2. Prove that $12! = 2^6 \cdot 6!(1 \cdot 3 \cdot 5 \cdot 7 \cdot 9 \cdot 11)$
3. $\frac{(n+2)!}{n!} = n^2 + 3n + 2$. Prove it.
4. $(2n)!\,(n-1)! = 2(n!)\,(2n-1)!$. Prove it.

ANSWERS

1. (a) 56 (b) 9

1.12 PERMUTATIONS AND COMBINATIONS

Permutations. The different arrangements that can be made with a given number of things taking some or all of them at a time are called permutations.

The symbol ^nP_r is used to denote the number of permutations of n things taken r at a time.

To find the value of ^nP_r

The number of permutations of n things taken r at a time is the same as the number of ways in which r places in a row can be filled with n different things.

Suppose that we have n things. The first place can be filled up by any one of these n things. Thus there are n ways of filling up the first place.

When the first place has been filled up by any one of the n ways, we are left with $(n-1)$ things and any one of them can be put in the second place. Therefore the second place can be filled up in $(n-1)$ ways. So by the principle of Association, the number of ways of filling up the first two places is $n(n-1)$.

When the first two places have been filled up in any one of the $n(n-1)$ ways, then we are left with $(n-2)$ things. So the third place can be filled up in $(n-2)$ ways.

By the principle of Association, the number of ways of filling up the first three places is $n(n-1)(n-2)$.

Proceeding in this way, the number of ways in which r places can be filled up is

$$^nP_r = n(n-1)(n-2) \text{ .... upto } r \text{ factors}$$
$$= n(n-1)(n-2) \text{ ....} (n-(r-1))$$
$$= n(n-1)(n-2) \text{ ....} (n-r+1)$$

Therefore $^nP_r = n(n-1) \text{ ....} (n-r+1)$

For example $^7P_4 = 7 \times 6 \times 5 \times 4 = 840$

$$^5P_4 = 5 \times 4 \times 3 \times 2 = 120$$

When $r = n$, $^nP_r = {}^nP_n = n(n-1)(n-2) \text{ .... to } n \text{ factors}$

$$= n(n-1)(n-2) \text{ ....} (n-(n-1))$$
$$= n(n-1)(n-2) \text{ ....} 1$$
$$= n!$$

So $^nP_n = n!$

Now to prove that $^nP_r = n \times {}^{n-1}P_{r-1} = \frac{n!}{(n-r)!}$

$$\text{L.H.S.} = {}^nP_r = n(n-1)(n-2) \text{ ....} (n-r+1)$$
$$= \frac{\{n(n-1)(n-2)\text{.......}(n-r+1)\}\{(n-r)(n-r-1)\text{.....}3\cdot2\cdot1\}}{(n-r)(n-r-1)\text{.....}3\cdot2\cdot1}$$
$$= \frac{n!}{(n-r)!}$$

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$$\text{R.H.S.} = n \times {}^{n-1}P_{r-1}$$

$$= n \times \frac{(n-1)!}{((n-r)\cdot(r-1))!}$$

$\because$ We have proved above ${}^nP_r = \frac{n!}{(n-r)!}$

$$\frac{n.(n-1)!}{(n-r)!} = \frac{n!}{(n-r)!}$$

$$\therefore \quad {}^nP_r = n \times {}^{n-1}P_{r-1} = \frac{n!}{(n-r)!}$$

***Example 1.* Find the value of ${}^{12}P_4$.**

Solution.

$$ {}^{12}P_4 = 12 \times 11 \times 10 \times 9 = 11880 $$

Example 2. If ${}^{n-1}P_3 : {}^{n+1}P_3 = 5 : 12$, find the value of n.

Solution.

$$\frac{{}^{n-1}P_3}{{}^{n+1}P_3} = \frac{5}{12}$$

or $$\frac{(n-1)(n-2)(n-3)}{(n+1)\,n(n-1)} = \frac{5}{12}$$

Simplifying $$\frac{(n-2)(n-3)}{(n+1)n} = \frac{5}{12}$$

Cross-multiplying , $12(n^2 - 5n + 6) = 5n\,(n + 1)$

$\Rightarrow \quad 12n^2 - 60n + 72 = 5n^2 + 5n$

$\Rightarrow \quad 7n^2 - 65n + 72 = 0$

$$\Rightarrow \quad n = \frac{65 \pm \sqrt{(-65)^2 - 4(7)(72)}}{2\times 7}$$

$$= \frac{65 \pm 47}{14} = 8 \quad \text{or} \quad \frac{9}{7}$$

Rejecting $\frac{9}{7}$ as n is a +ve integer.

Hence $n = 8$.

***Example 3.* In how many ways can the letters of 'Lahore' be arranged ?**

Solution.

Total number of letters in the word Lahore = 6

These are all different letters.

$\therefore$ Number of arrangements of these letters taken all at a time ${}^6P_6 = 6! = 720$.

***Example 4.* How many words can be formed from the letters of the word DAUGHTER so that the vowels are never together ?**

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Solution.

Total number of letters in the word DAUGHTER is 8. These 8 letters are all different.

First of all, let us find those arrangements in which vowels are always together.

When the vowels A, E, U are always together, they can be supposed to be put in a bracket and treated as one letter (A, E, U). So the number of letters becomes 6.

i.e., (8 – 3 + 1) (D, G, H, T, R (A, E, U))

These 6 letters can be arranged in $^6P_6$ ways = 6! ways

Now the three letters in the group (A, E, U) can be arranged among themselves in $^3P_3$ = 3! ways.

∴ Required numbers of such words = 6! 3! = 720 × 6 = 4320.

Now total numbers of arrangements of letters of the word DAUGHTER is 8!

∴ Number of words in which vowels are never together

= Total number of words – Numbers of words in which vowels are always together

= 8! – 4320

= 40320 – 4320 = 36000.

EXERCISES

1. How many different words can be formed with the letters of the word 'LUCKNOW'?
2. Prove that $^{2n}P_n = 1 \cdot 3 \cdot 5 \cdot \ldots\ldots (2n-1) \cdot 2^n$.
3. Find n if $^{n-3}P_6 : {}^{n-2}P_4 = 14 : 1$.
4. In how many ways 5 books on English and 4 books on Hindi can be placed on a shelf so that the books on the same subject always remain together?
5. How many words can be formed out of the letters of the word 'ORIENTAL' so that no two of the vowels are together?

ANSWERS

1. 7! = 5040
3. 4
4. 5! 4! 2!
5. 4! $^5P_4$ = 2880.

Combinations : The different selections or groups that can be made out of a given number of things taking some or all of them at a time are called combinations.

The symbol ^nC_r is used to denote the number of combinations of n things taken r at a time.

To find the value of ^nC_r

The number of combinations of n things taken r at a time is denoted by ^nC_r. Let these combinations be x. Because each combination contains r things and these r things in any one of the combinations can be arranged among themselves in $r!$ ways (as we know by permutations). Hence one combination will give rise to $r!$ permutations. So x combinations will give rise to $x \cdot r!$ permutations. But the number of permutation of n things taken r at a time is ^nP_r.

$$^nP_r = x \cdot r! = {}^nC_r \cdot r!$$

$$^nC_r = \frac{^nP_r}{r!} = \frac{n!}{(n-r)!\,r!}$$

$$\therefore \quad ^nC_r = \frac{n!}{r!(n-r)!}$$

To prove that $^nC_r = {}^nC_{n-r}$.

We know that $^nC_r = \dfrac{n!}{r!(n-r)!}$

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$$6n + 6 = 11r + 11 \quad \text{and} \quad n = 2r$$

$\Rightarrow \quad 6(2r) + 6 = 11r + 11 \qquad n = 2 \times 5$

$\Rightarrow \quad 12r + 6 = 11r + 11 \qquad = 10$

$\Rightarrow \quad r = 5.$

Hence $\quad n = 10, \; r = 5.$

EXERCISES

1. Evaluate (*i*) ${}^{51}C_{49}$ (*ii*) ${}^{100}C_{96}$
2. If ${}^{n}P_r = {}^{n}P_{r-1}$ and ${}^{n}C_r = {}^{n}C_{r-1}$, find n and r.
3. Prove that ${}^{2n}C_n = \dfrac{2^n \; 1 \cdot 3 \cdot 5 \cdot ......(2n-1)}{n!}$.
4. If ${}^{18}C_r = {}^{18}C_{r-2}$, evaluate ${}^{r}C_5$ and ${}^{11}C_r$.

ANSWERS

1. (*i*) 1275 (*ii*) 3921225
4. 56, 165

1.13 PROBABILITY

Probability means chance or possibility occurrence of some event.

Experiment. An experiment is defined as a process of well-defined outcomes.

Random experiment. A random experiment is defined as an experiment in which all possible outcomes are known in advance.

For example, If we toss a coin we will either get head or tail.

or, in throwing of a dice there are 6 possibilities 1 or 2 or 3 or 4 or 5 or 6.

Sample space. The sample space of a random experiment is the set of all possible outcomes.

For example,

	Random Experiment	*Sample Experiment*
1.	Throwing of a fair dice	$S = \{1, 2, 3, 4, 5, 6\}$
2.	Tossing of a coin	$S = \{H, T\}$
3.	Tossing of two coins	$S = \{HH, HT, TH, TT\}$
4.	A family of two children	$S = \{BB, BG, GB, GG]$

Event. An event is a subset of sample space. An event is called simple event, if it contains only one sample point. In the experiment of throwing a die, the event A of getting 3 is a simple event.

Equal likely outcomes. The outcomes of a random experiment are called equally likely, if all of these have equal preferences. In the experiment of tossing of a coin the outcomes head and tail are equally likely.

Exhaustive outcomes. The outcomes of random experiment are called exhaustive if they cover all the possible outcomes of the experiment. In throwing of a dice, the outcomes 1, 2, 3, 4, 5, 6 are exhaustive.

Probability. Suppose in a random experiment there are n equally likely, exhaustive outcomes. Let A be an event and there are m outcomes favourable to the happening of it.

Then the probability $P(A)$ of the happening of the event A is defined as

$$P(A) = \frac{m}{n}$$

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Changing r to $n-r$ we get

$$^nC_{n-r} = \frac{n!}{(n-r)!(n-(n-r))}$$

$$= \frac{n!}{(n-r)!\,r!}$$

$$\therefore \quad ^nC_r = {}^nC_{n-r}. \qquad \text{Hence the result.}$$

***Example 1.* Evaluate $^{50}C_{47}$.**

Solution.

$$^{50}C_{47} = {}^{50}C_{50-47} = {}^{50}C_3 = \frac{\lfloor 50}{\lfloor 3 \lfloor 47} = \frac{50\cdot 49\cdot 48 \lfloor 47}{\lfloor 3 \lfloor 47}$$

$$= \frac{50\cdot 49\cdot 48}{3\cdot 2\cdot 1} = 19600.$$

***Example 2.* If $^nC_{10} = {}^nC_{15}$, find the value of $^{27}C_n$.**

Solution:

Given $\quad ^nC_{10} = {}^nC_{15}$

Either $10 = 15$ or $10 + 15 = n$ $\quad \left| \because {}^nC_r = {}^nC_{n-r} \right.$

But $10 = 15$ is impossible

So $n = 10 + 15$

$\therefore \quad n = 25$

Now we have to calculate $^{27}C_n$ i.e., $^{27}C_{25}$ $\quad \left| \because n = 25 \right.$

$$^{27}C_{25} = \frac{27!}{25!\,2!} = \frac{27\cdot 26\cdot 25!}{25!\;2!}$$

$$= \frac{27\cdot 26}{2\cdot 1} = 351$$

So $\quad ^{27}C_{25} = 351.$

***Example 3.* If $^{n+1}C_{r+1} : {}^nC_r = 11 : 6$ and $^nC_r : {}^{n-1}C_{r-1} = 6 : 3$, find the values of n and r.**

Solution.

$$\frac{^{n+1}C_{r+1}}{^nC_r} = \frac{11}{6} \quad \text{and} \quad \frac{^nC_r}{^{n-1}C_{r-1}} = \frac{6}{3}$$

$$\Rightarrow \quad \frac{\dfrac{(n+1)!}{(r+1)!\{(n+1)-(r+1)\}!}}{\dfrac{n!}{r!(n-r)!}} = \frac{11}{6} \quad \text{and} \quad \frac{\dfrac{\lfloor n}{\lfloor r \lfloor n-r}}{\dfrac{(n-1)!}{(r-1)!\{(n-1)-(r-1)\}!}} = \frac{6}{3} = 2$$

$$\Rightarrow \quad \frac{(n+1)!}{(r+1)!(n-r)!} \times \frac{r!(n-r)!}{n!} = \frac{11}{6} \quad \text{and} \quad \frac{\lfloor n}{\lfloor r \lfloor n-r} \times \frac{(r-1)!(n-r)!}{(n-1)!} = 2$$

$$\Rightarrow \quad \frac{(n+1)!\;r!}{(r+1)!\,n!} = \frac{11}{6} \quad \text{and} \quad \frac{n!(r-1)!}{r!(n+1)!} = 2$$

$$\Rightarrow \quad \frac{(n+1)n!\;r!}{(r+1)\,r!\,n!} = \frac{11}{6} \quad \text{and} \quad \frac{n(n-1)!(r-1)!}{r(r-1)!\;(n-1)!} = 2$$

$$\Rightarrow \quad \frac{n+1}{r+1} = \frac{11}{6} \quad \text{and} \quad \frac{n}{r} = 2$$

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or $$P(A) = \frac{\text{Total no. of favourable cases in the happening of } A}{\text{Total no. of equally likely exhaustive cases}}$$

It is clear from the definition that

$$0 \le m \le n \quad \Rightarrow \quad 0 \le \frac{m}{n} \le 1$$
$$\Rightarrow \quad 0 \le P(A) \le 1$$

The number of cases favourable to the non-happening of the event A is $n - m$.

$$\therefore \quad P(\text{not } A) = \frac{n-m}{n}$$
$$= \frac{n}{n} - \frac{m}{n} = 1 - \frac{m}{n}$$
$$= 1 - P(A)$$
$$P(\bar{A}) = 1 - P(A) \qquad (\bar{A} = \text{not } A)$$
$$\Rightarrow P(\bar{A}) + P(A) = 1$$

Example 1. **What is the probability of getting an even number in the throw of an unbiased die?**

Solution.

In this experiment, there are 6 equally likely possible outcomes, *i.e.*, $\{1, 2, 3, 4, 5, 6\}$ and let A be the event of getting even number.

$$A = \{2, 4, 6\}$$

Favourable cases = 3

Total no. of cases = 6

$$P(A) = \frac{3}{6} = \frac{1}{2}$$

Example 2. **Find the probability of getting the sum 10 in a single throw of two dice.**

Solution.

Here $S = \{(1, 1), (1, 2), (1, 3) \ldots\ldots (6, 5), (6, 6)\}$

No. of possible outcomes are $6 \times 6 = 36$

Let A be the event of getting sum 10

$$A = \{(4, 6), (5, 5), (6, 4)\}$$

Favourable cases = 3

$$P(A) = \frac{3}{36} = \frac{1}{12}.$$

Example 3. **Find the probability of getting a 'King' or 'Queen' in a single draw from a well shuffled pack of playing cards.**

Solution.

Let A be the event of getting a King or a Queen in the draw.

No. of favourable cases for happening of the event A is $4 + 4 = 8$

Total number of cases = 52

$$P(A) = \frac{8}{52} = \frac{2}{13}.$$

EXERCISES

1. Find the probability of getting an odd number in a single throw of a fair dice.
2. Find the probability of getting a number less than 2 in a single throw of a fair dice.

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Total number of sample points in A or B

$$= m_1 + m_2 - m_3$$

$$P(A \text{ or } B) = \frac{m_1 + m_2 - m_3}{n} = \frac{m_1}{n} + \frac{m_2}{n} - \frac{m_3}{n} = P(A) + P(B) - P(AB)$$

***Example 1.* The probability that a company executive will travel by bus is $\frac{2}{3}$ and that he will travel by train is $\frac{1}{5}$. Find the probability of his travelling by bus or train.**

Solution.

Let A = the event that the company executive travels by bus

$$\therefore \quad P(A) = \frac{2}{3}$$

Let B = the event that the company executive travels by train

$$P(B) = \frac{1}{5}$$

Events in this question are mutually exclusive because either he can travel by bus or by train.

$\therefore$ The probability of his travelling by bus or by train

$$P(A \text{ or } B) = P(A) + P(B) = \frac{2}{3} + \frac{1}{5} = \frac{13}{15}.$$

***Example 2.* One number is drawn from numbers 1 to 150. Find the probability that it is either divisible by 3 or 5.**

Solution.

Here $S = \{1, 2, 3, \ldots\ldots, 149, 150\}$

Let A = the event that number is divisible by 3

$$A = \{3, 6, 9, \ldots\ldots, 147, 150\}$$

$$P(A) = \frac{50}{150}$$

B = The event that the number is divisible by 5

$$B = \{5, 10, 15, \ldots\ldots, 145, 150\}$$

$$P(B) = \frac{30}{150}$$

The events are not mutually exclusive because some points are common to both A and B. The common points are 15, 30, 45, ..., 150.

So $AB = \{15, 30, 45, \ldots\ldots, 135, 150\}$

$$P(AB) = \frac{10}{150}$$

So by the Addition theorem

$$P(A \text{ or } B) = P(A) + P(B) - P(AB)$$

$$= \frac{50}{150} + \frac{30}{150} - \frac{10}{150} = \frac{70}{150} = \frac{7}{15}$$

Hence the result.

EXERCISES

1. A bag contains 30 balls numbered from 1 to 30. One ball is drawn at random. Find the probability that number of the ball is a multiple of 5 or 6.

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3. In a simultaneous toss of two coins, find the probability of getting exactly two heads.
4. Find the probability of getting no head in a single toss of three coins.
5. A ball is drawn at random from a box containing 4 white, 7 red and 12 black balls. Determine the probability that the ball drawn is red.

ANSWERS

1. $\frac{1}{2}$ 2. $\frac{1}{6}$ 3. $\frac{1}{4}$ 4. $\frac{1}{8}$ 5. $\frac{7}{23}$

1.14 MUTUALLY EXCLUSIVE EVENTS

Two events are said to be mutually exclusive events if both cannot occur together with same trial. In experiment of rolling a die, the events $A = \{1, 3\}$ and $B = \{2, 4, 6\}$ are mutually exclusive events. In the same experiment, the events $A = \{1, 3\}$ and $C = \{1, 3, 5, 6\}$ are not mutually exclusive events because if 3 appears on the die it is favourable to both A and C.

Addition Theorem (For mutually exclusive events). If A and B are two mutually exclusive events associated with a random experiment, then

$$P(A \text{ or } B) = P(A) + P(B).$$

Proof: Let n be the total number of exhaustive, equally likely cases of the experiment.

Let m_1 and m_2 be the number of cases favourable to the happening of the events A and B respectively.

$$P(A) = \frac{m_1}{n}$$

and $$P(B) = \frac{m_2}{n}$$

As the events are given to be mutually exclusive, so there will be no sample point common to both events A and B.

$\therefore$ The event A or B can happen in exactly $m_1 + m_2$ ways

$$\therefore \quad P(A \text{ or } B) = \frac{m_1 + m_2}{n} = \frac{m_1}{n} + \frac{m_2}{n} = P(A) + P(B)$$

Hence $P(A \text{ or } B) = P(A) + P(B)$

Addition Theorem (For non-mutually events). If A and B are two non-mutually exclusive events associated with a random experiment, then

$$P(A \text{ or } B) = P(A) + P(B) - P(AB)$$

Proof. Let n be the total number of exhaustive and equally likely cases of the experiment.

Let m_1 and m_2 be the number of cases favourable to the happening of the events A and B respectively.

$$\therefore \quad P(A) = \frac{m_1}{n}$$

$$P(B) = \frac{m_2}{n}$$

As the events are given to be non-mutually exclusive, there will be some sample points common to both events A and B.

Let m_3 be the number of common sample points

$$P(AB) = \frac{m_3}{n}$$

These m_3 sample points are also included in the events A and B separately

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The momentum of the emitted γ-ray is given, according to the de Broglie relation, by

$$p = h/\lambda \qquad ...(65)$$

where λ is the γ-ray wave length. Since linear momentum must be conserved, the nucleus must recoil in the opposite direction, with the recoil energy R given by

$$R = p^2/2M \qquad ...(66)$$

where M is the mass of the recoiling nucleus. The target nucleus, too, must recoil with energy R on receiving the γ-ray, with the result that some of the energy of the γ-ray transition, E_γ, is converted into the recoil energy. Thus, for the emitting nucleus

$$E = E_\gamma - R \qquad ...(67)$$

and for the absorbing nucleus (absorber)

$$E = E_\gamma + R \qquad ...(68)$$

We see that the emission and absorption lines are centred $2R$ apart.

Since

$$E_\gamma = h\nu = hc/\lambda = pc \qquad ..(69)$$

we have, from Eqs. 66 and 69,

$$2R = E_\gamma^2 / Mc^2 \qquad ...(70)$$

For the resonance absorption to occur, Γ must be greater than or equal to the loss in γ-ray energy due to recoil, *i.e.*,

$$\Gamma \approx 2R \qquad ...(71)$$

The plot of the number of the emitted γ-rays versus energy is given in Fig. 55.

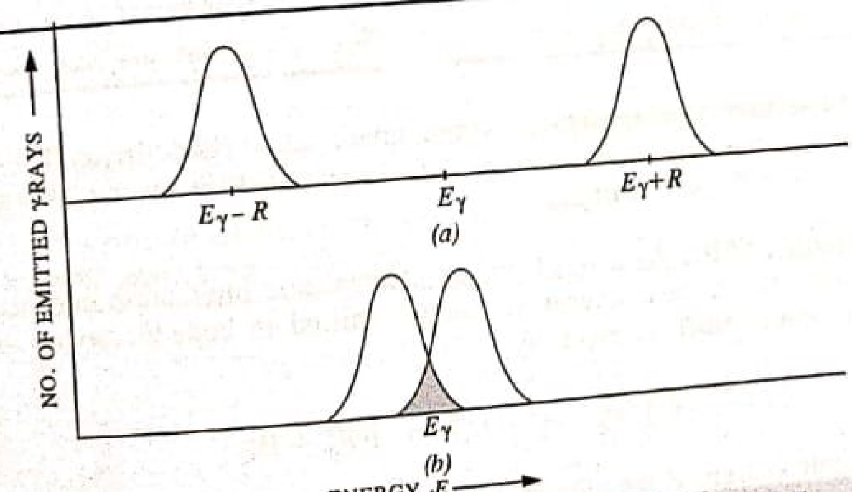

Fig. 55. *(a)* Resonance absorption and emission curves for $2R > \Gamma$.
(b) Resonance absorption and emission curves for $2R \approx \Gamma$.

Let us make an order-of-magnitude calculation. For the Mössbauer nuclide ^{57}Fe, it is found experimentally that $E_\gamma = 14{\cdot}4$ keV; and $M = 1{\cdot}67 \times 10^{-27}$ kg. Hence, using Eq. 70, $R = 2 \times 10^{-3}$ eV. The life-time of the lowest excited state of ^{57}Fe is 10^{-7} s which, using Eq. 64, corresponds to Γ-value of about 5×10^{-9} eV. In other words, $R >> \Gamma$. Obviously, the resonance absorption condition, *viz.*, $\Gamma \approx 2R$ (Eq. 71) is not obtained. Mössbauer devised a very ingenious method to obtain the γ-ray resonance condition. He took the sample (containing the emitter nuclei) in the form of a solid at low temperatures. In the solid the nuclear recoil energy is dissipated among the lattice vibrations or the solid as a whole. Thus, the emitted γ-rays have the energy, E_γ. Likewise, no energy is lost to recoil

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S_x, S_y are the components along x and y-axes, respectively; I = nuclear spin and I_x, I_y, I_z are the Cartesian components ; D, E are the zero-field splitting constants, Q is the nuclear quadrupole moment and A is the hyperfine coupling constant.

The constants g, D, E, A and Q are determined empirically from experiment. The terms involving B and S denote the interaction of electronic magnetic moment with the Zeeman field; they are generally anisotropic. The terms involving D and E give rise to fine structure, resulting from the second-order effects of crystal field exerted via spin-orbit interaction. The terms involving I and S denoting hyperfine interaction are also anisotropic, resulting from dipole interactions between the nuclei and the electrons. The quadrupole interaction term (for nuclei with nuclear spin, $I \geq 1$) is also anisotropic. The last term represents the direct interaction between the nuclear magnetic moment and the Zeeman field. Though g is positive, the signs of other constants are very difficult to obtain since they have to be determined from second-order effects. Of course, not all the terms in Eq. 63 are of equal importance for a given metal ion. For instance, if an ion has no nuclear spin, the terms containing I vanish. For a free electron, on the other hand, D, E, I, A, Q are all zero so that the Hamiltonian assumes the form $H = g_e \mu_B B$, where g_e is now a scalar quantity.

By convention, S is assigned a value that makes the observed number of energy levels equal to $2S+1$. In those spin systems, where only the lower energy levels are occupied, the higher energy levels cannot be detected experimentally. Thus, the spin determined from the $2S+1$ observed levels corresponds to a fictitious state ; hence the effective spin is sometimes referred to as 'fictitious spin'.

MÖSSBAUER SPECTROSCOPY (MB SPECTROSCOPY)

The discovery of **Mössbauer effect** or Mössbauer spectroscopy (also known as the recoil-less nuclear gamma resonance fluorescence (NRF) spectroscopy) in 1958 by the German physicist Rudolf Mössbauer was hailed as a breakthrough in nuclear and solid state physics. Mössbauer shared the 1961 Physics Nobel Prize with the American nuclear physicist Robert Hofstadter (who was honoured for electron–nuclear scattering concerning the structure of the nucleons). Mössbauer spectroscopy has found wide application in elucidating the nature of the chemical bond in inorganic solid state chemistry and biological science, for instance, bonding in haemoglobin and oxyhaemoglobin.

Basic Principle of NRF Spectroscopy. Consider the original experiment performed by Mössbauer. Here ^{57}Co decays to the excited state of iron, $^{57}Fe^*$ by electron capture (EC), which further decays to the stable ^{57}Fe by the emission of delayed gamma ray (Fig. 54). This latter phenomenon is called **γ–ray fluorescence**. In the presence of a target nucleus ^{57}Fe, this gamma ray can be resonantly absorbed. Since the excited state $^{57}Fe^*$ has a finite life–time (τ), the uncertainty in the enegy of the emitted γ–ray is governed by the Heisenberg uncertainty principle, $\Delta E \Delta t \approx \hbar$, which can be rewritten in a slightly different notation as

$$\Gamma\tau \approx \hbar \qquad ...(64)$$

where Γ is the line width and τ is the life–time of the excited state. From Eq. 46 we see that since 10^{-11} s $< \tau < 10^{-4}$ s, $10^{-4} < \Gamma < 10^{-11}$ eV.

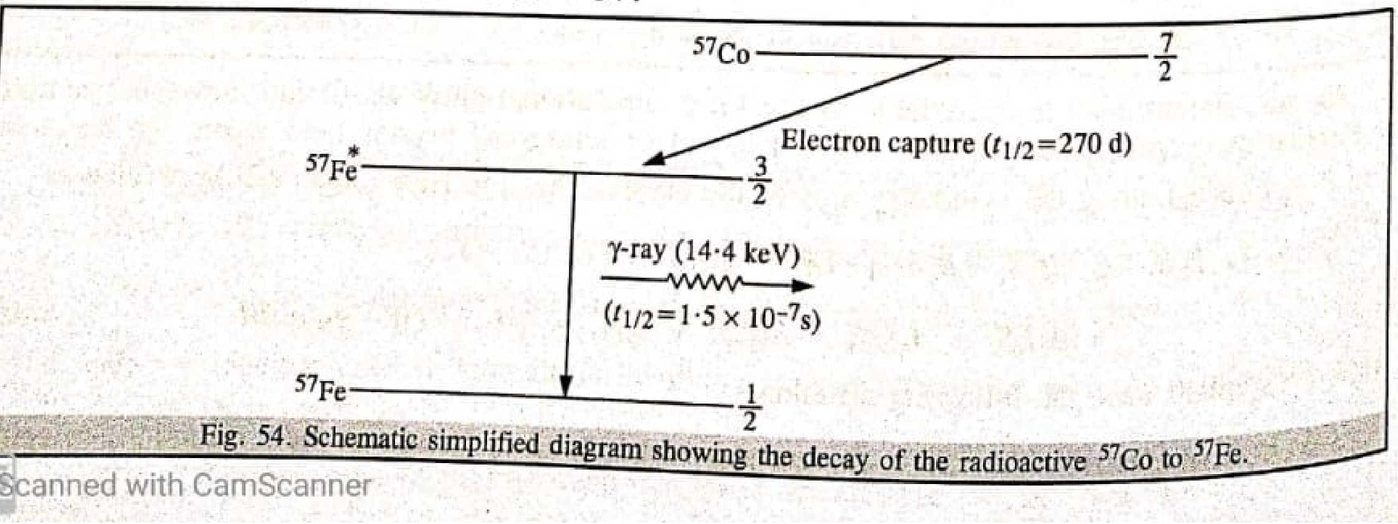

Fig. 54. Schematic simplified diagram showing the decay of the radioactive ^{57}Co to ^{57}Fe.

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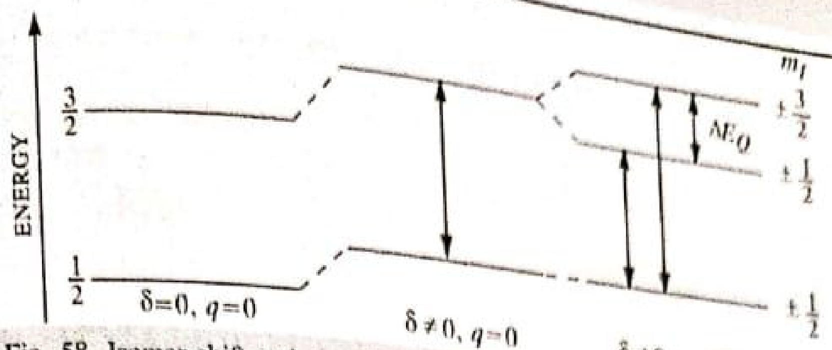

Fig. 58. Isomer shift and electric quadrupole splitting in ^{57}Fe energy levels.

Example 47. The Mössbauer spectrum of $K_4[Fe(CN)_6]$ consists of one line whereas that of $K_3[Fe(CN)_5NO]$ consists of two lines. Draw these spectra qualitatively and account for their appearance.

Solution : *(a)* $K_4[Fe(CN)_6]$. A single line Mössbauer spectrum shows only the effect of isomer shift because for the $[Fe(CN)_6]^{4-}$ anion, being spherically symmetric, $q=0$ (Fig. 59). Also, refer to Fig. 58.

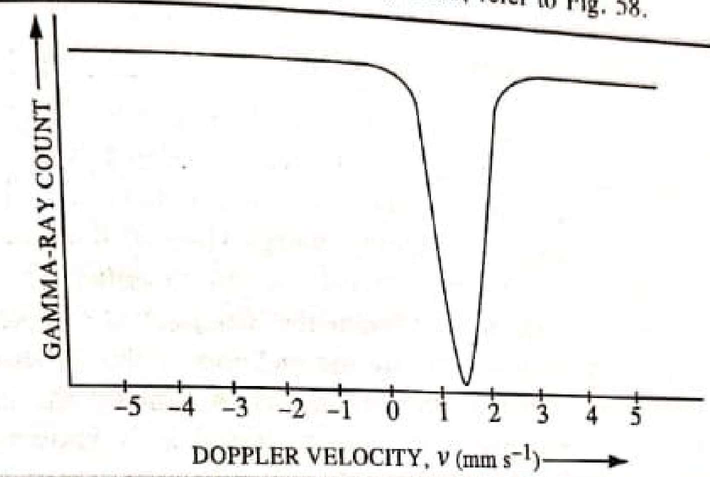

Fig. 59. The Mössbauer spectrum of $K_4[Fe(CN)_6]$. $\delta \neq 0$, $q = 0$

(b) $K_3[Fe(CN)_5NO]$. A two-line spectrum shows the effect of both the isomer shift and the quadrupole splitting because for the $[Fe(CN)_5NO]^{3-}$ anion, being not spherically symmetric, $q \neq 0$ (Fig. 60). Also, refer to Fig. 8.

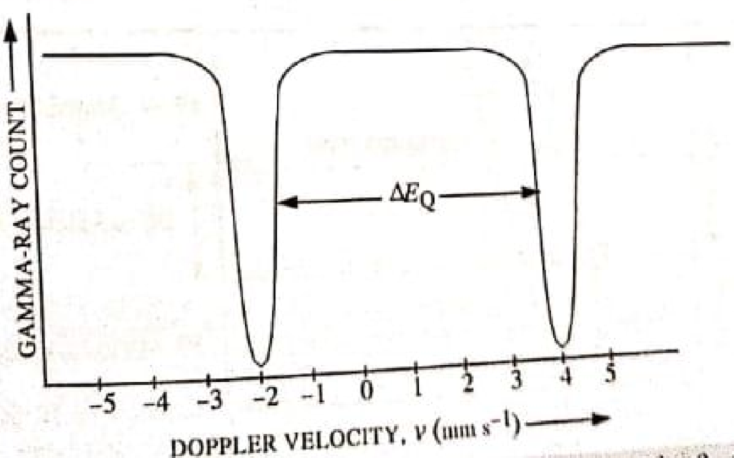

Fig. 60. The Mössbauer spectrum of $K_3[Fe(CN)_5NO]$. Here $\delta \neq 0$, $q \neq 0$.

3. **Nuclear Zeeman Splitting** (also called **magnetic hyperfine splitting**). The external nuclear Zeeman splitting is caused by the splitting of the nuclear energy levels by the magnetic field, *B*. In fact, in the metallic state of iron, very large internal magnetic field of the order of about 30 T, exists; this field, too, causes huge splitting. Fig. 61 shows the combined effect of isomer shift ($\delta \neq 0$)

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for the absorber nucleus. It should be noted that Mössbauer effect cannot be observed in liquids and gases because the recoil energy cannot be dissipated in these states of matter.

Mössbauer Experiment. The set-up that Mössbauer designed for his experiment is very simple (Fig. 56). The Doppler motion is given to the source, *i.e.*, the source is moved towards the absorber with velocity *v* by means of a velocity drive. The intersity of the emitted gamma rays is meausred as a function of the Doppler velocity, *v*. It must be remembered that the Doppler velocity given to the source relative to the absorber is necessary to bring the source and the absorber lines closer to meet the resonance absorption condition; it is *not* required to compensate the recoil energy because the recoil has already been eliminated by taking the sample in the form of a solid. When the source and the absorber move towards each other, the sign of Doppler velocity is taken to be positive. A typical Mössbauer spectrum is shown in Fig. 57.

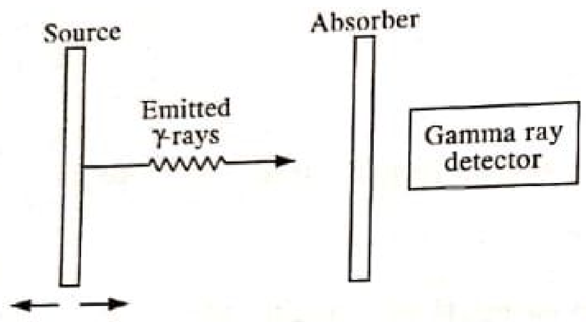

Fig. 56. The Mössbauer spectrometer.

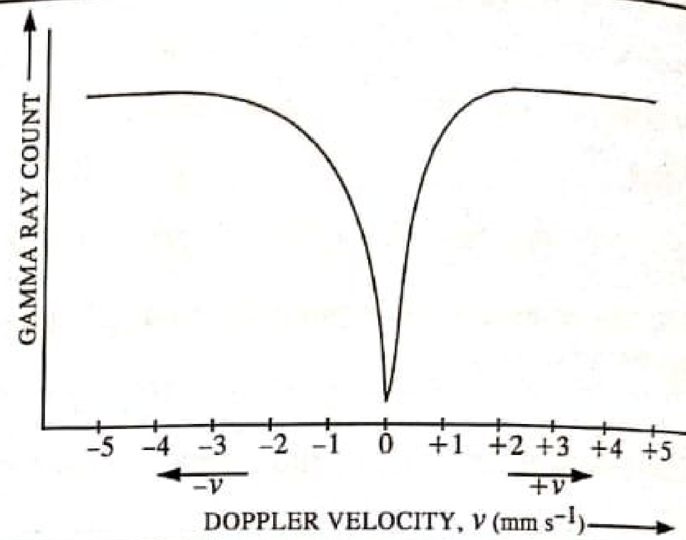

Fig. 57. A typical Mössbauer spectrum.

More about Mössbauer Spectroscopy. Three quantities, called **hyperfine interactions**, are studied by Mössbauer spectroscopy. There are *chemical (isomer) shift* (δ); *nuclear electric quadrupole splitting* (ΔE_Q) and *nuclear Zeeman splitting*.

1. Chemical (Isomer) Shift. As a result of the electrostatic interaction between the nucleus and the electrons in a solid, the nuclear energy levels are shifted in both the source and the absorber. This shift, called the **isomer shift**, is given by

$$\delta = \frac{2\pi}{5} Ze^2[|\psi_a(0)|^2 - |\psi_s(0)|^2](R_{ex}^2 - R_{gd}^2) \quad ...(72)$$

where e is the electronic charge, Z the atomic number and R_{ex} and R_{gd} are the radii of the nucleus in the excited and the ground states, respectively. $|\psi_a(0)|^2$ is the electron density evaluated at the nucleus for the absorber and $|\psi_s(0)|^2$ is the corresponding quantity for the source. Since only s electrons have a finite wave function at the nucleus and the p and d electrons have vanishing wave functions at the nucleus, it is only the s electrons which are responsible for the isomer shift.

2. Nuclear Electric Quadrupole Splitting, ΔE_Q. Sometimes, as in the case of ^{57}Fe, the excited state has a nuclear spin > 1; here I = 3/2. If the quadrupole moment eQ of the ^{57}Fe nucleus in the absorber interacts with the *EFG* (electric field gradient) that is not spherically symmetric, the resulting interaction splits the excited state energy level into two lines, the splitting being called electric quadrupole splitting, ΔE_Q. The quantity e^2Qq is called nuclear electric quadrupole coupling constant. Fig. 58 illustrates the concepts of isomer shift and electric quadrupole splitting.

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and magnetic field ($\delta \neq 0$, $B \neq 0$) on the Mössbauer spectrum of ^{57}Fe. The selection rule $\Delta m_I = 0, \pm 1$ gives six lines in the spectrum.

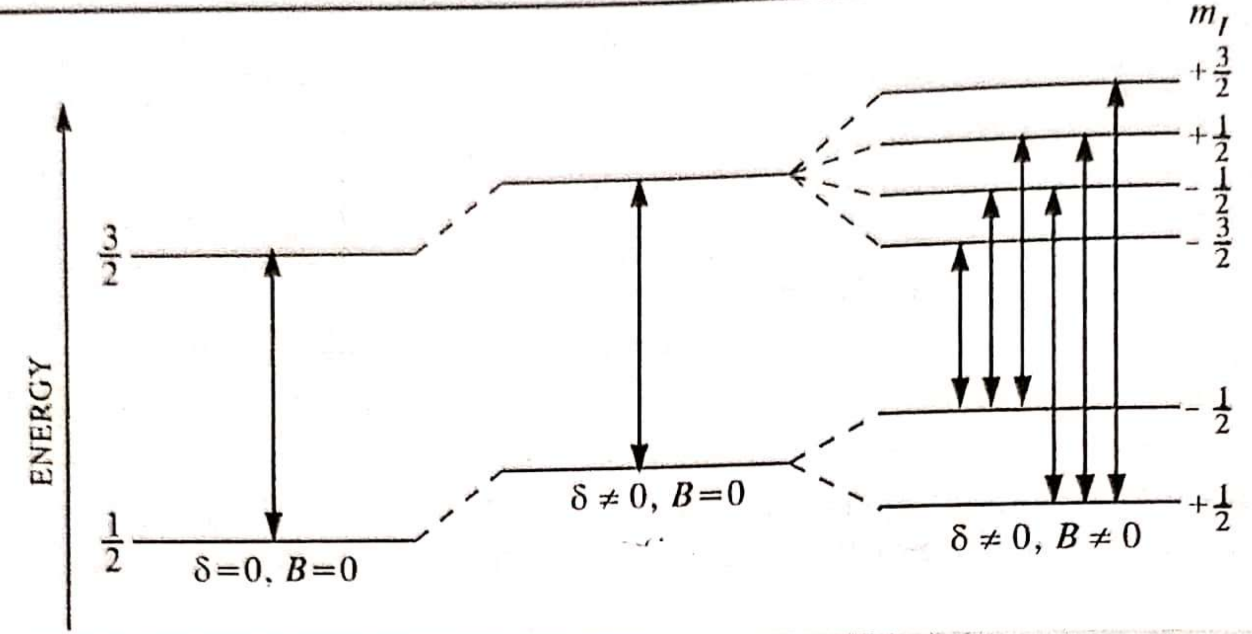

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Fig. 61. Isomer shift and nuclear Zeeman splitting in ^{57}Fe energy levels.