Chemical Principles II Professor Doctor Arnab Mukherjee Department of Chemistry Indian Institute of Science Education and Research Pune Module 07 Lecture 41 Permutation and Combination

(Refer Slide Time: 00:16)

What is permutation? Permutation is nothing but arranging distinguishable things in a particular order.

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(Refer Slide Time: 00:23)

Let us say, arrange, let us say we are suppose to, we are given the task of arranging 3 distinct balls in 3 boxes in a very specific order.

I have box 1, I have box 2, and I have box 3.

(Refer Slide Time: 00:37)

These 3 boxes are there.

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And I have 3 distinguishable balls. I can put one of them in one

(Refer Slide Time: 00:44)

box,

(Refer Slide Time: 00:45)

one of them in second box, and one of them in third box.

Note that I cannot have more than 1 ball in a box, Ok. In this kind of situation what will be my statistics? What will be the number of possibilities?

(Refer Slide Time: 01:00)

So first box can be filled by any of the 3 balls, Ok. That is the first thing. I have these 3 balls right, red, green and blue. And I have 3 boxes also. And these boxes are very distinguishable boxes, you see. I have numbered them 1, 2 and 3.

First ball I can put in any of the boxes. Or, rather let us say first box, first box, box number 1 I have to fill up. I can pick up any of the ball. Let us say I picked up a green one, a blue ball sorry. If I picked up the blue one, I will be left with red and green. So this is 3 ways I can do that, right.

(Refer Slide Time: 01:38)

And then since I am not doing with replacement, my blue is gone. I have only 2 ball, red and green. For the box number 2, I will have to choose one. I choose

(Refer Slide Time: 01:49)

red one. So I can choose 2 ways,

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either red or green. But then last case I am left with only one.

(Refer Slide Time: 01:56)

And that is a green ball.

So number of possibilities will be 6

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as I

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mentioned here.

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Or we can say, also as factorial 3.

(Refer Slide Time: 02:09)

Factorial 3, factorial n is typically n into n minus 1 into n minus 2 till 1.

So you see if I have n balls, n distinct balls and n distinct

(Refer Slide Time: 02:23)

boxes such that I can put only one ball in a box, I can do that in factorial n number of ways. That is called permutation. Permutation is nothing but arranging distinguishable things in a particular order.

For example I am giving you 3 letter A, B and C.

(Refer Slide Time: 02:45)

And I am telling you that how many possible words you can make, of course meaningless words let us say. How many possible words of 3 letter can you make?

So you can take any of the first 3, then any of the second 2, then any, then the last one you have to take. So there again n factorial 3 ways you can do that.

If I tell you that, Ok you have A, B, C, D

how many 4-letter word you can make out of this? Factorial 4, because you can make in any combinations, you can take any of the 4 as the first letter of the word, then you can take any of the other 3 as the second letter of the word.

Only condition here is that you are always picking one, not more than 1. Just like you are putting only 1 ball in a box, not more than 1.

And you see, you have a very nice arrangement here, blue, green; blue red

(Refer Slide Time: 03:39)

green arrangement. You could have red green blue arrangement also. You could have green red blue arrangement

(Refer Slide Time: 03:46)

also. In fact all possible, 6 possible arrangements you could have had with that and that is what is called permutation.

Permutation is actually making distinguishable things in a ordered, and how many such things will be possible. Now when you look at these particular configurations of blue, red and green you immediately see that as one configuration, you can say that as one microstate.

I change that combination I get another microstate. I change that combination I get another microstate. How many possible ones? 6. After the 6 it is just going to repeat. If it repeats it is no longer use, no longer of any use, right.

So you are not, no longer you are going to count it. It is almost, symmetry and group theory, symmetry measurements. So when you, while you rotate something, when you rotate 360 degree it will become the same one.

So you do not have, you know you cannot distinguish between the initial one or when you rotate it in full 360 degree. You cannot distinguish between them.

So therefore every system will have, that is called C 1 symmetry which you rotate 360 degree and you will not have anything, at least a C 1. There can be even more; by rotating less also you can get that. But that is a different topic altogether.

(Refer Slide Time: 05:01)

Now let us do little bit more complicated. Let us say I have only 3 boxes but 6 balls.

(Refer Slide Time: 05:07)

These 6, all 6 are there here.

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And I have only 3 boxes just like above. How can you do that?

So first one can be again, let us say there are 3 boxes.

(Refer Slide Time: 05:18)

So first box can be filled by 6, any of the 6 balls. But once I fill that, it is without replacement, remember. I am left with only 5. Then I am left

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with only 4.

So how many possibilities I will get? 6 into 5 into 4 which is 120

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possibilities. So 120 microstates I can create from these 3 boxes when I have 6 balls available with us. And

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this situation, as I said, that permutations are also sampling without replacement. Same thing.

I am, from the pool of these boxes,

(Refer Slide Time: 06:01)

from the pool of these balls I was putting them in the boxes. In fact I need not have put it. When I am picking up for the first time it can be my first box. When I am picking up the second time it is my second box. When I am picking up the third time it is my third box.

So only taking out

(Refer Slide Time: 06:18)

itself can be thought of as a permutation. So permutation and also sampling without replacement. See without.

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With replacement gave us to the power, n to the power r, but with replacement is giving us what you will see, put r ball in n cell without replacement such that one cell, a cell can have, no, cell can have

(Refer Slide Time: 06:44)

at most one ball. At most, that is very important. Why? We will come back in a moment.

(Refer Slide Time: 06:50)

So as you see that now I have 7 boxes, 7. I said at most, right. Did I say at most?

(Refer Slide Time: 07:00)

At most. You see this is

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very important. Why I say at most? Because if my number of boxes is greater than

(Refer Slide Time: 07:08)

number of balls then all the boxes will not be filled. Because I can put at most 1.

So it can be 0 or 1, all are distinguishable balls. All are distinguishable boxes. So how many ways you can do that? So again as you can see that my first box can be filled in 6 possible ways. Second box can be, you know accordingly.

(Refer Slide Time: 07:32)

First box let us say I have now; I have now n boxes right and r balls. So my first ball can be put in any of the n boxes. My second ball can be put in any of the n minus 1 boxes. Third ball can be put in any of the n minus 2 boxes. And then (0) $(07:55)$ like that I have r terms because I have r balls.

Only thing is that if let us say, in greater, equal, let us say n would be less than r, what will happen? If n is less than r, that means boxes are less then I must have to put more than 1 ball in a box. That situation will arise. But I have forbidden that. So this is not allowed.

(Refer Slide Time: 08:21)

n less than r is not allowed.

So you see this situation where the, where I am choosing any of the n boxes for my first ball and then I am left with only n minus 1 because I cannot put more than 1 ball, so n minus 1. And then my third box will have n minus 2.

And like that I have r balls, so r terms and that can be written as factorial n by

(Refer Slide Time: 08:42)

factorial n minus r. Because factorial n by factorial n minus r is exactly that one, if you can think of.

For example, let us say, let us talk about n 3 and r 1. So n 3 and r 1 is just 3, because I have only 1 box, right. So that can be written as 3 factorial by 3 minus 2 factorial,

(Refer Slide Time: 09:05)

sorry 3 minus 1 factorial, r 1.

So it is 3 factorial by 2 factorial, and 3 factorial is written as 3 into 2 into 1. 2 factorial is just 2 into 1. Cancels and gives me 3.

(Refer Slide Time: 09:18)

So this n factorial by n minus r factorial is called n P r, permutations of n particles into r, n into r levels, Ok. So this is a particular situation in which permutation is required and we can get an estimate of number of microstates.

So now you are getting a hang of things that when I am talking about a microstate, this is a distinguishable configurations of distinguishable things. It can be particles, it can be balls, it can be dice. It can be coins; it can be anything as long as I distinguish it.

In the context of chemistry, of course we need something more tangible like particles, like you know molecules but this is, this probability is not restricted to chemistry.

It is mathematics. It can be applied anywhere else. And therefore wherever we want to connect to a situation we can always associate probability. And if we want to call that entropy that is us to do that.

For example you can say that entropy of getting 2 different colored cards out of 4 cards in one hand is more. What you are saying is the probability is more.

So entropy of, of the situations in which we can put distinguishable balls in distinguishable boxes will be more. We are all saying that basically that the possibilities are more. They are equivalent.

So entropy is nothing but, as I said options or possibilities. Possibilities give us probabilities. More possibilities is more probability.

So these words are connected. Probability is a word that is associated with mathematics of calculating a ratio that how many possible ways I can get something out of all possible ways. That is the probability.

So now probability will increase when the numerator will increase. And numerator is how many possible ways we can get certain things which will decrease when the number of possibilities increase in the denominator.

So you see that, we will see that it is not, not even the, it is the, for particular thing that you want to get, the probability becomes important.

Even without probability the whole, all total possibility if it increases that also will increase the entropy. We will, we will be more clear later on on this aspect but now we understand what permutation is.

Now we will switch to more than 1 ball in a box. Till now we were concentrating ourselves to 1 ball in a box. But still we are, still we are talking about distinguishable particles, Ok.

(Refer Slide Time: 12:07)

Now we will see that if we have more than 1 ball in a particular box, then what kind of situations we will get. We will see that. It will be something called combination rather than permutation.

And combination is

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a choice. We have to choose. So what is the number of possible combination of r objects from set of n objects? Or you can say r balls, you know from n balls. And, so these are the typical examples of 6 balls

(Refer Slide Time: 12:38)

and that we have to choose, out of that I will, let us say choose only 3.

So our r equal to 3 and n equal to 6.

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In that situation we write that n choose r, n choose r and let us say we have only one box.

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In that we have to put 3 balls, in 1 box. Because see, remember we were saying earlier that we have to put 1 ball in a box for permutation.

But now in combination we can put more than 1 ball. So initially they are all distinguishable. Once we put in a box, in the box they are all indistinguishable, Ok.

So we have to put 3 balls from, out of 6 balls in the box. So how many possible ways you can choose? We can choose in something called n choose r or n C r ways, which by formula is factorial n by

(Refer Slide Time: 13:38)

factorial n minus 1, n minus r and factorial r. You see in that case I have an extra r factorial on n P r.

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So I had an n P r which is permutation. On top of that,

(Refer Slide Time: 13:53)

I have, I have divided that n P r by factorial r. Why we did that is because when I am choosing this one ball out of all possible, all possible 6 balls then I can pick any of 6, any 1 of them, any what you say, I can pick the first ball in any 6 ways.

I can pick my second ball in 5 ways. I can pick my third ball in 4 ways.

(Refer Slide Time: 14:21)

That is nothing but n P r or 6 P 3 like we discussed.

But once I choose my 3 ball and I put them here they are all

(Refer Slide Time: 14:31)

indistinguished balls. In the same box they do not have a separate identity.

We do not care which came first, which came later. We do not care about that as long as they are there. And that situation says that there are factorial r number of ways

> Combination (Choice) Number of possible combination of r objects from set of n objects δ $6x5x4$ O. Choose a set of 3 balls from 6 above without regard to the order = nC ,

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I can distribute them inside the box, which are all equivalent. So this is factorial r.

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Factorial 3 is nothing but 6, right.

(Refer Slide Time: 15:00)

So these are, let us say I have chosen, I have chosen this green, blue and you know brown ball, gray ball, green, blue and gray. Let us say I have chosen out of the 6 possibilities.

And, but these ones, all possible configurations are equivalent when I put in the box. So therefore I have divide by that. And that is the division of 1 by factorial r that I mentioned. And that reduces the number of configurations by factorial r.

So therefore this choice that we talked about, that reduces the number of possible microstates because we are, we do not care about which particle, which ball came first and which ball came second and which ball came third.

Once we do not care about that we have factorial 3 ways of doing that and

(Refer Slide Time: 15:51)

therefore from permutation we are getting a sense of combination that, you know, from permutation if you divide by the number of balls that are grouped together then that will give us combination.

So combination means you combine things. So you combine 3 balls and give them a single label just like what is mentioned here.

So 6 C 3 are 6 into 5 into 4 divided by factorial 3 and that becomes only 20. So how many ways 6 balls

(Refer Slide Time: 16:30)

can be chosen from a box given. So let us say I have to choose all 6. What will be the number of possibilities? All 6 I put in one box.

There is only one way of doing. I will take all of them and put in. There are no other possibilities. And that is happening because I put 6 factorial on the numerator but I divide 6 factorial back again when they are put in the box. Then they become indistinguishable.

So all 6 of them are inside the box and they are all indistinguishable. They lost their color which is seen here. Now in the box they lost their color.

(Refer Slide Time: 17:03)

There is only one way of doing it and that is what combination is. And you will see later on, when you put particles in levels, in a single level particles have no distinguishibility.

Before when you choose them, there is but in a single level they do not care which particle came first, which particle came later. Therefore all of them are, you know indistinguishable in the same level, in the same box. That gives us combination.

(Refer Slide Time: 17:38)

So combination to permutation we have discussed that how many ways 6 balls can be chosen from 6 boxes such that there is only one particle in a box, one particle in a box that was permutation.

So if I just put 1 particle in a box it will go back to my permutation. When you combine them that gives us combination.

(Refer Slide Time: 17:57)

Now let us look at a different situation. Now balls are indistinguishable but cells are distinguishable. Earlier both balls and cells were distinguishable. Now we are coming to a situation where balls are indistinguishable.

So earlier we had 3 balls like a, b and c. We can call them all a or you can call them all stars, will be indistinguishable. Boxes are still distinguishable by, so I have 3 balls,

(Refer Slide Time: 18:25)

they are all indistinguishable. I do not have any color anymore. But I have these 3

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particular boxes. Now how many ways do you think it is possible?

This is a typical problem of, you know star bar problem. We will show you that later on. But now we are just going to enumerate it in a different way. I will show you because this number is smaller. We will show you here all possible combinations.

But in future for any general combinations of choosing r indistinguishable balls from n distinguishable boxes can be done later on.

(Refer Slide Time: 19:02)

Now look at these possibilities here. I denote these balls as stars,

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and boxes as these spaces. This is box number 1, this is box number 2 and this is box number 3.

(Refer Slide Time: 19:17)

There are 3 boxes and I have 3 balls as stars. Now how many possible ways can be done? You can see that I can put these 5 plus these 5.

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possibilities As you can see here, 3 particles in that box is fine when for first box, 3 particles in second box is fine, 3 particle in third

(Refer Slide Time: 19:40)

box is fine. That is Ok, that is not a problem. But earlier I had, you know another kind of situation. So for example here I have 2 particles here and 1 particle here.

Now earlier I had more situations here. I had a, b and c. I had a, c and b. I had b, c and a.

(Refer Slide Time: 20:07)

But they all collapsed to only one possibility. Because if they are all star, then it is same as star, star; star, this also will be star, star; star, this also will be star, star and star.

See now these 3 are

(Refer Slide Time: 20:24)

indistinguishable, right. We cannot distinguish this from this from this from this, cannot distinguish. So therefore when the balls are indistinguishable, we reduce number of microstates. We get less number of microstates. And that is why from 27 we got only 10 possible distinguishable configurations.

For example look at here. I have 3 stars here. in 3 different boxes. Earlier I could have many more ways. I could have a b c, c b a, in fact I could have 6 possibilities; a c b, and c a b, and b a c and b c a. Did I write all that?

(Refer Slide Time: 21:18)

Yeah.

So all those 6 possibilities now are nothing but star star and star. The 6 possibilities collapse to only one possibility.

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Here 3 possibilities collapse to, I do not know there may be more possibilities than the 3 actually. So I can take this was any 3 of the...no, 3 possibilities. These 3 possibilities collapse to only one possibility.

Therefore 27 which was earlier n to the power r has become now only 10 possibilities and you will see that in this arrangements are something called n plus r minus 1 C n minus 1, where n is the number of cells and r is number of balls. We will discuss this

(Refer Slide Time: 22:11)

one a little bit more detail later on because this very important and we will come back to that.

For the time being we just wanted to show you how it looks. You can read this. So what is the number of microstates, what is the

(Refer Slide Time: 22:27)

number of such microstates of, so exactly?

That was I was saying, right, like how many microstates we can get when there are r indistinguishable ball and n, what is the number of such a microstates when r is indistinguishable balls and n is indistinguishable boxes.

So these number of boxes will be n and number of balls will be r. In that case

(Refer Slide Time: 22:51)

you can see that it will be this formula and we will come back to that later on.

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Now let us simplify even further. Let us make both balls and sets, and boxes are indistinguishable, what will happen?

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So I take 3 indistinguishable balls and 3 indistinguishable boxes.

(Refer Slide Time: 23:14)

So I have 3 indistinguishable balls and 3 boxes.

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You see I have not labeled the boxes any more. So they are indistinguishable boxes right.

This situation, again I can say that this is star and boxes are of course,

(Refer Slide Time: 23:28)

you know it does not matter whether it 1, 2, or 3 or not. You can see it reduces only to 3 possibilities,

For example I showed you earlier that if balls were distinguishable and boxes were distinguishable this would correspond to 6 possible configurations. Now there is only 1.

(Refer Slide Time: 23:46)

I showed you here also that this, if balls were distinguishable this would be 3 possible configurations.

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And when both were distinguishable this had many, many more configuration, this situation, 2 1. Many more configurations.

But here it is either all the 3 particles in 1 box or not or there is 2 particle and 1 particle situation or there is 3 particle situation... It is almost like I am breaking my 3 into this situation. I am breaking my 3 into 3 0 0, or 2 1 1 sorry, 2 1 0, or 1 1 1.

(Refer Slide Time: 24:37)

Now what will happen if I have r indistinguishable balls in n indistinguishable cells? Now how

(Refer Slide Time: 24:46)

we get r indistinguishable balls in n indistinguishable boxes? So this is again something that I have to come back later on. But I will just give a glimpse of it. It is called integer partitions, partition on the integer.

We will briefly discuss about that however

it is not so important for this particular course. This is just to give you an idea if you are curious enough that in a situation I have let us say 11 indistinguishable balls and I have to place it into 3 indistinguishable boxes. How many such things will come up?

And also you will see these 3 situations are kind of 3 different distributions.

(Refer Slide Time: 25:27)

And each of them will have its own microstates when the balls and boxes will be distinguishable.

We will come back to that later on. It is just to give you an idea that how the ball can be put in the boxes and what is that (1) $(25:42)$ is indistinguishable. The reason is that you will see

that the classical particles are typically distinguishable particles. Whereas quantum particles like electrons, protons are indistinguishable particles.

So therefore while developing the statistics we have to consider whether the particles are distinguishable or not. For example we do classical statistics that such as Maxwell Boltzmann statistics, we need to consider particles to be distinguishable.

If we calculate particles like (()) (26:10) Bose Einsteinian statistics which come from quantum statistics which are called quantum statistics for a reason, and there you will see that the indistinguishibility of the particle will come into the picture.

And also the restrictions were that there may be 1 or more particle in a box that also give rise to (()) Newtonian statistics. The point is that we can always consider or calculate the statistics whether the particle is distinguishable or not.

That is Ok for us to do so and get different numbers but we have to always check with experiments that what we are getting out of that experiment. If our experiment matches with the theory that requires indistinguishability, then we will know that they are indistinguishable.

For example we looking at, looking at a glass of water we cannot distinguish from one water to another water, even if we use microscope we will not be able to. But our inability to distinguish a particle has nothing to do with the statistics that experimentally comes in.

Because it, that means the distinguishability is inherent in the system, or in the particle such a way that giving us a statistics that corresponds to indistinguishable particle statistics. So that is the important point. It is nothing to do with our indistinguishability.

It is to do with the indistinguishability that is inherent to the system or looking at the statistic that is coming out of the experiment. And that is what is more interesting to note.

Now that you go forward, you know balls and boxes situation, let us see what happens when calculate on the, calculations of, you know on two-level systems.