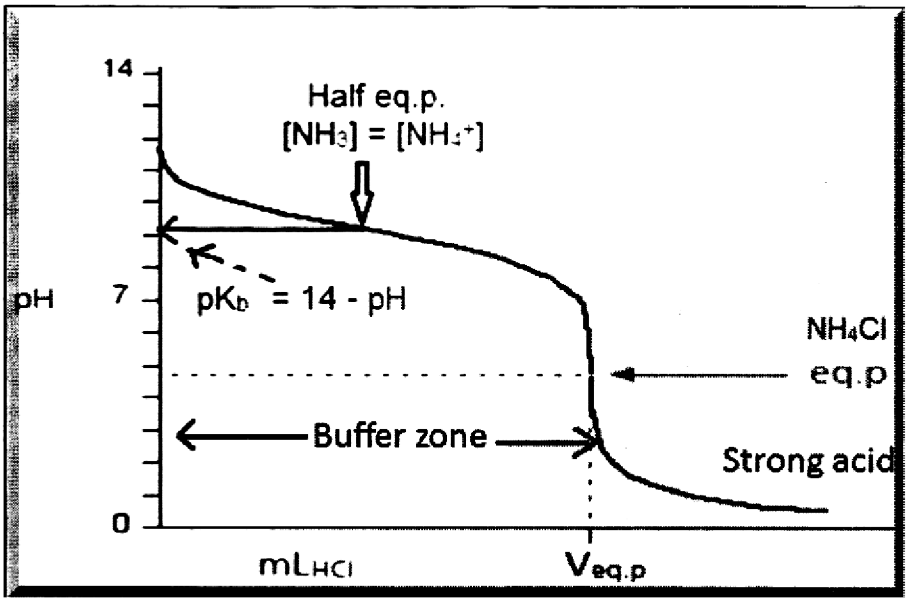
6.13.2. Weak acid and strong base titration curve

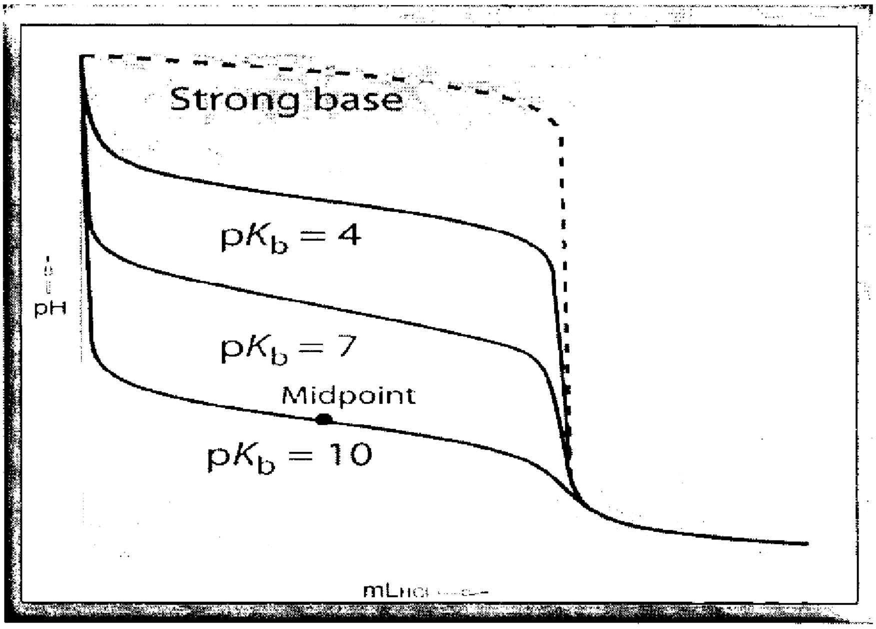


6.13.3. Weak acid and strong base titration curve

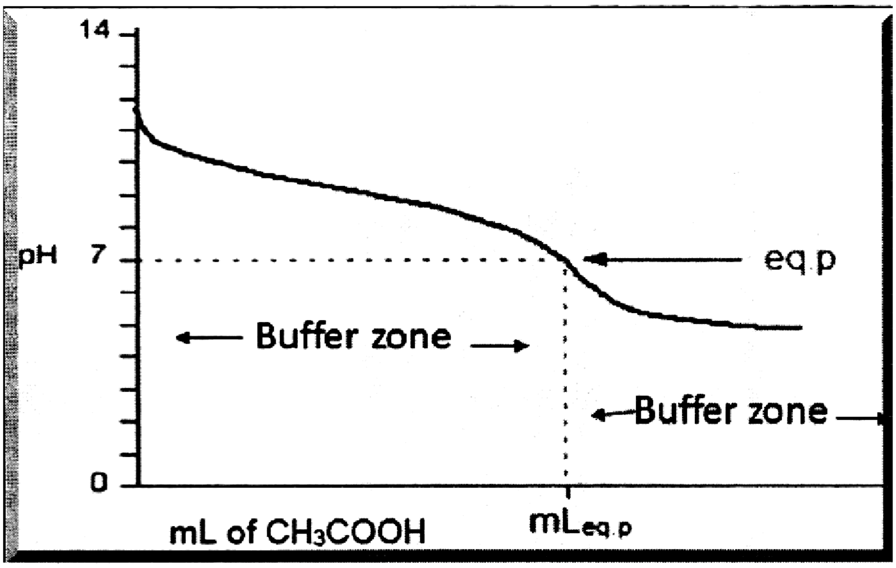


6.13.4. Weak base and strong acid titration curve

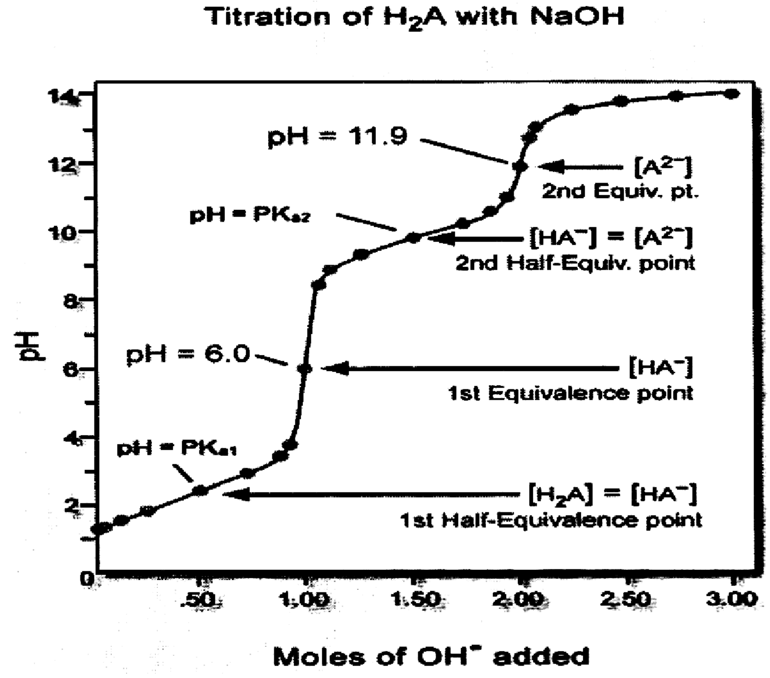




6.13.5. Weak base and weak acid titration curve



6.13.6. Curves for polyprotic acids titration



6.14 Choice of indicators in acid–base titrtions

Acid-base titration indicators are usually weak acids (HIn) which ionise as follows :

$$HIn(aq) \overset{Ka}{\rightleftharpoons} H^+(aq) + In^-(aq)$$

(colour 1) (colourless) (colour 2)

$$pH = pKa + \log[In^-(aq)]/[HIn(aq)]$$

For the reaction mixture to impart colour 1 with confidence, $[In\text{–}(aq)]/[HIn(aq)]$has to be ≤ 1/10

For the reaction mixture to impart colour 2 with confidence, $[In\text{–}\ (aq)]/[HIn(aq)]$has to be ≥ 10.

In other words, for the reaction mixture to impart colour 1 with confidence, pH value of the solution should be $pKa{-}1$ or lower, and for the reaction mixture to impart colour 2 with confidence, pH value of the solution should be $pKa{+}1$ or higher. Hence pH range of an indicator = $pKa \pm 1$.

6.15 Gas phase acidity

The proton affinity and gas phase acidity are quite similar in this contest. The term proton affinity of a species B is determined from the enthalpy change of the following process :

$B_{(g)} + {H^+}_{(g),} \rightleftharpoons BH^+_{(R)} - \Delta Hp = PA$ of B; $HA(g) \rightleftharpoons {H^+}_{(g)} + {A^-}_{(g).}$ (Gas phase acidity of HA)

ΔHp can be estimated by constructing a suitable Borm-Haber cycle. If A^- is the conjugate base of HA, then the higher proton affinity of $A-$ indicates the weaker gas phase acidity of HA. In terms of Born – Haber cycle, gas phase acidity of HA depends on the three energy terms i.e. HA bond dissociation energy, ionization energy of H and electron affinity (EA) of A. Higher stability of A-(g) will enhance the gas phase acidity of HA. In the case of aqueous phase acidity, solvation of the involved species is to be considered.

Gas phase acidity of the hydrides of 2nd period elements run as :

PA affinity : $CH_3 > NH_2 > OH > F^-$

Gas phase acidity : $HF^- > H_2O > NH_3 > CH_4$, (same sequence in aqueous phase)

Beside the A-H bond strength (which does not change remarkably in a period), the electron affinity of A is also an important factor to determine the gas phase acidity. The higher electron affinity (or electronegativity roughly) of A will favour the process more. In a period, EA increases from left to right. This reflected in above series.

A-H bond strength decreases for the heavier congeners in a particular group because of the increasing trend of $A - H$ bond length. In fact, the heavier congenrs, the valence orbitals of larger size cannot effectively overlap with the small 1s orbital of H. Thus the bond strength decreases in the following sequence :

$H-O(H_2O) > H-S(H_2S) > H-Se(H_2Se) > H-Te(H_2Te)$;

$H-N(NH_3) > P-S(PH_3)$; $H-F > H-Cl > H-Br > H-I$

Gas phase acidity : $H_2Te > H_2Se > H_2S > H_2S > H_2O$;

$HI > HBr > HCl > HF$; $PH_3 > NH_3$

Proton affinity : $OH^- > HS^- > HSe^- > HTe^-$; $F^- > Cl^- > Br^- > I^-$;

${NH_2}^- > {PH_2}^-$

In a group in general electron affinity decreases in moving from top to bottom. Thus in terms of EA, hydrides of heavier congeners should show reduced gas phase acidity. The observed reverse sequence can be explained by considering the bond strength which decreases for the heavier congeners, Thus we can conclude :

(i) In a period, the gas phase acidity (and also aqueous phase acidity) of the hydrides increases in moving from left to right and it is mainly due to the increasing trend of electron affinity.

(ii) In a group, the gas phase acidity (and also aqueous phase acidity) of the hydrides increases from top to bottom and it is governed mainly by the bond strength sequence though opposed by the electron affinity sequence.

Gas phase acidity : $C_2H_5OH > CH_3OH > H_2O$ (opposite sequence in aqueous phase)

The alkyl groups are the better electron pushing grups compared to hydrogen. Thus H_2O is expected to be stronger acid than ROH but it is not true in gas phase. To explain the sequence, we are to consider the relative stability of the conjugate bases i.e. $C_2H_5O^-$, CH_3O^- and OH⁻. Now let us consider the inherent group electronegativity(a1) and charge capacity parameters $(\sigma \infty 1/b)$

$a : H(2.1) < Me(2.3) < Et(2.32);\ \sigma : H(1) < Me(2.8) < Et(3.9)$

Thus inherent electronegativities of the groups H, Me and Et are more or less the same but their charge capacity parameters are quite different. In terms of the σ values, the charge accommodating capacity of the groups is in the sequence : Et > Me > H. The ion induced dipole interaction due to the polarization of the R-group in R-O⁻ also follows the same trend. Thus stability of the conjugate bases due to charge delocalization through the polarization of R run in the sequence : $EtO^- > MeO^- > OH^-$.

Gas phase acidity order of primary, secondary and tertiary alcohols : It runs in the sequence $R(3°)OH > R(2°)OH > R(1°)OH$.

The sequence can not be explained in terms of simple electron pushing inductive effect of *R* but it can be explained in terms of electron capacity charge parameters of the R groups and the resultant stability sequence of the conjugate bases. The charge capacity is large for the more branched chain alkyl groups and consequently such alkyl groups are the better moieties to accommodate the charge. Thus the stability order of the conjugate base in terms of charge delocalization runs as $R(3°)O > R(2°)O^- > R(1°)O^-$

Gas phase acidity $CH_3OH > H_2O$ but $CH_3SH < H_2S$

The size of the orbitals of carbon and sulfur differ significantly while the orbitals of carbon and oxygen are comparable in size. Thus stabilization of CH_3S^- through charge delocalization by hyperconjugation is not efficient but CH_3O^- is efficiently stabilized through charge delocalization by hyperconjugation.

Similarly, the gas phase acidity orders are $CHCl_3 > CHF_3$; $C_6H_5CH_3 > CH_4$; $CH_3NO_2 > CH_4$

6.16 Summary

In the present unit different types of acid base theories are discussed in detailed, According to Arrhenius acids produce H^+ ion in aqueous solution whereas bases produce OH" ion in aqueous solution. According to Bransted Lowry concept acids are proton donor whereas bases are proton acceptor. In Lewis concept acids are lone pair acceptor and bases are lone pair donor. In Lux flood concept acids are oxide ion acceptor and bases are oxide ion donor. The nucleophilicity trends of some species like as:

$OH^- > F^-$; $NH_3 > H_2O$; $I^- > Br^- > Cl^- > F^-$; $CH_3S^- > CH_3O^-$

Drago and Wayland equation: $\Delta H = E_A E_B + C_A C_B$ for reaction $A_{gas} + B_{gas} \rightarrow AB_{gas}$

In this study the leveling and differentiating effect are discussed.

Here many examples of the relative acid strengths are shown. Like $CH_3COOH < HNO_2 < HSO_4^-$;

$HF < HCl < HBr < HI$; $H_3PO_4 > H_3PO_3 > H_3PO_2$ etc.

Hammett acidity function is used to measure the acidity function of super acids. According to HSAB principle a hard acid prefers to combine with a hard base and a soft acid prefers to combine with a soft base to form a more stable adduct.

When acid dissociation constant is greater than 1, then it is called strong acid and when acid dissociation constant less than 1, then it is weak acid. pH is a negative logarithm of hydrogen ion $[H^+]$ concentration. It is given as: pH = 14 – pOH at 25°C. A buffer is a mixture that resists changes in pH when a limited amount of acid or base is added to it. Buffer capacity can be defined as the measure of the efficiency of a buffer in resisting its change in pH. The most common approach for the calculation of titration curves is based on approximations depending on the relative strength of the acid and base, concentration levels, and the actual region of the titration curve relatively to the equivalence point. Gas phase acidity of the second period elements run as:

$HF > H_2O > NH_3 > CH_4$;

$H_2Te > H_2Se > H_2S > H_2O$; $HI > HBr > HCl > HF$; $PH_3 > NH_3$

6.17 Questions

(1) What are the different types of Lewis acids and bases ? Discuss the merits and demerits of Lewis concept.

(2) What are the basic features of Bronsted – Lowery concept of acid and bases ? Discuss its merits and demerits.

(3) Discuss the basic idea of Lux-Flood concept of acids and bases ?

(4) What do you mean by the leveling effect of water ? How do you express the acid strength ?

(5) Discuss the relative strength and factors of mononuclear oxyacids ?

(6) What do you mean by the Hammett acidity function (H_0) ? What do you mean by H_0. H_+, H_- ? What do you mean by the superacids ?

(7) Discus the basic concept of SHAB principle. What are the basic characteristics of hard and soft species ?

(8) What do you mean by buffer ? How does a buffer show its actionT? Show that buffer capacity is maximum at the *pH* close to the *pKa* value of the conjugate weak acid.

(9) Discuss the basic principle involved in selecting the indicator in acid base titration.

(10) What do you mean by gas phas acidity ? Which factor affecting the strength of gas phas acidity ?

6.18 Answers

(1) See the section 6.2.5

(2) See the section 6.2.3

(3) See the section 6.2.4

(4) See the section 6.4 and 5.5

(5) See the section 6.6

(6) See the section 6.7

(7) See the section 6.8 and 6.8.1

(8) See the section 6.11 and 6.12

(9) See the section 6.13

(10) See the section 6.14

6.19 Further Reading

1. *Inorganic Chemistry : Principles of Structure and Reactivity* James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi
2. *Advanced Inorganic Chemistry* F. A. Cotton and G. Willkinson
3. *Fundamental Concepts of Inorganic Chemistry :* Volume 3, A. K. Das
4. *General & Inorganic Chemistry,* Volume 1 & 2, R. Sarkar
5. *Concise Inorganic Chemistry,* J. D. Lee

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