BHARATHIDASAN UNIVERSITY

Tiruchirappalli- 620024

Tamil Nadu, India

Programme: M.Sc., Physics

Course Title : Thermodynamics and Statistical Physics

Course Code : 22PH202

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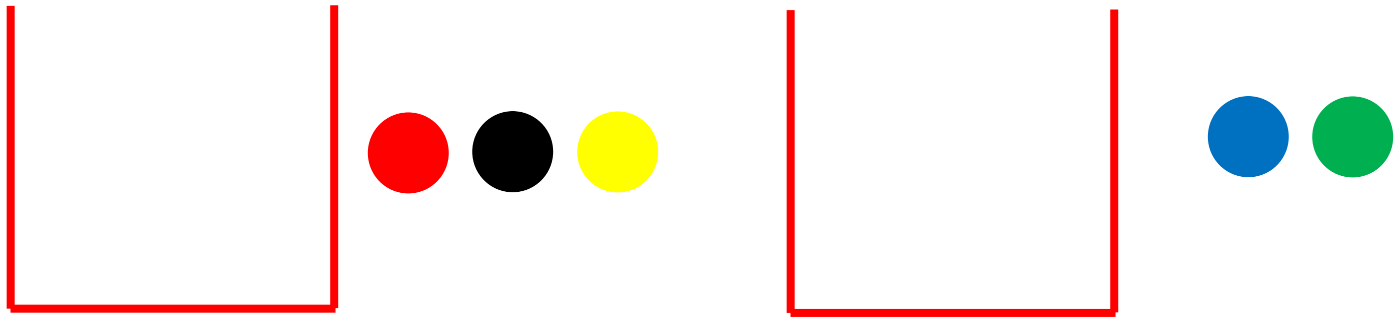
UNIT - III

QUANTUM STATISTICS

Combinational Problems

❖ Consider two boxes



Box 1 Box 2

❖ I want to take one ball from the first set and put it in the first box and one ball from the second set and put it in the second box.

<u>Question</u>

❖ How many numbers of ways the combined system of Box – 1 and Box – 2 can be filled? (or) Find the total number of possible distributions.

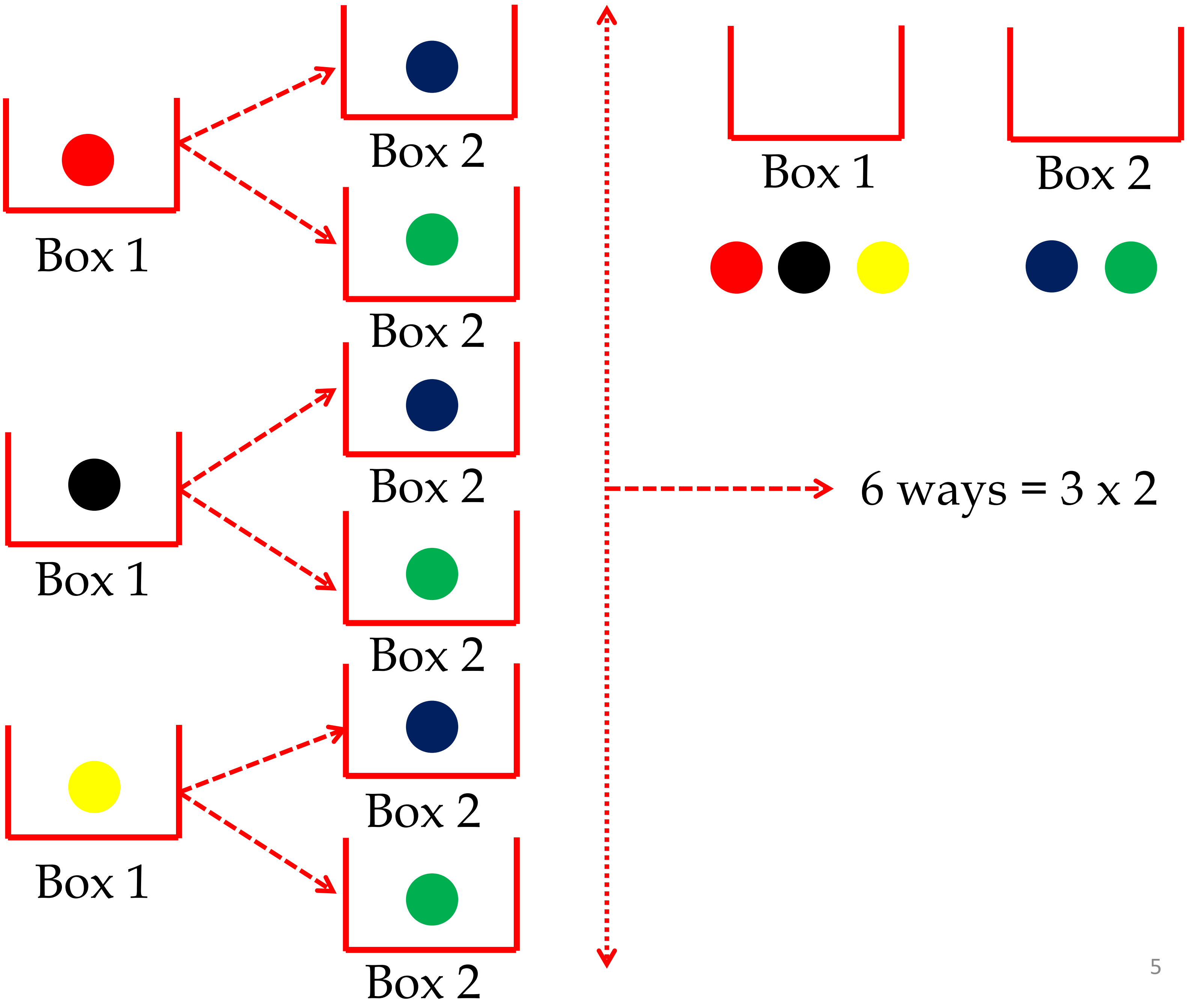
(a) 2 + 3 ? (b) 2 x 3 ?

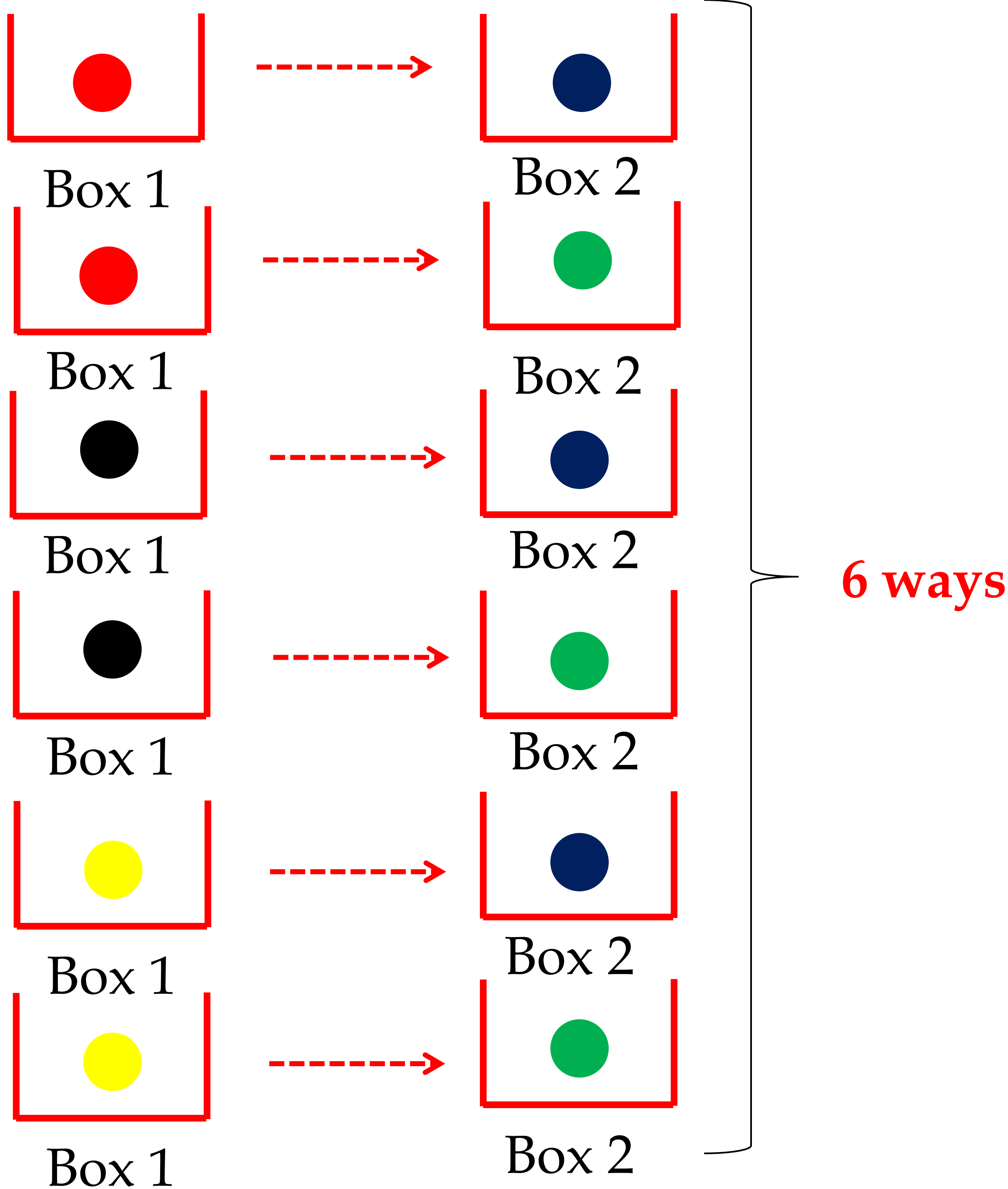
Basic Combinational Problems

- ❖ Box – 1 : can be filled with either a red ball (or) a black ball (or) with a yellow ball.
- ❖ Box – 2 : can be filled with either a blue ball or with a green ball.

<u>In short</u>

- ❖ Box – 1 can be filled in 3 different ways and Box – 2 can be filled in 2 different ways.


Box 1
Box 2
Box 2
Box 1
Box 2
Box 2
Box 1
Box 2
Box 2
Box 1
Box 2
6 ways = 3 x 2

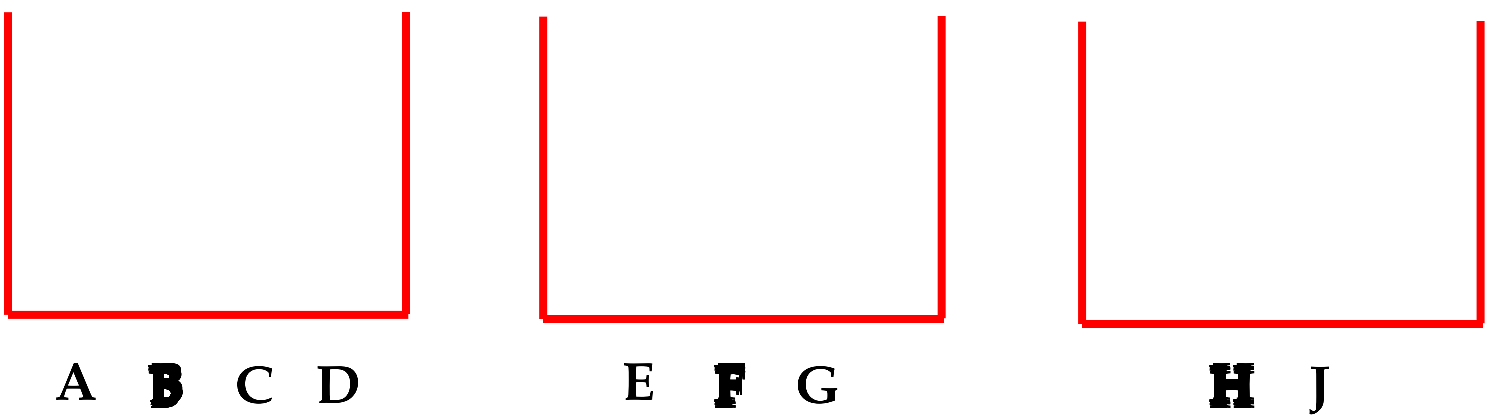

Box 1
Box 2
Box 1
Box 2
Box 1
Box 2
Box 1
Box 2
Box 1
Box 2
Box 1
Box 2
6 ways

Extension to 3 Boxes

❖ I want to take one ball from the first set and put it in the first box and one ball from the second set and put it in the second box and one ball from the third set and put it in the third box

<u>Question</u>

❖ How many numbers of ways the combined system of Box – 1, 2 & 3 can be filled?



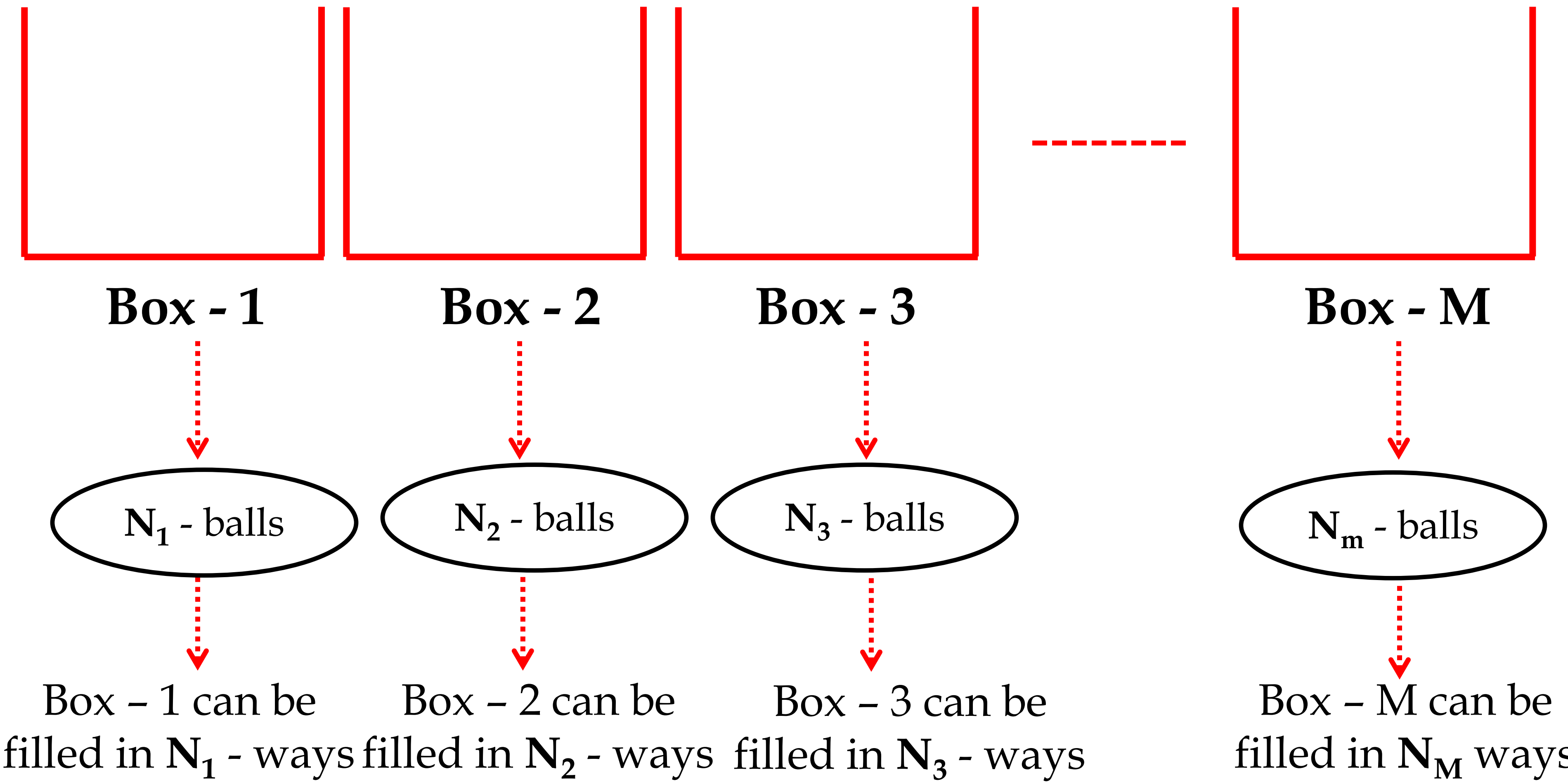
A, B, C, D **E, F, G** **H, J**

A E H	A E J	A F H	A F J	A G H	A G J
B E H	B E J	B F H	B F J	B G H	B G J
C E H	C E J	C F H	C F J	C G H	C G J
D E H	D E J	D F H	D F J	D G H	D G J

$$4 \times 3 \times 2 = 24$$

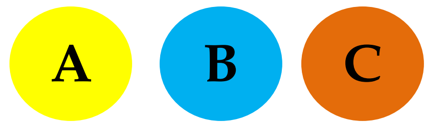
First Ball	Second Ball	Third Ball
First Box	Second Box	Third Box
(First Letter)	(Second Letter)	(Third Letter)

Suppose there are M boxes and N balls.



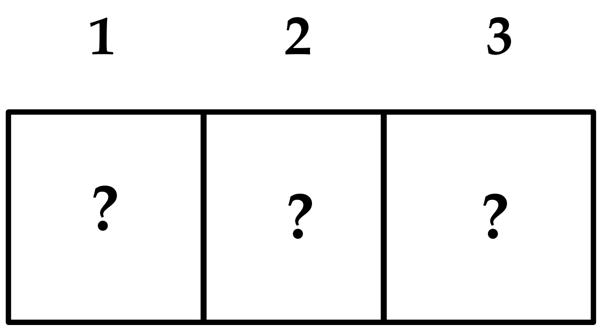
Total number of possible distributions = $N_1 \times N_2 \times N_3 \times .... \times N_M$

Problem 2 :

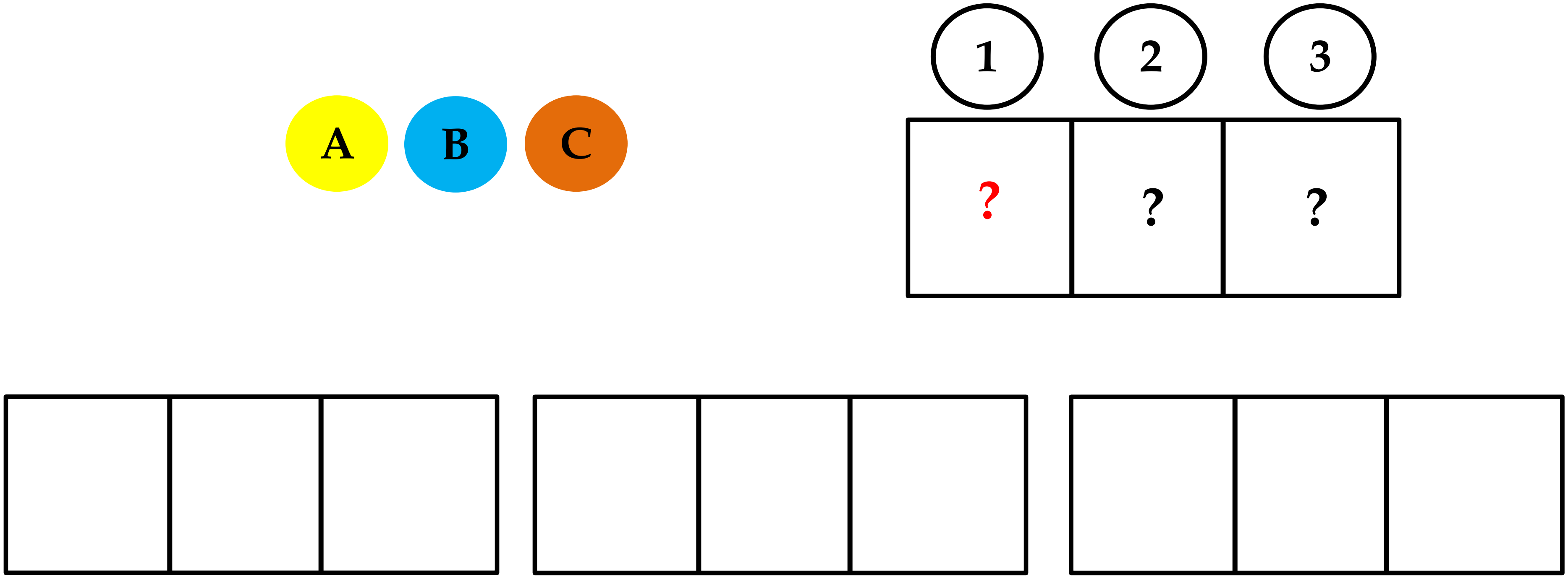


We have to arrange these three balls in a line.

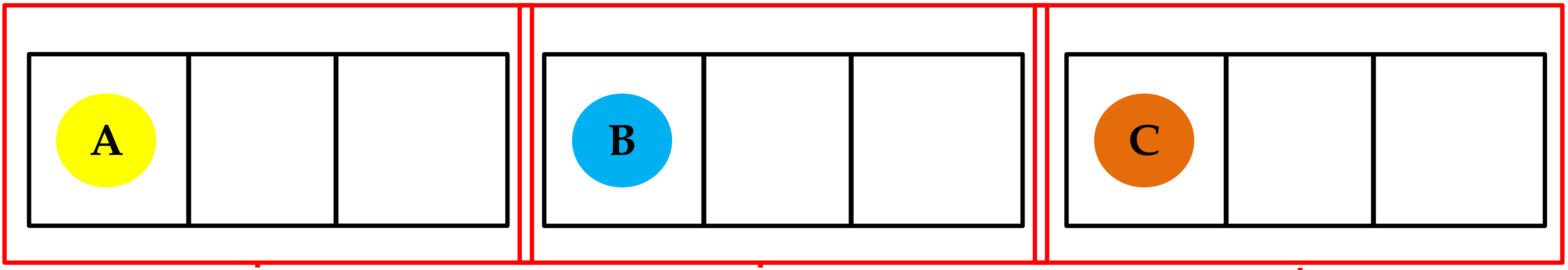
How many ways will you arrange it?



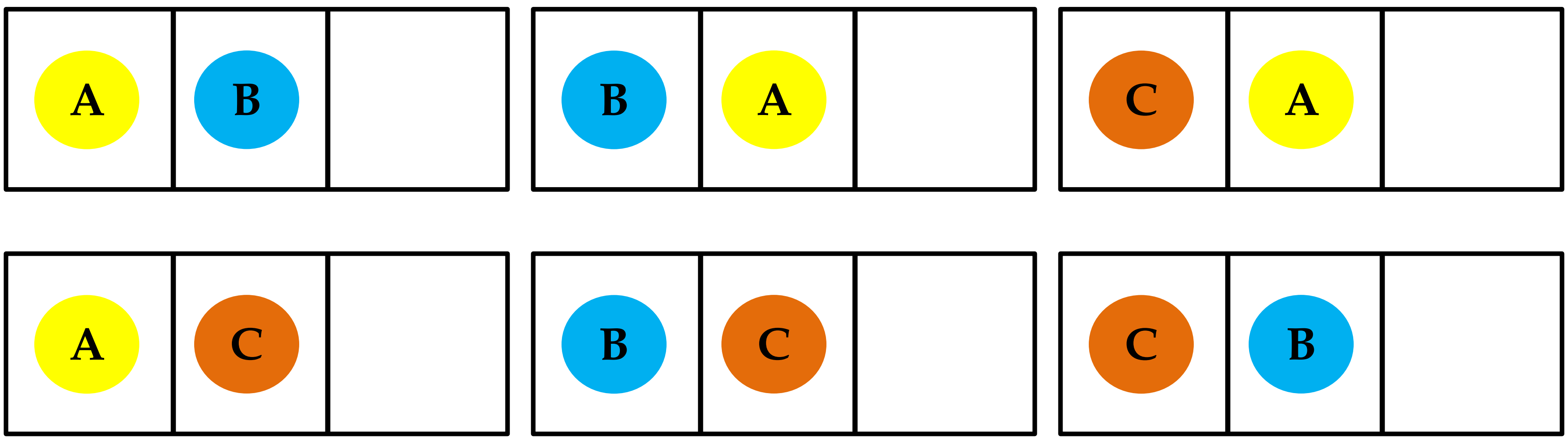
How many ways the first particle can be chosen?



The first particle can be chosen in three ways



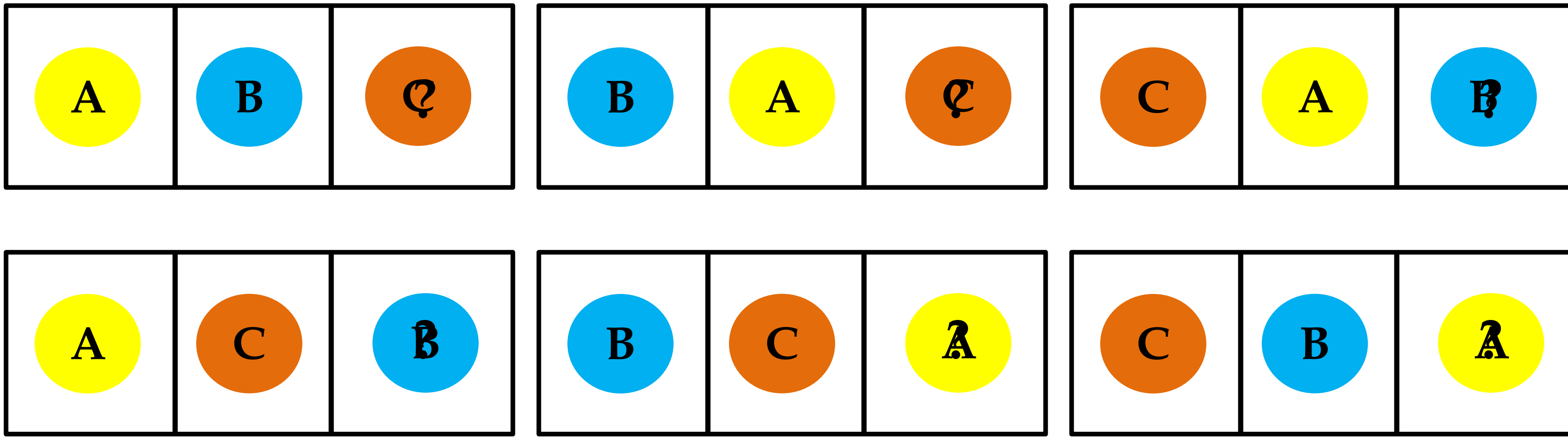
How many ways the second box can be filled.



2 ways 2 ways 2 ways

Total number of ways the first two boxes can be filled = 3 x 2

Now filling up the third box



There is only one way to fill up the third box.

Total number of ways that the three balls can be arranged = 3 x 2 x 1 = 3!

If we consider N balls, then in how many ways that those balls can be arranged?

N!

Extension

We have to arrange four balls in a line. How many number of ways we can do it?

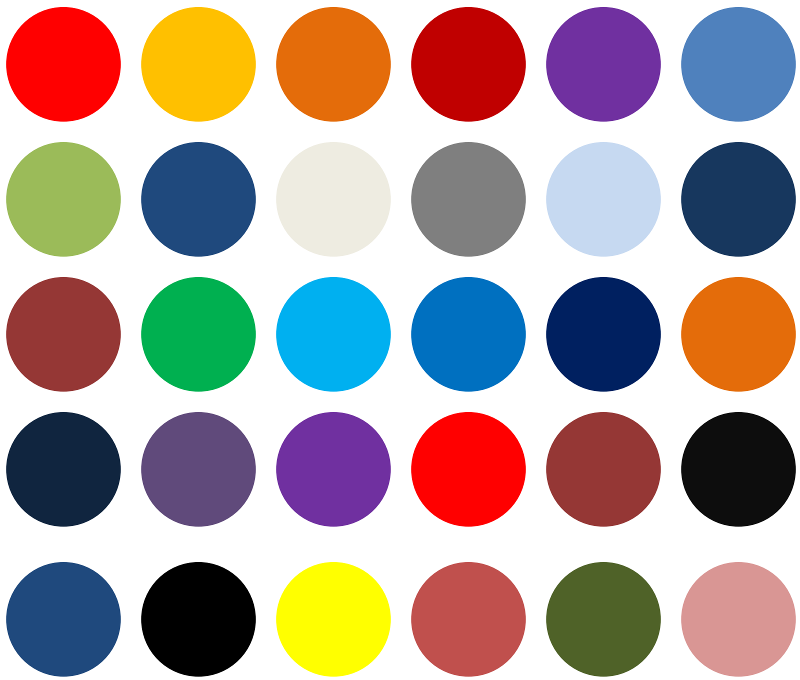
Answer : 4 x 3 x 2 x 1 = 24

A B C D	B A C D	C A B D	D A B C
A B D C	B A D C	C A D B	D A C B
A C B D	B D C A	C D B A	D B A C
A C D B	B D A C	C D A B	D B C A
A D B C	B C A D	C B A D	D C A B
A D C B	B C D A	C B D A	D C B A

Arranging N Distinguishable Object

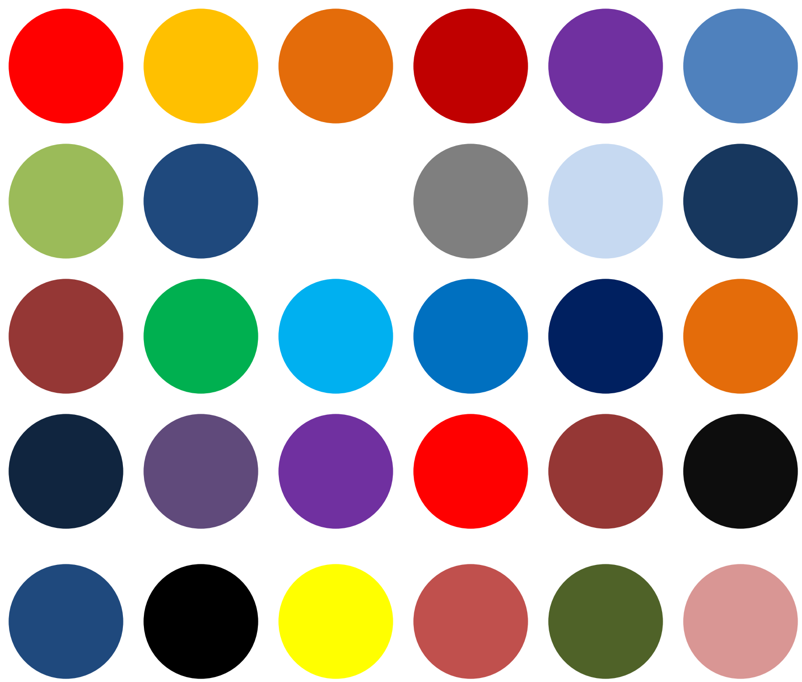
We look upon the problem that in how many number of ways the balls can be arranged in a line

Number of ways the first ball can be chosen **N Ways**



N Balls

Number of ways the second ball can be chosen (N – 1) Ways

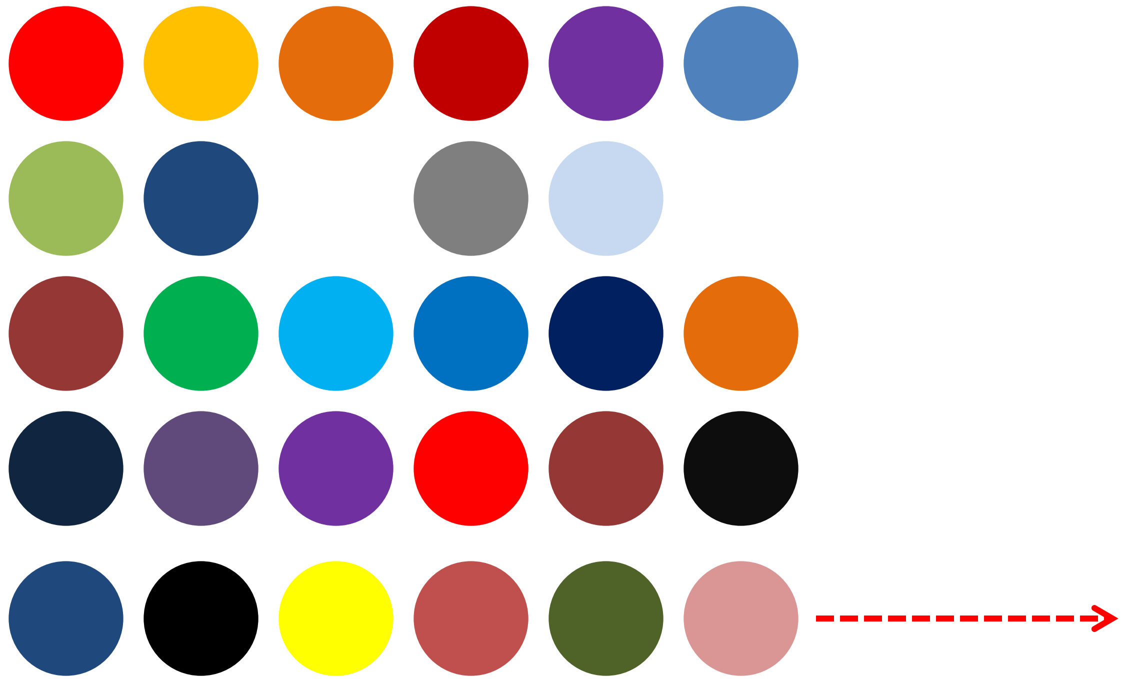


(N - 1) Balls

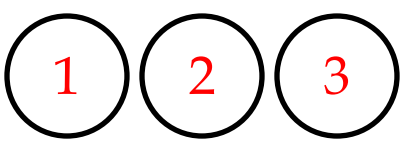
1 2

Total Number of ways the first two particles can be chosen = N(N – 1)

Number of ways the third ball can be chosen (N – 2) Ways

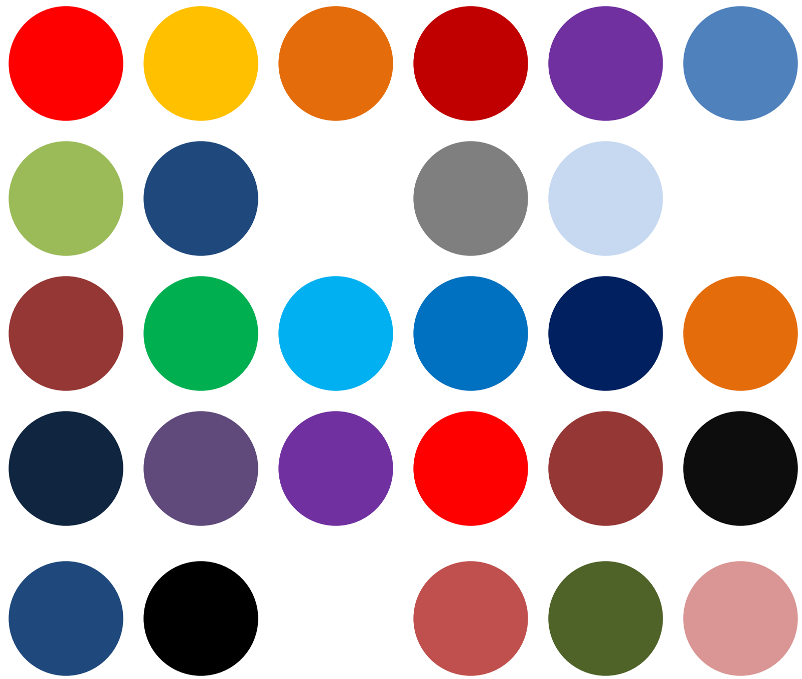


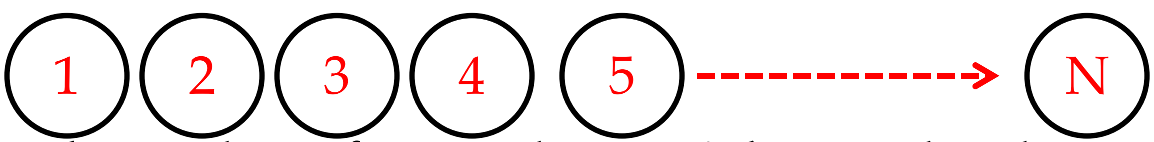
(N - 2) Balls



Total Number of ways the first three particles can be chosen

$$= N(N-1)\,(N-2)$$





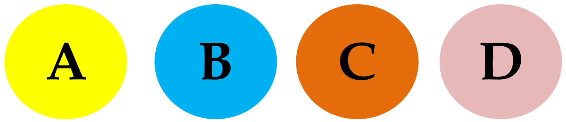
Total Number of ways the particles can be chosen

$$= N(N-1)(N-2)(N-3)(N-4) \dashrightarrow 3 \times 2 \times 1$$

$$\boxed{= N!}$$

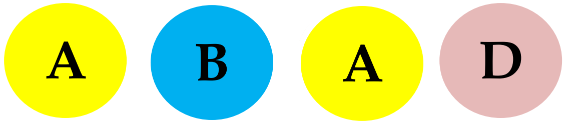
Problem 3 :

4 Objects



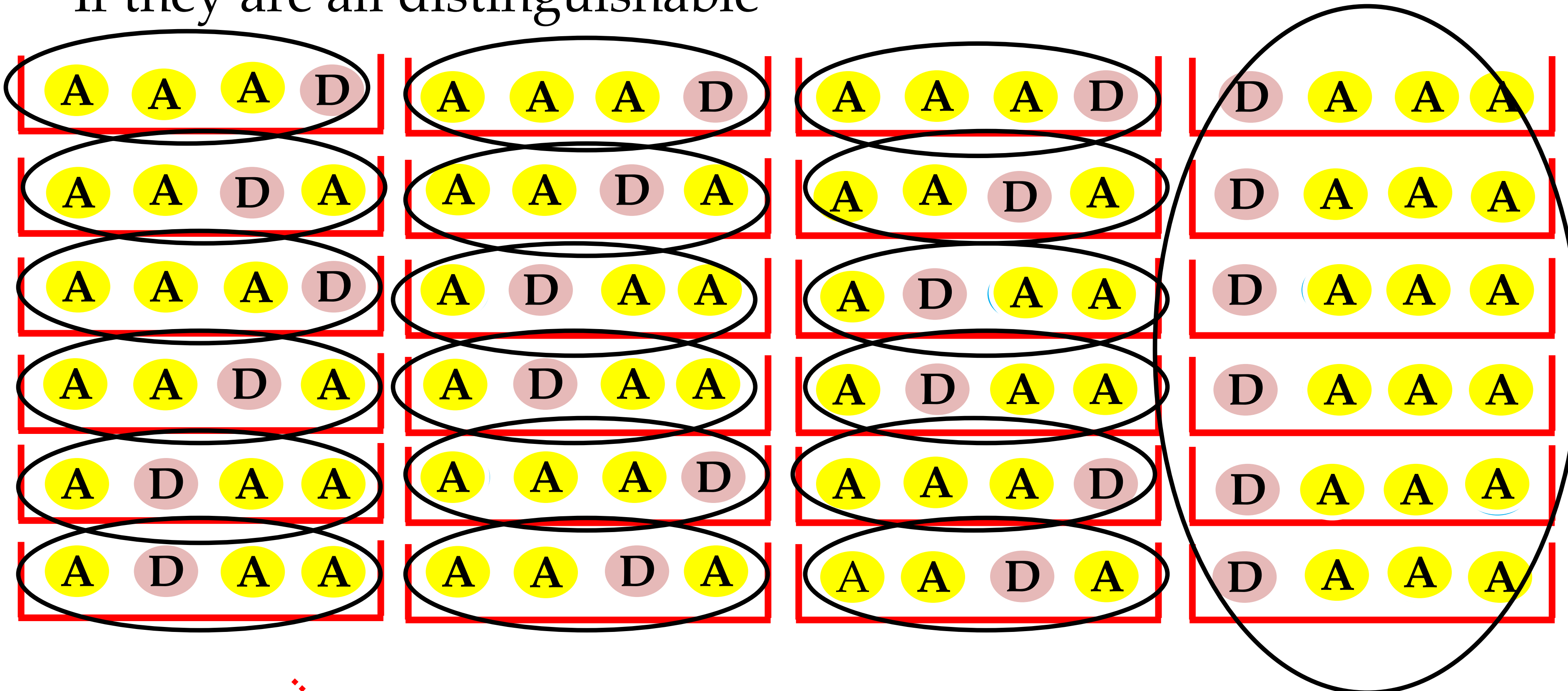
Number of ways of arranging these 4 distinguishable objects = 4!

Now if suppose, 3 of them are indistinguishable



Number of ways of arranging = ?

If they are all distinguishable

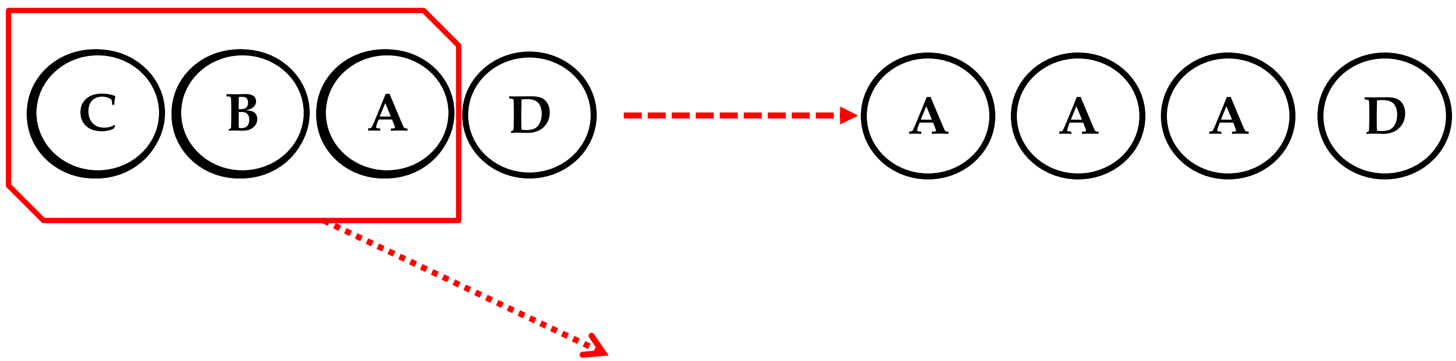


A, B, C→ A

Same ! Same ! Same ! Same !

indistinguishable

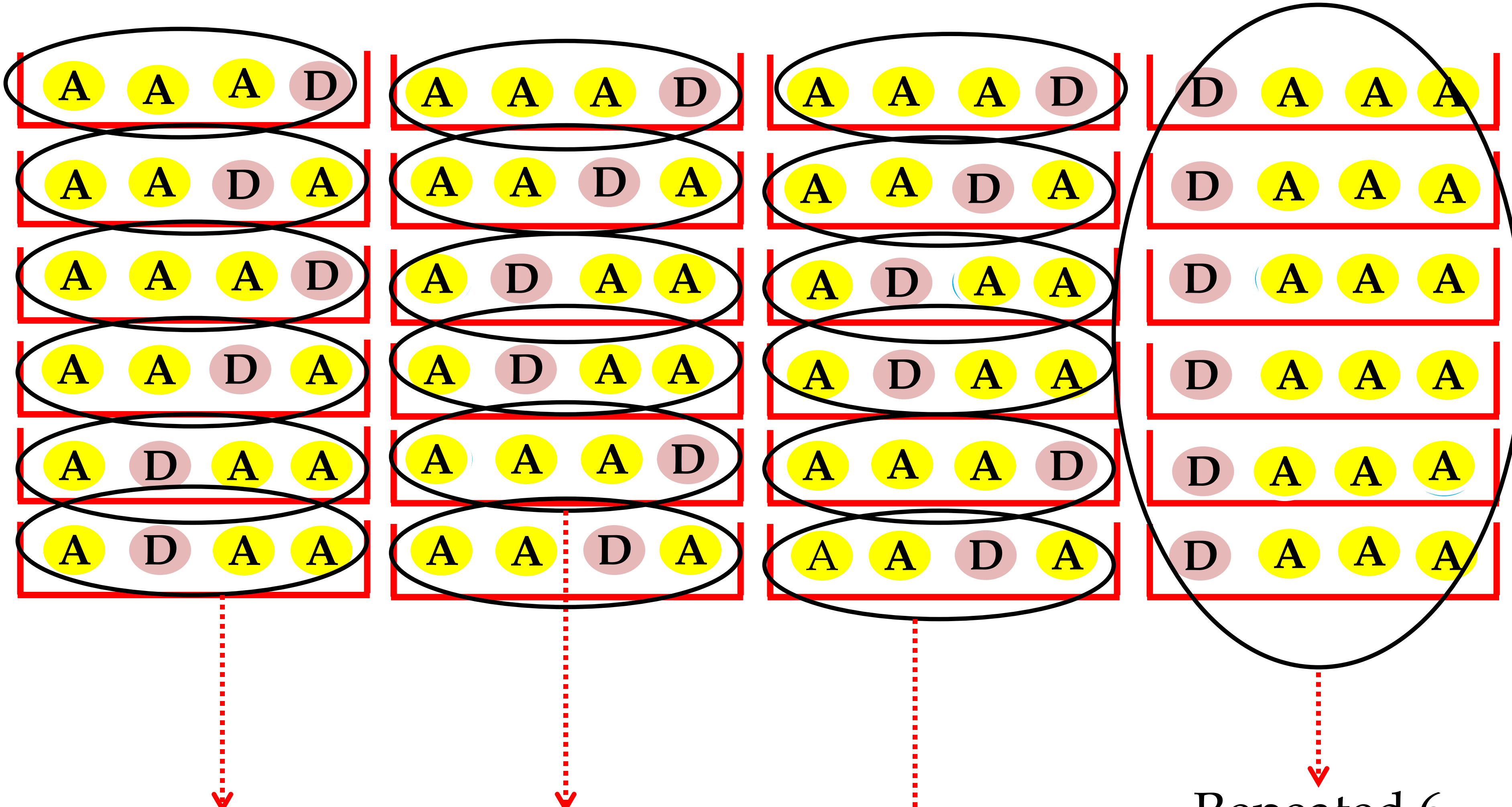
For example,



How many ways these **three** can be arranged = **3**!

This denotes that each possible configuration is repeated 3! Times (or) 6 times.

Actual number of ways of arranging 4 objects (with 3 indistinguishable) objects $= \frac{4!}{3!} = 4$

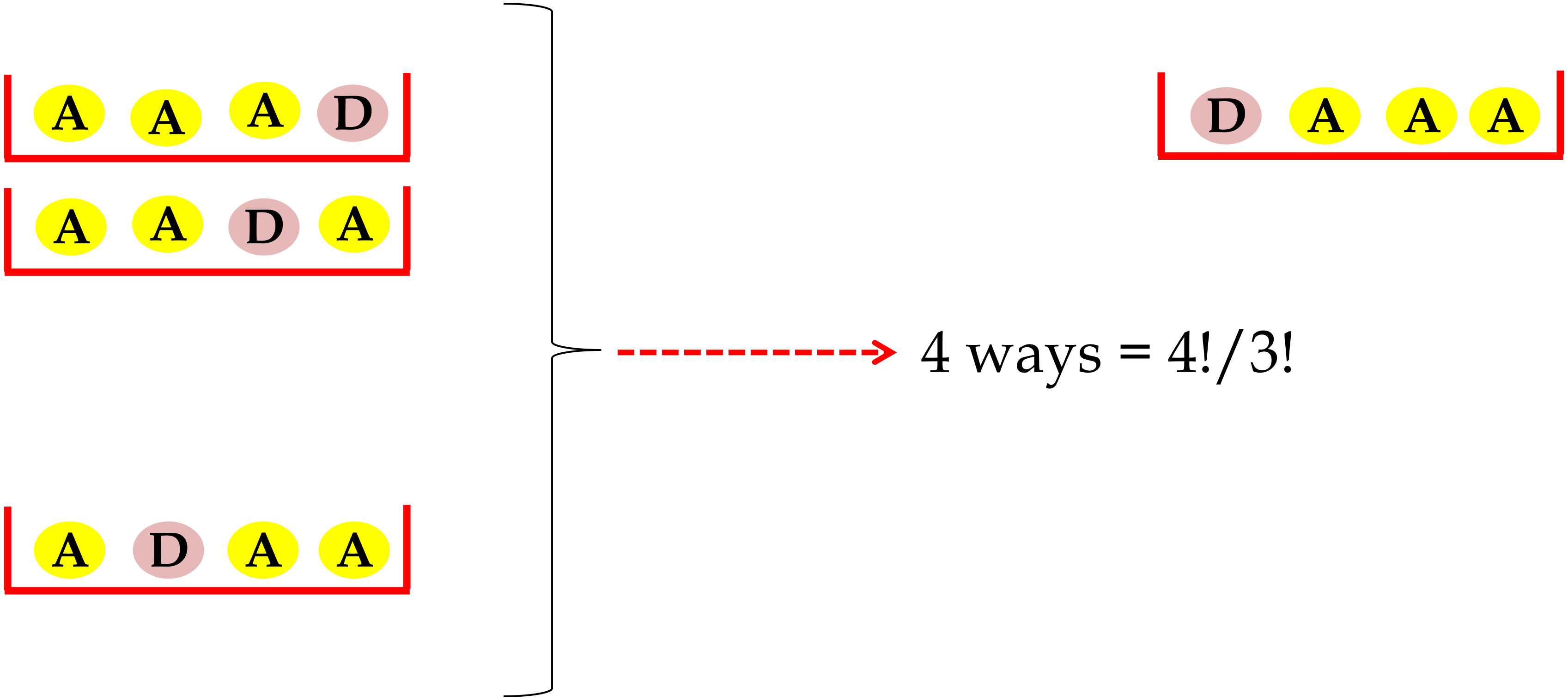


Repeated 6 Times

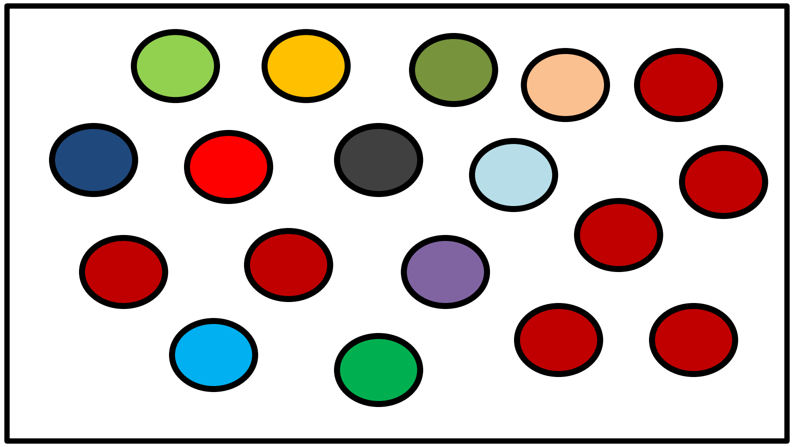
Repeated 6 Times

Repeated 6 Times

Repeated 6 Times


A A A D
A A D A
A D A A
D A A A
4 ways = 4!/3!

Suppose we have N distinguishable objects



If M object are indistinguishable.

$$\text{Total ways of arranging} = \frac{N!}{M!}$$

In the N objects , if M_1 and M_2 number of objects are identical among themselves then the total ways of arranging

$$= \frac{N!}{M_1! \times M_2!}$$

Recall :

Suppose we have N distinguishable objects. If M objects are indistinguishable.

$$\text{Total ways of arranging} = \frac{N!}{M!}$$

Suppose we have 5 objects

A B C D E

A A C D D

In the 5 objects, two sets of objects are identical among themselves then the total ways of arranging

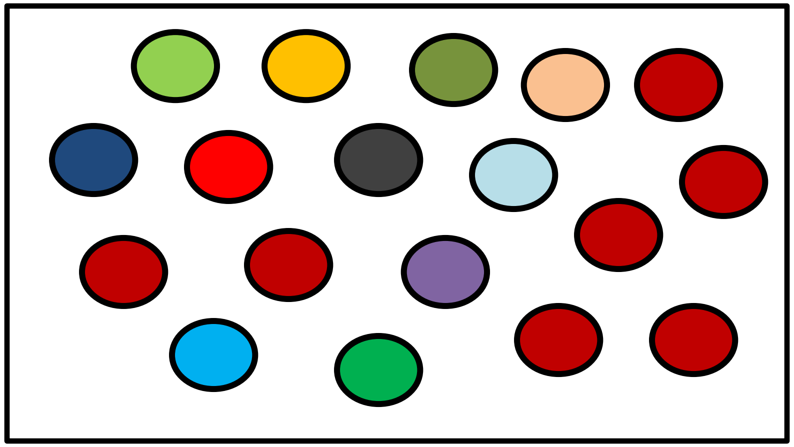
$$= \frac{5!}{2!\times 2!}$$

❖ If 5 objects are different (A, B, C, D, E) the number of ways arranging = 5! = 120.

❖ Since A and B (AA) are identical and D and E (DD) are identical the number of ways arranging is $= \dfrac{5!}{2! \times 2!} = 30$

A A B D D	A D D B A	D D B A A	D A A B D	B A A D D
A A D D B	A D B D A	D D A A B	D A B A D	B A D A D
A A D B D	A D B A D	D D A B A	D A B D A	B A D D A
A A A D D	A D A D B	D B D A A	D A D A B	B D D A A
A B D A D	A D D A B	D B A D A	D A A D B	B D A D A
A B D D A	A D A B D	D B A A D	D A D B A	B D A A D

Suppose we have N objects



If M objects are indistinguishable.

$$\text{Total ways of arranging} = \frac{N!}{M!}$$

In the N objects , if M_1 and M_2 number of objects are identical among themselves then the total ways of arranging

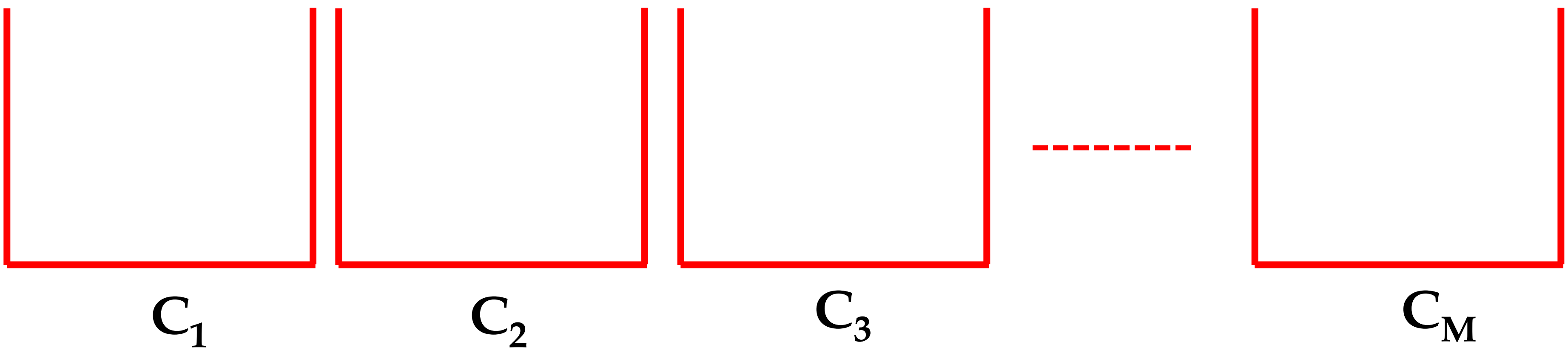
$$= \frac{N!}{M_1! \times M_2!}$$

Problem 4 :

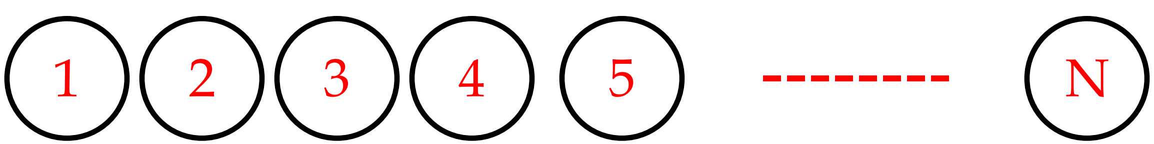
Arranging N distinguishable objects in M distinguishable (No restriction) containers.

How many number of ways possible?

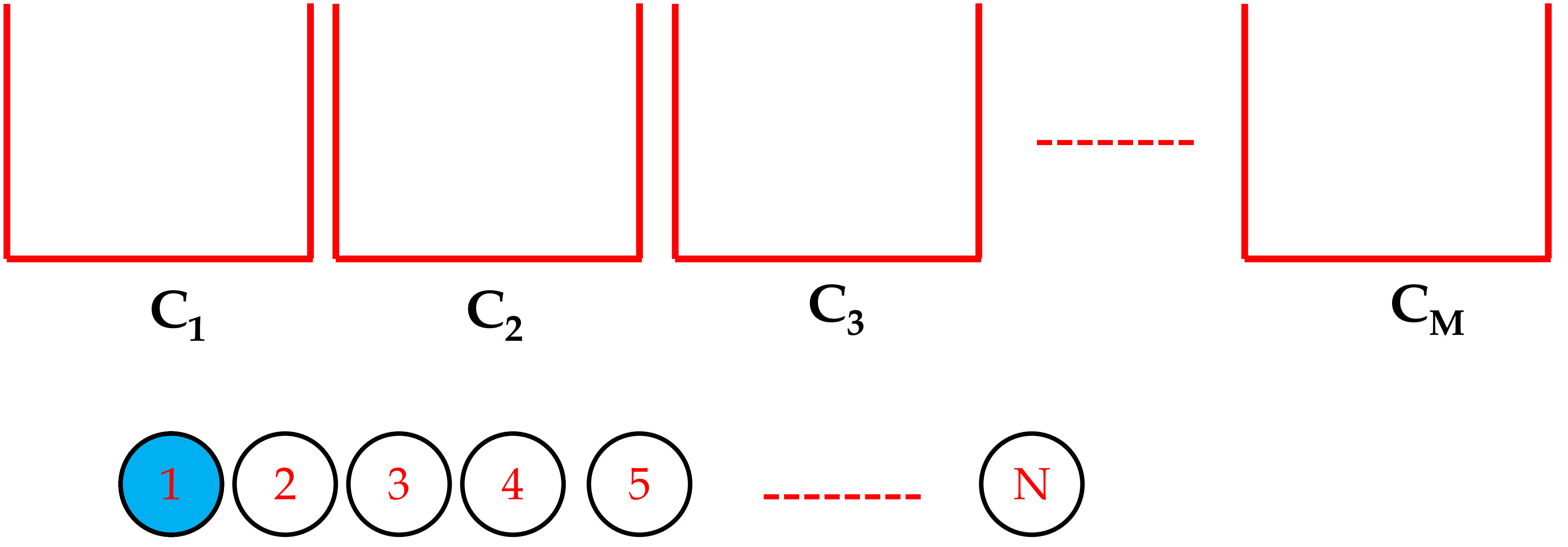
$M \rightarrow$ Containers



$N \rightarrow$ Objects

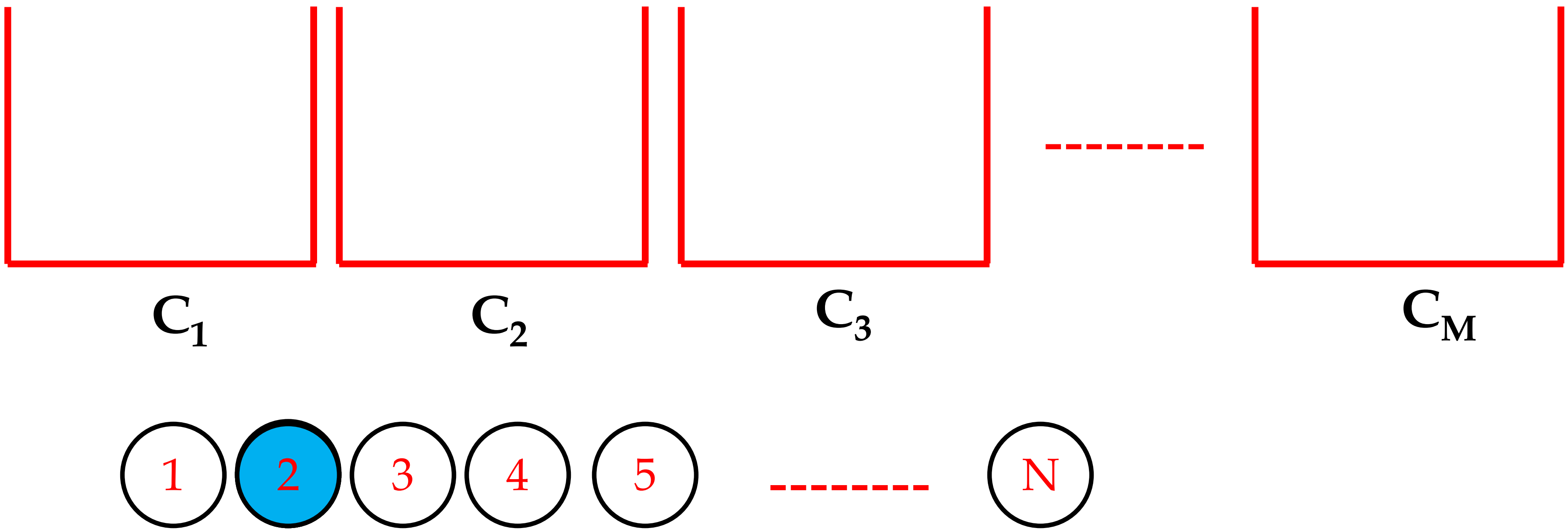


The first object can be put in any one of the M containers



Total number of ways first object is placed = M

The Second object can be put in any one of M ways



Total Number of ways the first two objects can be placed

$= M \times M = M^2$

In the similar manner,

Total number of ways the first three can be placed = M^3

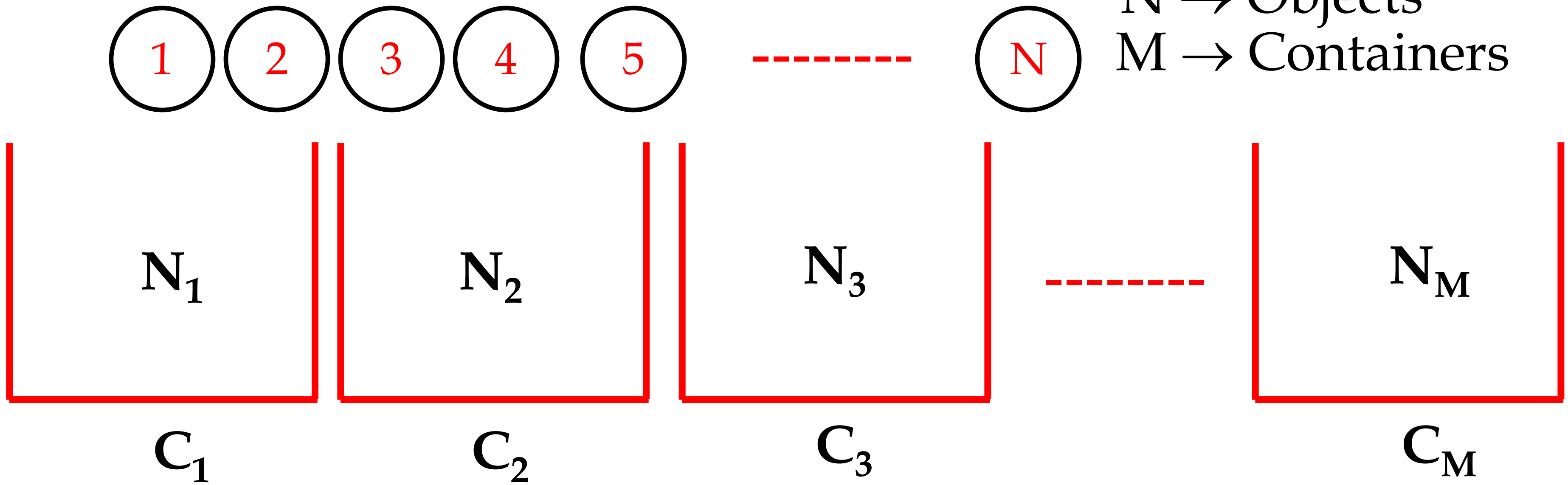
Total number of ways the first four can be placed = M^4

Total number of ways the N objects can be placed M containers = $\boxed{M^N}$

Now, if the number of particles in each container is restricted

$N \rightarrow$ Objects

$M \rightarrow$ Containers



Say $\rightarrow$ C_1 is restricted to have N_1 number of particles

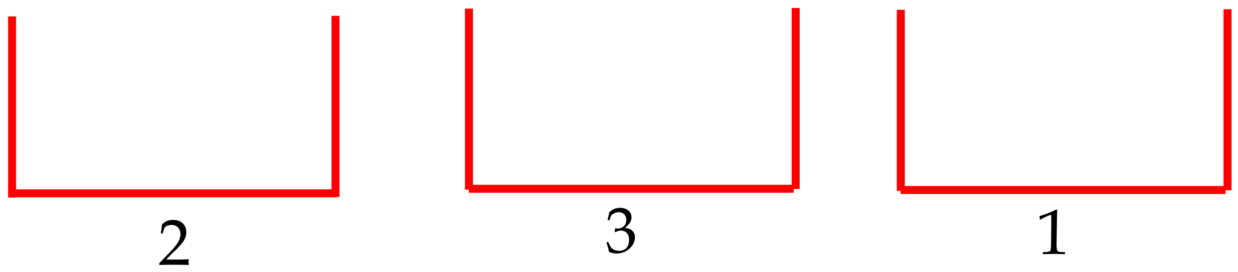
C_2 is restricted to have N_2 number of particles

C_3 is restricted to have N_3 number of particles

C_M is restricted to have N_M number of particles

$$N_1 + N_2 + N_3 + \ldots\ldots\ldots\ldots + N_M = N$$

❖ To begin, let us consider three boxes and 6 particles



❖ Suppose we want to put

2 particles in box 1 3 particles in box 2 1 particles in box 3

❖ 1^{st} Box 1^{st} Particle

A B C D E F

❖ 1st Box 2nd Particles

Only different choices

Repeating

AB	AC	AD	AE	AF
BA	BC	BD	BE	BF
CA	CB	CD	CE	CF
DA	DB	DC	DE	CF
EA	EB	EC	ED	EF
FA	FB	FC	FD	FE

$$= \frac{30}{2} = 15\ ways$$

AB	AC	AD	AE	AF
	BC	BD	BE	BF
		CD	CE	CF
			DE	CF
				EF

- 2nd Box 3 Particles
- Suppose in the 1st box we have AB. The remaining 4 particles on CDEF. We have to choose 3 from 4.

AB : <u>CDEF</u>

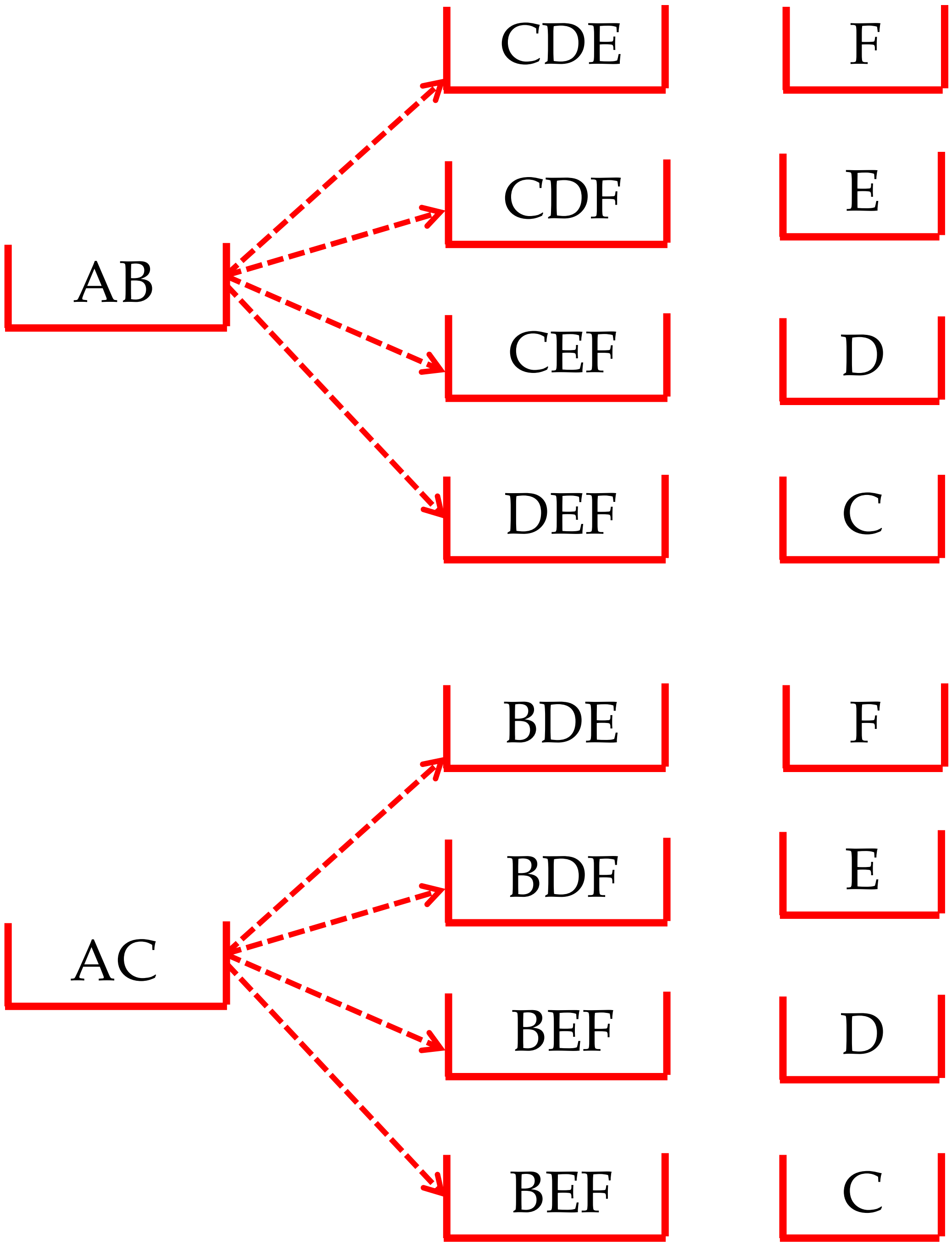
	CDE	CDF	CEF	CED	CFD	CFE
Repeat	DEF	DEC	DFC	DFE	DCE	DCF
	EFC	EFD	ECD	ECF	EDF	EDC
	FCD	FCE	FDE	FDC	FEC	FED

<u>4 ways :</u>

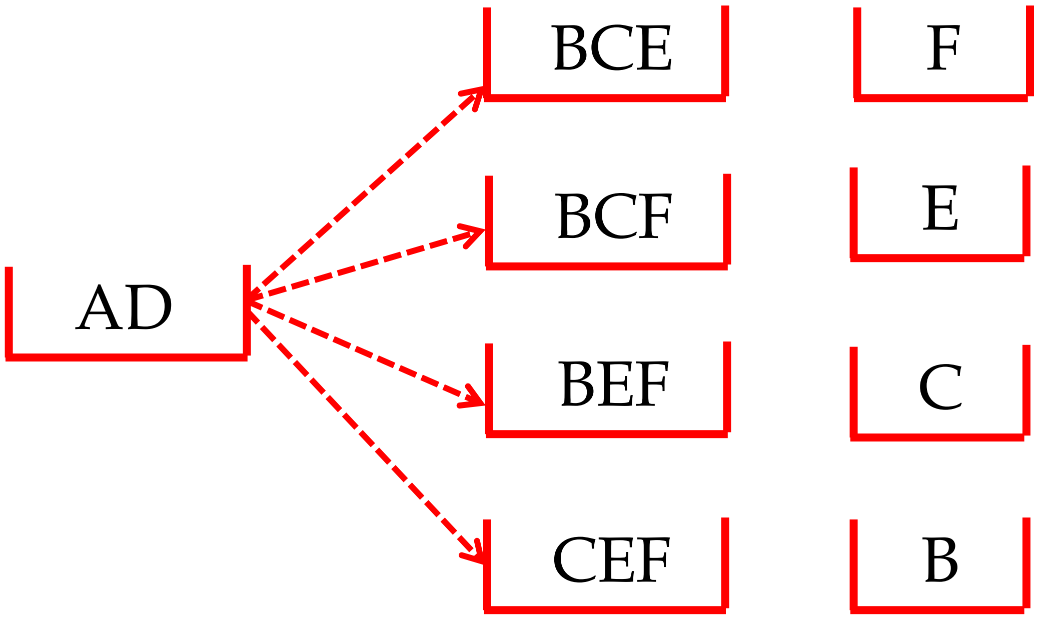
CDE CDF CEF DEF

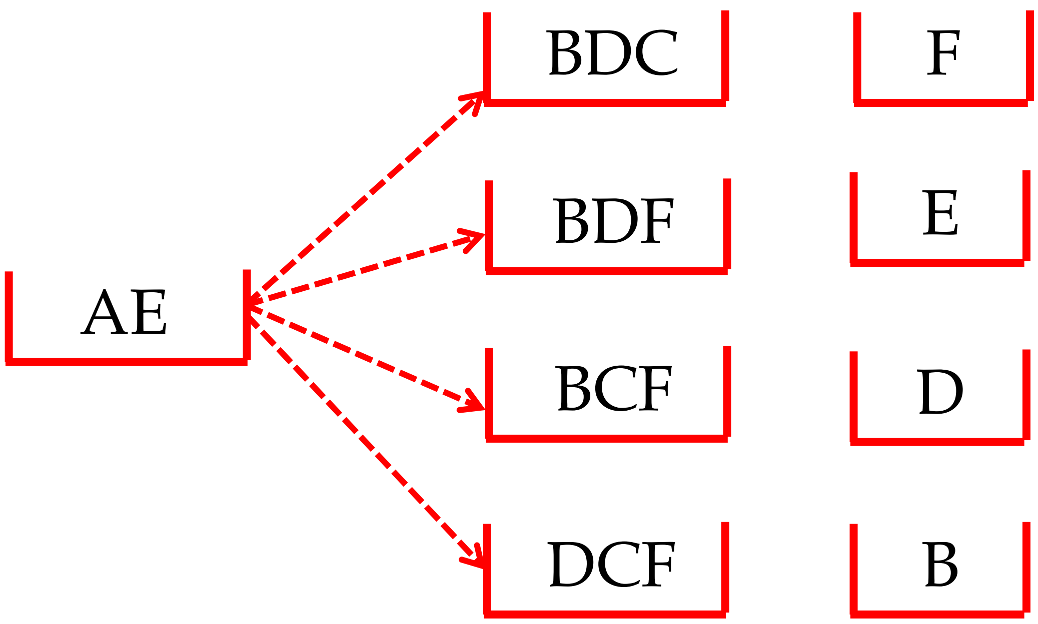
Total = 15 x 4 = 60 ways

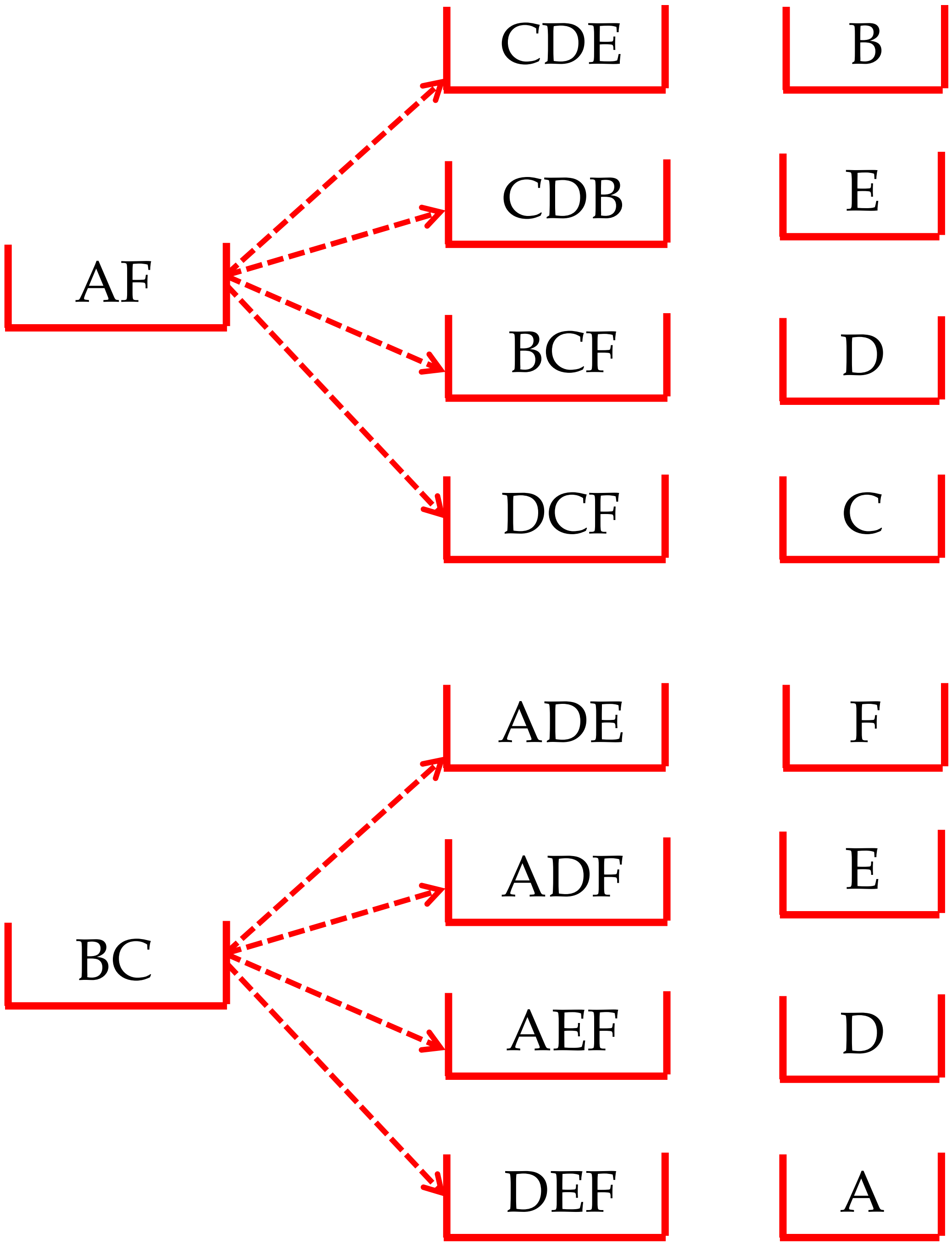
- 3^{rd} Box 1 Particle
- Suppose in the 1^{st} box we have AB and in the 2^{nd} box CDE the only option left out for the 3^{rd} box is F.
- Suppose in the 1^{st} box we have AC and in the 2^{nd} box BDF the only option left out for the 3^{rd} box is E.
- Sine there are 60 ways the 1^{st} and 2^{nd} box are filled we find totally 60 ways for the 3^{rd} box.

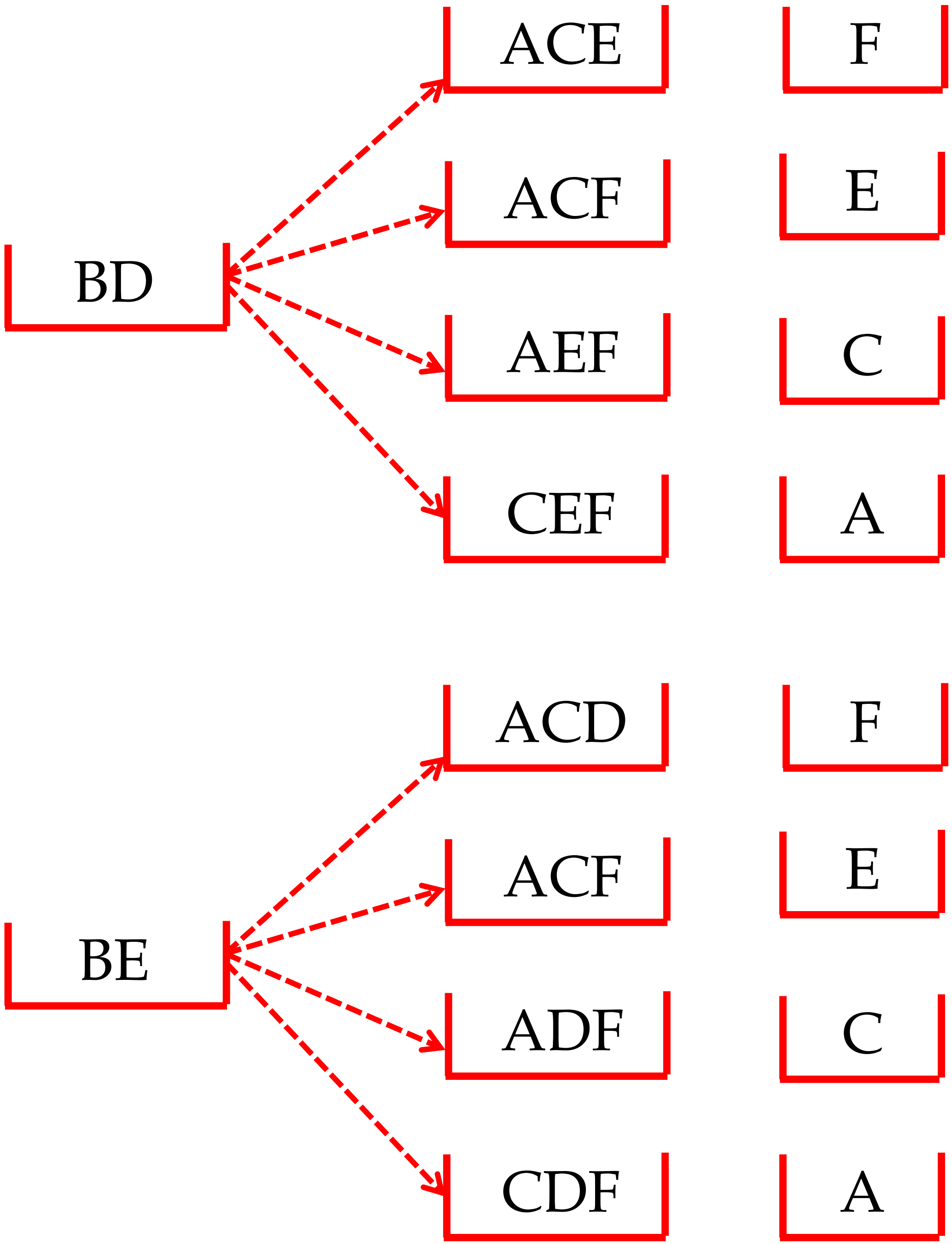


CDE
F
CDF
E
AB
CEF
D
DEF
C
BDE
F
BDF
E
AC
BEF
D
BEF
C


AD
BCE
F
BCF
E
BEF
C
CEF
B

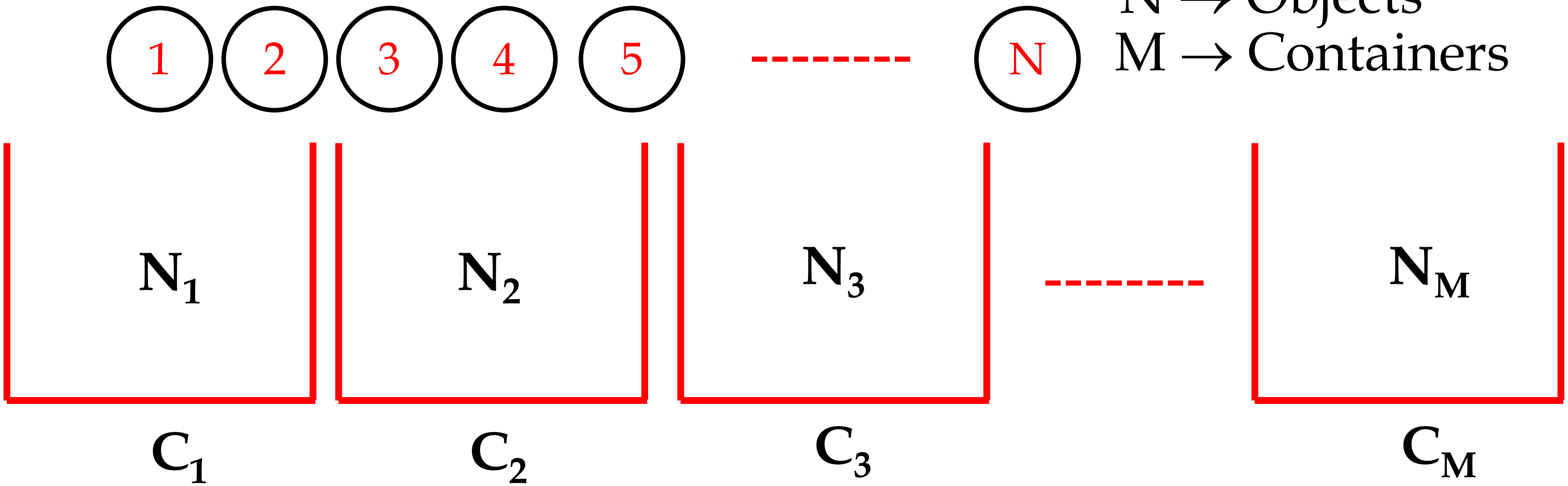

AE
BDC
F
BDF
E
BCF
D
DCF
B


AF
CDE
B
CDB
E
BCF
D
DCF
C
BC
ADE
F
ADF
E
AEF
D
DEF
A


BD
ACE
F
ACF
E
AEF
C
CEF
A
BE
ACD
F
ACF
E
ADF
C
CDF
A

Now, if the number of particles in each container is restricted

$N \rightarrow$ Objects
$M \rightarrow$ Containers



Say $\rightarrow$ C_1 is restricted to have N_1 number of particles

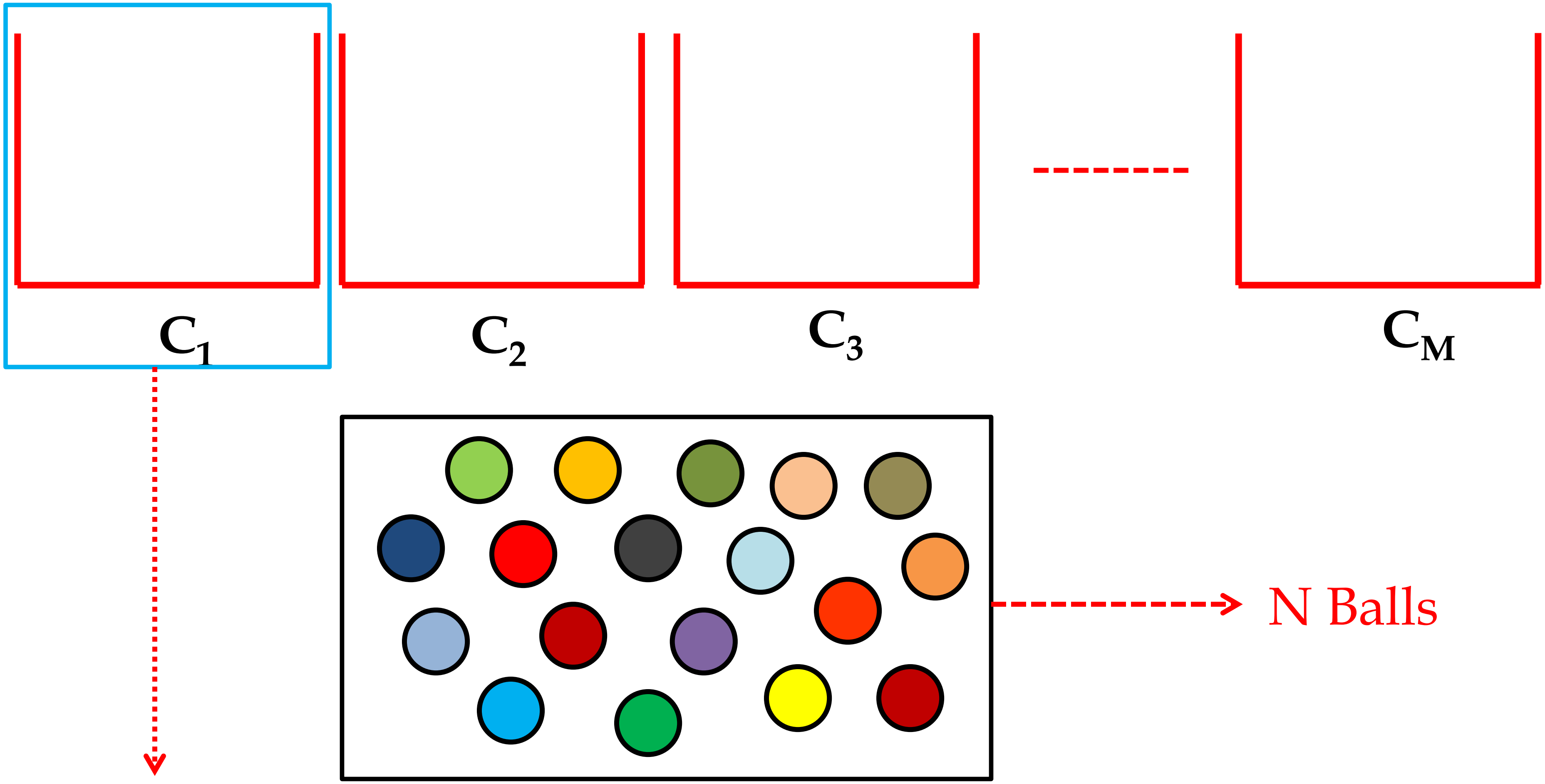
C_2 is restricted to have N_2 number of particles

C_3 is restricted to have N_3 number of particles

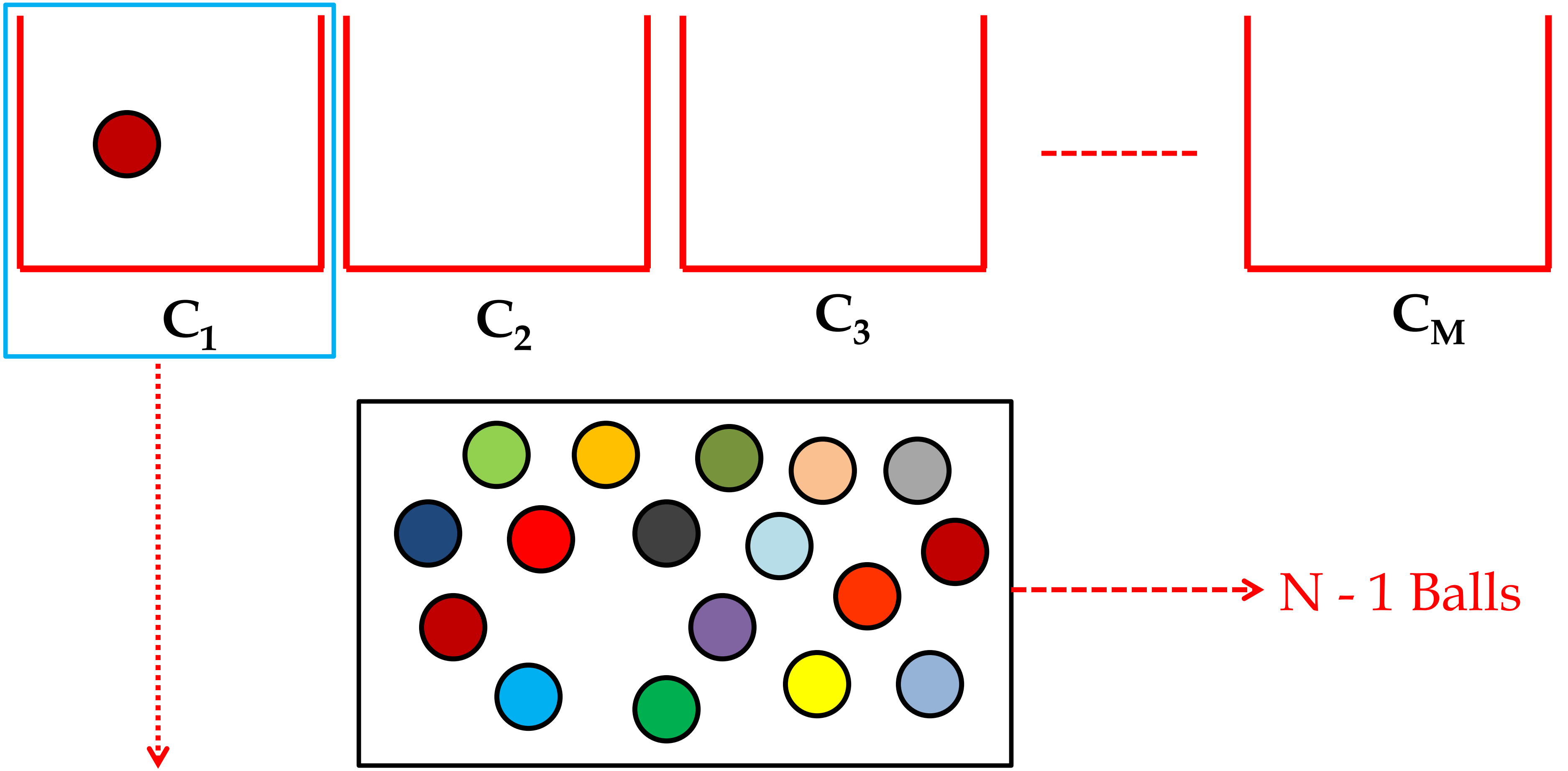
C_M is restricted to have N_M number of particles

$$N_1 + N_2 + N_3 + \ldots\ldots\ldots\ldots + N_M = N$$

For this case, how many ways the N particles can be distributed in the M – containers.



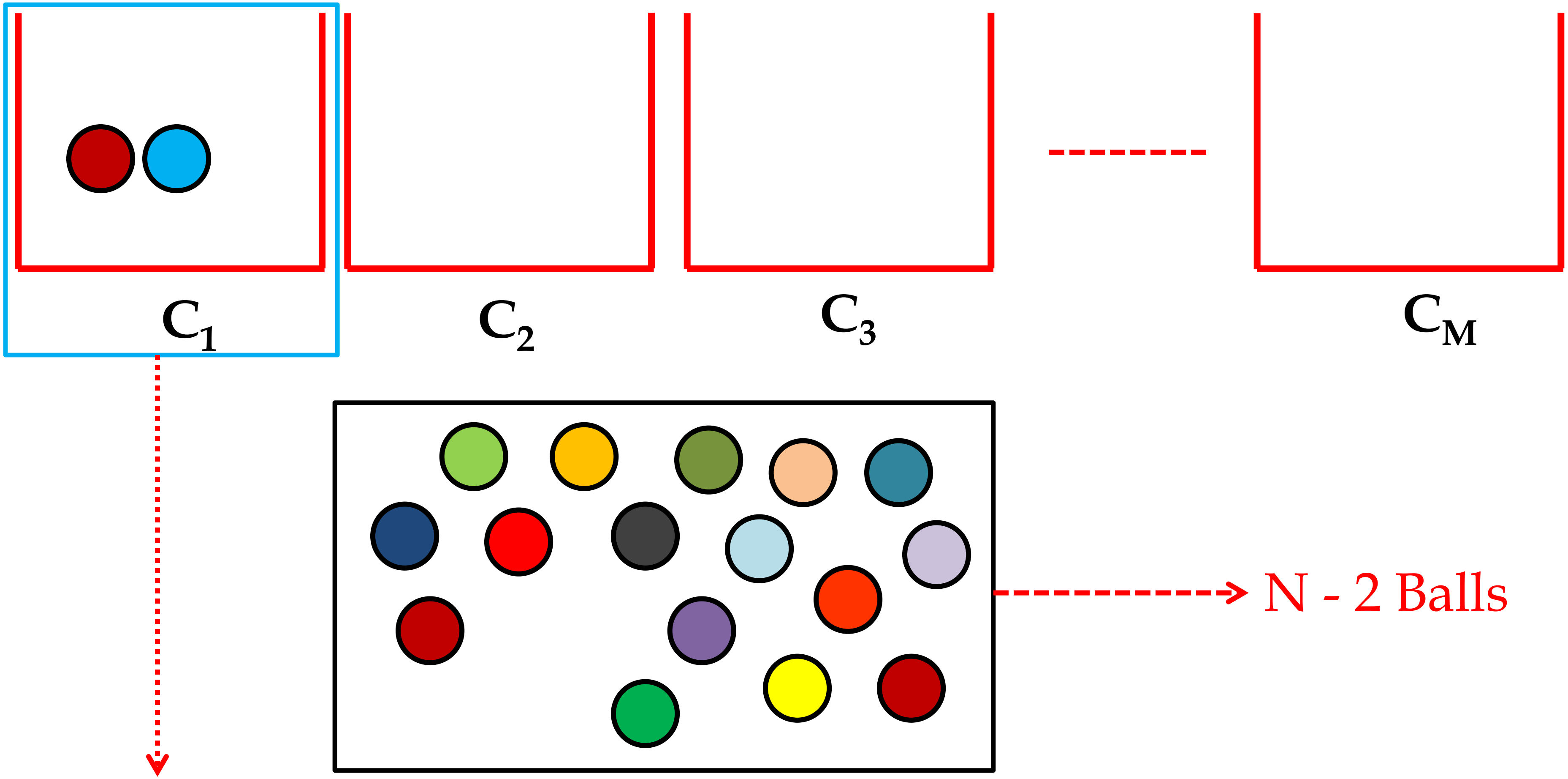
First particles to the container c_1 can be chosen in $\underline{\boxed{\mathbf{N}}}$ ways.



Number of ways to choose second particle to the container c_1

(N-1) ways

How many ways the first two particles can be chosen = N x (N – 1)

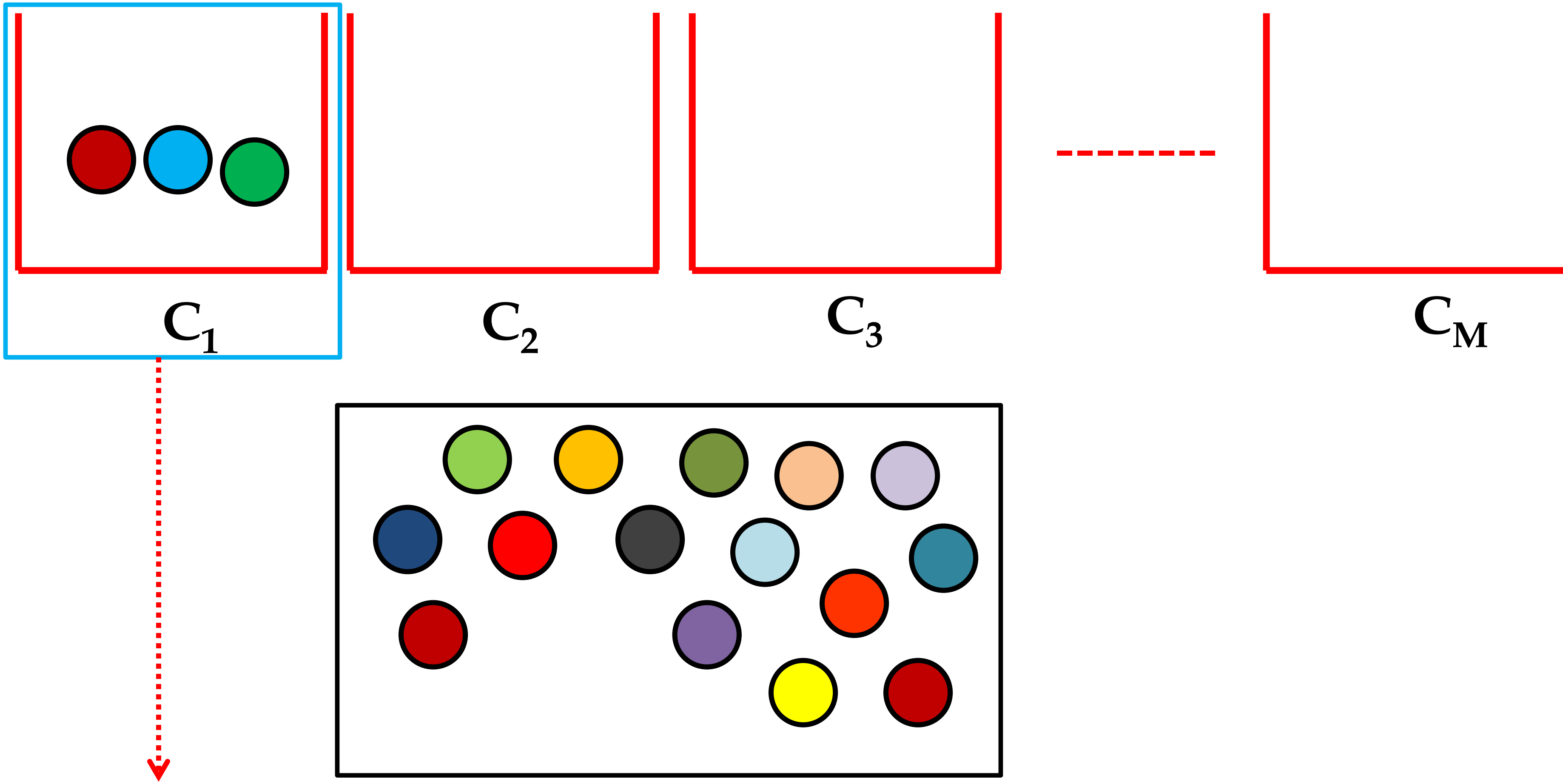


Number of ways to choose third particle to the container c_1

(N - 2) ways

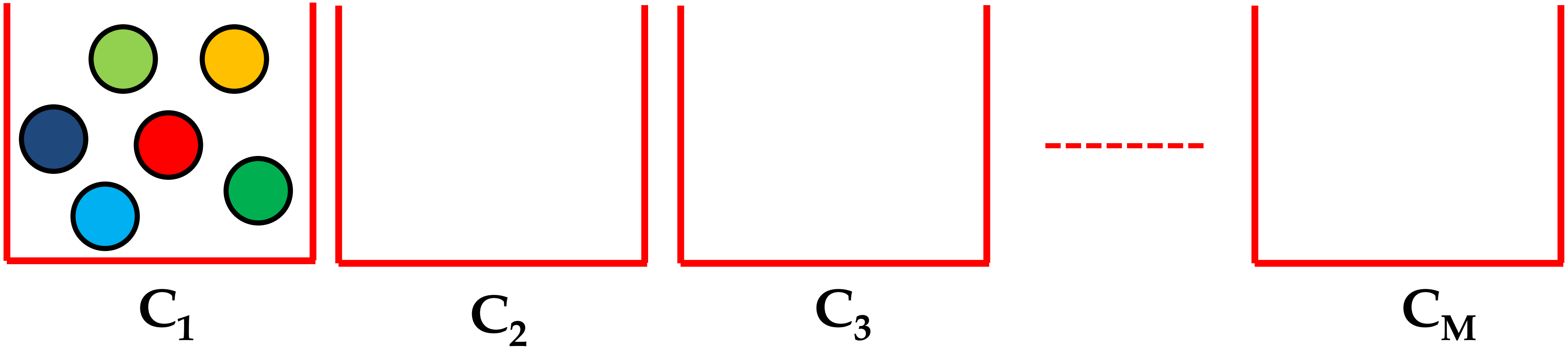
How many ways the first three particles can be chosen

$= N(N - 1)(N - 2)$



Number of ways to choose N^{th} particle = $N (N - 1)(N - 2) \ldots.(N - (N_1 - 1))$

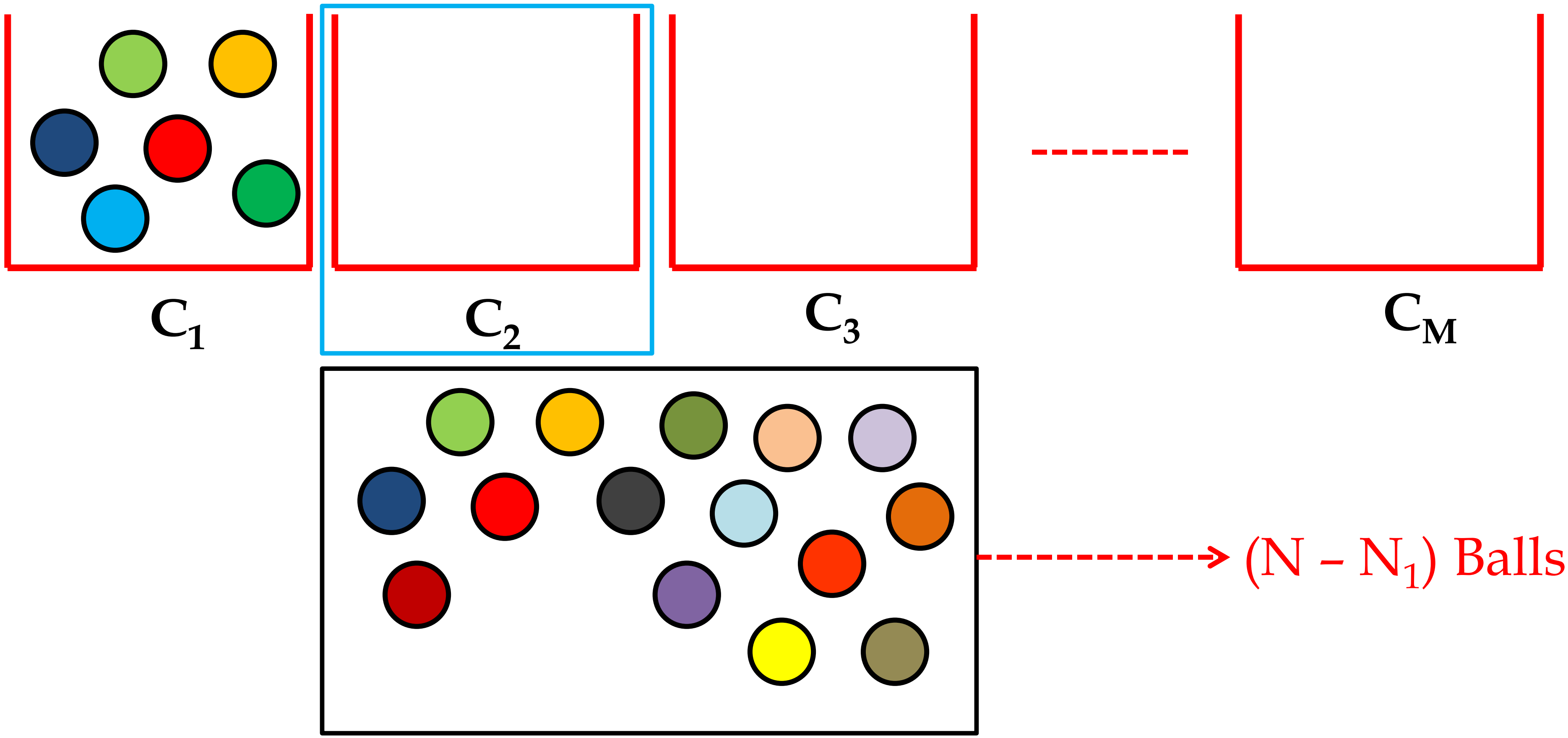
Here, we note that the order of choosing the particle is not important.



So the exact number of ways to choose N_1 particles for container C_1

$$w_1 = \frac{N(N-1)(N-2)\ldots\ldots(N-(N_1-1))}{N_1!}$$

Now, consider second container



How many number of ways

The first particles to c_2 can be chosen $(N - N_1)$ ways

The second particles to c_2 can be chosen $(N - \{N_1 - 1\})$ ways

Total number of ways to choose N_2 particle for second container.

$$= \frac{(N-N_1)(N-N_1-1)\ldots\ldots(N-(N_1+N_2)+1)}{N_2!}$$

So, number of ways of choosing N_1 particles for container c_1

$$(w_1) = \frac{N(N-1)(N-2)\ldots\ldots(N-N_1+1)}{N_1!}$$

So, number of ways of choosing N_2 particles for container c_2

$$(w_2) = \frac{(N-N_1)(N-N_1-1)\ldots\ldots(N-(N_1+N_2)+1)}{N_2!}$$

So, number of ways of choosing N_3 particles for container c_3

$$(w_3) = \frac{(N-(N_1+N_2))(N-(N_1+N_2)-1)\ldots\ldots(N-(N_1+N_2+N_3)+1)}{N_3!}$$

So, number of ways of choosing N_M particles for container c_M

(w_M)

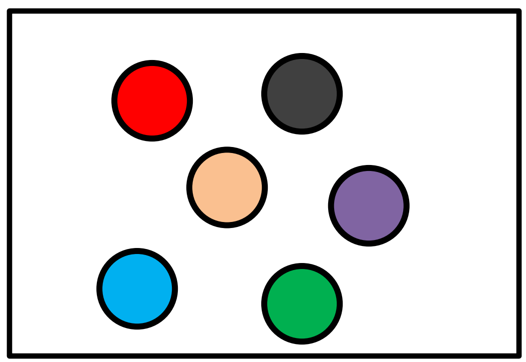
$$= \frac{\left(N - \left(N_1 + N_2 + \ldots\ldots + N_{M-1}\right)\right)\ldots\ldots 2.1}{N_M\,!}$$

Total number of ways of distributing N particles in M container

$$W = W_1\, W_2\, W_3 \ldots\ldots W_M$$

$$= \frac{N!}{\prod_{i=1}^{M} N_i\,!}$$

Example :



$N = 6$

First particle to container c_1

Number of ways = 6

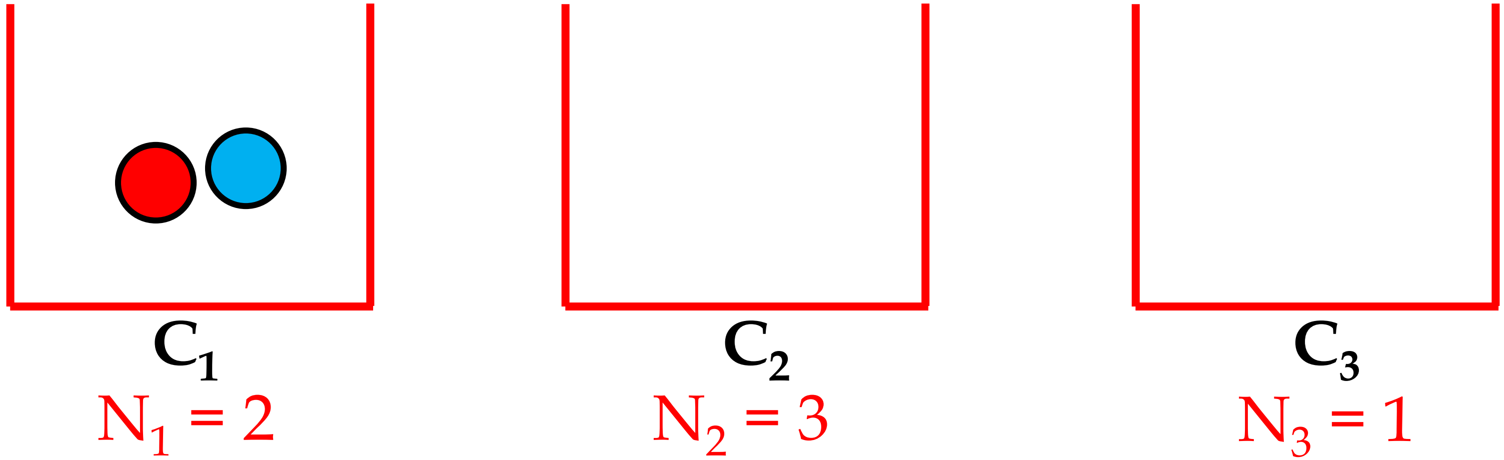
Second particle to container c_2

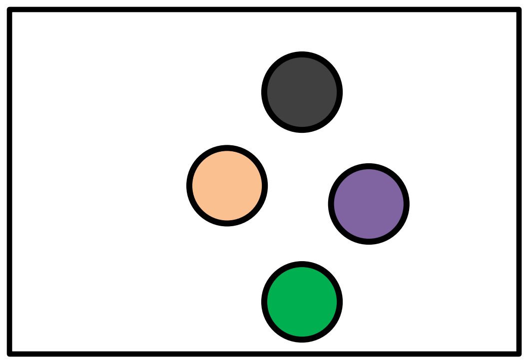
Number of ways = 5

$$\frac{6 \times 5}{2!}$$

Number of ways chose 2 particle for container c_1

Example :





Number of ways to chose first particle = 4

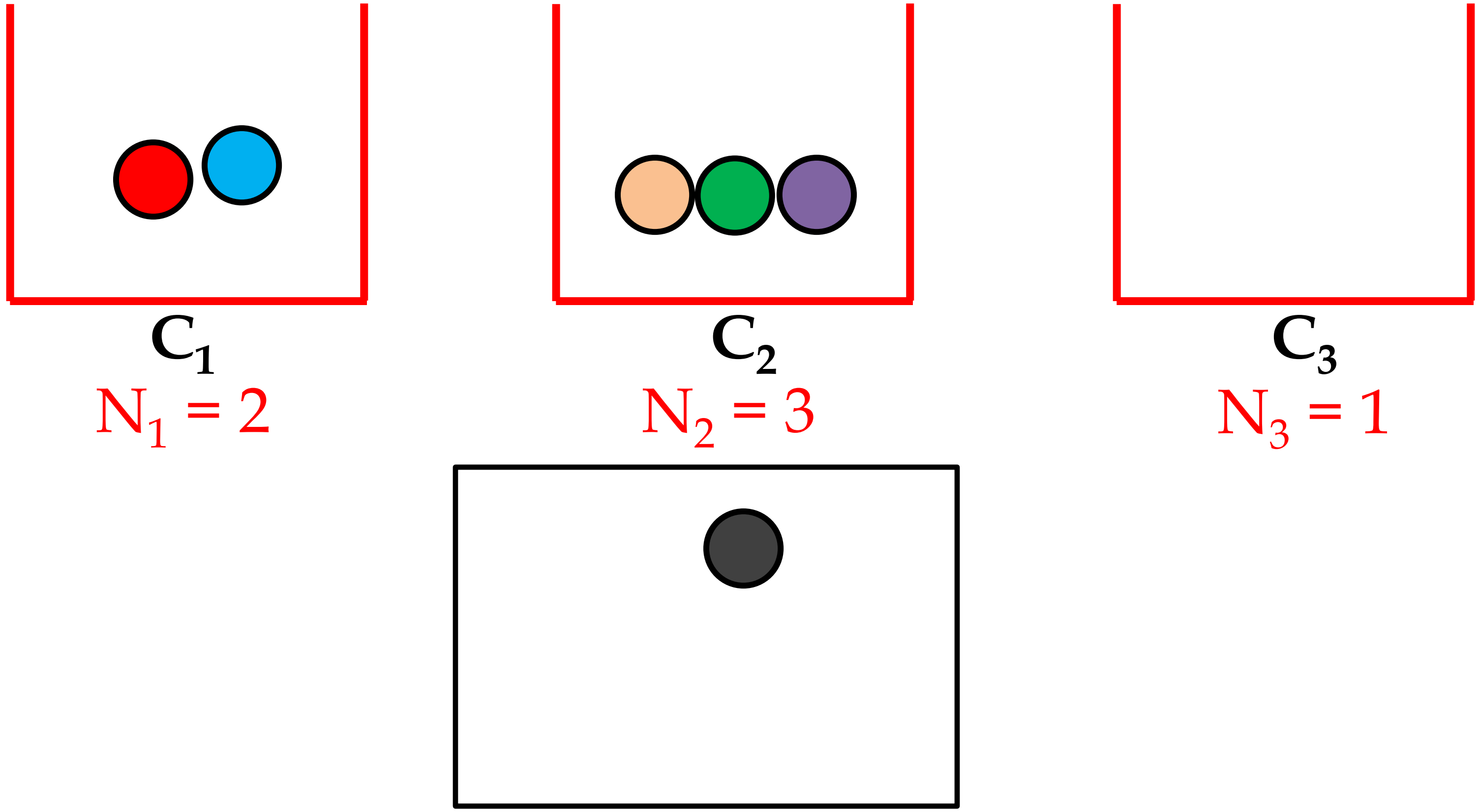
Number of ways to chose second particle = 3

Number of ways to chose third particle = 2

$$\frac{4 \times 3 \times 2}{3!}$$

Number of ways choose 3 particle for container c_2

Example :



Number of ways to chose 1 particle for $c_1 = \dfrac{1}{1!}$

Number of ways to chose (N_1 = 2) particle for c_1 $= \dfrac{6\times 5}{2!}$

Number of ways to chose (N_2 = 3) particle for c_2 $= \dfrac{4\times 3\times 2}{3!}$

Number of ways to chose (N_3 = 1) particle for c_3 $= \dfrac{1}{1!}$

So number of ways of distributing (N = 6) particles in 3 containers

$$= \frac{6\times 5}{2!}\times\frac{4\times 3\times 2}{3!}\times\frac{1}{1!}$$

$$= \frac{6!}{2!\ 3!\ 1!}$$

$$= \frac{N!}{N_1!\ \mathrm{N}_2!\ \mathrm{N}_3!}$$

Summary :

If you have N distinguishable particles, then number of ways to arrange N particles in a line = N!

If you have N particles where n particles are indistinguishable, then number of ways to arrange them $= \dfrac{N!}{n!}$

If you have N particles among them n_1 particles are identical to each other and n_2 particles are identical to each other, the number of ways of arranging the particular $= \dfrac{N!}{n_1! n_2!}$

If you have N particles, which have to be distributed in M containers (with no restriction on the number of particles per container) number of ways of distribution = M^N

If we have restriction on the number of particles in each container, that is, N_1 particles for container c_1, N_2 particles for c_2,….

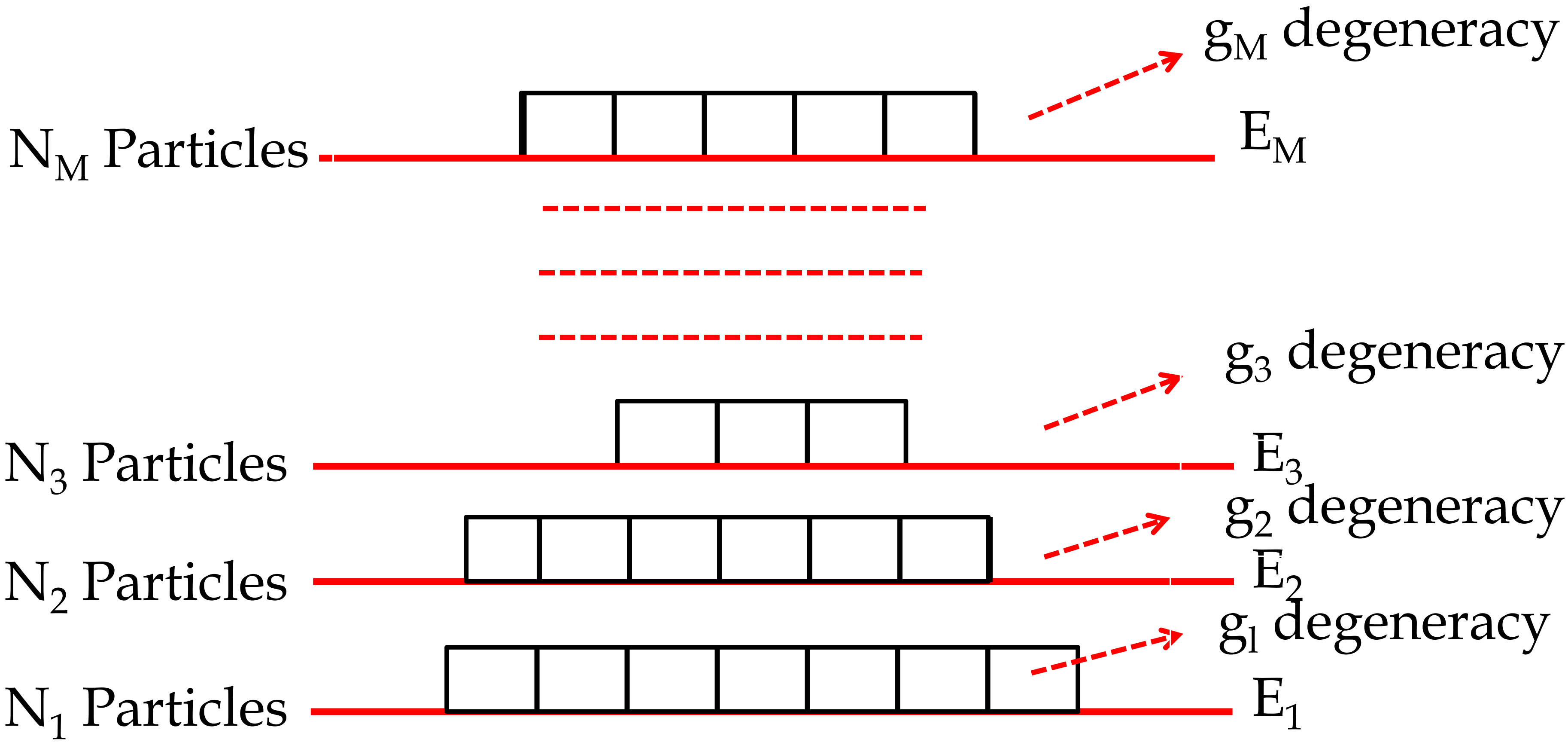
$$= \frac{N!}{N_1!N_2!N_3!.......N_M!} = \frac{N!}{\prod_i N_i!}$$

Maxwell Boltzmann Distribution

Particles are distinguishable.

Any number of particles can be accommodated a particular quantum energy state.

So let us consider that the system has N particles where N_1 particles have energy E_1, N_2 particles have energy E_2....N_M particles have energy E_n. Here, $N_0 + N_1 + N_2 + \ldots\ldots N_M = N$. Note that the Energy level E_i has g_i amount of degeneracy.

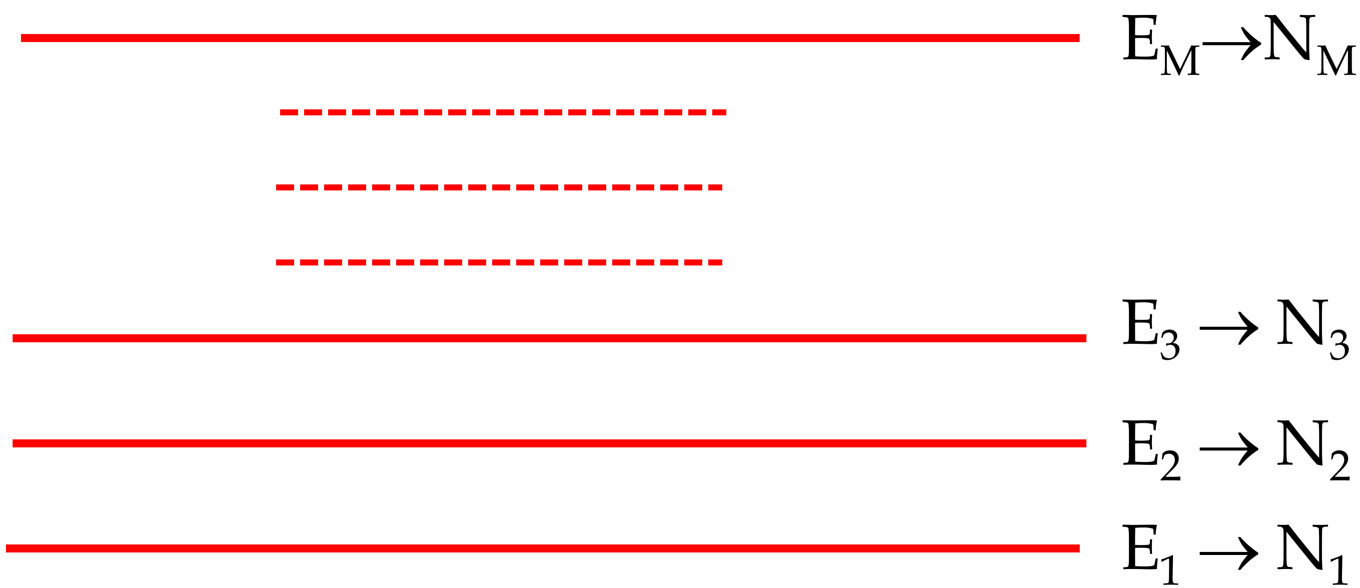


Problem :

"How many number of ways the particles can be distributed among the 'M' energy levels".

First, forget about the degeneracy of energy levels

How many ways $N_0 \rightarrow E_0$, $N_1 \rightarrow E_1$ ….. $N_M \rightarrow E_M$ can be distributed ?



The problem is like distributing N particles in E_i containers , i = 1, 2, ……..,M (with restriction on the number of particles in each containers.

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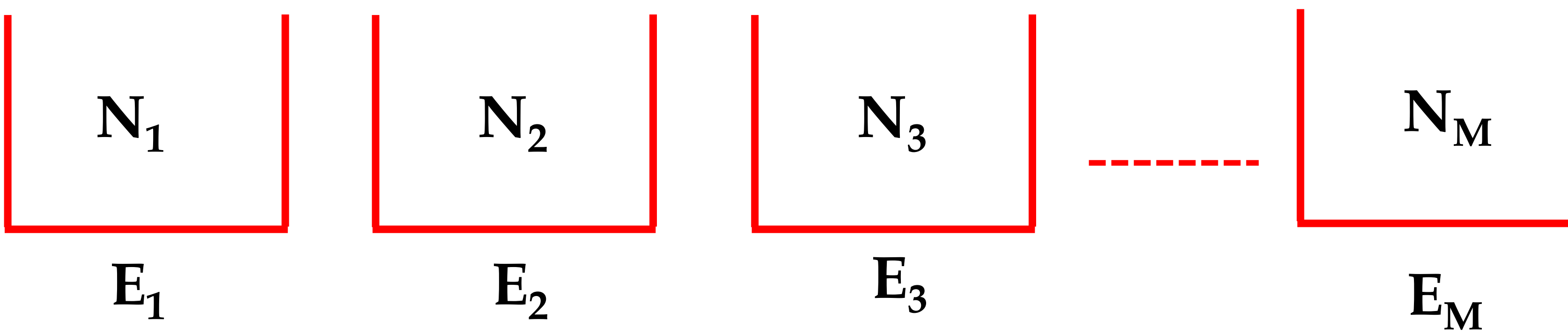
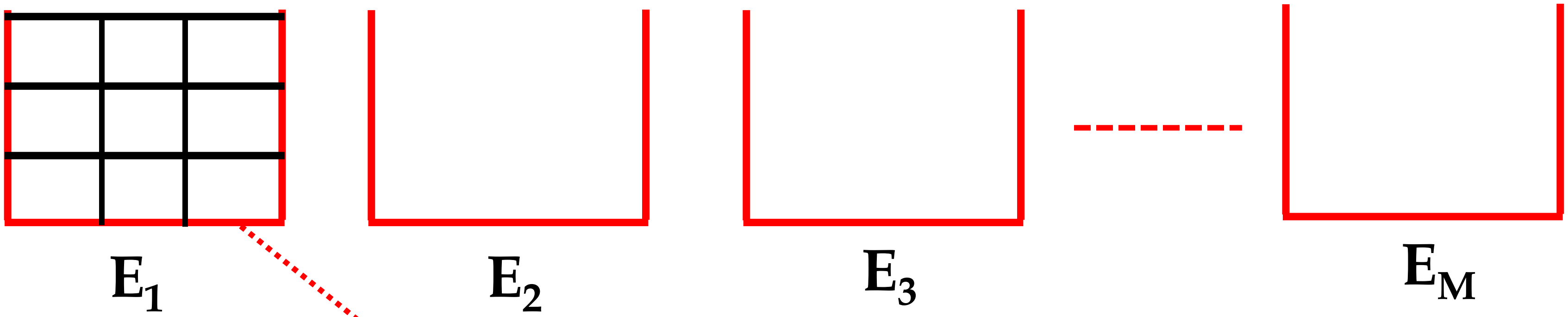
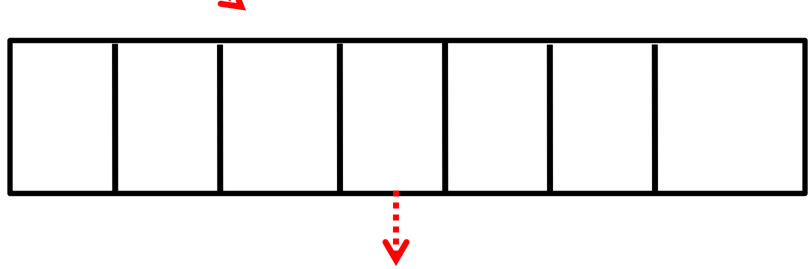


$$\text{Ans}: \frac{N!}{N_1!N_2!N_3!\ldots\ldots.N_M!} (or) \frac{N!}{\prod_{i=1}^{M} N_i}$$

Now, consider degeneracy. For example, the energy level E_1 has g_1 degeneracy.



How many ways N_1 particles can be distributed among g_1 boxes.



g_1 boxes

Note: No restriction on the number of particles per box.

$$\boxed{Answer = g_1^{N_1}}$$

(like in the case of distributing N particle in M containers (with no restriction on number of particles per container)(= M^N))

How many ways N_2 particles can be arranged in E_2 energy level with g_2 degeneracy = $g_2^{N_2}$

How many ways N_3 particles can be arranged in E_3 energy level with g_3 degeneracy = $g_3^{N_3}$

How many ways N_M particles can be arranged in E_M energy level with g_M degeneracy = $g_M^{N_M}$

So answer to original problem.

How many ways N particles can be arranged in E_i energy level with g_i degeneracy (where i = 1, 2, ……M)

$$W = \underbrace{\left(\frac{N!}{N_1!\,N_2!\,N_3!\ldots\ldots.N_M!}\right)}_{\text{Arranging N particles in } E_M \text{ energy levels}} \times \underbrace{\left(g_1^{N_1} g_2^{N_2} \ldots\ldots g_M^{N_M}\right)}_{\text{Arranging } N_i \text{ particles of } E_i \text{ th level in } g_i \text{ quantum states}} = N! \prod_{i=1}^{M} \frac{g_i^{N_i}}{N_i!}$$

Maxwell-Boltzmann Distribution Law

M-B Energy Distribution Law in General Form :

Taking logarithms of $W = N! \prod_i \left(\frac{g_i^{ni}}{n_i!}\right)$ we have

$$\log W = \log N! + \log\left[\prod_i \left(\frac{g_i^{ni}}{n_i!}\right)\right]$$

$$\log\left(\frac{g_1^{n_1}}{n_1!} \times \frac{g_2^{n_2}}{n_2!}\right) = \log\left[\frac{g_1^{n_1}}{n_1!}\right] + \log\left[\frac{g_2^{n_2}}{n_2!}\right]$$

$$= n_1 \log g_1 - \log n_1! + n_2 \log g_2 - \log n_2!$$

$$= \sum_{i=1}^{2}(n_i \log g_i - \log n_i!)$$

$$= \log N! + \sum_{i=1}^{k}(n_i \log g_i - \log n_i!) \quad \rightarrow (5)$$

Since the number of particles is very large,. $N!$ and $n_i!$ May be approximated by Sterling's $formula$, according to which

$$\log N! = N \log N - N \quad \rightarrow (6(a))$$

and

$$\log n_i! = n_i \log n_i - n_i \quad \rightarrow \big(6(b)\big)$$

$$\therefore \quad \log W = N \log N - N + \sum_{i=1}^{k}(n_i \log g_i - n_i \log n_i + n_i) \quad \rightarrow (7)$$

Condition for most Probable Distribution

- The most probable distribution of the particles among the energy states in equilibrium is that for which the probability of occurrence is maximum, i.e. for which **W is maximum.**
- For mathematical convenience, we consider the condition for maximum value of $\log W$. The condition for maximum value of $\log W$ is

$$d\log(W) = 0 \qquad \rightarrow (1)$$

where W is a function of $n_1, n_2, \ldots \ldots n_k$.

Differentiating Eq. (1), we get

$$d\log(W) = \frac{\partial \log W}{\partial n_1} dn_1 + \frac{\partial \log W}{\partial n_2} dn_2 + \ldots\ldots + \frac{\partial \log W}{\partial n_k} dn_k$$

$$= \sum_{i=1}^{k} \frac{\partial \log W}{\partial n_i} dn_i$$

Applying the condition from eqn. (1), we get

$$\sum_{i=1}^{k} \frac{\partial \log W}{\partial n_i} dn_i = 0 \qquad \rightarrow (2)$$

The solution of this equation is subject to the condition laid down by

$$N = \sum_i n_i\,; \quad dN = \sum_i dn_i = 0 \quad \rightarrow (A); \quad E = \sum_i n_i E_i\,; \quad E = \sum_i E_i dn_i = 0 \rightarrow (B)$$

These conditions are introduced into Eq. (2) by using the method of Langrange's undetermined multipliers.

Let α and β be these multipliers independent of n_i 's. We multiply Eq.(A) by $-\alpha$ and Eq.(B) by $-\beta$ and adding these equations to Eq.(2), we have

$$\sum_{i=1}^{k} \left(\frac{\partial \log W}{\partial n_i} - \alpha - \beta E_i \right) dn_i = 0 \qquad \rightarrow (3)$$

For maximum value of $\log W$, Eq.(3) must be true for the magnitudes of the individual increments dn_i. Hence, for all values of i, the term in the bracket must be zero.

$$\therefore \quad \frac{\partial \log W}{\partial n_i} - \alpha - \beta E_i = 0 \qquad \rightarrow (4)$$

$$\log W = N \log N - N + \sum_{i=1}^{k}(n_i \log g_i - n_i \log n_i + n_i)$$

Differentiating Eq.(7) partially with respect to n_i and remembering that the partial derivatives of the terms, except the ith term, are zero. Thus,

$$\frac{d \log W}{dn_i} = \log g_i - \left(\log n_i - \frac{n_i}{n_i}\right) + 1$$

$$= \log g_i - \log n_i$$

$$= -\log\left(\frac{n_i}{g_i}\right) \qquad \rightarrow (8)$$

Substituting this equation into (4), we have

$$\frac{\partial \log W}{\partial n_i} - \alpha - \beta E_i = 0$$

$$-\log\left(\frac{n_i}{g_i}\right) - \alpha - \beta E_i = 0$$

$$\log\left(\frac{n_i}{g_i}\right) = -\alpha - \beta E_i$$

$$n_i = g_i e^{(-\alpha - \beta E_i)}, \qquad i = 1,2,3, \dots . k \rightarrow (9)$$

This equation is known as the **Maxwell – Boltzmann energy distribution law** in the general form.

The value of undetermined multiplier β is evaluated as

$$\beta = \frac{1}{kT} \qquad \rightarrow (10)$$

Substituting in Eq.(10), we get

$$n_i = g_i e^{-\alpha} e_i^{-E_i/kT} \qquad \rightarrow (11)$$

Where k is Boltzmann constant and T its absolute temperature. The quantity $e^{-E_i/kT}$ is known as the **Boltzmann factor.**

From the fundamental postulates of statistical mechanics, we write, $N,$ the total number of particles as

$$N = \sum_i n_i = \sum_i g_i \, e^{-\alpha} \, e^{-E_i/kT} = e^{-\alpha} \sum_i g_i \, e^{-E_i/kT}$$

$$\therefore \qquad e^{-\alpha} = \frac{N}{\sum_i g_i \, e^{-E_i/kT}} \qquad \rightarrow (12)$$

Substituting this value in $n_i = g_i e^{-\alpha} \, e_i^{-E_i/kT}$ we get

$$n_i = \frac{N \, g_i \, e^{-E_i/kT}}{\sum_i \, g_i \, e^{-E_i/kT}} \qquad \rightarrow (13)$$

The quantity $\sum_i \, g_i \, e^{-E_i/kT}$ is the sum over all the states of the system and is called the **partition function** of the system devoted by Z. Thus

$$Z = \sum_i g_i \, e^{-E_i/kT} \qquad \rightarrow (14)$$

Recall

$n_i = g_i e^{-\alpha} \, e_i^{-E_i/kT}$

Substituting in equation (13), we have

$$n_i = \frac{N}{Z} \, g_i \, e^{-E_i/kT} \qquad \rightarrow (15)$$

Evaluation of the Multiplier α.

From eqn.(12), we write

$$e^{-\alpha} = \frac{N}{\sum_i \; g_i \; e^{-E_i/kT}}$$

Since the variation of energy of free particles of an ideal gas is continuous, we will replace g_i by $g(E)dE$ and E_i by E and the sign of summation is replaced by the sign of integration. Thus, we get

$$e^{-\alpha} = \frac{N}{\int_0^\infty \; g(E)dE.e^{-E/kT}}$$

$$= \frac{N}{\int_0^\infty \; g(E) \; e^{-E/kT} dE} \qquad \rightarrow (22)$$

Here the limit of integration is taken from $0\ to\ \infty$, because energy of the particles of an ideal gas is entirely kinetic and so they can have any kinetic energy. The value of $g(E)dE$ for particles with **no spin** is given by

$$g(E)dE = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{\frac{1}{2}}\, dE$$

Substituting in eqn.(22), we get

$$e^{-\alpha} = \frac{N}{2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty E^{\frac{1}{2}} e^{\frac{-E}{kT}}\, dE} \qquad \rightarrow (23)$$

Let us evaluate the definite integral as under :

For this, let $\frac{E}{kT} = x$, so that $dE = kTdx$.

$$\therefore \quad \int_0^\infty E^{\frac{1}{2}}\, e^{-E/kT}\, dE = \int_0^\infty (kTx)^{\frac{1}{2}}\, e^{-x}\, kTdx$$

$$= (kT)^{3/2} \int_0^\infty x^{\frac{1}{2}}\, e^{-x}\, dx$$

$$\therefore \quad \int_0^\infty E^{\frac{1}{2}}\, e^{-E/kT}\, dE = (kT)^{\frac{3}{2}}\, \frac{\sqrt{\pi}}{2}$$

Substituting in eqn.(23), we get

$$e^{-\alpha} = \frac{N}{V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}} \quad \rightarrow (24)$$

$$e^{\alpha} = \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \quad \rightarrow (25)$$

Taking logarithms of both sides, we get

$$\alpha = -\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}\right] = \log\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] \quad \rightarrow (26)$$

Here e^{α} is called the **degeneracy parameter.**

Condition for Application of M.B. Statistics.

The M. B. Statistics is applicable to a system of particles for which the mean distance between the particles is greater than the De Broglie wavelength of the particles.

$$\text{The volume of per particle} = \left(\frac{V}{N}\right)$$

$\therefore$ The mean distance between the particles $= \left(\frac{V}{N}\right)^{\frac{1}{3}}$

The De – Broglie wavelength associated is given by

$$\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}}$$

Thus, the condition for M.B. statistics to became applicable is

$$\left(\frac{V}{N}\right)^{\frac{1}{3}} \geq \left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}}$$

$$\left(\frac{V}{N}\right) \geq \left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}$$

Condition to Apply of M.B. Statistics

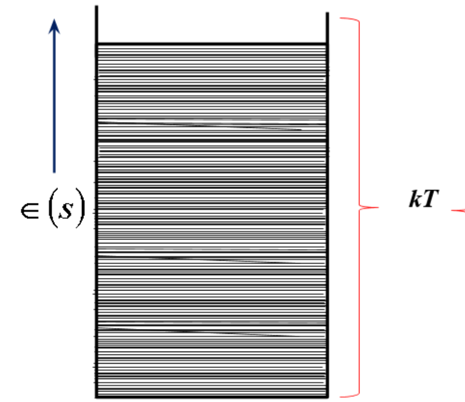
$$\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \geq 1$$

$$e^{\alpha} \geq 1 \qquad (\because Eqn. 25) \qquad \rightarrow (27)$$

Three cases :

Case(i) : When the degeneracy parameter e^{α} satisfies this condition, the gas is said to be **non degenerate.** i.e.

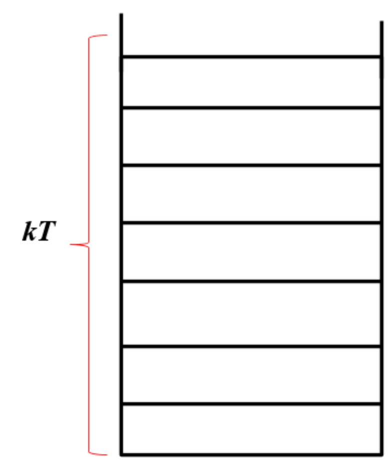
$$e^{\alpha} \geq 1$$



Non degenerate

Case(ii) : When $e^{\alpha} > 1$, but not too large, the gas is said to be **weakly degenerate.**

Case(iii) : When $e^{\alpha} < 1$, the gas is said to be **strongly degenerate.**



Degenerate

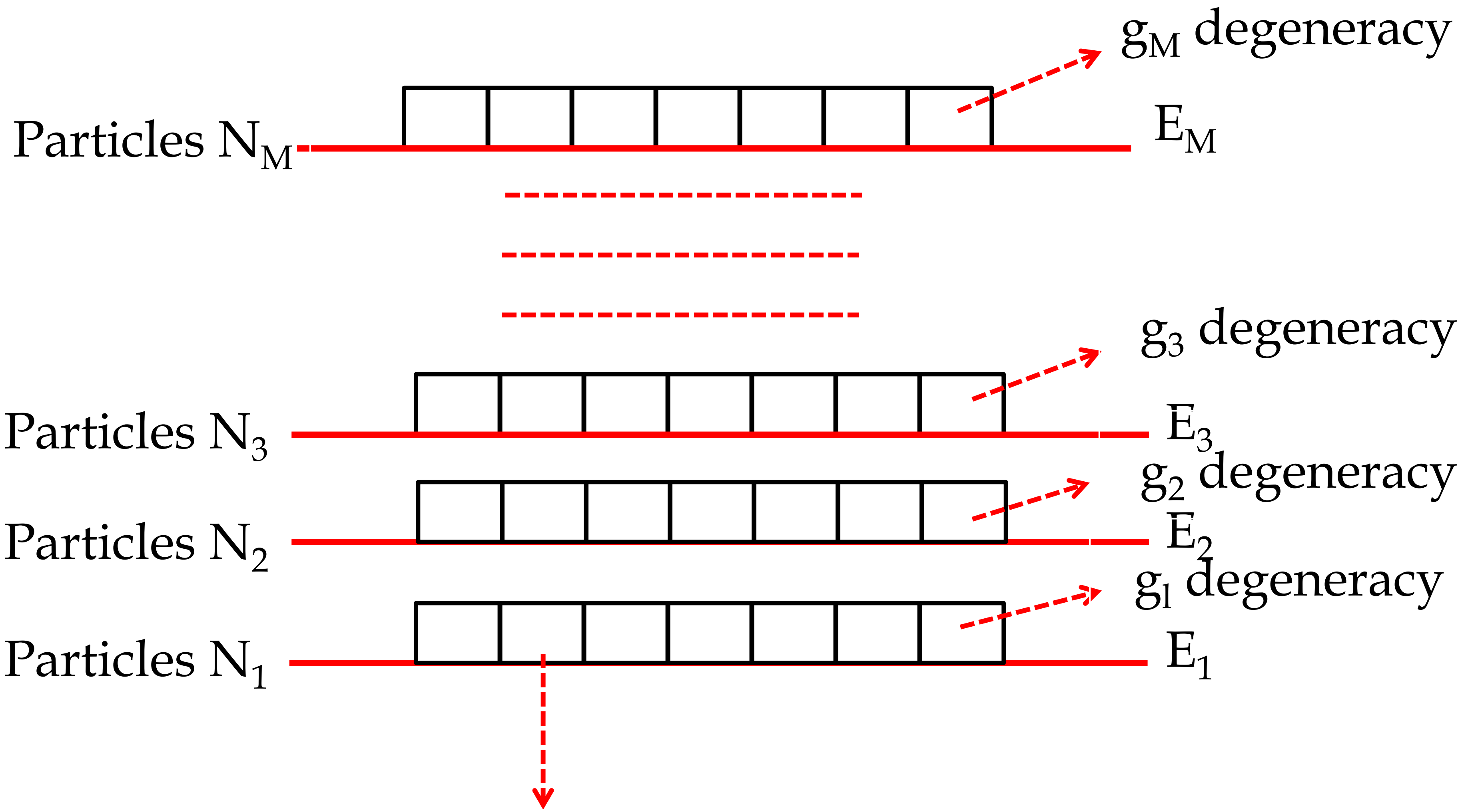
From inequality (27), we infer that the M.B. statistics is valid for systems at high temperature i.e., at low densities $\frac{N}{V}$ has a low value.

Fermi - Dirac Statistics

- Particles are indistinguishable
- Number of particles that can occupy a particular quantum state is strictly **ONE**.

Now consider the same (above mentioned) problem with fermions.

Find how many ways they can be arranged?

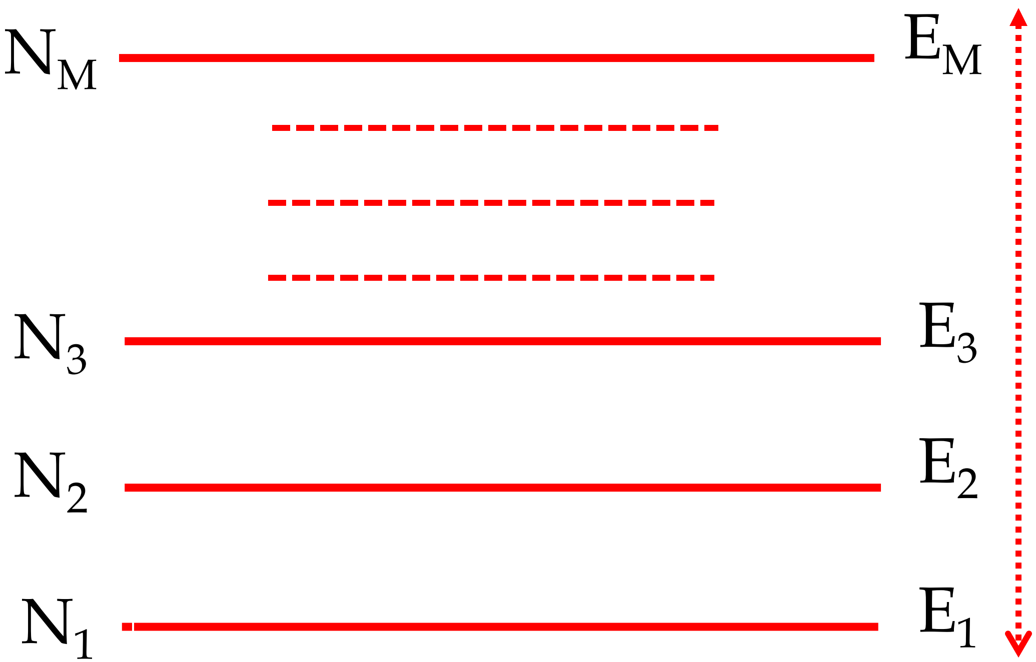


Only one particles per quantum state and $g_i >> N_i$.

Why $g_i >> N_i$? So that all particles will find place.

Similarly, first forget about degeneracy.

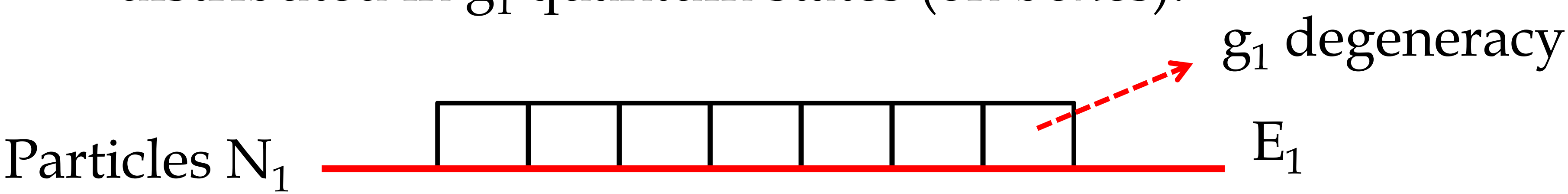
Find number of ways that the E_M energy levels can be filled respectively with N particles.



As particles are indistinguishable, there is only one way to distribute.

- Problem is solely on how many ways the particles in each energy levels can be distributed among g_i degenerate states.

- First, how many ways N_1 particles in energy E_1 can be distributed in g_1 quantum states (on boxes).



Note : there is only one particles per state and $g_i >> N_i$.

To find the above, we follow the below way:

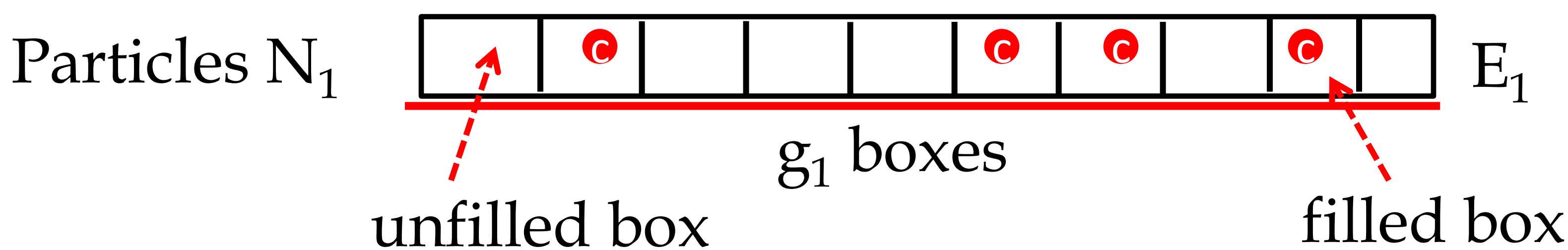
Instead of arranging N_1 particles in g_1 boxes we commute the filled boxes (boxes with a particles) with unfilled boxes.

❖To find the above, instead of arranging N_i in g_i boxes, we follow the below way:

❖First, fill up all the N_i particles in g_i boxes (Restriction: Not more than one particle per box)

❖As $g_i >> N_i$, obviously we will have few filled boxes and unfilled boxes.

❖Count the number of ways the filled and unfilled boxes can be arranged among themselves = the number of ways of distributing N_i in g_i boxes



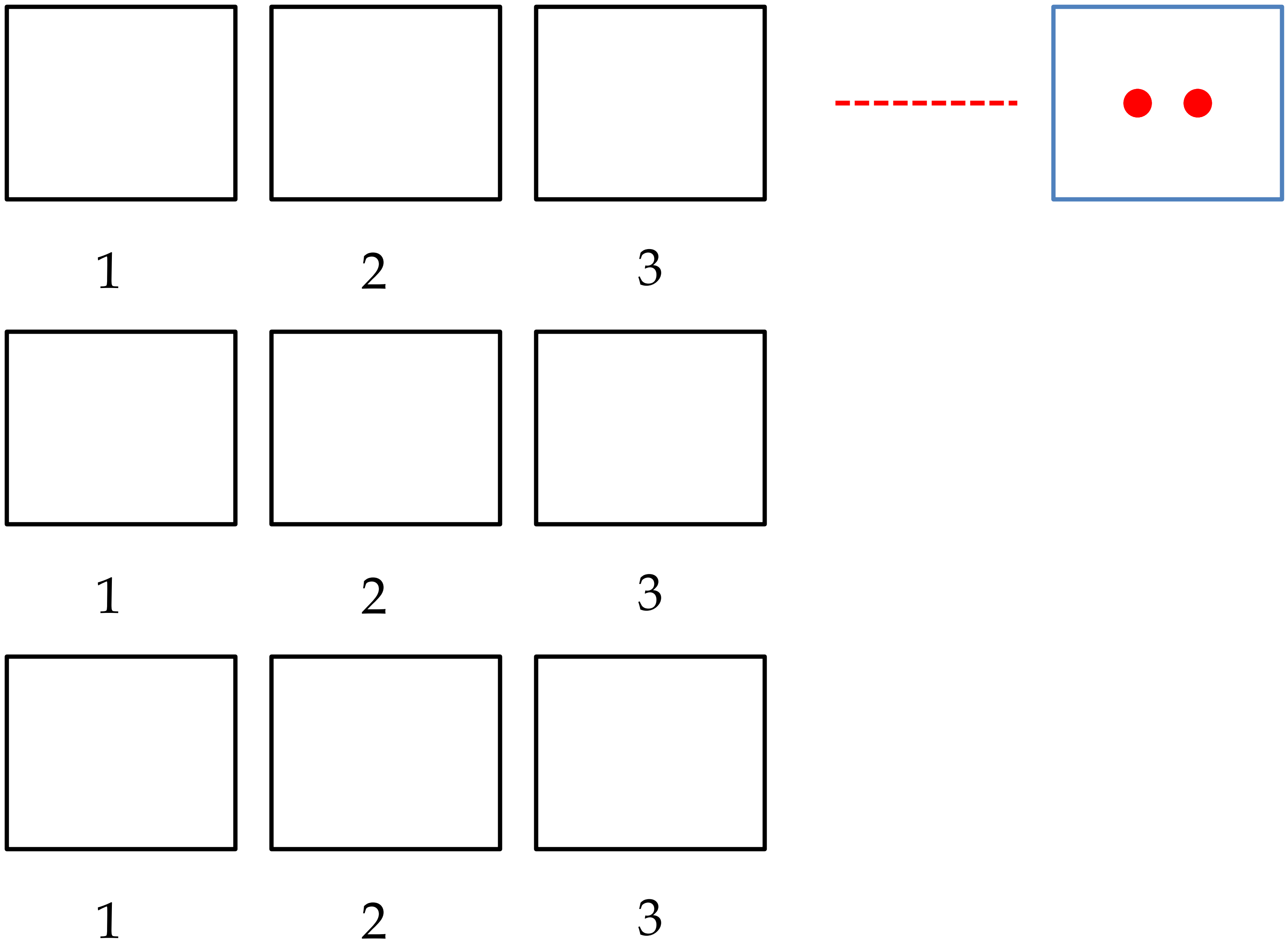
- ❖ Total number of filled boxes = N_1
- ❖ Total number of unfilled boxes = $(g_1 - N_1)$
- ❖ Total number of boxes = filled + unfilled boxes = g_1.
- ❖ Number of ways of arranging g_1 boxes = $g_1!$
- ❖ (as $N_1 \rightarrow$ filled boxes are identical among and

$(g_1 - N_1) \rightarrow$ unfilled boxes are identical among each other)

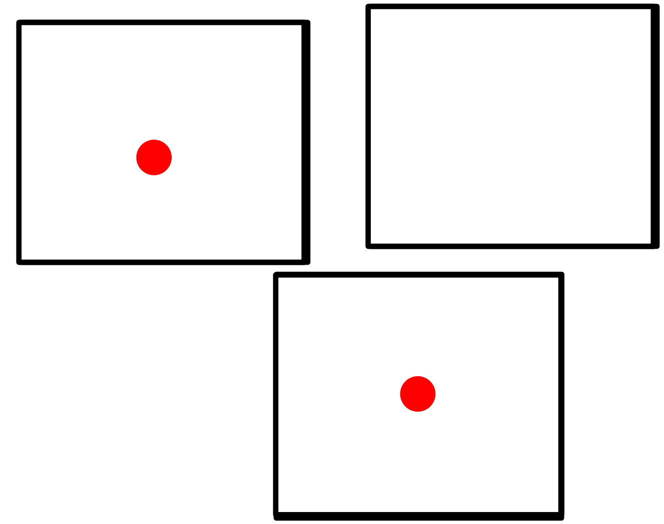
- ❖ Actual number of ways of arranging N_1 particles in g_1 boxes

$$= \boxed{\frac{g_1!}{N_1!(g_1 - N_1)!}}$$

❖ For example, $N_1 = 2$, $g_1 = 3$



❖ This can also be done by



1 2 3

1 2 3

1 2 3

There are two filled box and an unfilled box

$$\frac{g_1!}{N_1!\left(g_1 - N_1\right)!} = \frac{3!}{2!1!} = 3$$

- ❖ Similarly, N_2 particles can be distributed among g_2 quantum states (or boxes) in

$$= \frac{g_2!}{N_2!(g_2 - N_2)!} ways$$

- ❖ N_1 particles can be distributed among g_l quantum states (or boxes) in

$$= \frac{g_l!}{N_l!(g_l - N_l)!} ways$$

- So Total number of ways of arranging N particles in E_l energy levels

$$= \frac{g_l!}{N_l!(g_l - N_l)!} \frac{g_2!}{N_2!(g_2 - N_2)!} \cdots\cdots \frac{g_l!}{N_l!(g_l - N_l)!}$$

$$\boxed{w = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}}$$

Bose – Einstein Distribution

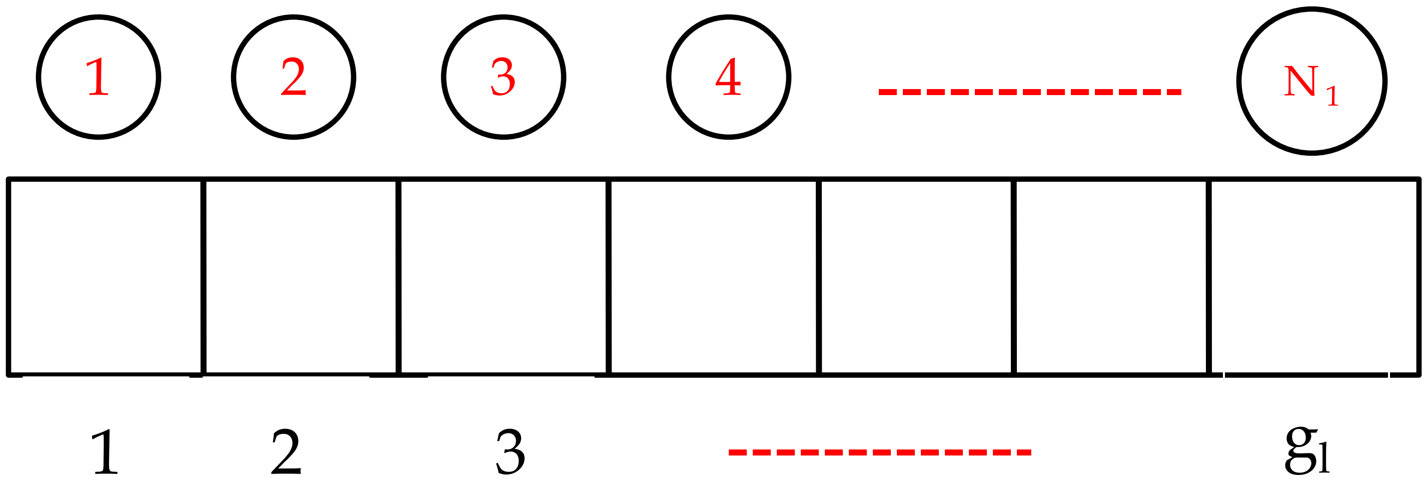
- Particles are indistinguishable.
- Any number of particles can occupy a particular quantum state.

Problem

- How many ways N Bosons can be distributed in energy levels E_1, E_2, E_3……E_l with degenerecies g_1, g_2, g_3, …..g_l.
- Here, N_1 Bosons occupy energy level E_1, N_2 Bosons occupy E_2, …….N_l Bosons occupy E_l energy level.

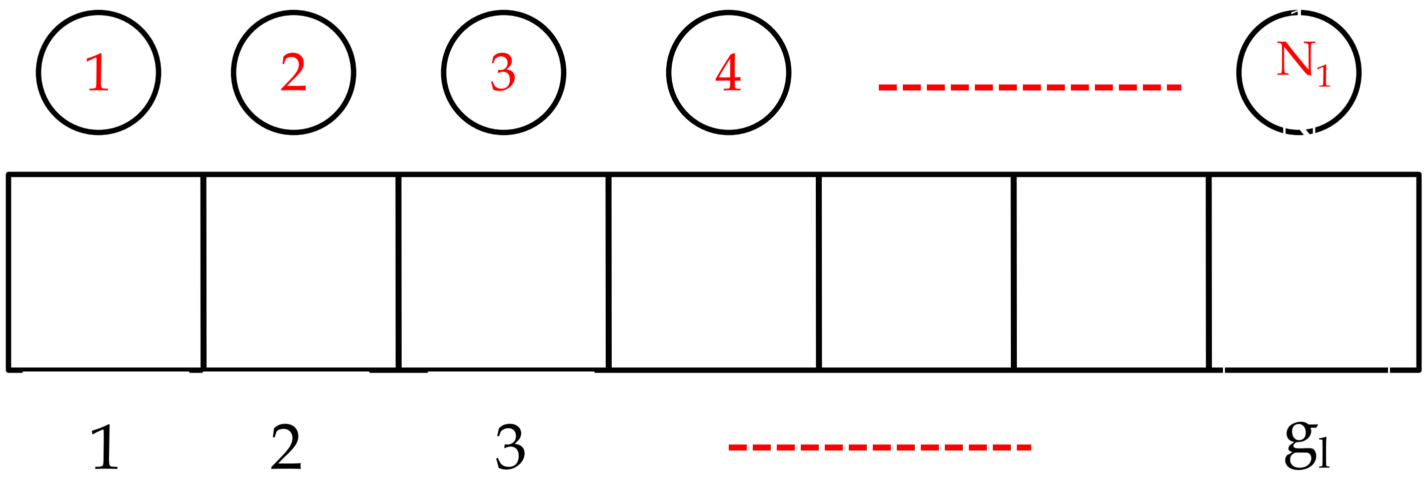
- ❖ As we did earlier, first consider the problem without degeneracy.
- ❖ In that case as particles are indistinguishable, there is **only one way** to distribute N_1, N_2, N_3, ……. N_l Bosons respectively in energy levels E_1, E_2, E_3, …….E_l .
- ❖ Thus the problem solely relies on the number of ways N_i number of particles can be distributed in g_i degenerate levels.

- How many ways will you distribute N_1 particles in g_1 states



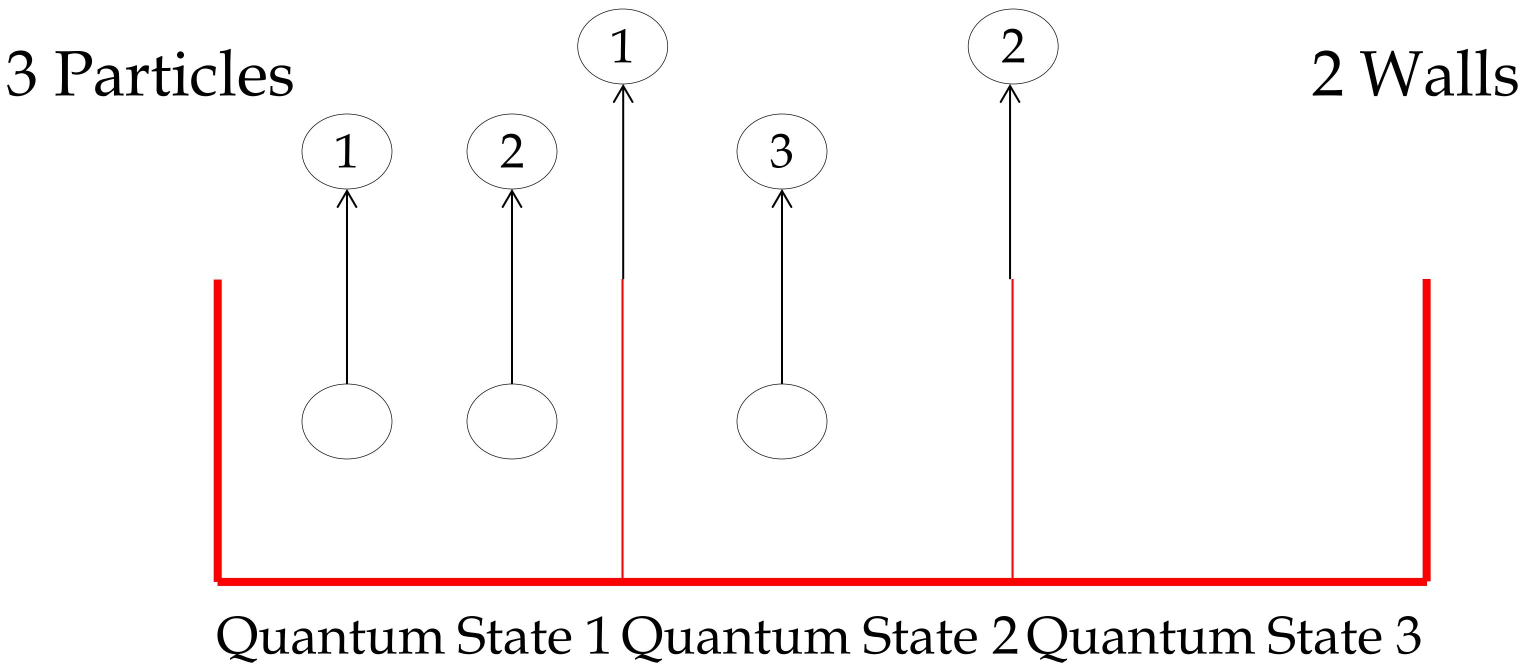
- (As we considered in the Harmonic Oscillator problem, there $(g_l - 1)$ walls and N_1 particles that have to be shuffled to get different distributions.

- How many ways will you distribute N_1 particles in g_1 states

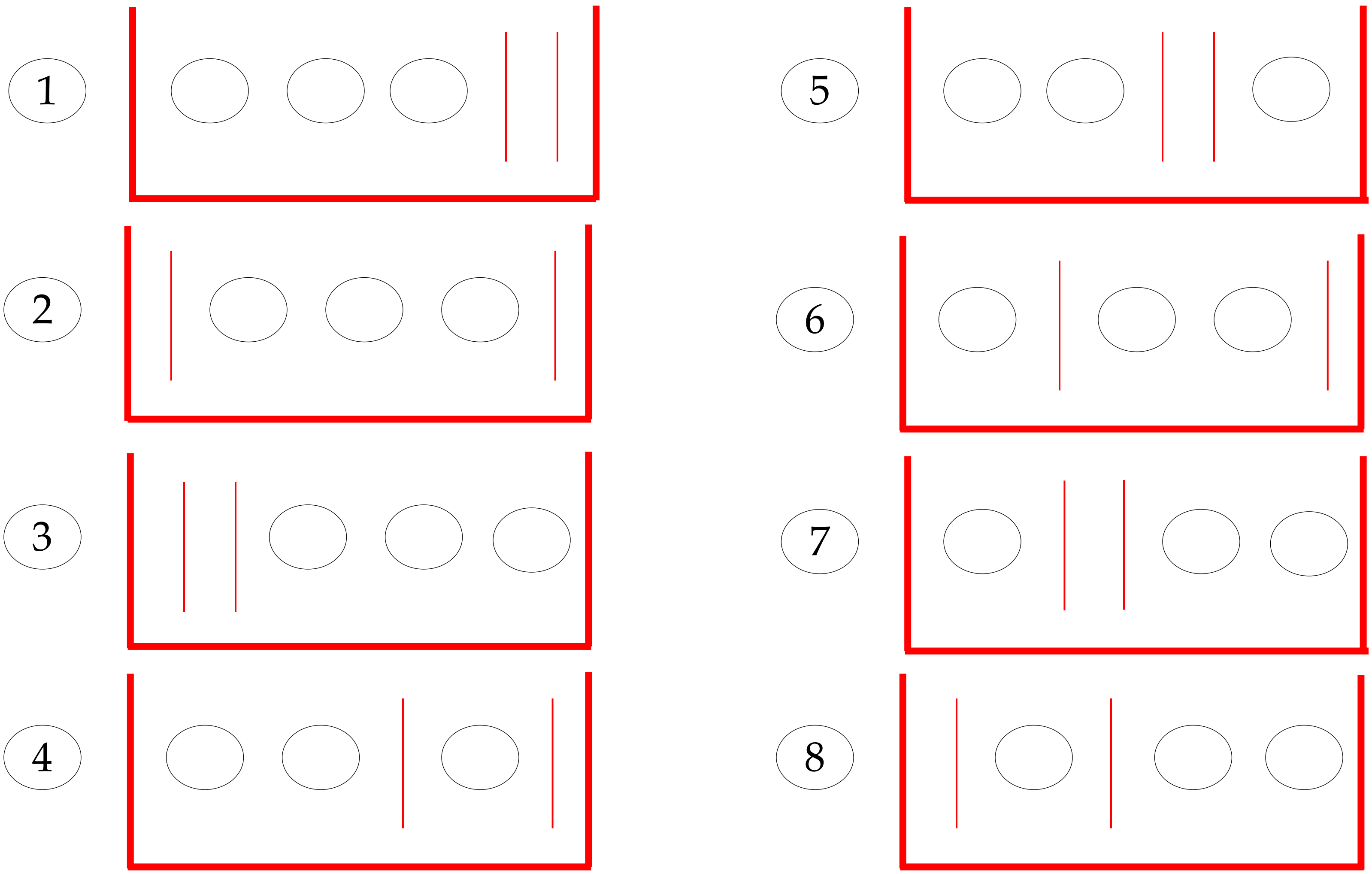


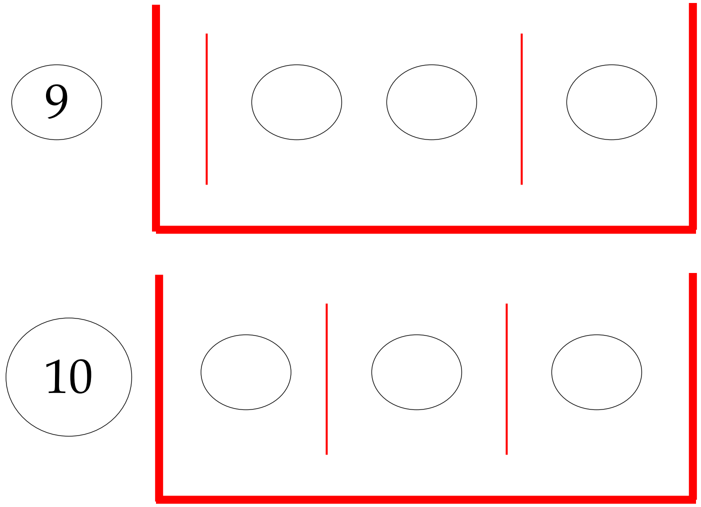
- (As we considered in the Harmonic Oscillator problem, there are (g_1 – 1) walls and N_1 particles that have to be shuffled to get different distributions.
- Total number of ways = $\dfrac{(g_1 + N_1 - 1)!}{(g_1 - 1)!\,N_1!}$

- For example, let us consider that in the energy level E_1 there are 3 degenerate states in which 3 particles has to be distributed
- $g_1 = 3$, $N_1 = 3$.
- Problem can be solved by counting number of ways the three particles and (3-1 = 2) walls can be arranged.



❖ Number of possible distributions





❖ Total number of ways 3 packets + 2 walls be arranged = (3+2)!

❖ 3 packets & 2 walls are indistinguishable among themselves.

$$\text{The Actual Count is} = \frac{(3+2)!}{3!\,2!}$$

❖ Total number of ways N_1 particles can be arranged in Energy level E_1 with g_1 degeneracy $= \frac{(g_1 + N_1 - 1)!}{(g_1 - 1)!\,N_1!}$

❖ Total number of ways N_2 particles can be arranged in Energy level E_2 with g_2 degeneracy $= \frac{(g_2 + N_2 - 1)!}{(g_2 - 1)!\,N_2!}$

❖ Total number of ways N_l particles can be arranged in Energy level E_l with g_l degeneracy $= \frac{(g_l + N_l - 1)!}{(g_l - 1)!\,N_l!}$

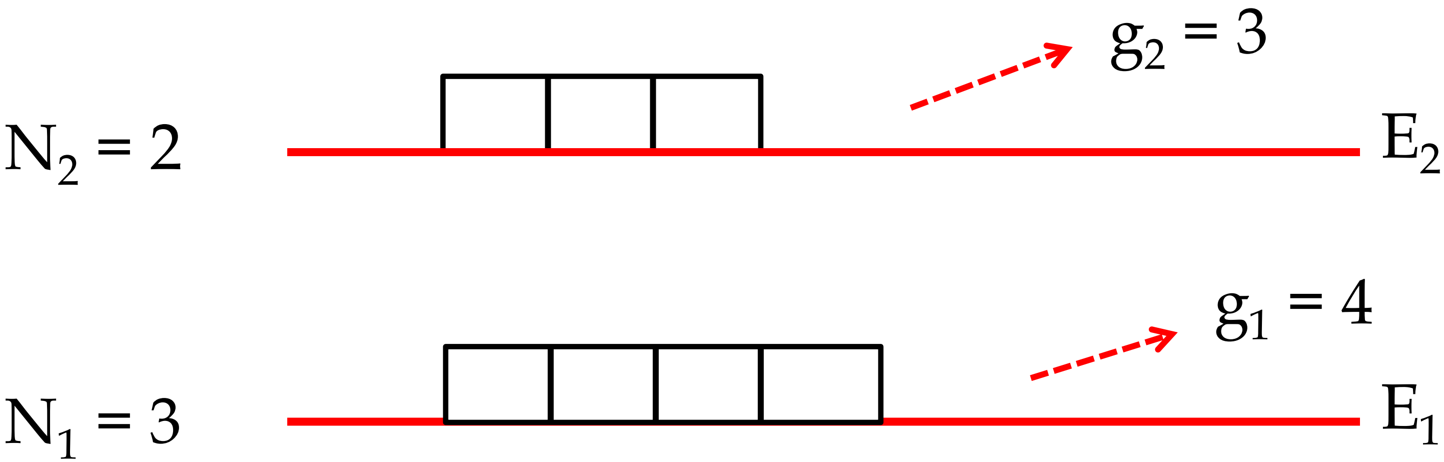
❖ Total number of ways of arranging N bosons in E_1, E_2, E_3,…..energy levels $= \prod_i \frac{(g_i + N_i - 1)!}{(g_i - 1)!\,N_i!}$

Fermi – Dirac Statistics : Example

Problem

- Consider a system of five particles that has to be distributed among two energy levels E_1 and E_2.
- In this case, three particles occupy E_1 and the other particles occupy energy E_2.
- Also note that the energy level E_1 is four fold degenerate and E_2 is three fold degenerate.
- Find the Fermi – Dirac distribution function for this case.

Given Information



$$N = N_1 + N_2 = 3 + 2 = 5$$

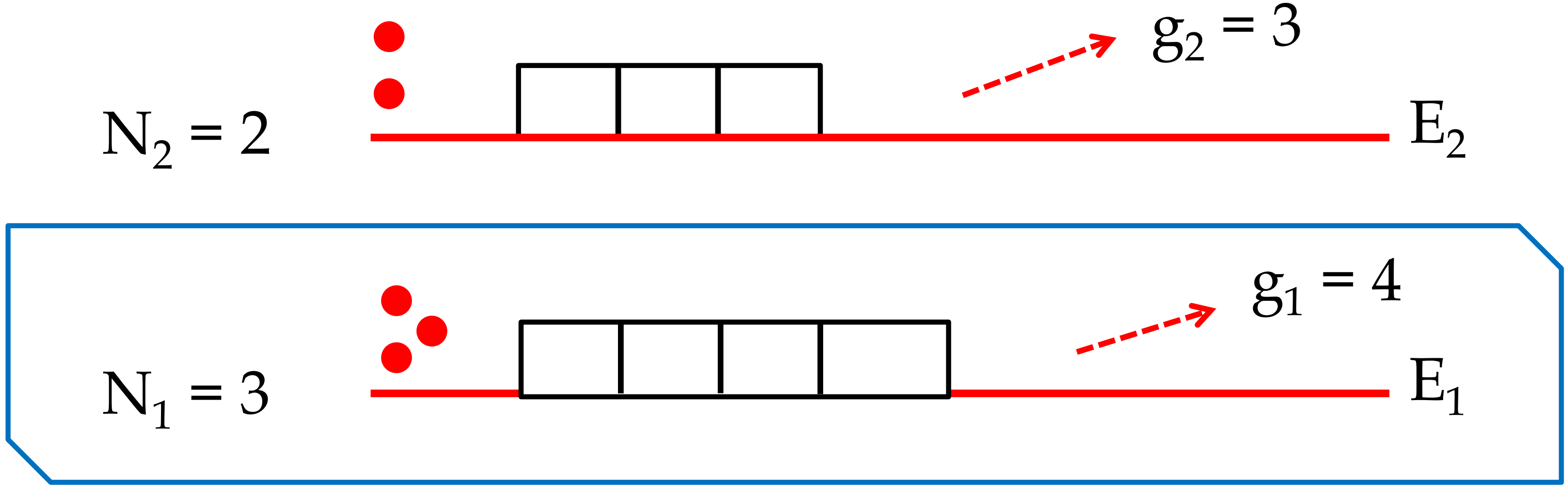
Note : $g_1 > N_1$

$g_2 > N_2$

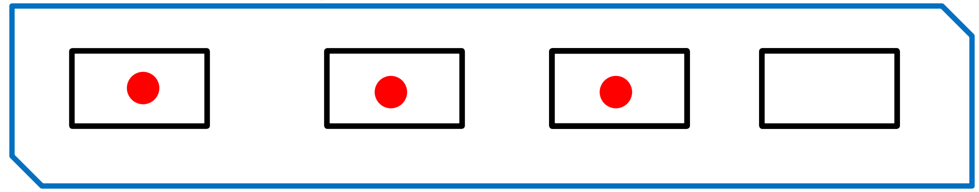
❖ Now, how many ways will you distribute the five Fermions in E_1 & E_2 (forget about degeneracy).

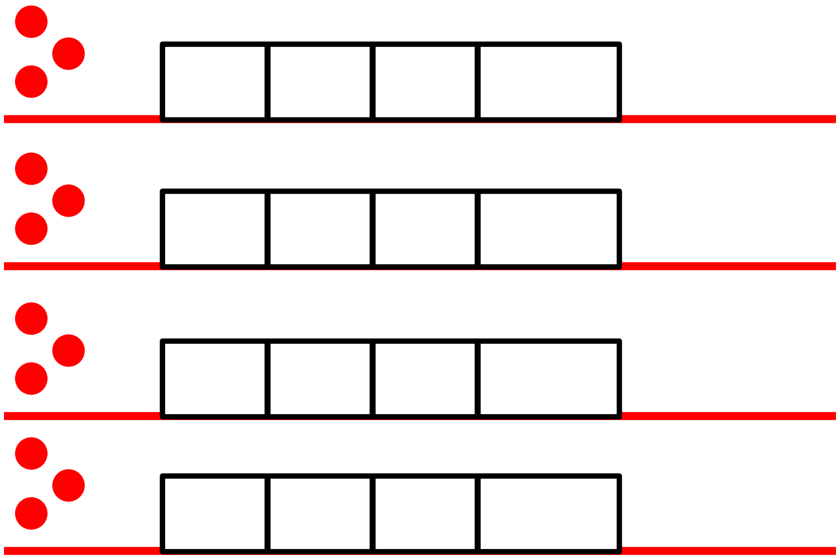
ONLY ONE WAY

Now, include degeneracy



Commuting filled & unfilled boxes





Four Ways

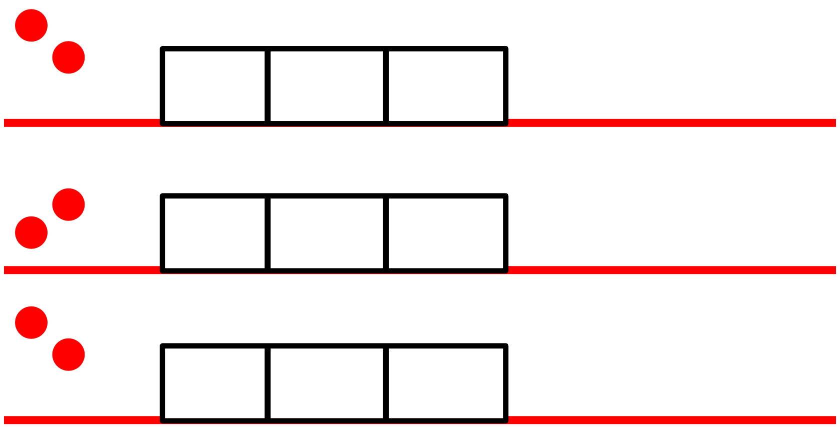
As mentioned earlier $g_1 = 4$; $N_1 = 3$.

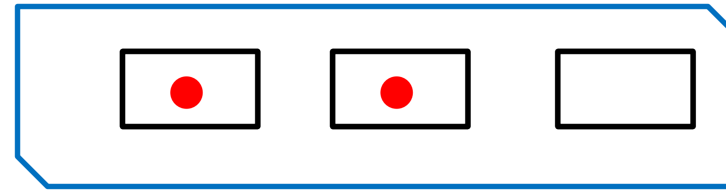
$$\text{Total Number of ways} = \frac{g_1!}{N_1!(g_1 - N_1)!}$$

$$= \frac{4!}{3!(4-3)!} = 4$$

Similarly, if you consider second energy level

$N_2 = 2$ E_2





Three Ways

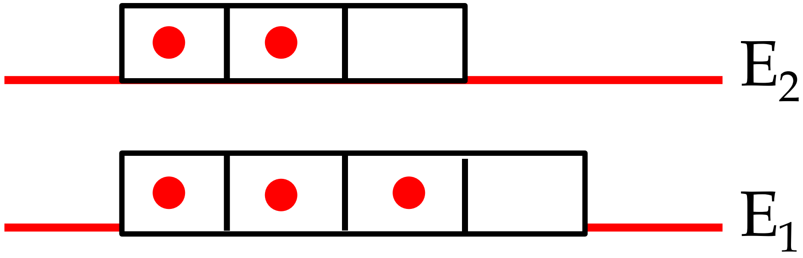
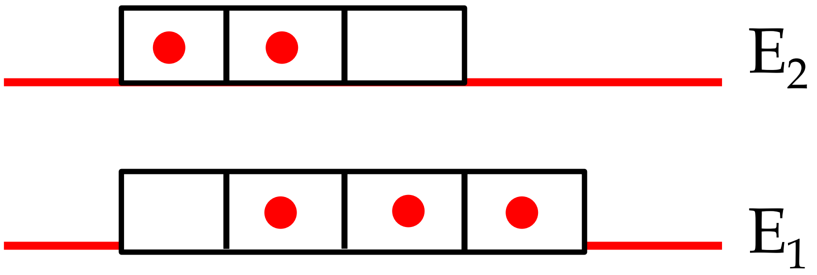
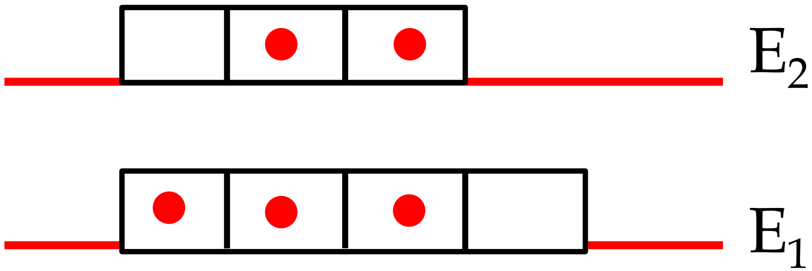
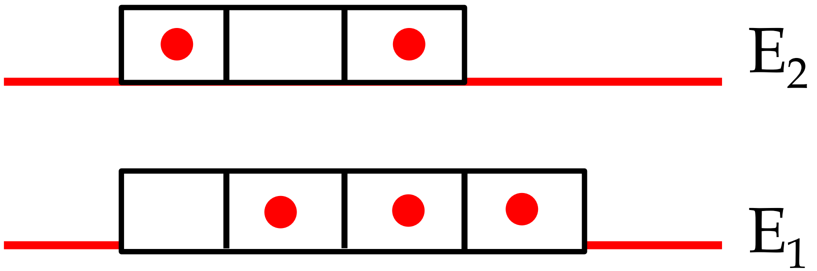
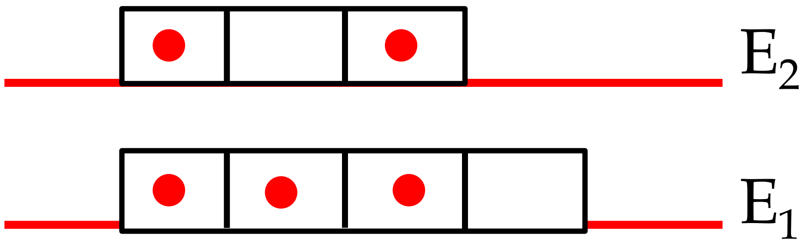
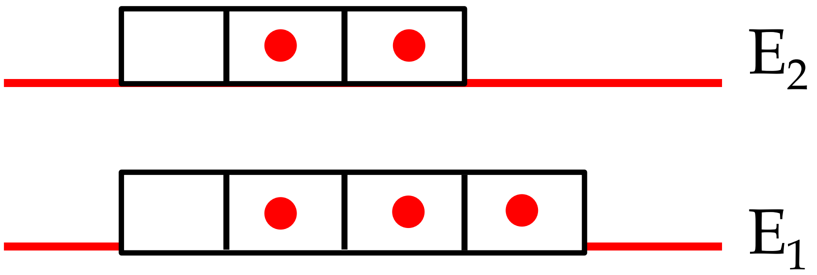
Total Number of ways of arranging fermions in Three Ways

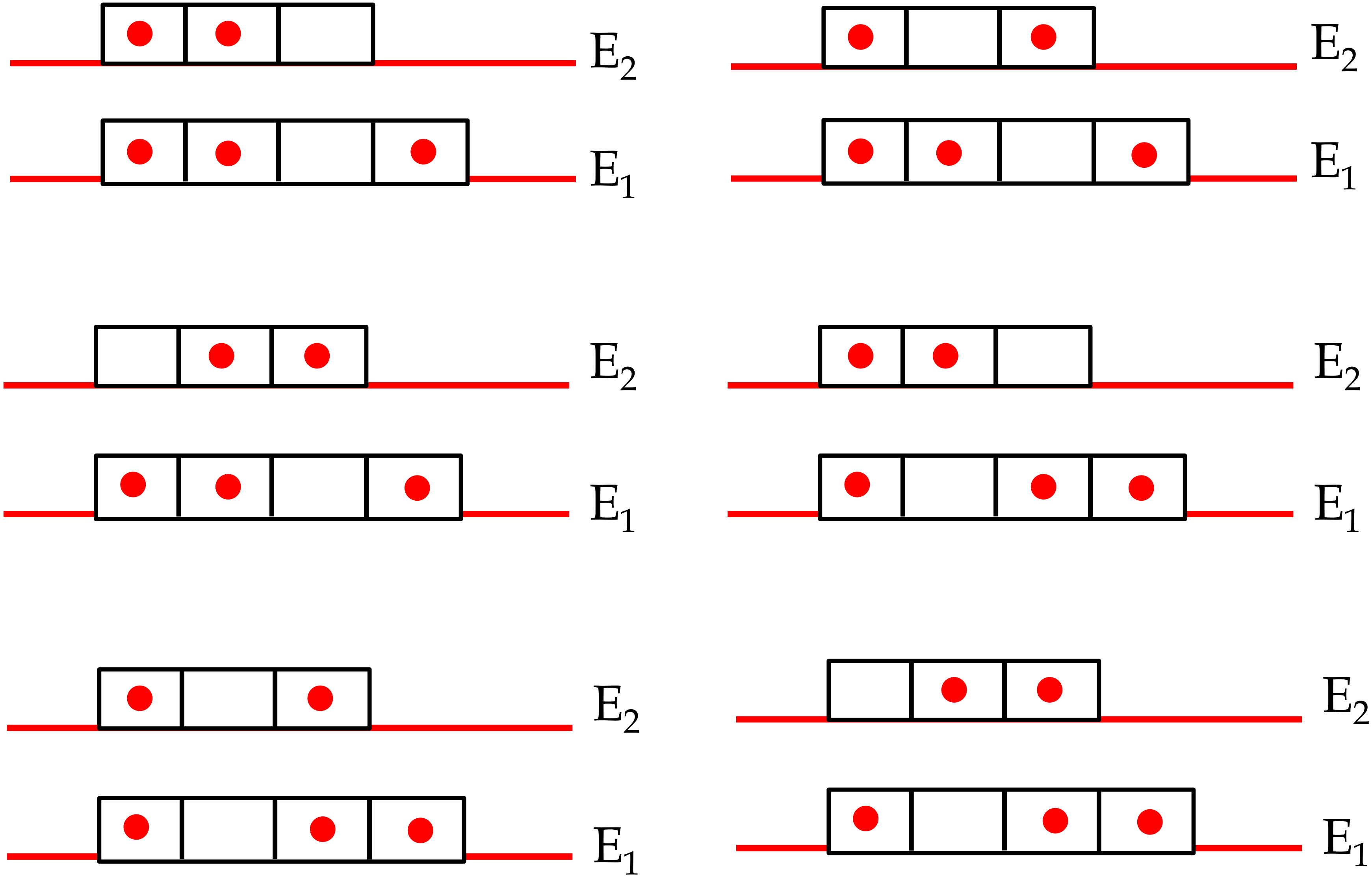
$$E_2\,(w_2) = \frac{g_2!}{N_2!\left(g_2 - N_2\right)!}$$

$$= \frac{3!}{2!\left(3-2\right)!} = 3$$

Total Number of ways of arranging fermions in the two

energy levels = $w_1\, w_2 = 4 \times 3 = 12$


E_2
E_1

E_2
E_1

E_2
E_1

E_2
E_1

E_2
E_1

E_2
E_1

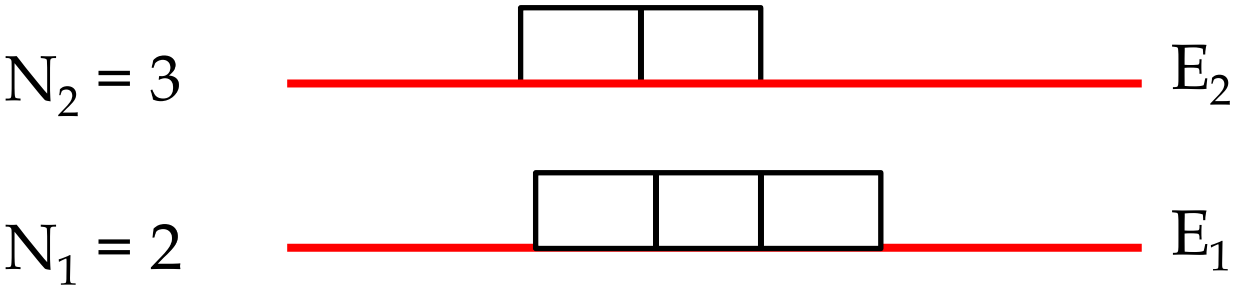

E2
E1
E2
E1
E2
E1
E2
E1
E2
E1
E2
E1

Bose Einstein Distribution : Example

<u>Problem</u>

- ❖ Consider a system of five Bosons that have to distributed among two energy levels E_1 and E_2 in such a way that two Bosons occupy the level E_1 and three other Bosons occupy the level E_2.
- ❖ In this case, the energy level E_1 is three fold degenerate and E_2 is two fold degenerate.
- ❖ Find the total number of ways to distribute those Bosons.

<u>Given Information</u>

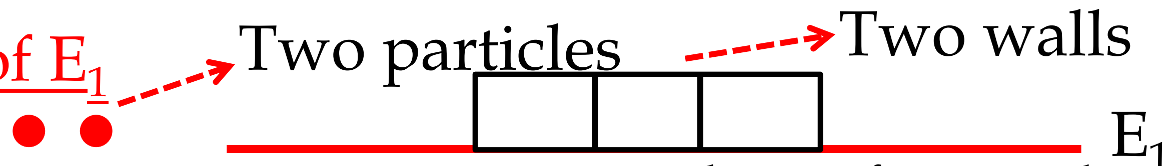


- (First forgot about the degeneracy) How many ways will you distribute (N_1 =) 2 particles in E_1 and (N_2 =) 3 particles E_2?
- As Bosons are indistinguishable, there is only one way.

ONLY ONE WAY

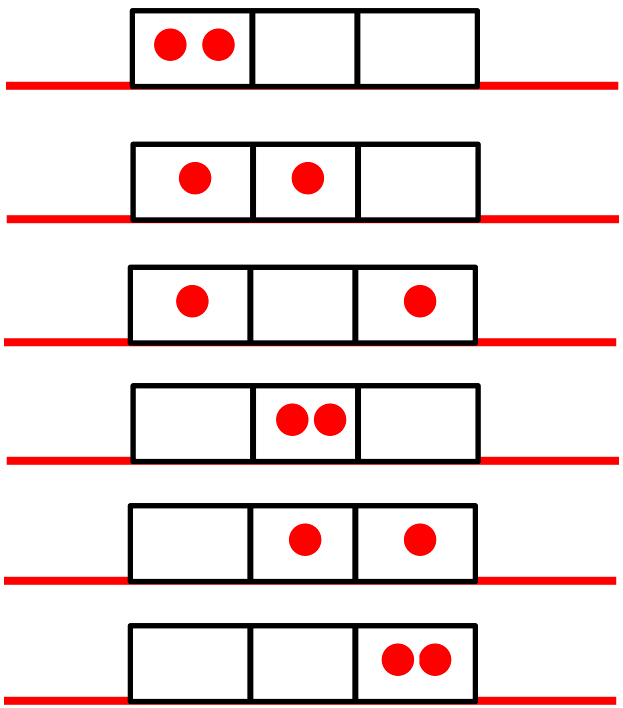
Now, include degeneracy

Distribution of the two particles among the degenerate quantum states of E_1

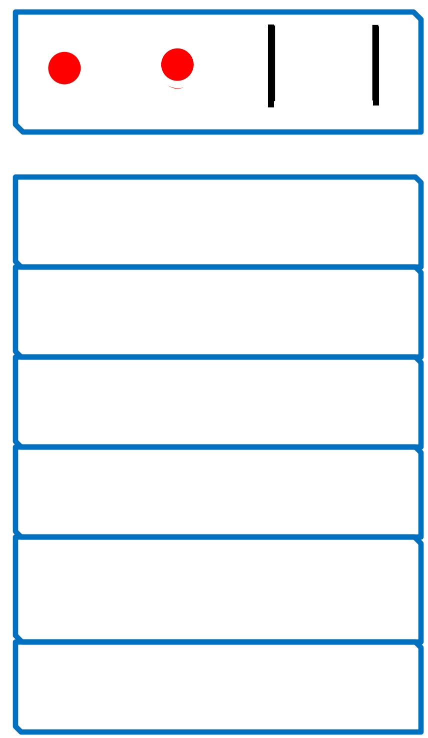


❖ As they are Bosons, any number of particles can occupy a particular quantum state.

The possible configurations can be obtained by arranging two walls and the two particles in different ways.



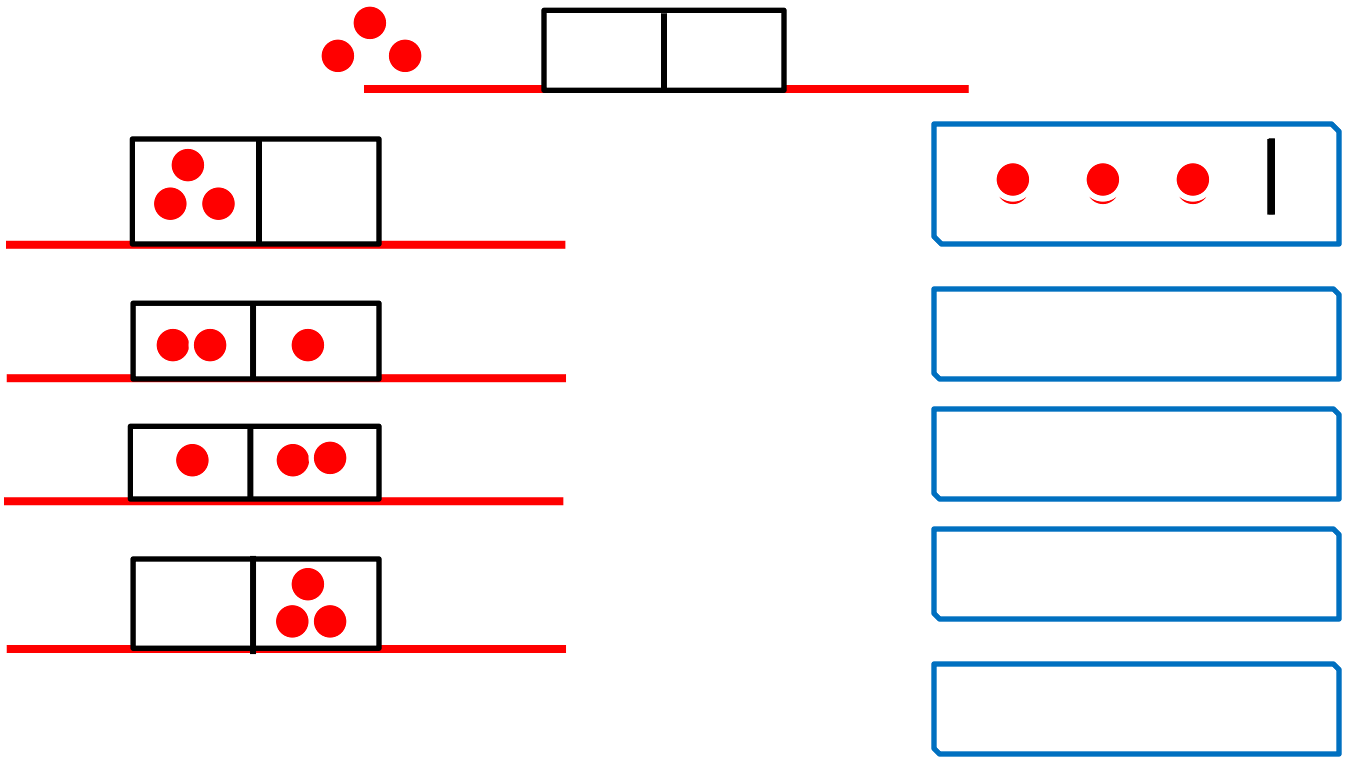
6 ways



As we discussed earlier w_1 = $$\frac{(g_1 + N_1 - 1)!}{(g_1 - 1)!\, N_1!}$$

$$= \frac{4!}{2!\, 2!} = 6$$

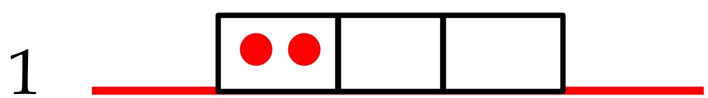
Distribution of the three particles among two degenerate quantum states of E_1



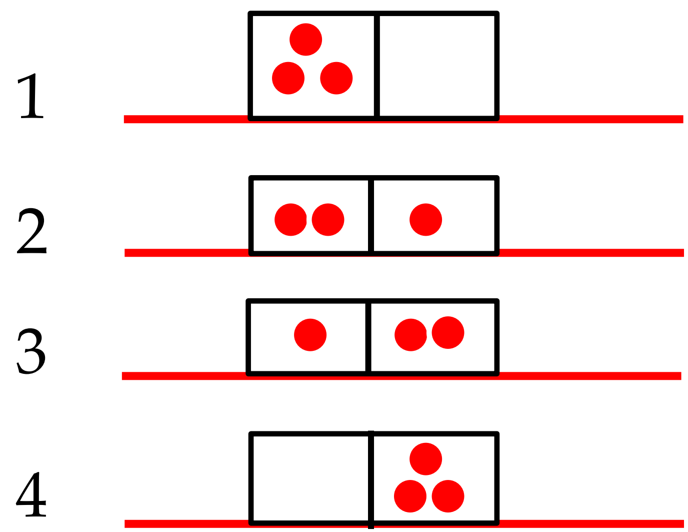
As we discussed earlier w_1 = $\dfrac{(g_2 + N_2 - 1)!}{(g_2 - 1)!\,N_2!} = \dfrac{4!}{1!\,3!} = 4$

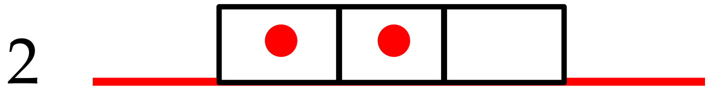
❖ Thus the total number of ways of distributing five Bosons in the two energy levels E_1 and E_2.

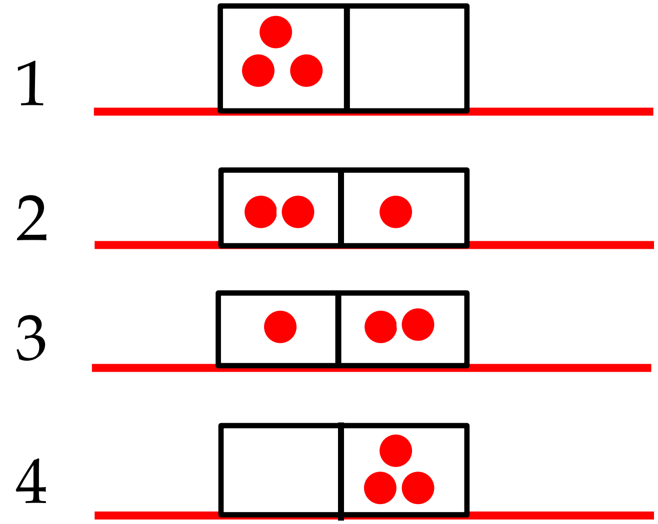
Possible distributions in Energy level E_1

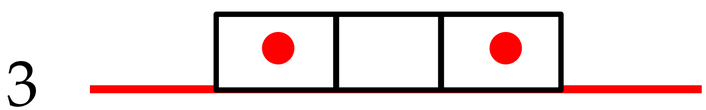


Possible distributions in Energy level E_2




2


1
2
3
4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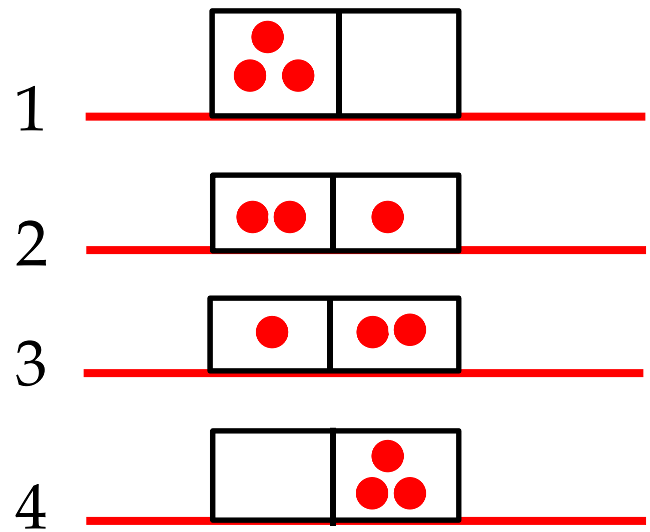
1
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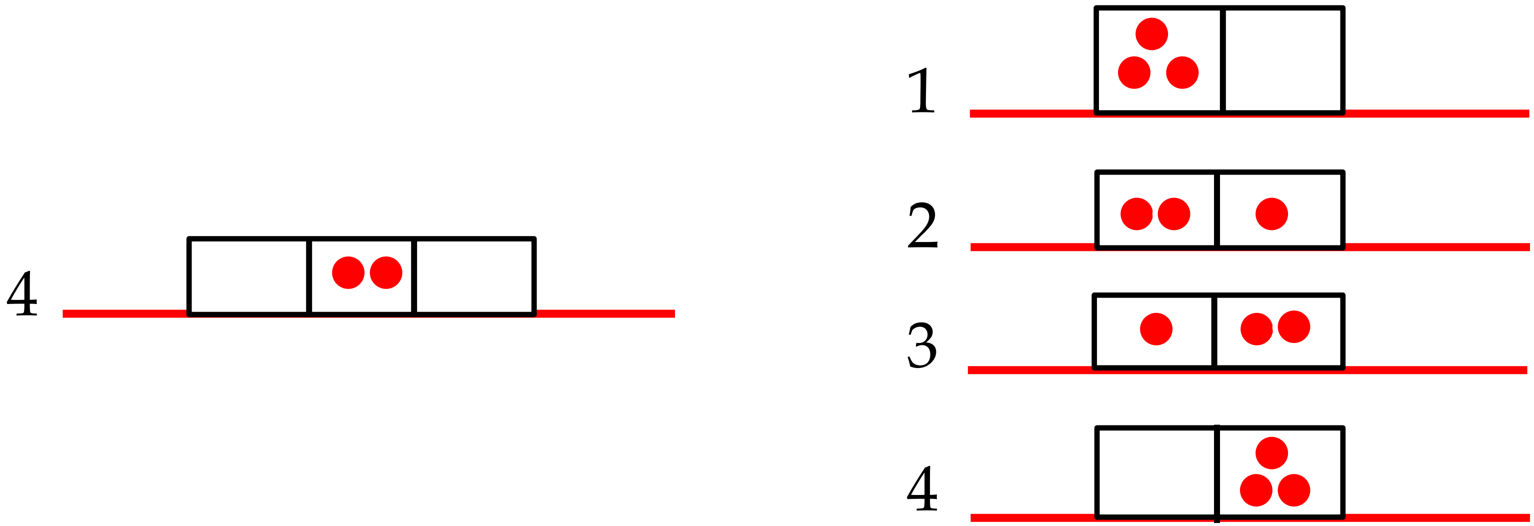
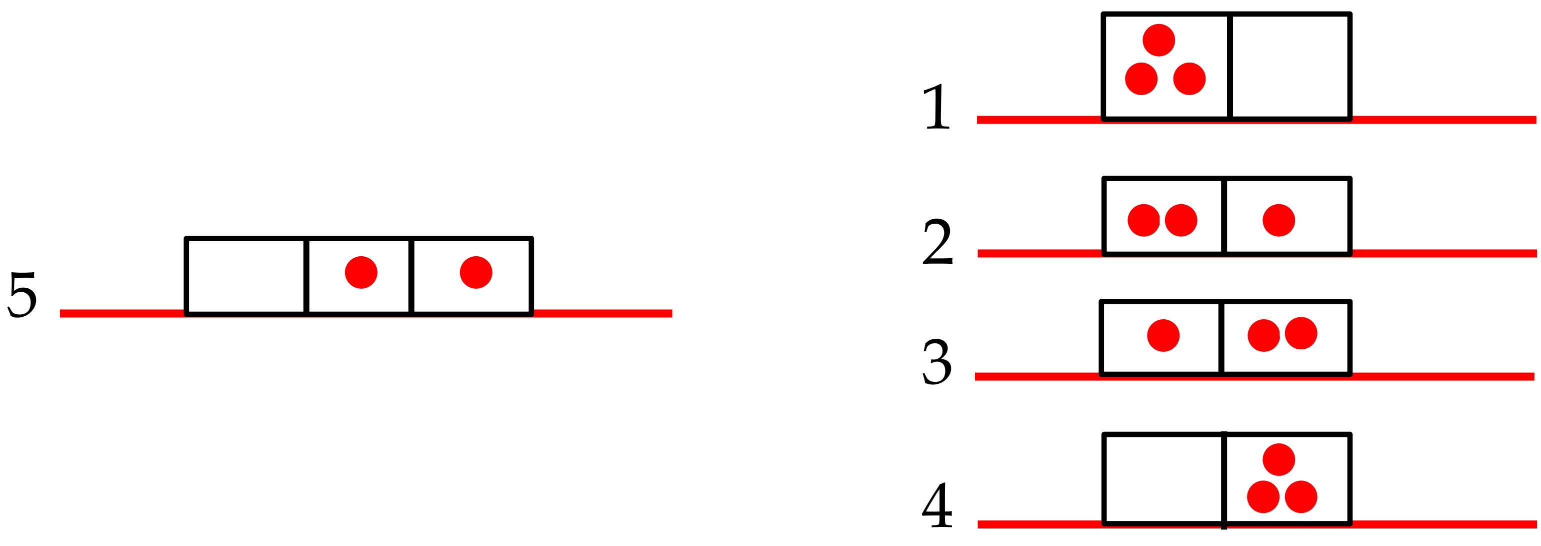
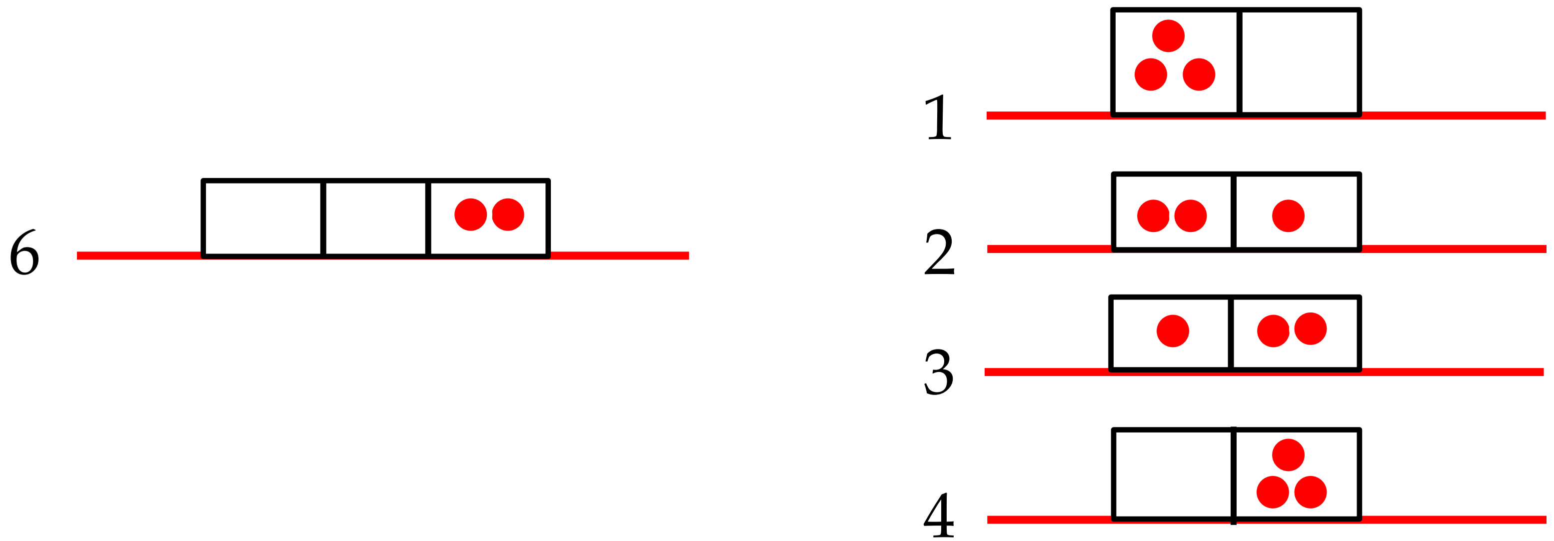
4


4
1
2
3
4


5
1
2
3
4



Total number of ways = 24 ways

$w_1 \times w_2 = 24$ ways

Lagrange Multipliers

Method of Lagrange Multipliers

- Lagrange multiplier method is a technique for finding a maximum or minimum of a function $F(x, y, z)$ subject to a constraint (also called side condition) of the form $G(x, y, z) = 0$.
- We start by trying to find the extreme values of $F(x, y)$ subject to a constraint of the form $G(x, y) = 0$.
- In other words, we seek the extreme values of $F(x, y)$ when the point (x, y) is restricted to lie on the level curve $G(x, y) = 0$.

❖ We have from chair rule,

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy = 0, \qquad dG = \frac{\partial G}{\partial x} dx + \frac{\partial G}{\partial y} dy = 0,$$

❖ Multiplying the second equation by λ and add to first equation yields

$$\left(\frac{\partial F}{\partial x} + \lambda \frac{\partial G}{\partial x} \right) dx + \left(\frac{\partial F}{\partial y} + \lambda \frac{\partial G}{\partial y} \right) dy = 0$$

❖ By choosing λ to satisfy

$$\frac{\partial F}{\partial x} + \lambda \frac{\partial G}{\partial x} = 0$$

❖ For example, so that

$$\frac{\partial F}{\partial y} + \lambda \frac{\partial G}{\partial y} = 0$$

❖ As can be seen, the above two equations are components of the vector equation

$$\vec{\nabla} F - \lambda \vec{\nabla} G = 0$$

❖ Thus, the maximum and minimum values of F(x, y) subject to the constraint G(x, y) = 0 can be found by solving the following set of equations.

$$\frac{\partial F}{\partial x} + \lambda \frac{\partial G}{\partial x} = 0$$

$$\frac{\partial F}{\partial y} + \lambda \frac{\partial G}{\partial y} = 0$$

$$G(x, y) = 0$$

❖ This is a system of three equations in the three unknowns x, y, and λ, but it is not necessary to find explicit values for λ.

Examples

- Use Lagrange multipliers to find the maximum and minimum values of the function subject to the given constraint $x^2 + y^2 = 10$.

  - $f(x, y) = 3x + y$

- For this problem, $f(x, y) = 3x + y$ and $g(x, y) = x^2 + y^2 = 10$.
- Let's go through the steps:

$$\vec{\nabla} F = 3\hat{i} + \hat{j}$$
$$\vec{\nabla} G = 2x\hat{i} + 2y\hat{j}$$

- This gives us the following equation

$$3\hat{i} + \hat{j} = \lambda\left(2x\hat{i} + 2y\hat{j}\right)$$

❖ We break up the above equation and consider the following system of 3 equations with 3 unknowns (x, y, λ).

$$3 = 2\lambda x \quad (1)$$

$$1 = 2\lambda y \quad (2)$$

$$x^2 + y^2 = 10. \quad (3)$$

❖ Now we want to solve for each variable.

❖ At this point, you should take a moment and try to cleverly think of a way to solve for one of the three.

❖ Let's plug in equations (1) and (2) into (3).

❖ This allows us to solve for λ.

$$\left(\frac{3}{2\lambda}\right)^2+\left(\frac{1}{2\lambda}\right)^2=10\Rightarrow\lambda=\pm\frac{1}{2}$$

❖ Now, we plug λ back into our original equations and get $x = \pm 3$ and $y = \pm 1$.

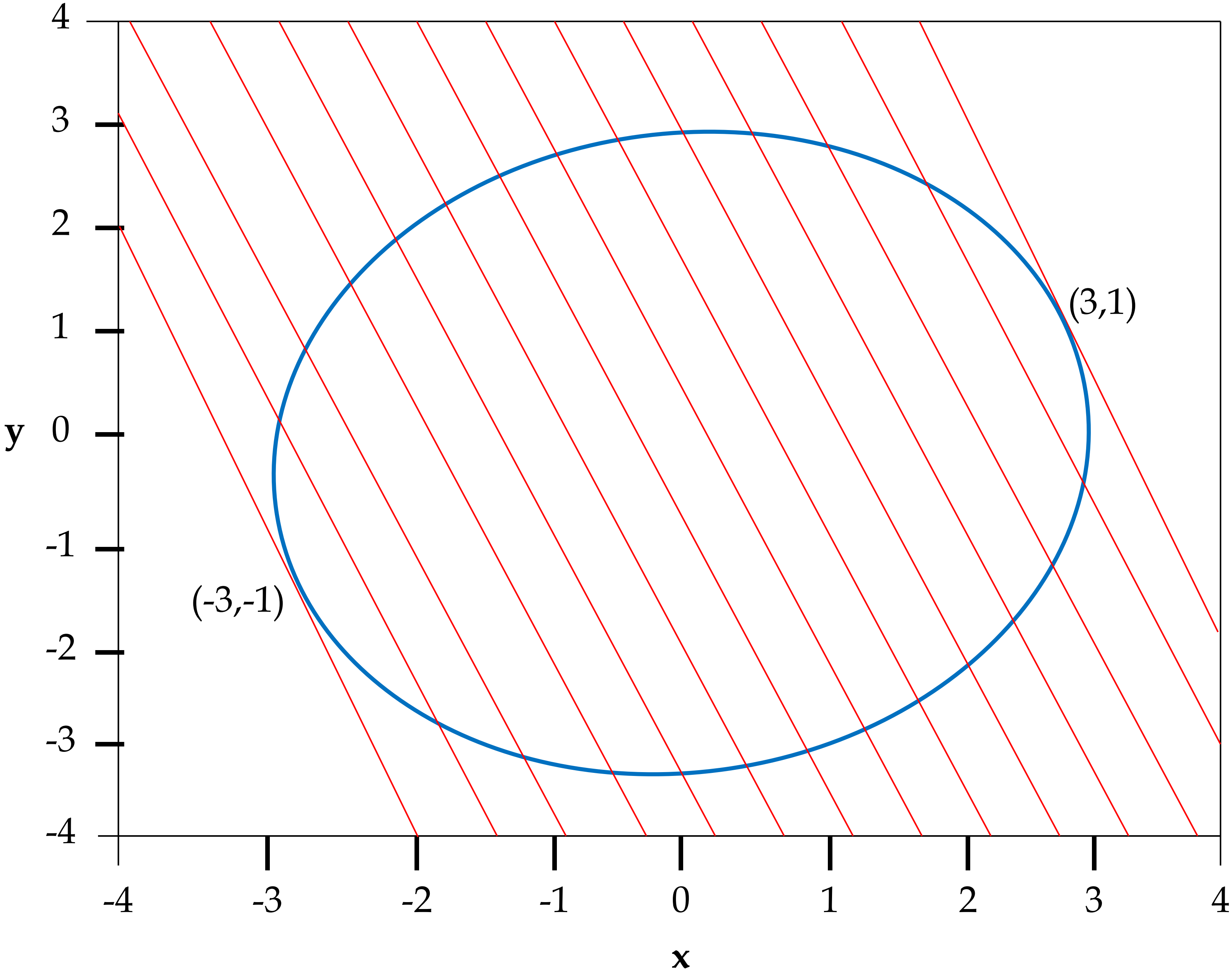
❖ We get the following extreme points (3, 1), (-3, -1)

❖ We can classify them by simply finding their values when plugging into f(x, y).

- $f(3, 1) = 9 + 1 = 10$
- $f(-3, -1) = -9 - 1 = -10$

❖ So the maximum happens at $\boxed{(3, 1)}$ and minimum happens at $\boxed{(-3, -1)}$.

$f(x, y) = 3x + y \qquad x^2 + y^2 = 10$



Fermi Dirac Distribution Law

Most Probable Microstate

Total number of ways of arranging N particles in E_i energy levels

$$w = \prod_i \frac{g_i!}{N_i!\,(g_i - N_i)\,!}$$

The most probable microstate corresponds to the state of maximum thermodynamics probability. Taking natural logarithm on both sides of Eq.(3),

$$\ln\ W\ = \sum_{i=1}^{k} [\ln g_i! - \ln n_i! - \ln(g_i - n_i)!]$$

As n_i *and* g_i are very large numbers, we can use Sterling approximation.

$$\ln n! = n\ \ln n - n$$

Applying Sterling approximation, we get

$$\ln\ W\ = \sum_{i=1}^{k} [\, g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i - n_i)\ \ln(g_i - n_i) + (g_i - n_i)]$$

$$= \sum_{i=1}^{k} [(n_i + g_i)\ \ln(n_i + g_i) - n_i\ \ln n_i - g_i \ln g_i]$$

Here g_i is not subject to variation whereas n_i varies continuously.

Differentiating both sides, we have

$$\delta(\ln W) = \sum_{i=1}^{k}\left[-n_i\frac{1}{n_i}\,\delta n_i - \ln n_i\,\delta n_i + (g_i - n_i)\frac{1}{(g_i - n_i)}\delta n_i + \ln(g_i - n_i)\,\delta n_i\right]$$

$$= \sum_{i=1}^{k}[\ln(g_i - n_i) - \ln n_i]\delta n_i$$

To get the state of maximum thermodynamic probability

$$\delta(\ln W) = 0$$

$$\therefore \quad \sum_{i=1}^{k}[\ln(g_i - n_i) - \ln n_i]\delta n_i = 0 \Rightarrow \sum_{i=1}^{k}\left[\ln\frac{g_i - n_i}{n_i}\right]\delta n_i = 0$$

$$\Rightarrow -\sum_{i=1}^{k}\left[\ln\frac{n_i}{g_i - n_i}\right]\delta n_i = 0 \Rightarrow \sum_{i=1}^{k}\left[\ln\frac{n_i}{g_i - n_i}\right]\delta n_i = 0 \qquad \rightarrow (4)$$

In addition, our system must satisfy the two auxillary condition:

(i) Conservation of total number of particles, i.e., N$=a$ constant.

$$\therefore \qquad N = \sum_i n_i = constant.$$

$$i.e. \qquad \delta N = \sum_i \delta n_i = 0 \qquad \rightarrow (5)$$

(ii) Conservation of total energy of the system, i.e., $E = a\ constant$.

$$\therefore \qquad E = \sum_i n_i E_i = constant.$$

$$i.e. \qquad \delta E = \sum_i E_i\, \delta n_i = 0 \qquad \rightarrow (6)$$

We shall now apply Lagrangian method of undetermined multipliers. For this let us multiply Eq.(5) by α and Eq.(6) by β , and add the resulting expression to Eq.(4),

$$\sum_{i=1}^{k}\left[\ln\left(\frac{n_i}{g_i - n_i}\right) + \alpha + \beta E_i\right] \delta n_i \ = \ 0$$

The variations δn_i are independent of each other, we get

$$\ln\left(\frac{n_i}{g_i - n_i}\right) + \alpha + \beta E_i \ = \ 0$$

or

$$\frac{n_i}{g_i - n_i} \ = \ e^{-(\alpha+\beta E_i)}$$

or

$$\frac{g_i - n_i}{n_i} \ = \ e^{\alpha+\beta E_i}$$

or

$$\frac{g_i}{n_i} - 1 \ = \ e^{\alpha+\beta E_i}$$

or

$$\frac{g_i}{n_i} = e^{\alpha+\beta E_i} + 1$$

or

$$n_i = \frac{g_i}{e^{\alpha+\beta E_i} + 1} \qquad \rightarrow (7)$$

This equation represents the most probable distribution of the particles among various energy levels for a system obeying Fermi-Dirac statistics and is therefore, known as **Fermi-Dirac Distribution Law** for an assembly of **fermions.**

The parameter $\beta = \frac{1}{kT}$, where k is Boltzmann's constant, has the same role as in case of M.B. distribution law. Substituting in equation (7), we have

$$n_i = \frac{g_i}{e^{\alpha}.\, e^{\beta E_i} + 1} = \frac{g_i}{e^{\alpha}.\, e^{E_i/kT} + 1} \qquad \rightarrow (8)$$

Fermi-Dirac energy distribution function.

Since there can be a maximum of one particle per quantum state, the function $f(E_i)$ is the ratio of the number of quantum states of energy E_i. Therefore, the value of $f(E_i)$ for the Fermi-Dirac distribution at a particular energy E_i is the probability that under equilibrium a quantum state of that energy is occupied by a particle.

From equation (8), $f(E_i)$ is given by

$$f(E_i) = \frac{n_i}{g_i}$$

$$f(E_i) = \frac{1}{e^{\alpha}\, e^{E_i/kT} + 1} \qquad \rightarrow (9)$$

For continuous distribution of energy E, the distribution function is written as

$$f(E) = \frac{1}{e^{\alpha}\, e^{E/kT} + 1} \qquad \rightarrow (10)$$

F-D energy distribution law for continuous variation of energy.

If the energy levels are very close together, then the distribution of energy of the particles may be considered continuous. For this distribution the number of particles $n(E)dE$ whose energies lie between $E\ and\ E + dE$, then $n_i = n(E)dE$ and is given by

$$n(E)dE = f(E)\ g(E)\ dE \qquad \rightarrow (11)$$

Where $g(E)dE$ is the number of quantum states of energy between $E\ and\ E + dE$.

Substituting the value of $f(E)$ in Eq. (11), we get

$$n(E)\,dE = \frac{g(E)dE}{e^{\alpha}.e^{E_i/kT}+1} \quad \rightarrow (12)$$

For particles like electron of spin angular momentum $\pm\frac{1}{2}\hbar$, there are two possible spin orientations. Substituting the expression for $g(E)dE$, we get

$$n(E)dE = 2\times 2\pi V\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \frac{E^{\frac{1}{2}}dE}{e^{\alpha}.e^{E/kT}+1} \quad \rightarrow (13)$$

This is the **Fermi-Dirac energy distribution law** continuous variation of energy among free particles with spin $\frac{1}{2}$.

Fermi - Dirac statistics : A Genesis

1. Pauli's exclusion principle was first derived by Fermi (1926) and a little later in the same year by Dirac (1926) independently.

2. Electron was a spin ½ particle was already proposed by Pauli (1925) though not well understood.

3. In late 1926 the work of Fermi and Dirac laid the foundations of second quantization- QM of many particle system.

4. They have demonstrated that the system as a whole has to respect a rule such as Pauli's exclusion principle.

5. They have analyzed systems in equilibrium at a finite temperature and found that at high temperature the results agree with MB statistics and at low temperatures (degeneracy limit) the results agree with qualitative predictions of Nernst on the degeneracy of gas at low temperature.

- Surprisingly two years prior (1924), a similar successful attempt was made towards understanding ‘degeneracy’ of a gas of another type of identical particles now called bosons.(Box of Einstein). Unfortunately spin of particles other than that of electrons was not known at that time.
- The theoretical connection between spin of identical particles and their statistics, FD or BE was established only 1940 in the form of spin- statistics theorem.
- Categorization of atoms as either bosons or fermions started around 1940
- Fermi - Dirac statistics has found numerous applications in nuclear physics, semiconductor physics, low- dimensional physics, plasma physics, astrophysics, GUT, string theory, carbon nanotube physics, ultracold atoms, graphene physics, topological insulator physics.

Applications of FD statistics

1. Metals: Electron gas model :

- The specific heat capacity calculated through FD statistics matches with experimental data.
- In the low temperature region the results coming out from FD statistics take over MB statistics.
- It provides a physically acceptable value for μ_σ Lorentz number for a metal.

2. Astrophysics – White Dwarfs :

- Using FD statistics to an ideal inhomogeneous gas of relativistic electrons Chandrasekar obtained a value of critical mass in terms of solar mass (M_0) as $M_e \approx 1.44\ M_0$ for the stability of the white dwarf star.
- Landau obtained the value of critical mass not only white dwarf stars but also for the neutron stars (even before the discovery of neutron by Chadwick).

3. Nuclear physics :

- 1927 – Thomas – Fermi model was proposed as an application of FD statistics.
- 1934 – Majorana and weizsalker proposed Fermi gas model to calculate the binding energy of the nucleons in the nucleus.

4. Solid State Physics :

- 1927 – Pauli explained temperature dependence of the paramagnetic susceptibility with the help of FD statistics.
- Landau studies magnification of metals in strongly magnetic fields using FD statistics.
- The existence of "holes" was proposed by Heisenberg as a consequence of FD statistics.
- The positron was proposed by Dirac during the same time.

5. Some direct / indirect applications :

- Quantum hydrodynamic theory, QED, Abrikosov flux lattice, Anderson localization, Asymptotically free Gauge theory, QFT

Bose –Einstein Distribution Law

Most Probable Microstate

The most probable microstate corresponds to the state of maximum thermodynamics probability.

In equation (1), $n_i \; and \; g_i$ both are very large numbers. Hence we may neglect 1 in the above expression

$$\therefore \quad W_{(n_1,n_2,\ldots.n_i,\ldots n_k)} = \prod \frac{(n_i + g_i)!}{n_i! \, g_i!} \qquad \rightarrow (2)$$

Taking natural logarithm on both sides, we have

$$\ln \; W = \sum_{i=1}^{k} [\ln(n_i + g_i)! - \ln n_i! - \ln g_i!]$$

As $n_i \; and \; g_i$ are very large numbers, we can use Sterling approximation.

$$\ln n! = n \; \ln n - n$$

Applying Sterling approximation, we get

$$\ln\ W\ =\ \sum_{i=1}^{k}[(n_i+g_i)\ln(n_i+g_i)\ -(n_i+g_i)\ -n_i\ \ln n_i+n_i-g_i\ln g_i+g_i\ ]$$

$$=\ \sum_{i=1}^{k}[(n_i+g_i)\ \ln(n_i+g_i)\ -n_i\ \ln n_i\ -g_i\ln g_i] \qquad \rightarrow (3)$$

Here g_i is not subject to variation whereas n_i varies continuously

To get the state of maximum thermodynamics probability, we differentiate equation (3) and equate it to zero; i.e.,

$$\delta(\ln W)=\ 0$$

$$\therefore\quad \delta(\ln W)\ =\ \sum_{i=1}^{k}\left[\delta n_i\ln(n_i+g_i)+\ (n_i+g_i)\frac{1}{(n_i+g_i)}\delta n_i\ -\delta n_i\ \ln n_i\ -n_i\frac{1}{n_i}\ \delta n_i\right]$$

$$=\ \sum_{i=1}^{k}\delta n_i\ \ln(n_i+g_i)\ -\delta n_i\ \ln n_i \qquad (g_i\ \text{ is a mere number } \delta g_i=0)$$

$$\text{or}\quad \delta(\ln W)\ =\ \sum_{i=1}^{k}\left[\ln\frac{(n_i+g_i)}{n_i}\right]\delta n_i=-\sum_{i=1}^{k}\left[\ln\frac{n_i}{(n_i+g_i)}\right]\delta n_i=0$$

$$or \qquad \sum_{i=1}^{k}\left[\ln\frac{n_i}{(n_i+g_i)}\right]\delta n_i = 0 \qquad \rightarrow (4)$$

In addition, our system must satisfy two subsidiary or auxillary condition:

(i) Conservation of total number of particles, i.e., N= a constant.

$$\therefore \qquad N = \sum_i n_i = constant.$$

$$i.e. \qquad \delta N = \sum_i \delta n_i = 0 \qquad \rightarrow (5)$$

(ii) Conservation of total energy of the system, i.e., $E = a\ constant$.

$$\therefore \qquad E = \sum_i n_i\, E_i = constant.$$

$$i.e. \qquad \delta E = \sum_i E_i\, \delta n_i = 0 \qquad \rightarrow (6)$$

Now we shall apply the Lagrangian method of undetermined multipliers. For this let us multiply Eq.(5) by α and Eq.(6) by β , and the resulting expression to Eq.(4) so that we get

$$= \sum_{i=1}^{k} \left[\ln\left(\frac{n_i}{n_i + g_i}\right) + \alpha + \beta E_i \right] \delta n_i = 0 \qquad \rightarrow (7)$$

The variations δn_i are independent of each other. Hence we get

$$\ln\left(\frac{n_i}{n_i + g_i}\right) + \alpha + \beta E_i = 0$$

or

$$\ln\left(\frac{n_i}{n_i + g_i}\right) = -\alpha - \beta E_i$$

or

$$\frac{n_i}{n_i + g_i} = e^{-\alpha - \beta E_i} = e^{-(\alpha + \beta E_i)}$$

or

$$\frac{n_i + g_i}{n_i} = e^{(\alpha + \beta E_i)}$$

or

$$1 + \frac{g_i}{n_i} = e^{\alpha + \beta E_i}$$

or

$$\frac{g_i}{n_i} = e^{\alpha + \beta E_i} - 1$$

or

$$n_i = \frac{g_i}{e^{\alpha + \beta E_i} - 1} \qquad \rightarrow (8)$$

This equation represents the most probable distribution of the particles among various energy levels for a system obeying Bose-Einstein statistics and is therefore, known as **Bose-Einstein's Distribution Law** for an assembly of **bosons.**

Substituting for $\beta = \frac{1}{kT}$, the equation (8) becomes

$$n_i = \frac{g_i}{e^{\alpha}.\, e^{\beta E_i} - 1} = \frac{g_i}{e^{\alpha}.\, e^{E_i/kT} - 1} \qquad \rightarrow (9)$$

B-E energy distribution function.

The energy distribution function $f(E_i)$ is the average number of particles per quantum state in the energy level E_i, It is given by

$$f(E_i) = \frac{n_i}{g_i}$$

Substituting the value of n_i/g_i from equation (9), we get

$$f(E_i) = \frac{1}{e^{\alpha}\, e^{E_i/kT} - 1} \qquad \rightarrow (10)$$

For continuous distribution of energy, the distribution function is written as

$$f(E) = \frac{1}{e^{\alpha}\, e^{E/kT} - 1} \qquad \rightarrow (11)$$

B-E energy distribution law for continuous variation of energy.

When the energy levels of the system are very closely packed, they from a quasi-continuous spectrum. In such a case, if $g(E)dE$ is the number of energy states between the energy range E and $E + dE$, then

$$g_i = g(E)\, dE$$

If $n(E)\,dE$ is the number of particles whose energy lies between $E\ and\ (E + dE)$, then $n_i\ =\ n(E)\,dE$. Substituting in Eq. (9), we get

$$n(E)\,dE\ =\ \frac{g(E)dE}{e^{\alpha}.\,e^{E_i/kT} - 1} \qquad \rightarrow (12)$$

The quantity $g(E)$ denotes the density of states.

For the system consisting of free particles with no spin $g(E)dE$ is given by

$$g(E)dE\ =\ 2\pi V\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}\,dE \qquad \rightarrow (13)$$

Substituting this value in Eq.(10), we get

$$n(E)dE\ =\ 2\pi V\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \frac{E^{\frac{1}{2}}dE}{e^{\alpha}.\,e^{E/kT} - 1} \qquad \rightarrow (14)$$

This is **Bose-Einstein energy distribution law** for continuous distribution of energy among free particles with no spin.

Distribution Laws

Boltzmann

$$\ln \frac{n_s}{g_s} = \alpha + \beta \varepsilon_s$$

$$\boxed{\frac{n_s}{g_s} = e^{\alpha + \beta \varepsilon_s}}$$

Bose-Einstein

$$\ln \frac{n_s}{n_s + g_s} = \alpha + \beta \varepsilon_s$$

$$\boxed{\frac{n_s}{g_s} = \frac{1}{e^{\alpha + \beta \varepsilon_s}}}$$

Fermi-Dirac

$$\ln \frac{n_s}{g_s - n_s} = \alpha + \beta \varepsilon_s$$

$$\boxed{\frac{n_s}{g_s} = \frac{1}{e^{\alpha + \beta \varepsilon_s} + 1}}$$

Determination of β

Recall , $N = \sum n_s$ and $E = \sum n_s \epsilon_s$

Distribution, $n_s = g_s e^{\alpha + \beta \epsilon_s}$

$$\sum n_s = N = \sum g_s e^{\alpha+\beta\epsilon_s}$$

$$\sum n_s \epsilon_s = E = \sum \epsilon_s g_s e^{\alpha+\beta\epsilon_s}$$

$$\sum x_i p_i = \sum \epsilon_i p_i = \frac{\sum \epsilon_i g_i e^{\alpha+\beta\epsilon_i}}{\sum g_i e^{\alpha+\beta\epsilon_i}}$$

$$= \frac{\int \epsilon \, g(\epsilon) e^{\alpha+\beta\epsilon} \, d\epsilon}{\int g(\epsilon) e^{\alpha+\beta\epsilon} \, d\epsilon}$$

$$g(\epsilon) d\epsilon = 2\pi v (2m)^{\frac{3}{2}} \epsilon^{1/2} d\epsilon$$

$$\text{In phase} - \text{space } \bar{\epsilon} = \frac{\int \epsilon \, g(\epsilon) e^{\alpha+\beta\epsilon} \, d\epsilon}{\int g(\epsilon) e^{\alpha+\beta\epsilon} \, d\epsilon}$$

where $g(\epsilon) = 2\pi v (2m)^{\frac{3}{2}} \epsilon^{1/2}$.

$$\bar{\epsilon} = \frac{\int_0^\infty \epsilon^{3/2} e^{\beta\epsilon} \, d\epsilon}{\int_0^\infty \epsilon^{1/2} e^{\beta\epsilon} \, d\epsilon} = \frac{3}{2\beta}$$

It is well known that from kinetic energy theory, $\bar{\epsilon} = \frac{3}{2} kT$

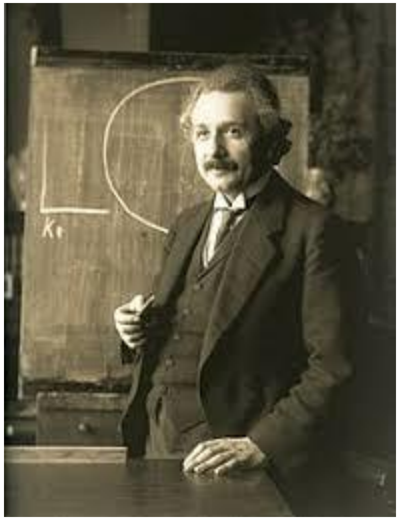
Comparing,

$$\beta = \frac{1}{kT}$$

Bose's Contribution

- Distribution was derived before Quantum Mechanics was formally established.
- June 1924: Bose $\rightarrow$ Einstein.
- Bose derived Planck's radiation law. He derived the formula by counting the number of states of photon.
- Bose assumed photons were indistinguishable.
- Einstein recommended the paper for publication.

Einstein's Contribution



- Einstein applied this approach to an Helium atom.
- He found that there was a maximum possible values for the total number N_0 of particles of non-zero energy that the system can have.
- $N\text{-}N_0 \rightarrow$ Ground state. (BEC)

Bose – Einstein's Work

- The idea was not accepted as physically important.
- It was felt that a mathematical trick used by Einstein.
- A sum over states by an integration, was responsible for the result.
- 1938 London suggested that BEC as an explanation for the superfluid properties of Helium.
- London was awarded Nobel prize for this work.
- 2001 – Cornell, Wieman and Ketterle awarded Nobel prize for achievement of BEC in dilute gases alkali atoms and for their studies of the properties of the condensate.

Determination of α

$$n_s = g_s e^{\alpha+\beta\epsilon_s} = A g_s e^{\beta\epsilon_s}, \qquad A = e^{\alpha}$$

$$\sum n_s = N = A \sum g_s e^{\beta\epsilon_s}$$

$$A = \frac{N}{\sum g_s e^{\beta\epsilon_s}} = \frac{N}{2\pi v(2m)^{\frac{3}{2}} \int_0^{\infty} \epsilon^{1/2} e^{\beta\epsilon}\, d\epsilon}$$

$$A = \frac{N}{v\left(\frac{-2\pi m}{\beta}\right)^{\frac{3}{2}}} = \frac{N}{v(2\pi mkT)^{\frac{3}{2}}}$$

$$\alpha = \log A = log\left[\frac{N}{v(2\pi mkT)^{\frac{3}{2}}}\right]$$

Maxwell- Boltzmann distribution

$$n_s = g_s e^{\alpha+\beta\epsilon_s}$$

Suppose $g(\epsilon)\, d\epsilon$ is the number of states with energies in the range ϵ to ϵ+$d\epsilon$. Then,

$$n(\epsilon)d\epsilon = \frac{2\pi N}{(\pi kT)^{\frac{3}{2}}} e^{\frac{-\epsilon}{kT}} \epsilon^{1/2} d\epsilon$$

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