Chemical Principles II
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Module 07
Lecture 40
Microstates and Distributions

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Last class you have seen that entropy is proportional to the number of microstates. And the reason behind the increase of entropy with time was discussed as that entropy is nothing but options. When you have more options you have more entropy.

So in order to show that, I have shown that movie of water in which you could see that every time instant the number of the configurations of the particles were changing. So therefore at every instance of time new microstates were being generated.

Now there for a very complicated systems like water in a glass the string of numbers constituting their position and momentum can be thought of as a microstate. Let us say if we have one particle, one water molecule then it will have 3 atoms therefore 9 positions and therefore 9 different momentum.

So this 18 number will constitute one microstate. If you change any of these 18 numbers then a new microstate will be generated. So today we are going to talk about much simpler system. And then we will come back to this complicated water systems may be later on.

Water system is also complicated because there are interactions between the water which will also change the possibility of certain microstate being there or not being there.

So in order to understand what is a microstate we will discuss some simpler problems. Before that also we will just, you know remind you that we have also discussed about little bit of probability and we discussed about the and probability, or probability and the combination of them.

We showed you that when the number is large then only the probability values are coming to the, the desired value. For example when we toss a coin it becomes point 5 only when you toss many number of times.

And the distributions of probability mass functions for 2 die throw becomes perfect only when you do very high number, in our case we have shown 10,000 trials, 100,000 trials actually gave a right symmetric distributions at the sum equal to 7.

So today we are going to talk about distributions and microstate. So by distribution what we mean is that, imagine that die throw. So there we could see that there were 11 different possibilities. Sum as 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12.

So there were these 11 possibilities and by distribution it means that out of 10,000 or 100,000 trials each of these possibilities occurred some number of times. And which means that our sum of 2 dice got distributed in these numbers between 2 and 12.

So when you talk about distribution and then each distribution had some possibilities, some probability. So here we talk about much simpler thing. When you talk about cards

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we know

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what distribution is, right.

So typically you know, if you know about playing a card then typically there are games called bridge where there are 52 cards and you distribute 13 to each of them.

And so that is called distribution, right. So let us say there are 4 players, 1, 2, 3, and 4. I distribute 4 cards in 4 players. Make it simpler and let us say there are only 2 players. So I will distribute 1 card, 2 card, another card, another card.

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So I distribute my 4 cards into 2 different people, 2 hands or 2 sets.

Now each hand has some cards. For example here you could see that there is one heart

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and one diamond. By the way these all 4 cards are aces. So they are all A as you can see A here, and there are only 4 such cards. One from diamond, one from heart and one from club and one from spade.

They are all distinguishable cards because I know

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aces of heart and aces of club, aces of diamond, aces of spade. I know these 4 cards, distinguishable cards.

But forget about that, they are hearts, spades, clubs and diamonds. Look at their colors. What do you see? In one hand I saw 2 red, in another hand I see 2 black. Now this is just one occurrences of my distribution. I can distribute again. I shuffle it and then let me distribute it again.

What do I see? I see

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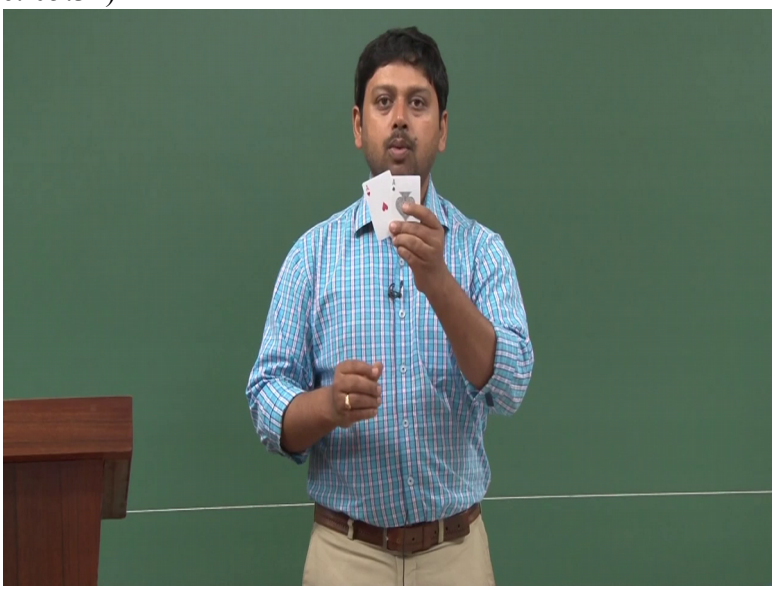

1 black and 1 red. And I see in the other hand, of course

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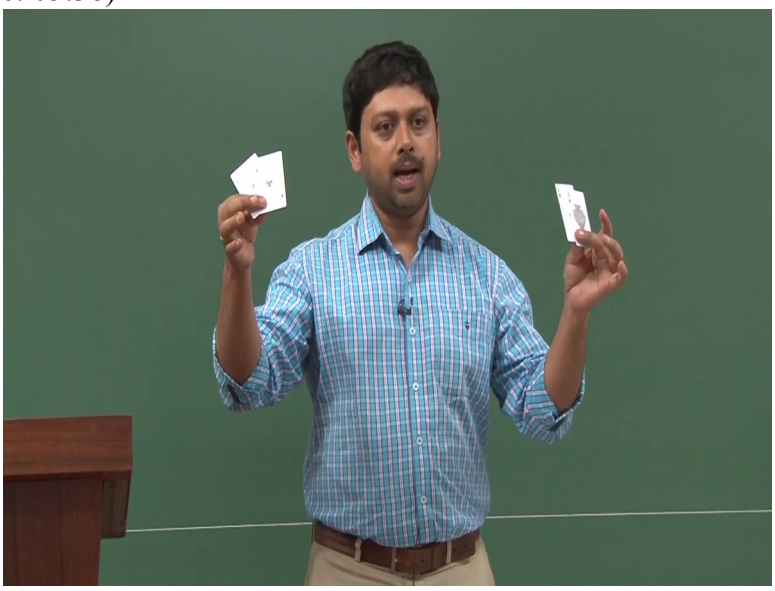

one black and one red. Now what do you think whether this is a better possibility?

Or the other one in which one hand had black card and another hand had red card is the possibility, higher possibility? So which one will be more probable?

So in order to understand that let us see that all possible combinations of these 4 cards distributed among 2 hands.

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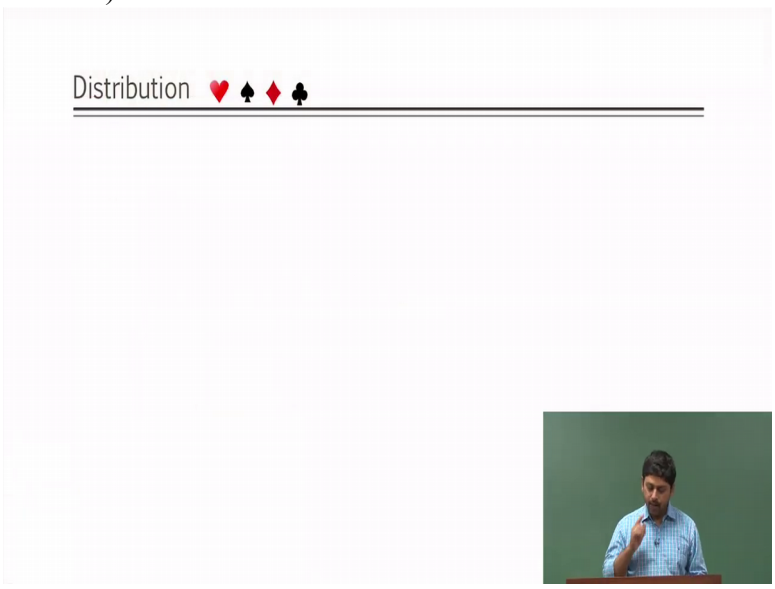

So here again as you can see, they are all aces; just think about it that they are all aces. I have not specified that. And now I am going to distribute

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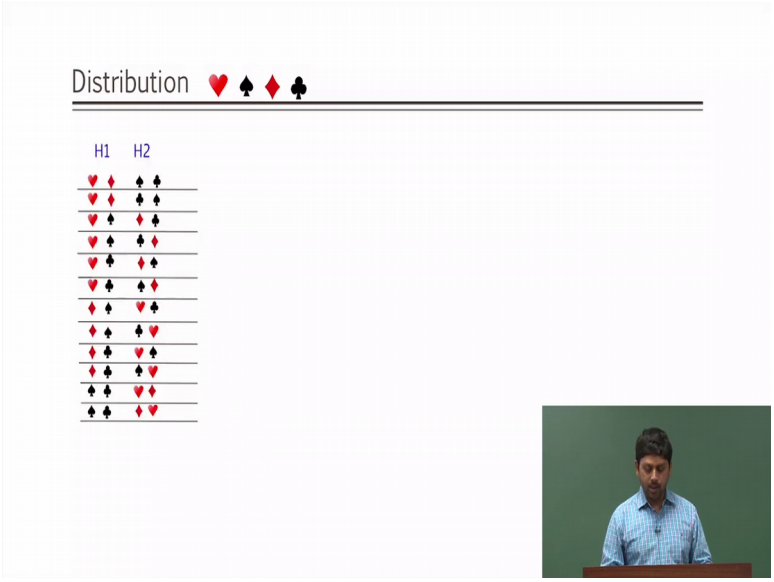

them in the hand 1 and hand 2.

And you can see I distribute heart and diamond to hand 1, and spade and club to hand 2 in one of the distribution, once when I give. And then I can also give heart and diamond and club and spade, another possibility.

And if I go on like that

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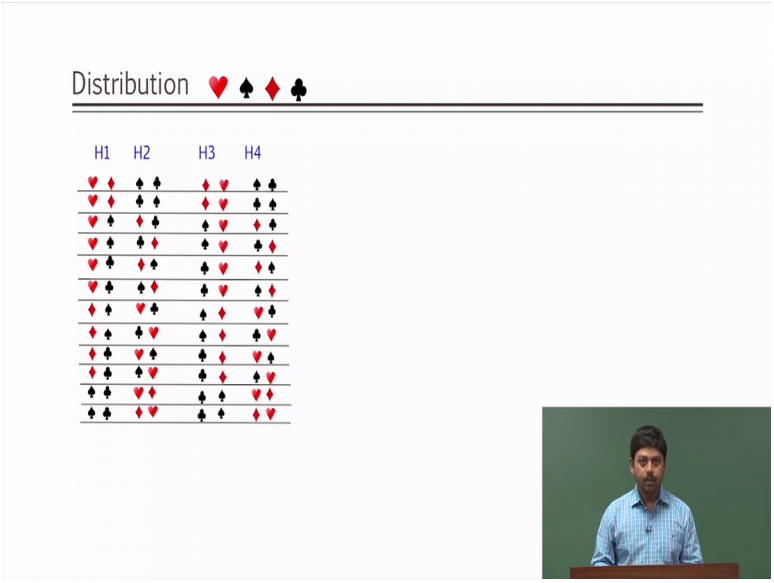

then as you can see there are 24 possible distribution of this, you know 4 cards into 2 hands. The reason is that why there is 24 possibilities because they are 4 different cards, hearts, spade, club and diamond.

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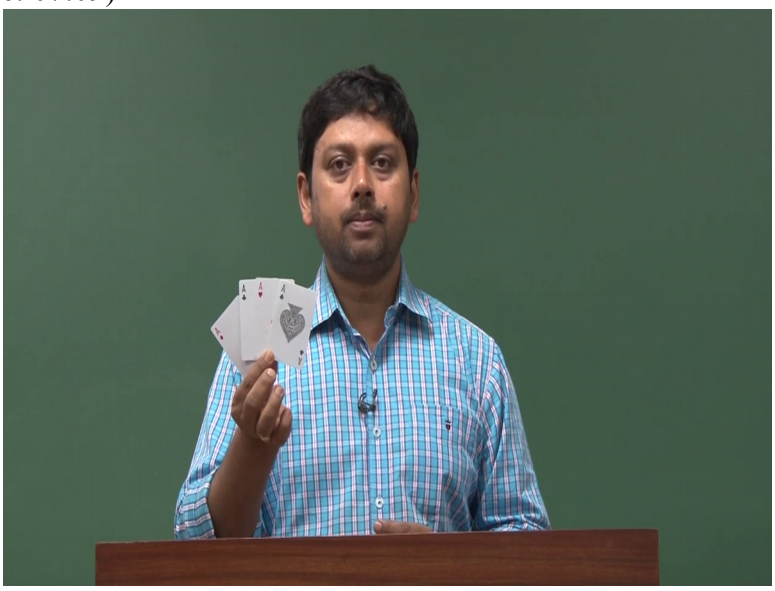

Now when you give the first card, first card I can pick any of the 4 possibilities. This first

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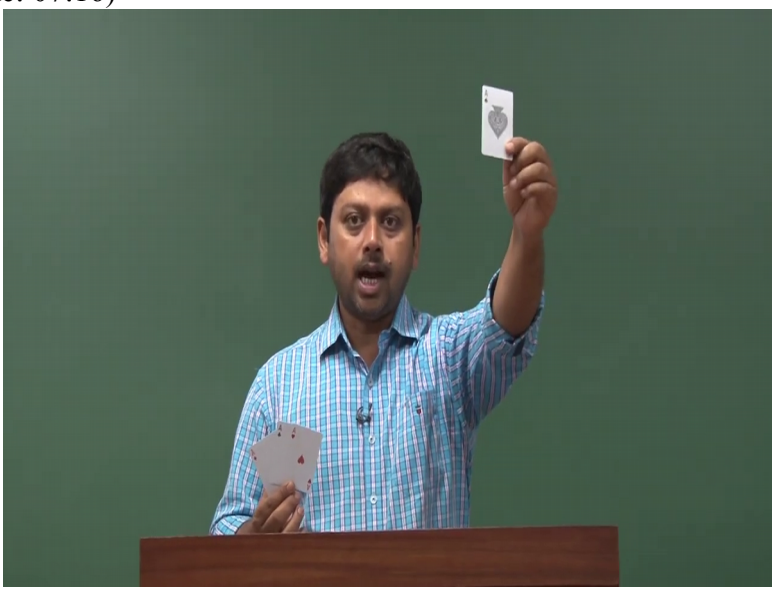

card I do not know, I am not looking at it, therefore it can be, I can choose and pick and I can actually take any of the 4.

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Once I take any of the 4, I have then, I am left with 3 more cards.

Second one I can take any of the 3.

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So 4 into 3 is 12. Out of the last 2 cards I can take any of

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the 2, 4 into 3 into 2. And then

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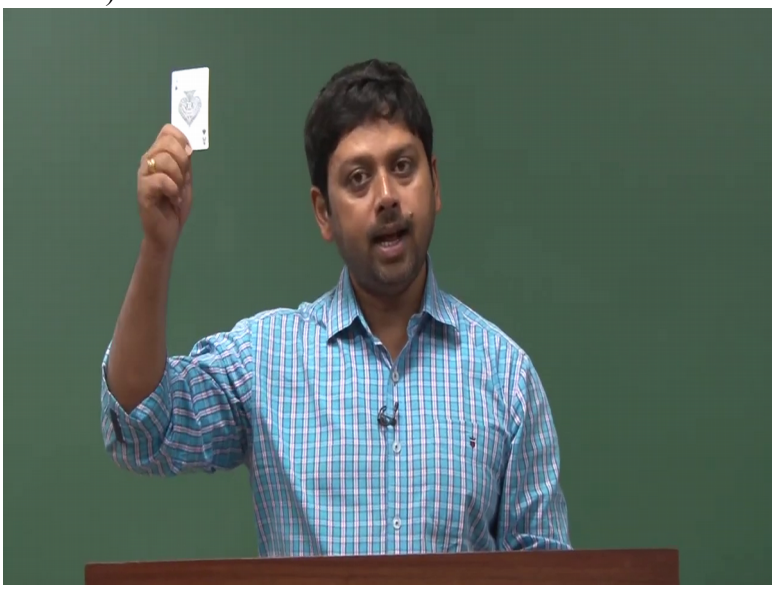

I am left with only one choice, into 1. So the number of possibilities as you can see is 4 into 3 into 2 into 1 is equal to 24. And that

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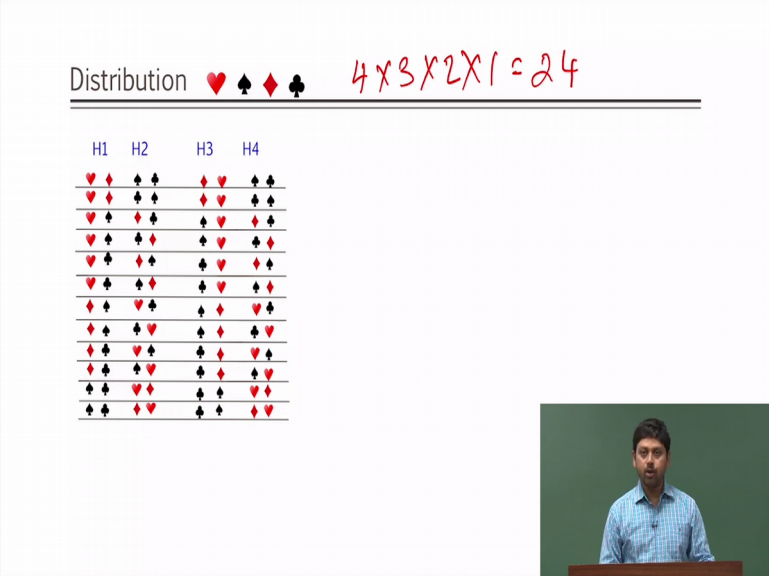

24 is actually given here, that 24 possibilities.

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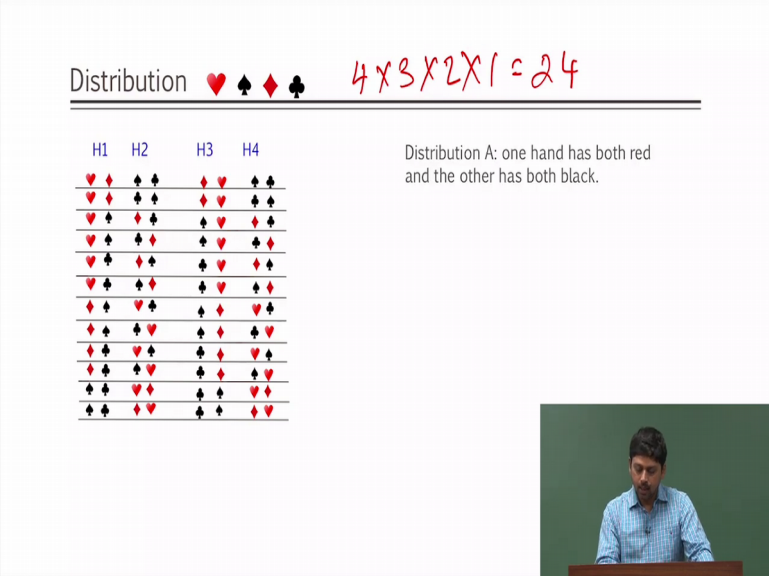

So now I say that Ok, I have these 24 possible ways of giving this card but I want to summarize this into 2 main distributions. In one distribution, I say that one hand had both red cards which we saw the first time.

How many such occurrences are there? Let us see where one hand red card and another hand black card and hands are independent, that means it is Ok that the first guy gets both the red or the second guy gets both the red. So let us see such occurrences.

This is 1, 2 and then 3, 4 and then 5, 6, 7 and 8.

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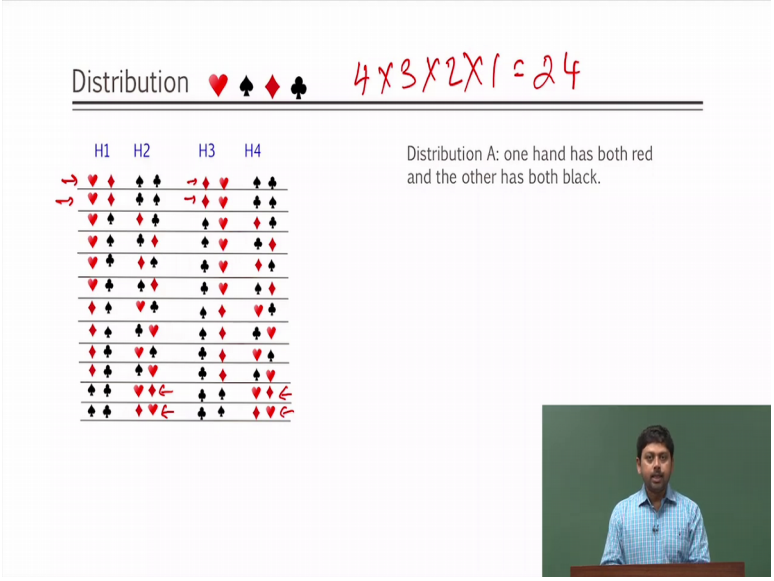

There are 8 possible situations where one hand gets one particular color, red or black. The other hand gets another particular color, red or black. There are 8 such situations.

If that is the case

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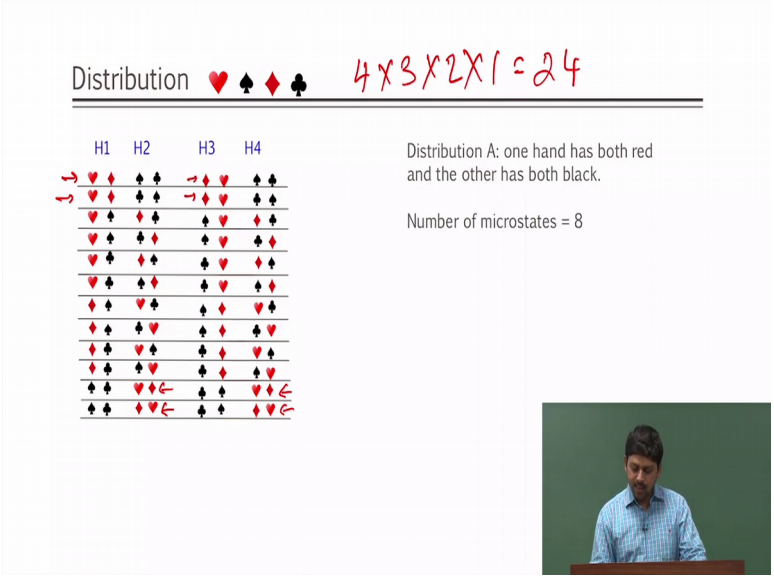

we can say that the number of microstates corresponding to a particular hand getting one particular color is only 8. Total number of microstates again is 24.

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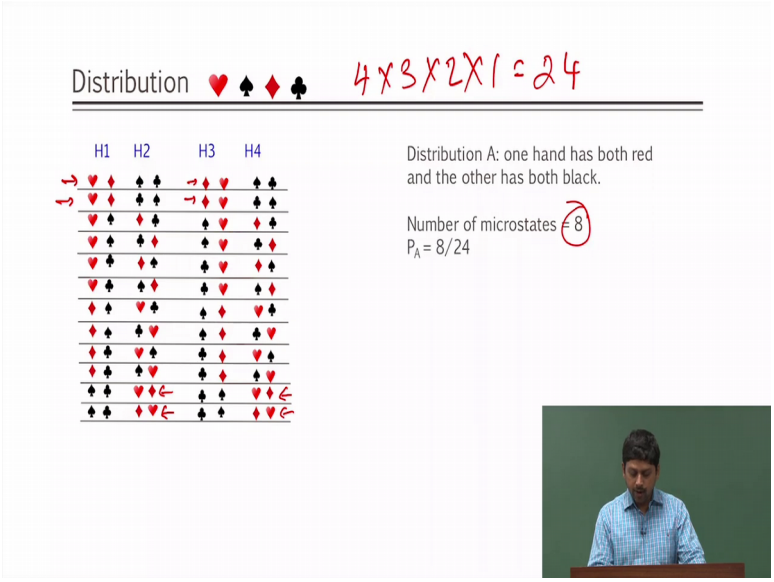

Therefore probabilities of this particular distribution which we call distribution A

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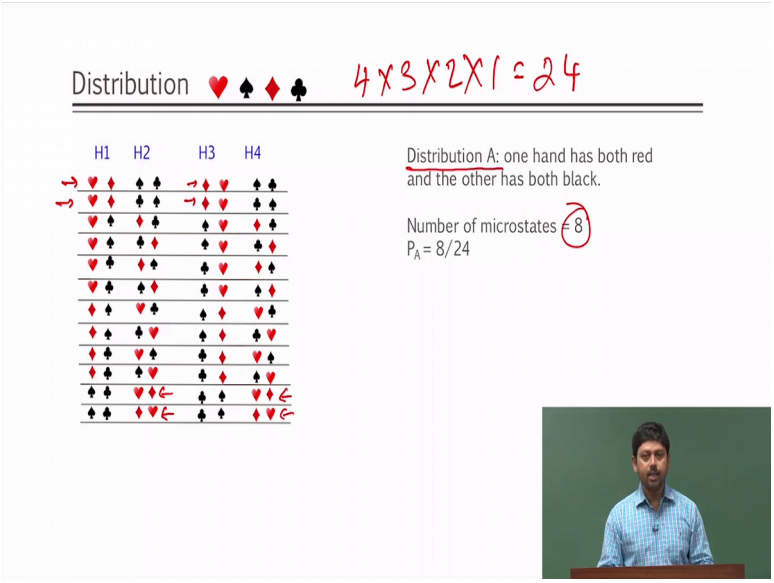

is 8 by 24 or basically 1 by 3.

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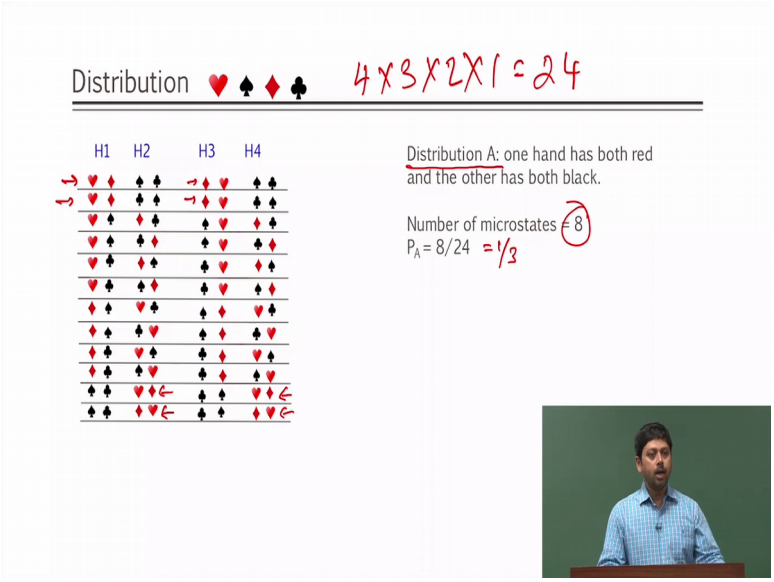

Now let us say,

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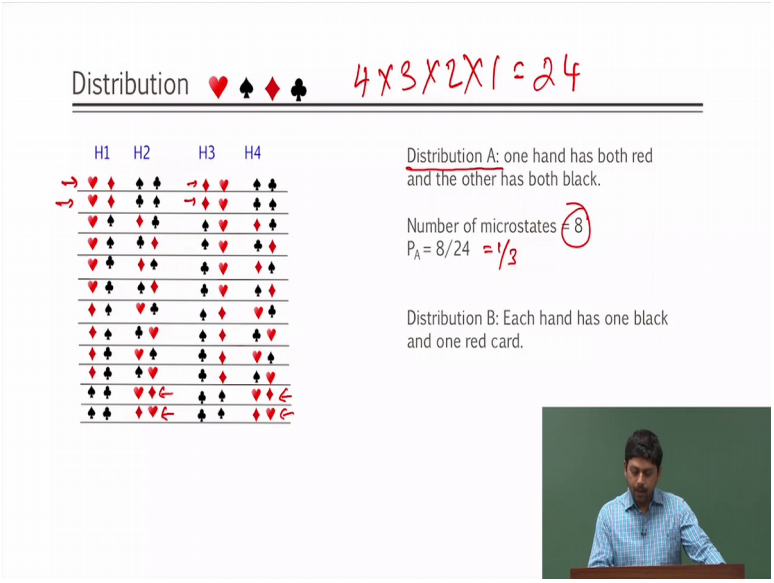

I talk about distribution B. I say that each hand has 1 black and 1 red card. So mixed card. So what is the mass probability that you will get a mixed card?

In that case all other things, all other things, other than the 8 they are all mixed. So there are 16

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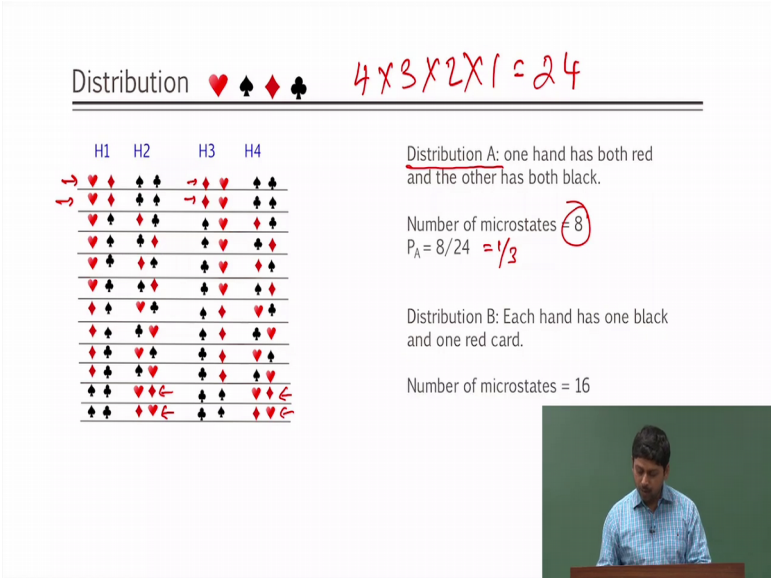

possible mixed, situations are there.

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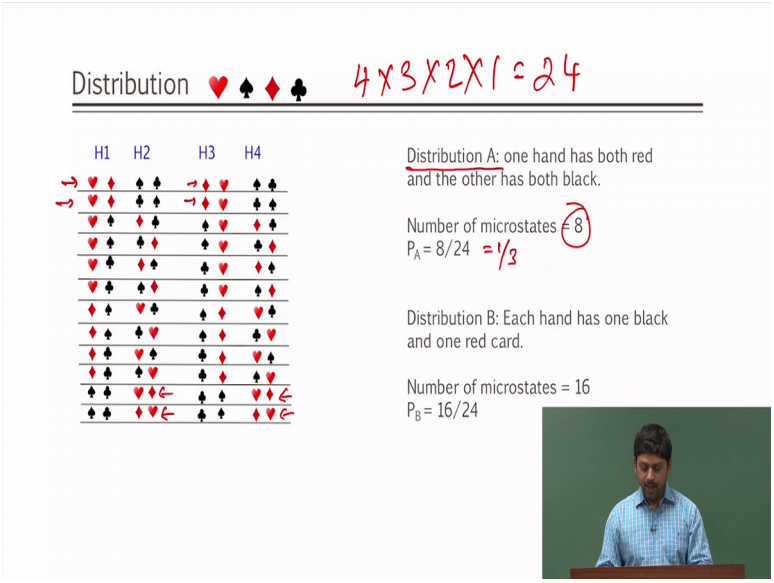

And then the probability of that distribution will be 16 by 24 or 2 by 3.

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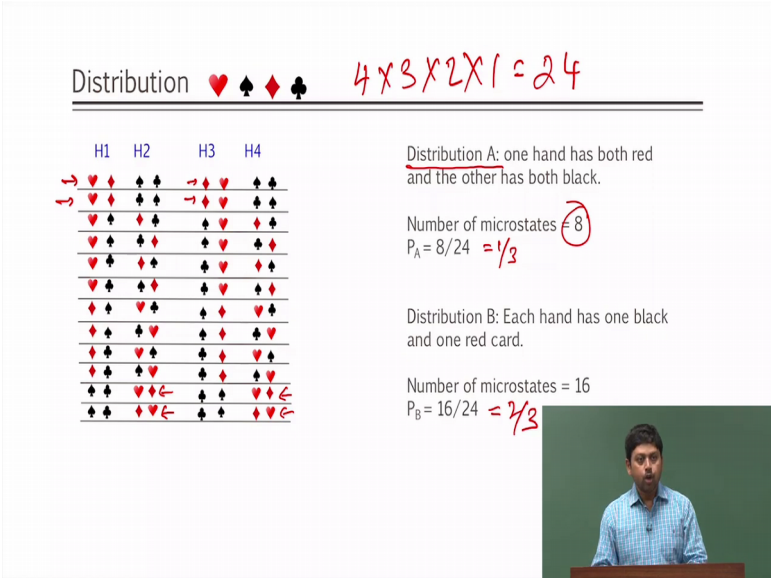

So without doing or distributing this, using the probability we can say that when you distribute the card these 4 ace, 4 cards then the probability that you will get a mixed color card is much higher, is higher. It is actually double than the probability that you get same colored cards, even without doing that.

But remember you may get 2 red cards or you may get 2 black cards, you know in one occurrences. However when you do several times, multiple times, then it will be more probable that you will get a mixed card.

So microstates are again, we can say that all possible arrangements. What are the possibilities of distributing these 4 cards is what we can think of as microstates. Remember that if 2 distributions are identical or 2 arrangements are identical then we will count only 1. So we will not count them twice.

For example when you define that there are black cards and red cards, 2 red or 2 black then we already define the situations and we count in that all possible, all possible, all possible variation.

So what do you mean by the distribution? So distribution is that when you distribute either a card or particle or something into two or more people. So let us say we distribute cards to people. That is a distribution.

Or distribute particles to different energy levels, that is a distribution. So distribution literally means that you are giving it, you are dividing it to, you know certain parts. And then number of microstates will be how many possible ways you can do that for one such distribution.

So for, when you have, you know one hand getting same color that is a distribution. And number of possibilities is 8. One hand getting mixed color is a distribution. And the number of possibilities is 16.

So that is what we will distinguish between distribution and microstate. Let us do more about that.

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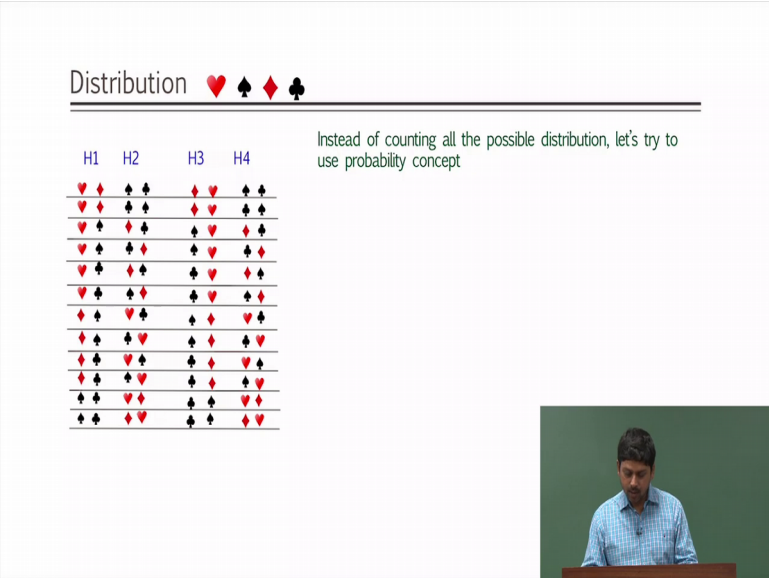

So instead of counting all possible distributions like we showed we actually enumerated all 24 and we actually showed you that there are 8 possible situations in which one hand gets black card and another hand gets completely red card. We can use probability and

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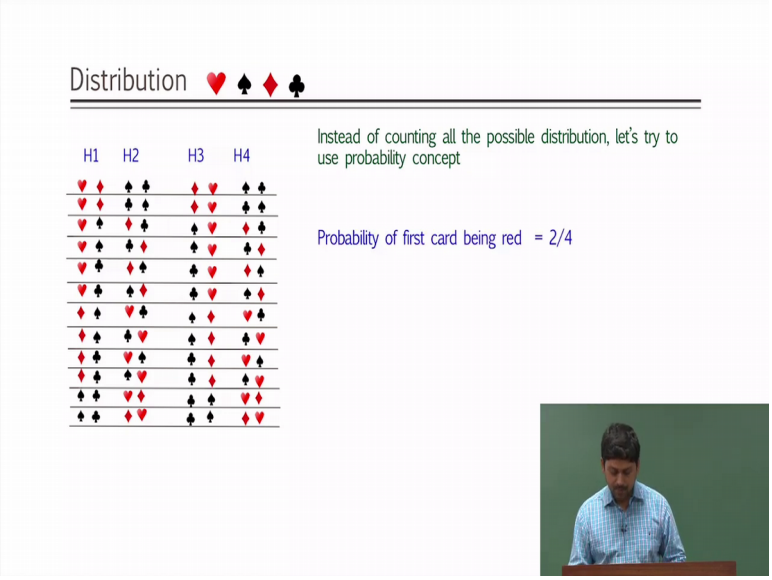

calculate the same thing.

So when I pick up, when I give the first card to somebody

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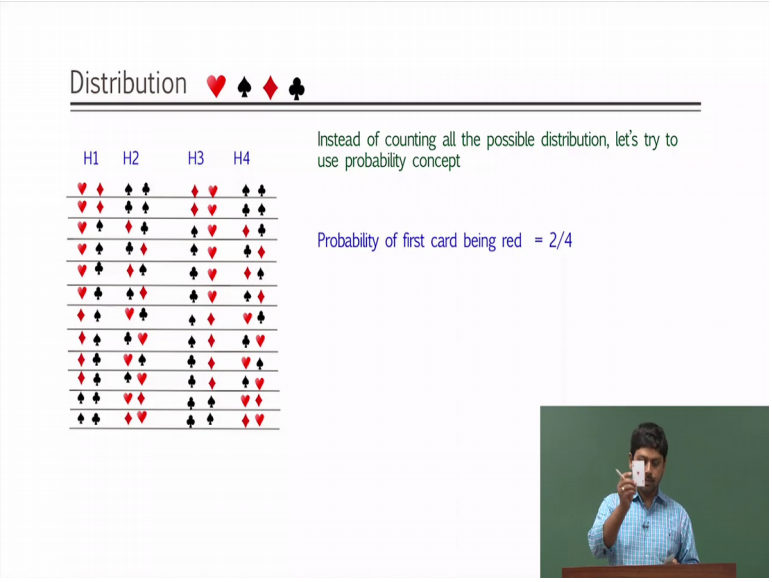

what is the probability that I am giving a red card? 2 by 4. Because there are 2 red cards out of 4 cards. So the probability that the first card gets a red is 2 by 4.

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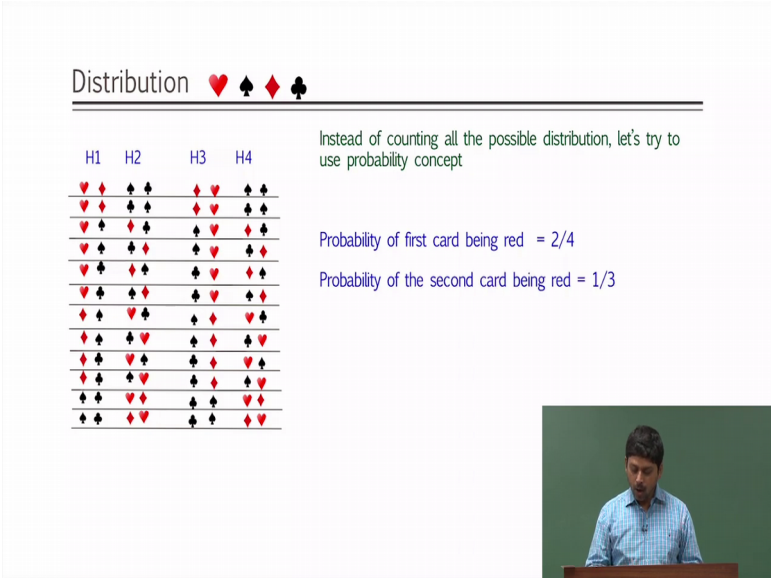

Probability that the second card is red, because there is only 1 more red card left there, right, out of these 3 cards. It should be 1 by 3.

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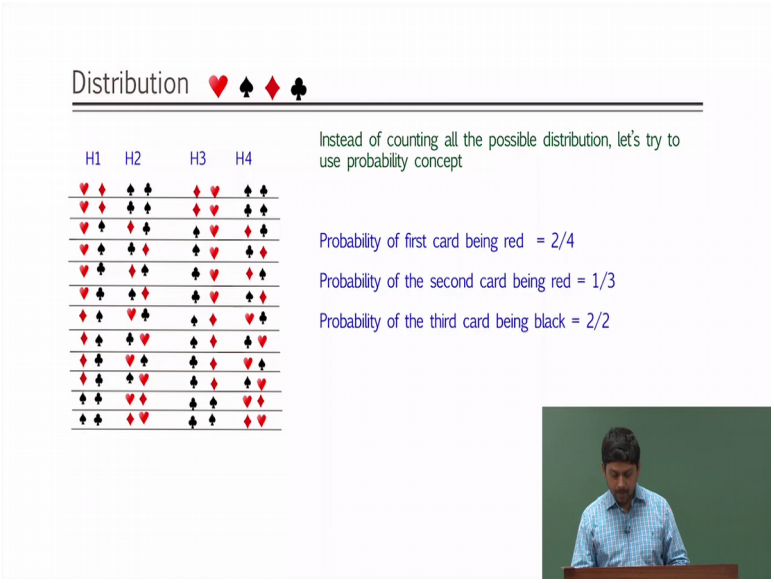

Probability that the third card being black, now I have only 2 cards left and I know they are both black, right.

So the probability that the third card is black is 2 by 2 and

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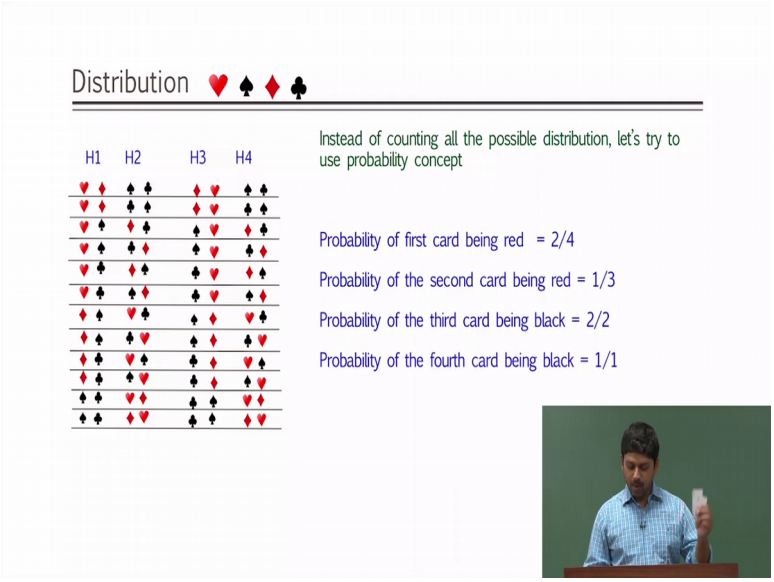

probability that fourth card is black is 1 by 1, there is only one card and that is also black.

So

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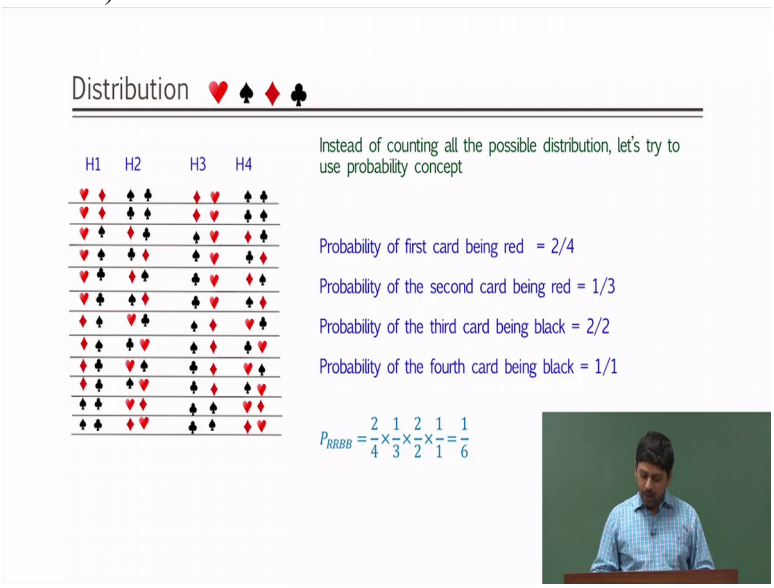

the total probability, now see we are invoking the and probability situation here, that first card being red and the second card being red and the third card being black and the fourth card being black, so I am multiplying all of them and I am getting 1 by 6.

But that is not the only situation in which one hand gets red and another hand gets black, right. Because there is a situation

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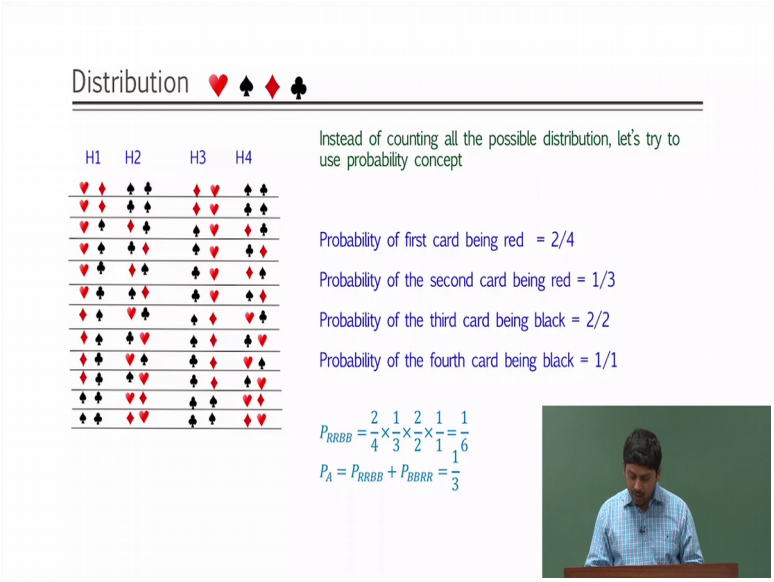

in which I can, instead of giving that second guy that red card I can give them black card.

So I also have to count that the first, probability that the first card being black, probability the second card being black, probability that the third card being red and fourth card being red.

So in that situation that will be same as 1 by 6, right. And I can, and denoting that

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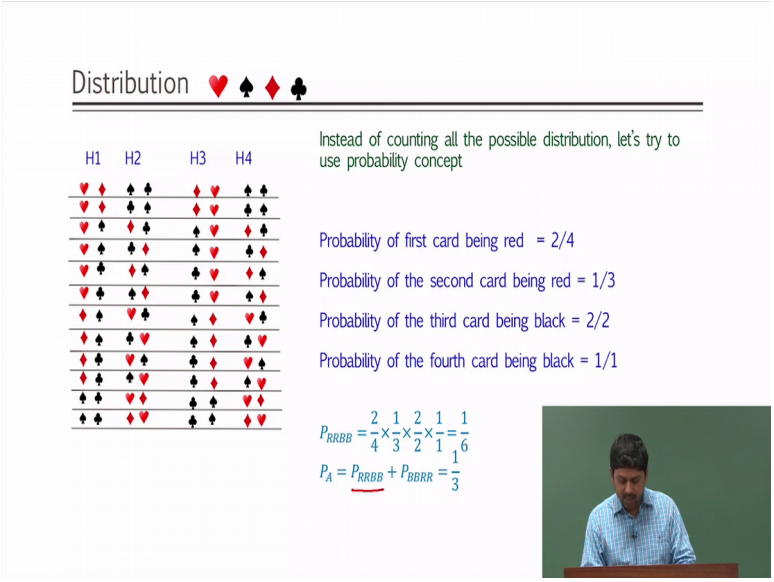

probability as R R B B that is first card red, second card red, third card black, fourth card black. This will make two hands R R and B B,

And in the second case, first card black, second card black, third card red, fourth card red,

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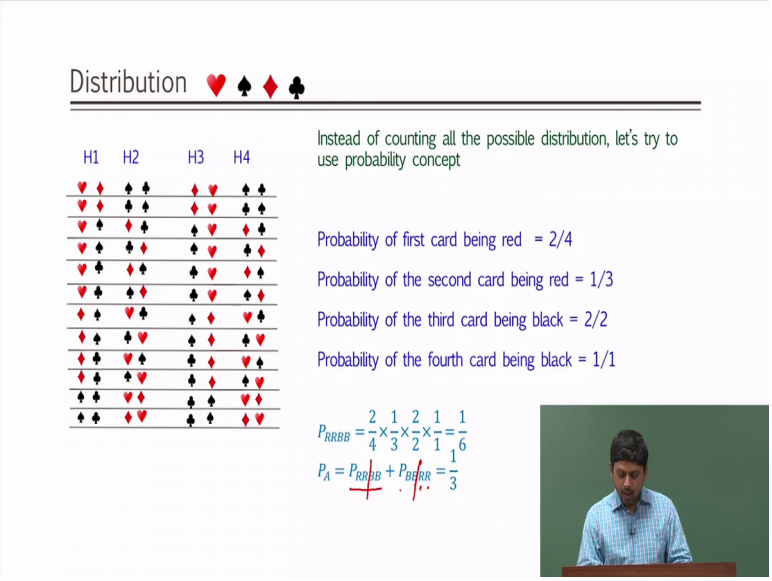

and I am getting another possibility. You see here that I am not distinguishing between two hands. I am not saying that hand 1 has to get red and hand 2 has to get black.

That I am not saying here. I am saying any of the hands should get any of the color, but same color. And that is why I need a or probability. And the or probability, as you know adds. And because of that my total probability that one hand gets one color, the other hand gets the other color is 1 by 3.

You see now, without doing, without any (()) (15:12), instead of 4 cards if I had 20 cards, or 20 different colors, should I be enumerating all of them, writing all of them down?

No. I have to use the probability to estimate that what will be the number of possible microstates and what will be the probability of that distribution.

Why I am talking about probability of the distribution? You have to differentiate between distribution and its probability. So we will see later on that there are many possible ways of doing a, performing a distribution.

And in that there is one distribution which will be maximum probable. And you will see that the situation will go towards those probability.

What I mean by that is that if you keep on shuffling the card, you will see more and more mixed color card, one hand is getting mixed color card, that is going towards a more probable situation.

Here there are only 2 possible distribution so that is why you know you go from one to the other not (()) (16:15) so but where there will be many possible distributions and there we will see that one possible distribution will be max.

So now

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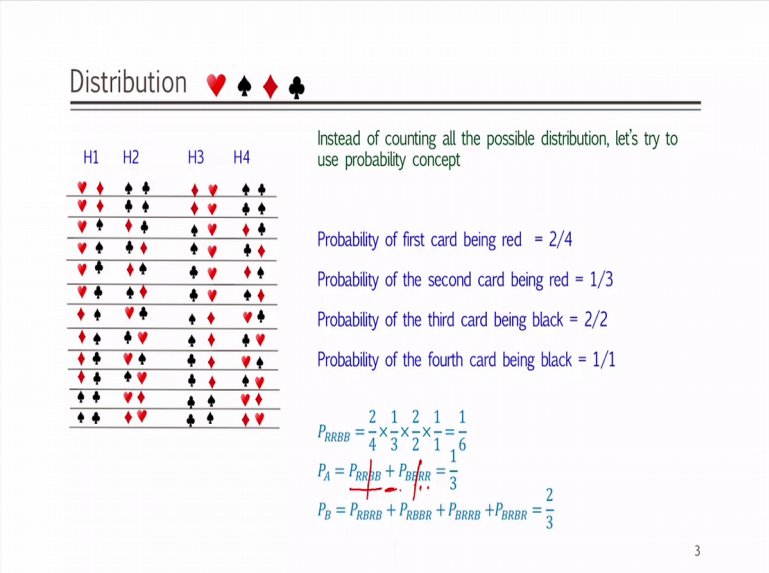

let us do the P B the same way. First card black, second card, first card red, second card has to be black for the hand 1,

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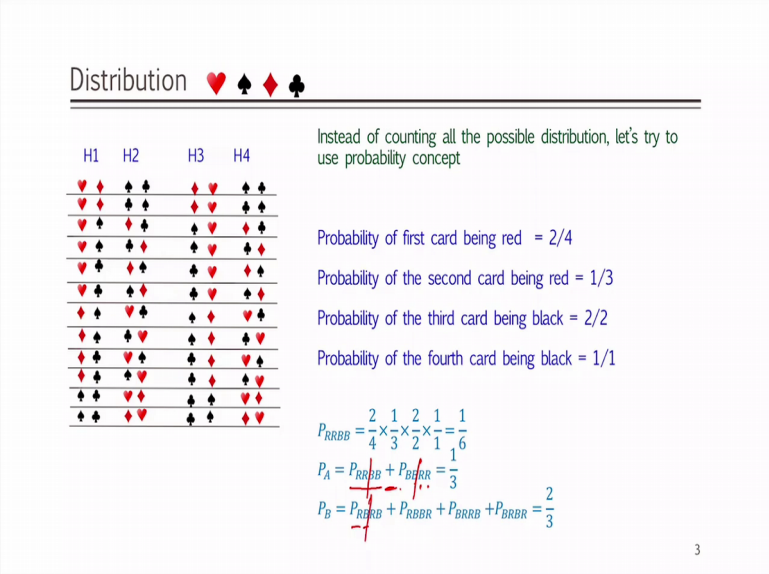

and then the, for the hand 2, it should be red and black.

That is one possibility, right. In that case hand 1 and hand 2 will get mix color. Hand 1 and hand 2 will get mix color when first card red,

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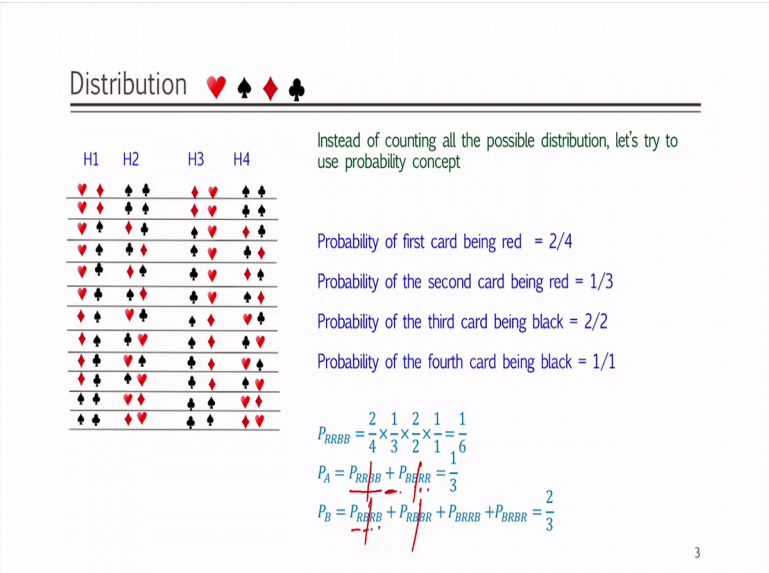

second card black, third card black and fourth card red.

Also the another

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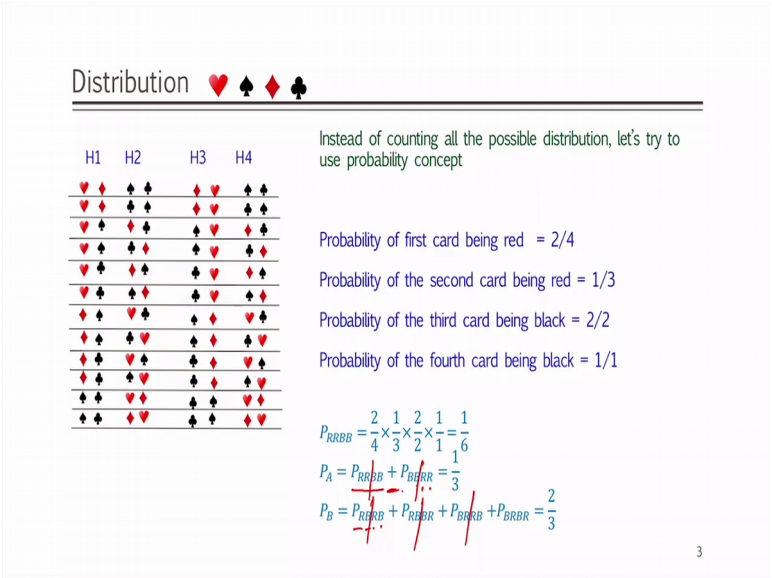

situation will happen when first card black, second card red, third card black and black so basically if do it in a short notation it is R B R B or R B B R or B R R B and B R B R, all possible

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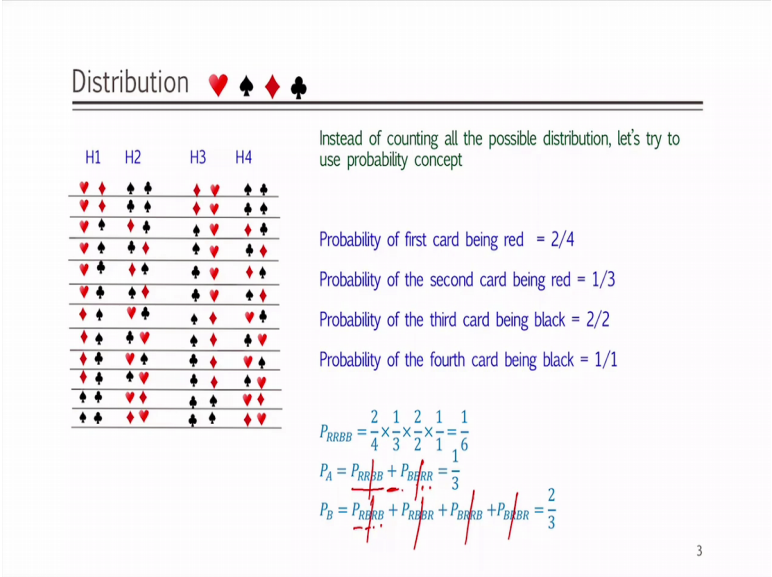

situations will give that. Each of them has 1 by 6 possibilities. When you add them up

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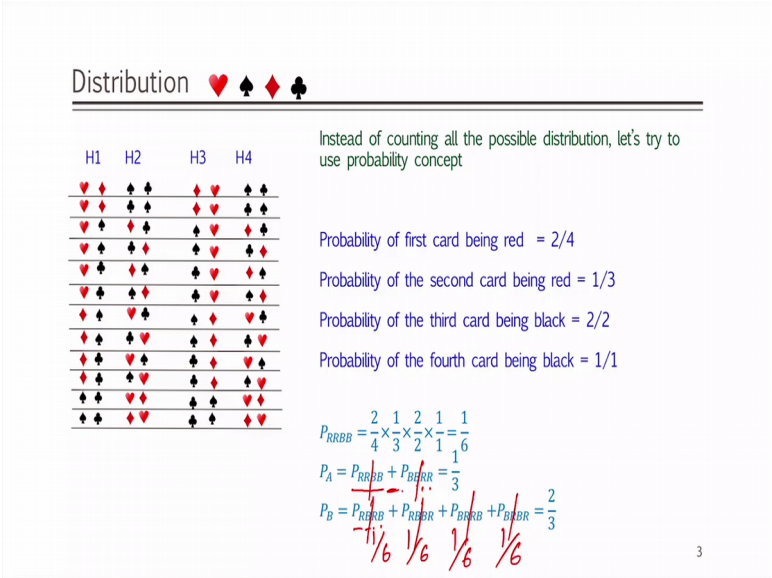

you will get 4 by 6 or 2 by 3.

So mixed color cards as you can see will have double probability than the same color card.

So now we know that what distribution is? How you are using probability to estimate the probability of one particular distribution? Why it is important? You will come to know soon enough.

Why we are talking about cards? Because it is simple enough. We can understand from this and then we can apply to a realistic situation later on.

So scientists always try to think about think from a very simplistic point of view so that they understand what happens in simple things. Once they understand that completely then only they apply to a more complicated systems like a glass of water. Believe me this is extremely complicated.

Even the theories of that will not be even discussed in this particular course and sometimes even, you know later courses. We still deal with very simple situations and try to understand that. Only very complicated situations we will try to deal with, systems like water.

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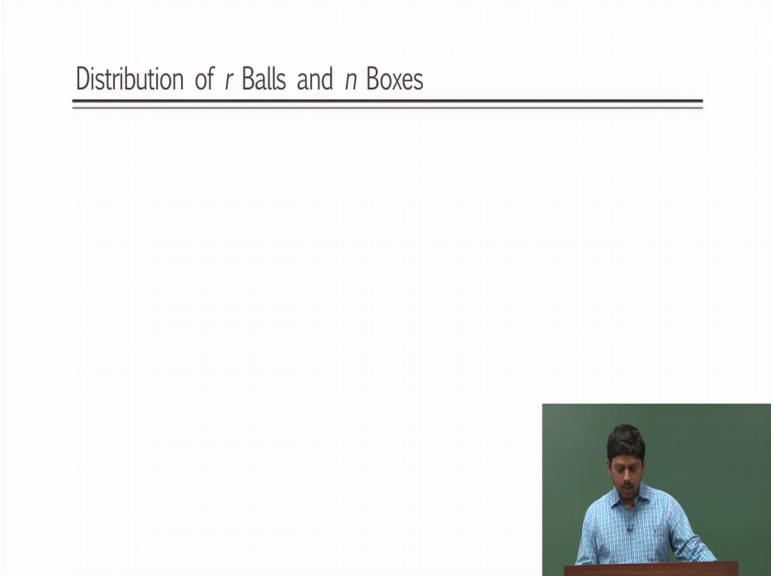

So now the situation that I talked about, distributing cards in hands, the similar situations or most common probabilistic situations is distribution of r balls in n boxes, we can say in n boxes.

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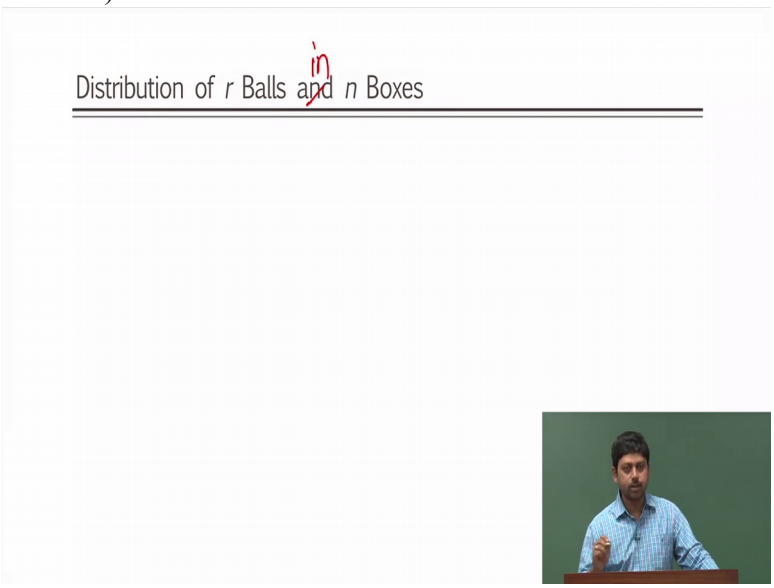

This is, this particular problem, r balls in n boxes is so common that it can be used in many different situations.

It can be mapped or it can be thought of or projected in many, many different situations including that of our current discussions of number of microstates of particles and then chemical systems and things like that.

I will give you some example.

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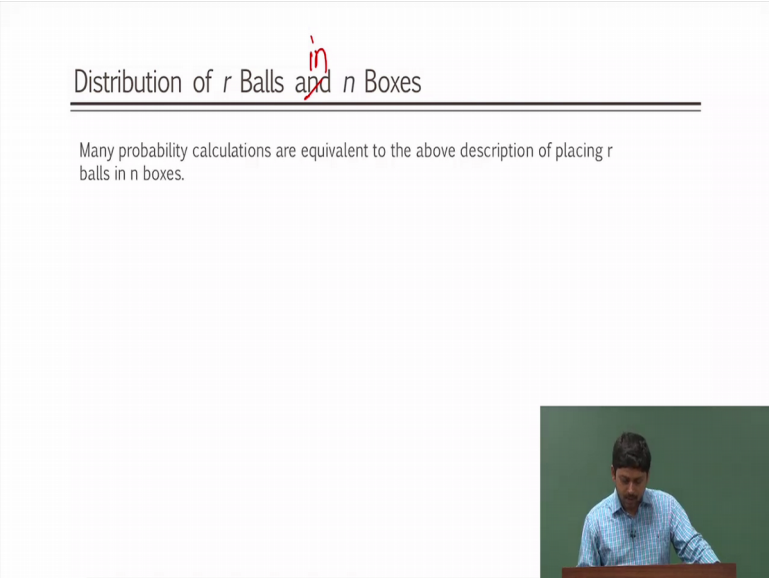

So as I said many probability calculations are equivalent to the above description of placing r balls in n boxes. For example

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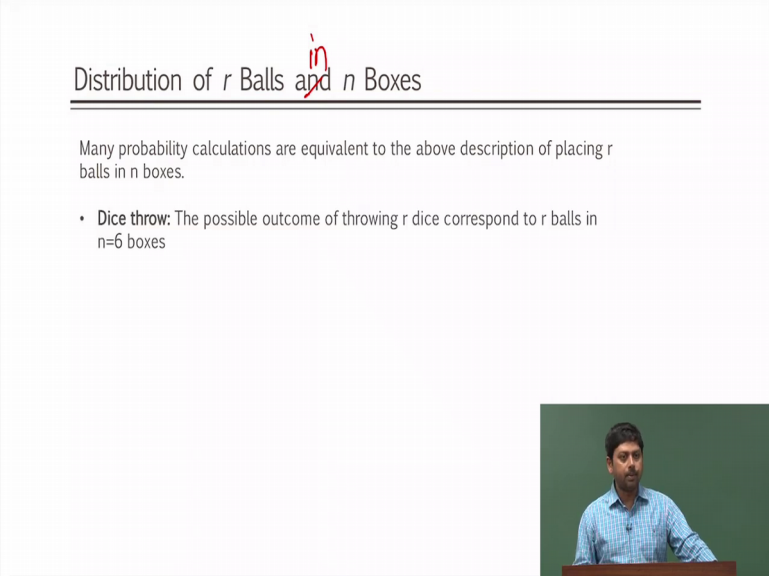

we talked about dice throw, right. Dice is what; there are all 6 possibilities, right for one particular dice.

When I throw the second die, what you say, again 6 possibilities, right? So you can think of the possible outcome of throwing r dice, let us say, is corresponding to placing r balls in n equal to 6 boxes.

Why that is a, why we are saying that? For example if you have n equal to 6 boxes means the box are distinguishable. That means if I get 1 by throwing a dice it means I am putting a ball in box number 1.

If I get 5 by throwing a dice I will say that I am putting a ball in box number 5. And my balls are distinguishable because I throw the first dice, I throw the second dice.

So my dices are distinguishable because I have first dice, I have second dice, I have third dice and

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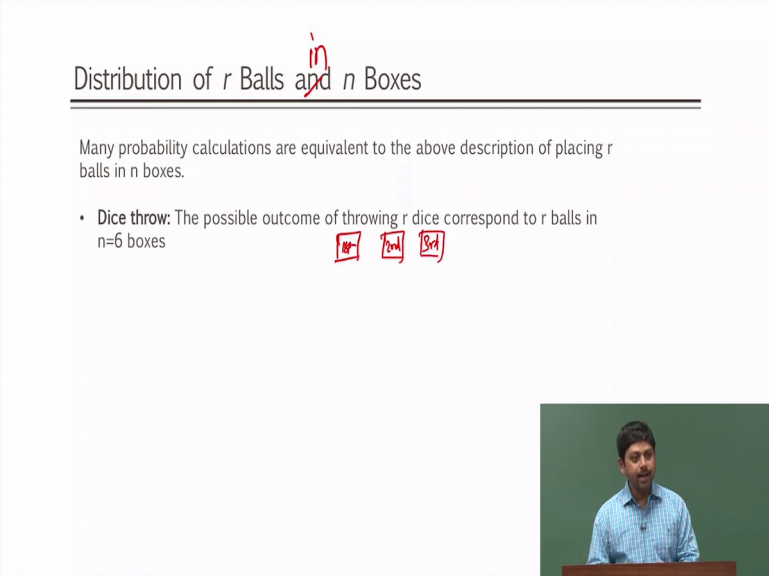

the boxes are

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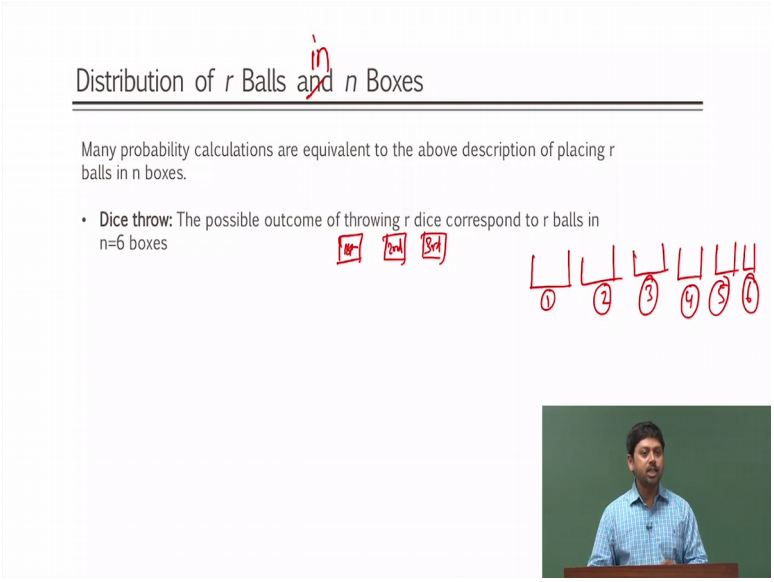

denoting, the boxes are denoting what is the outcome of throwing a die?

So in a way you are looking at situations of placing r distinguishable particles, why distinguishable, because first dice, second dice, third dice we know, in 6 distinguishable boxes. Why distinguishable boxes because outcomes are distinguishable.

So that means if I throw 2 dice for example, so if I throw 2 dice then my r equal to 2

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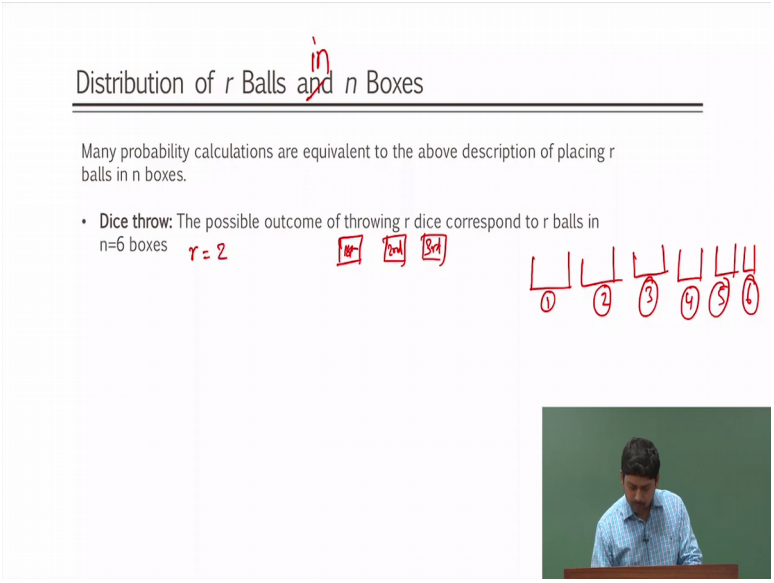

and n equal to 6.

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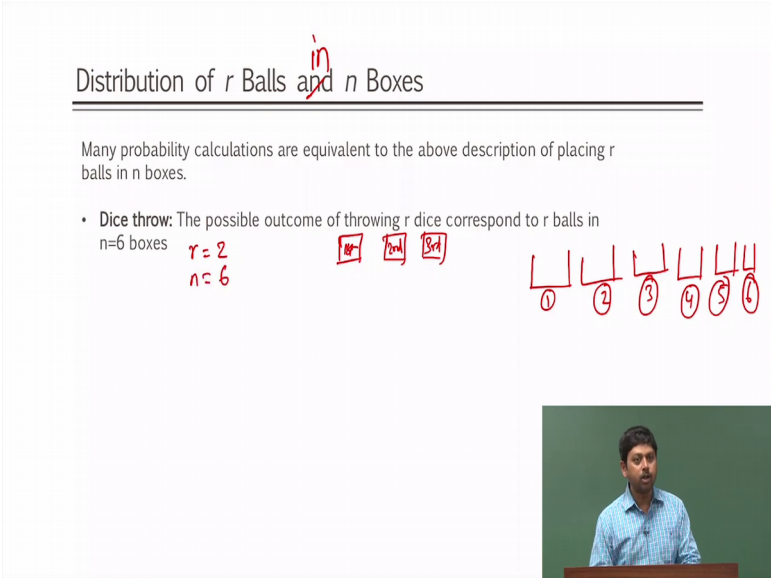

What are the possibilities that I can get?

I can get any of the 6, I can put in any of the 6, any of the 6 boxes, the outcome is 6. Second time also I have the outcome of 6. So when I throw 2 dice

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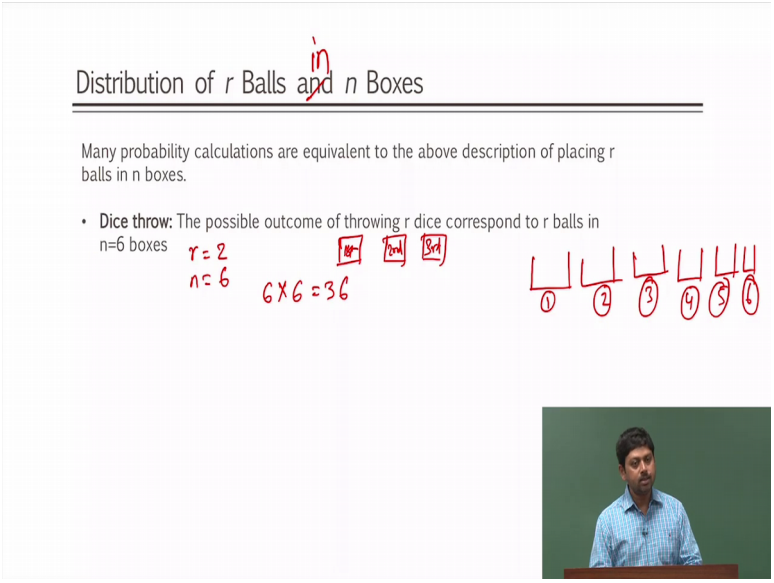

it is 6 into 6, or 6 to the power 2.

If I throw it 3 times it is this, 6 to the power 3.

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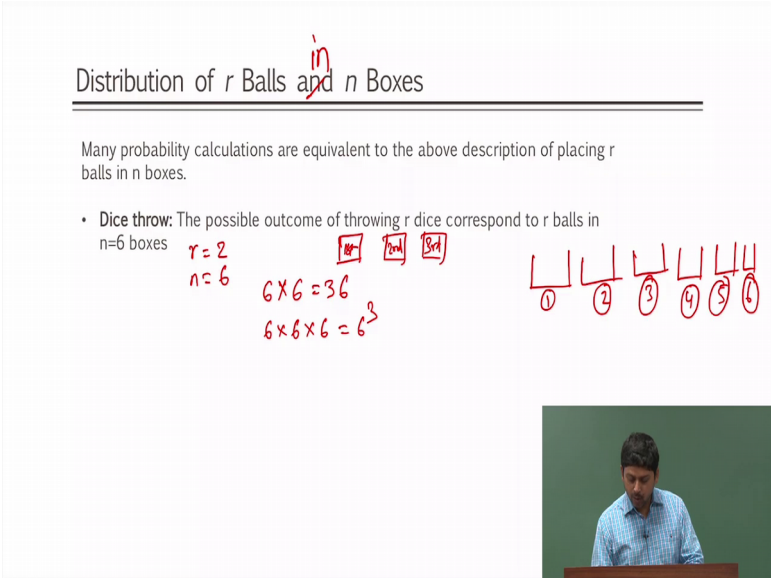

If I throw it how many times, r times, right it will be 6 to the power r. So in general my formula of placing r distinguishable ball in n boxes is n to the power r,

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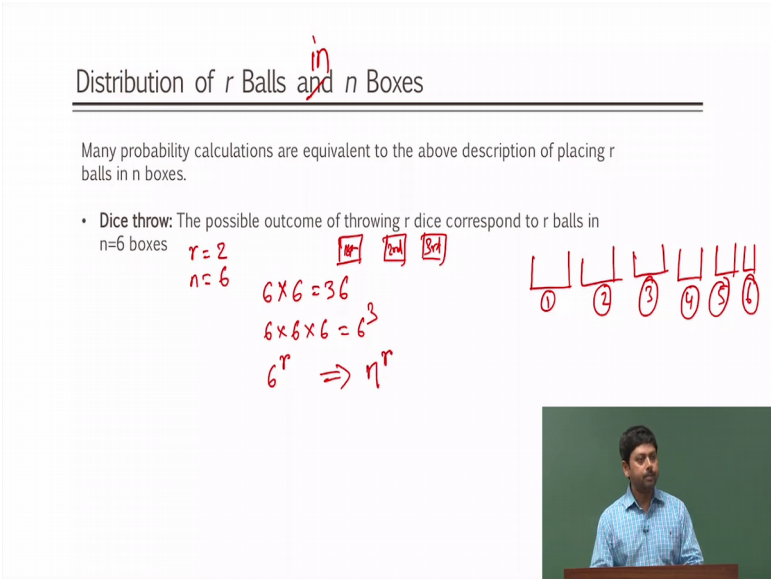

because....I will come back to that more on this.

Another situation

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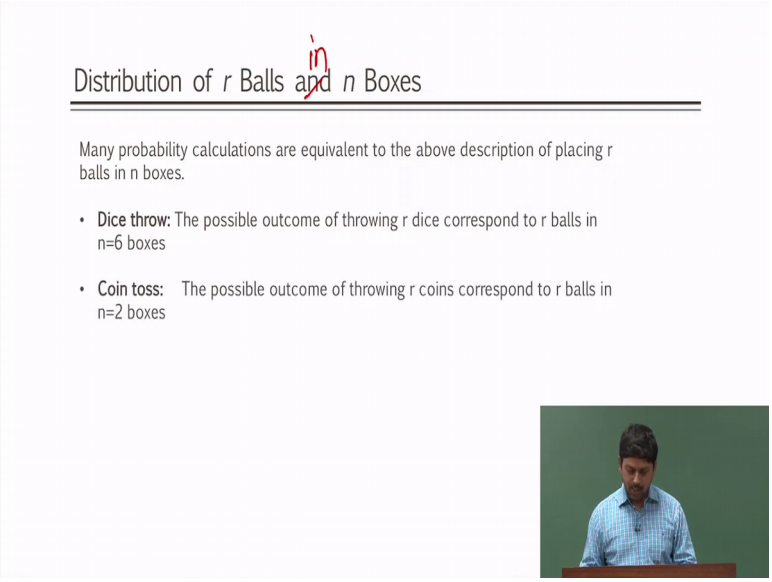

is that of coin toss. Now can you tell me that how the coin toss can be associated with putting ball in the boxes?

So coin tosses has two outcomes, head or tail. So I can say that 1 box is head, another box is tail. And my first coin is a, you know one ball, my second coin is another ball, my third coin is another ball.

So it is putting r balls into 2 boxes. So first box, first ball can be in any of the 2 boxes, so 2 possibilities. Second ball can be in any of the two boxes so 2 possibilities. So like that if I have r balls it will be 2 to the power r possibilities.

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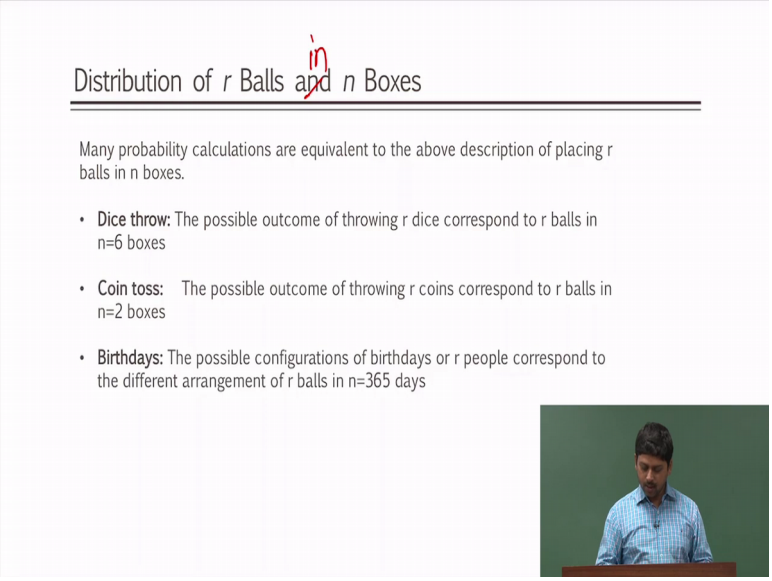

Birthdays, another example that the possible configurations of the birthdays of r people. So first person can have birthday any of one 365 days. Second person can have birthday any of 365 days. Third person can have, so here n is 365. So boxes are 365 boxes. You can number them according to the number of the days.

And people are like balls. So you are putting them on the first day on the calendar, this is a calendar. And my birthday is let us say, for example 8 August. So I will be on that day, I will be standing on that day. Somebody else will be standing on some other day.

So you can imagine that birthdays are nothing but putting distinguishing balls like you and me into distinguishable boxes like that particular day of the calendar.

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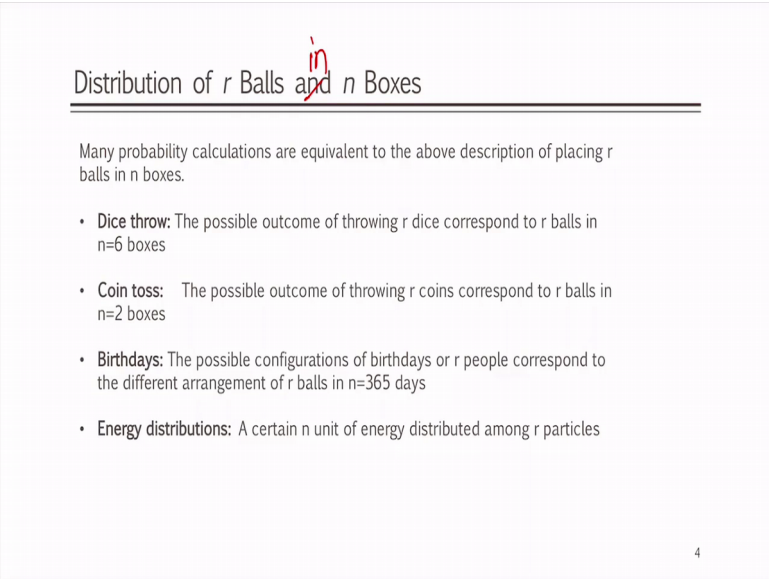

Another example, energy distribution. A certain n units of energy distributed among r particles, that is a possibility, right. So you can say that in this case, you know, of course the energies are not distinguishable in some sense but you can say, we are talking about balls and boxes

So we can say that we are putting some, you know definitive energy values, either epsilon, 2 epsilon, 3 epsilon into, you know r particles.

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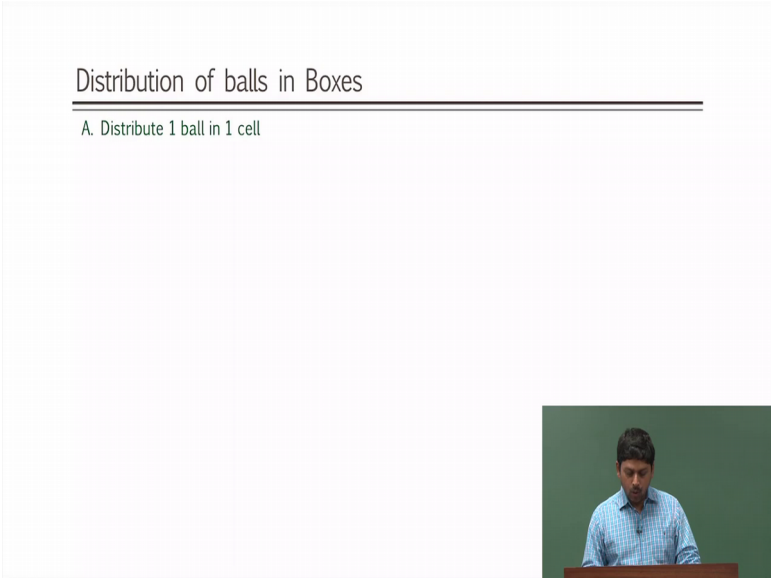

So let us first start with very simple system. So we have seen that by working on the distinguishable, working on this placing balls in boxes we can understand different situations related to creating new microstates including, you know talking about the cards for example we had like 4 cards, right.

We saw that there are 4 cards and there are 4 distinct possibilities, heart, spade, club and diamond. So you can say that there are 4 possibilities and you know in that 4 possibilities if you have multiple number of cards, for example 52 cards then you will actually get placed them accordingly, right, anyway.

So let us start with very simple system. Distribute 1 ball in 1 box,

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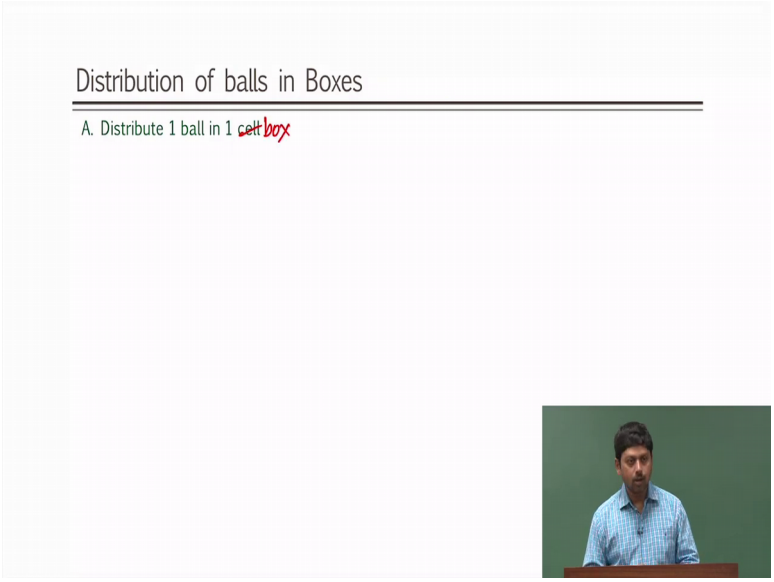

1 ball in 1 box. How can you do that? You have only 1 ball and 1 box.

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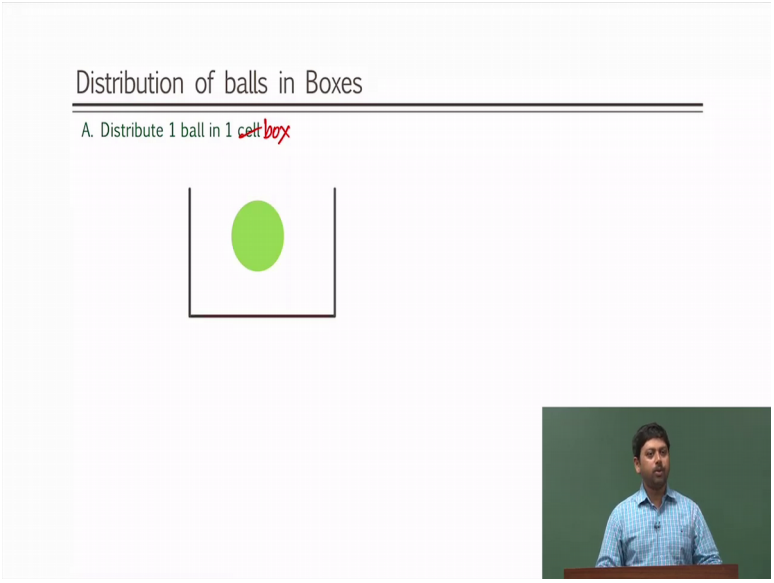

How many possibilities can you imagine? 1 ball and 1 box, just 1 possibilities.

So I will say number of possibilities we are denoting by W, remember? We said that W is number of microstates; we can say number of possibilities as well.

And since microstate is equivalent to entropy then entropy is equivalent to possibilities or options, that is what we discussed, right?

So let us call that as W. And that

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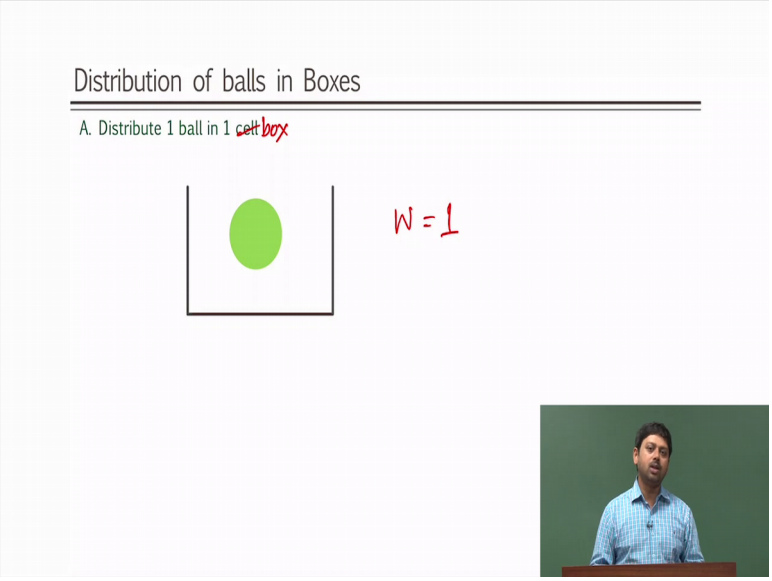

can be only 1. We can no other way. If I have to place it I have to place it, but let us say I have to place it, Ok. I may not choose to place it, that is another possibility.

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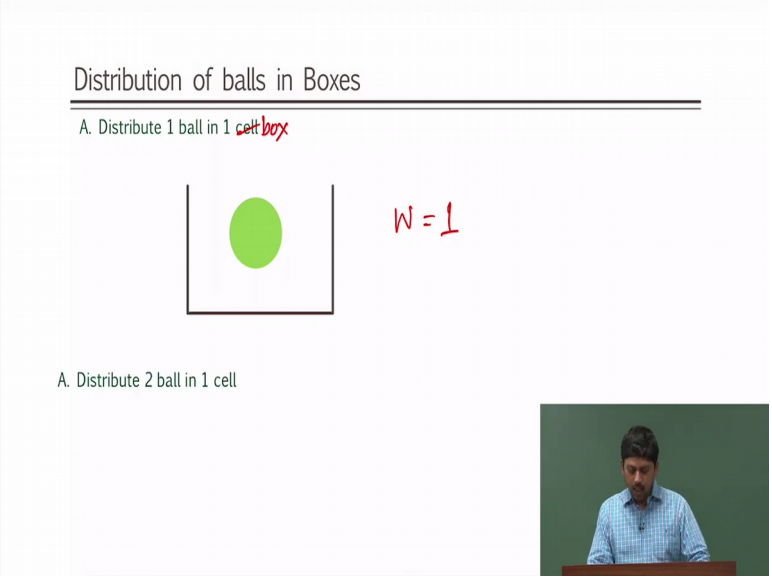

Distribute 2 balls in 1 box.

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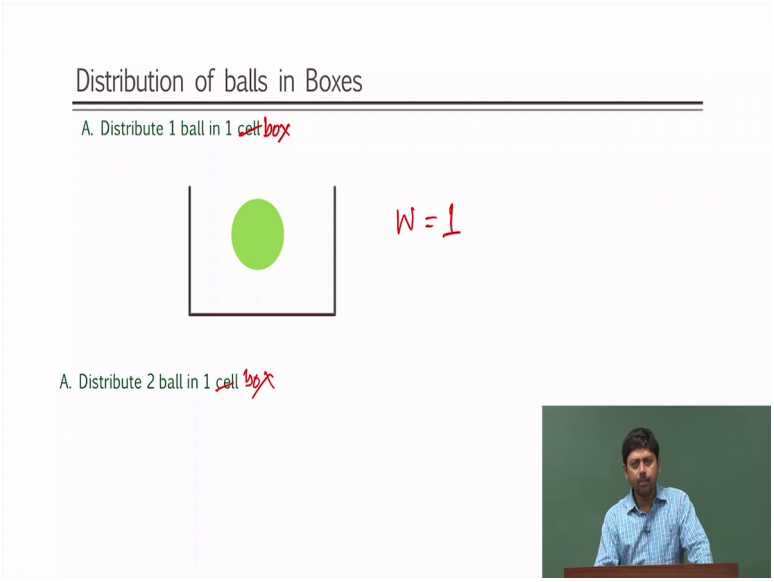

Cell and box are actually the same thing but just specifying box. These are our box, right, these are typical box and this is the ball that we are talking about, Ok.

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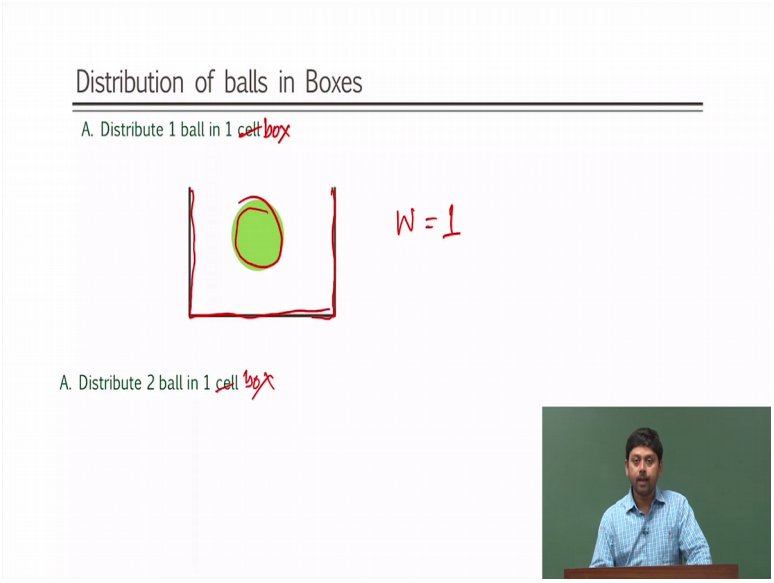

2 balls in 1 box.

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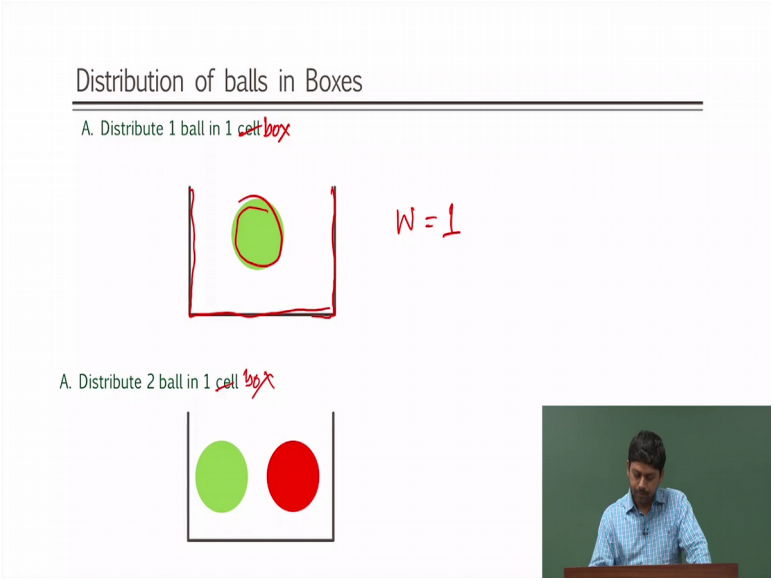

How many ways you can do that? I have to place 2 balls. Only 1. I do not see any other way.

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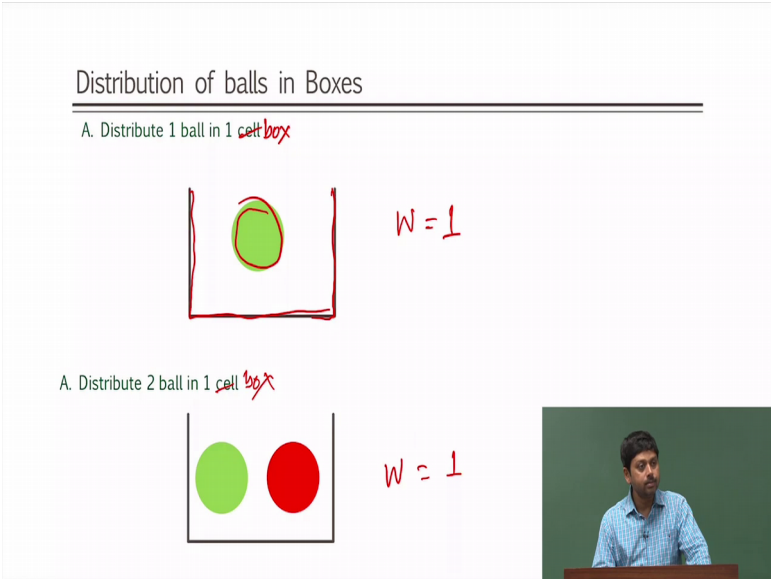

So box is important. So you remember I was saying, imagine the, what is the formula we got?

Number of boxes to the power balls, is not it?

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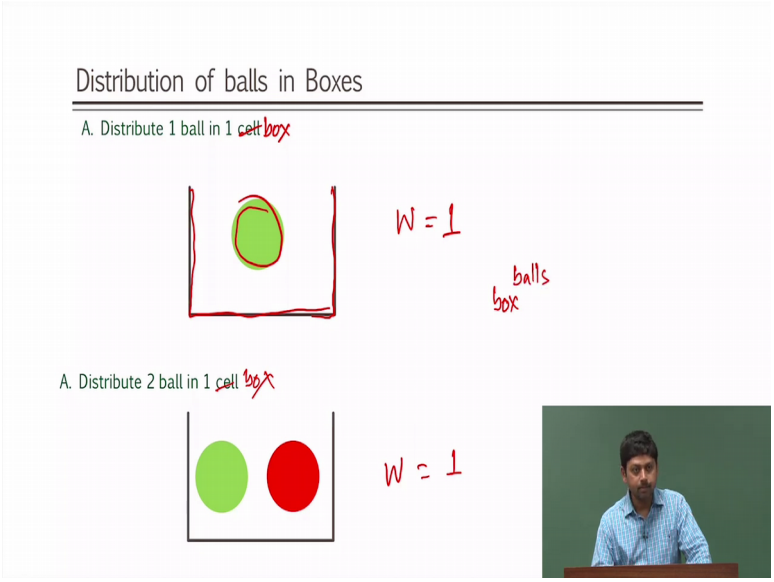

So in this case it is 1 to the power 1 equal to 1. In this

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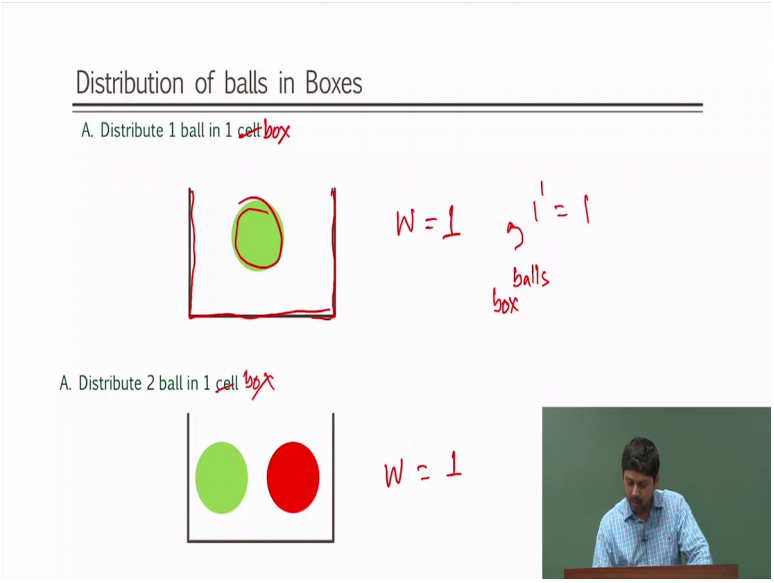

case it is 1 to the power 2 is also 1.

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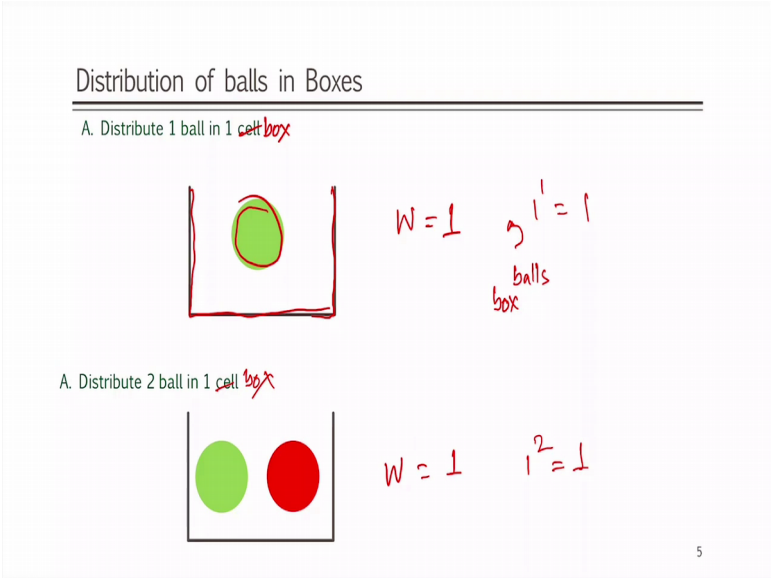

Now let us go to little bit more

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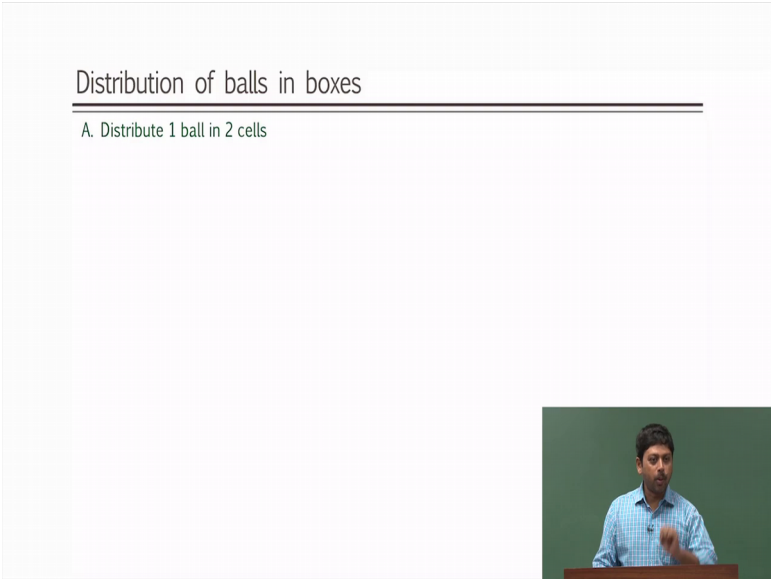

complicated situation. One ball in 2 boxes. I have these

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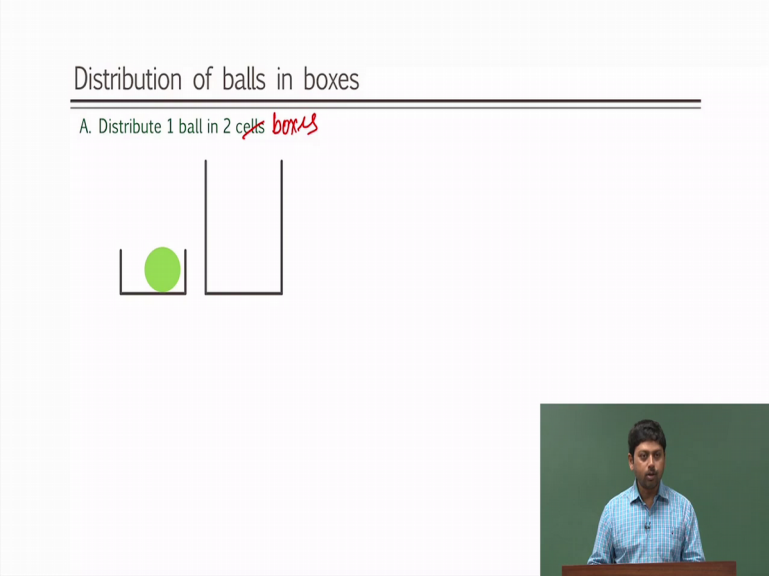

2 box. And I have one ball. I can place it either in the left box or on the right.

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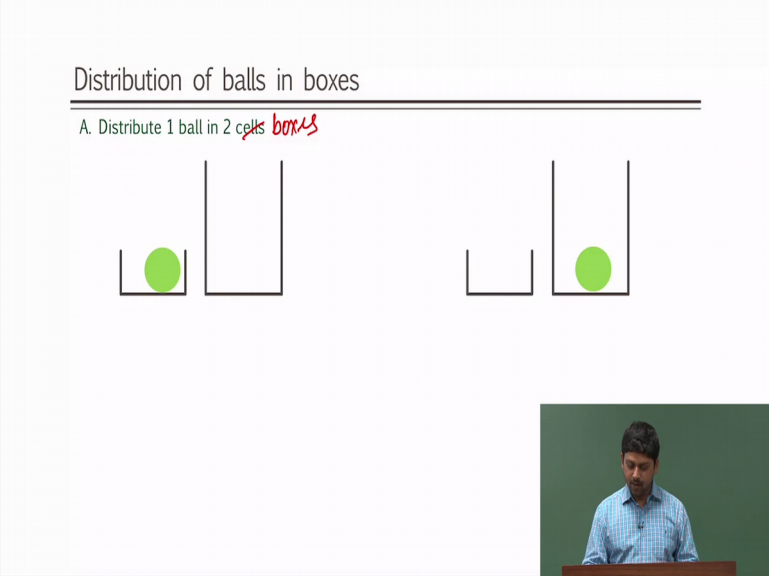

I can place it on the left box or on the right box. So I am getting

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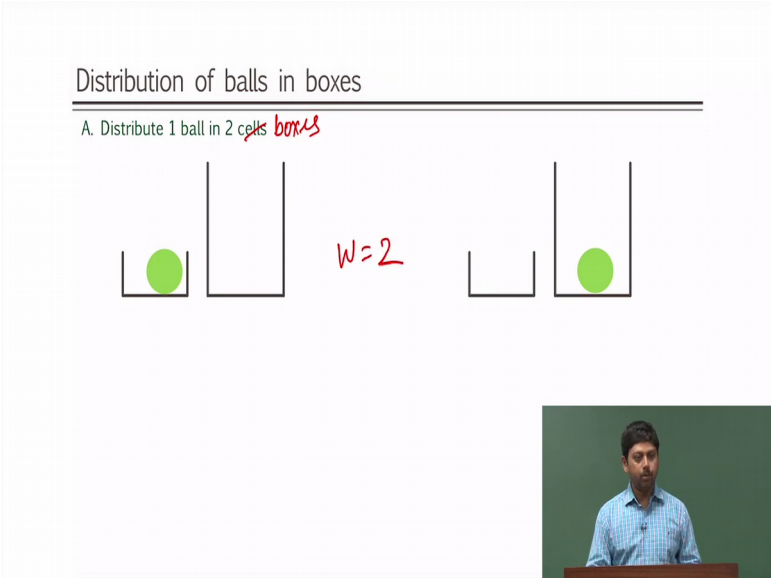

W equal to 2.

So here what is the situation? Box to the power ball, right, box is 2, ball is 1, is equal to 2.

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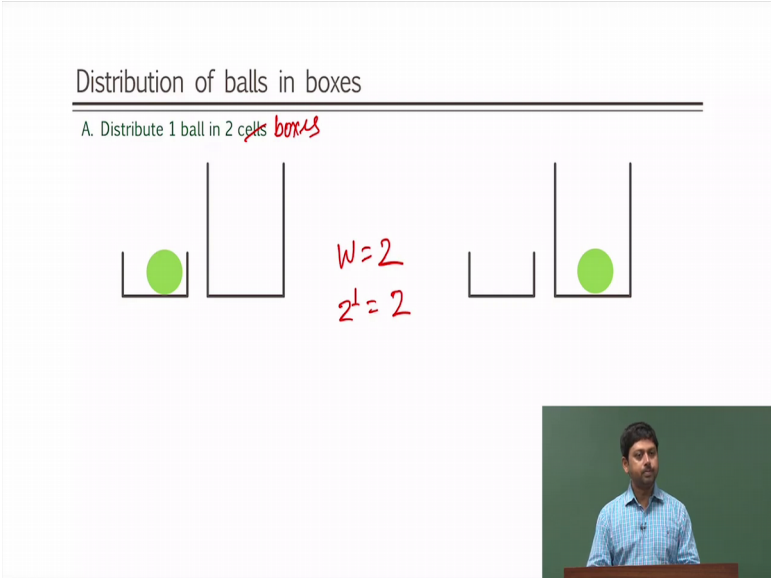

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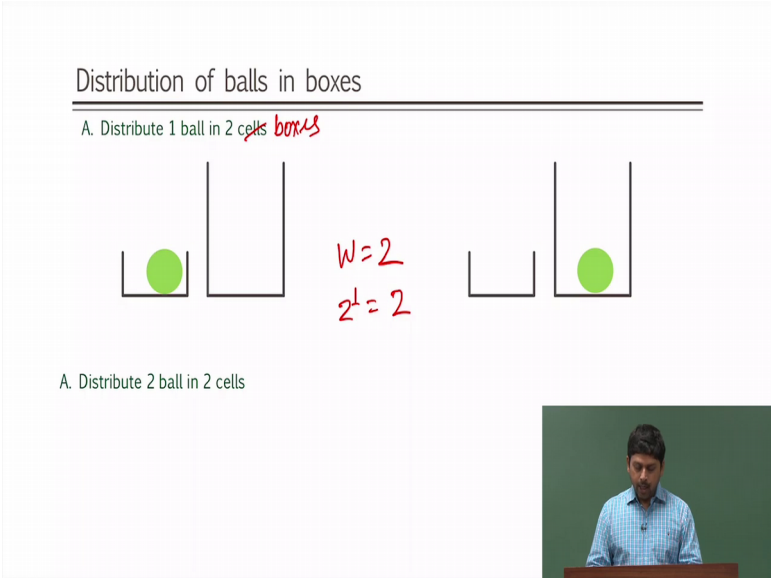

n to the power r is the situation where balls and boxes are both distinguishable. That is why I draw, I drew the boxes are both distinguishable. That is why I draw; I drew the boxes in a distinguishable fashion.

Distribute 2 balls in 2 boxes,

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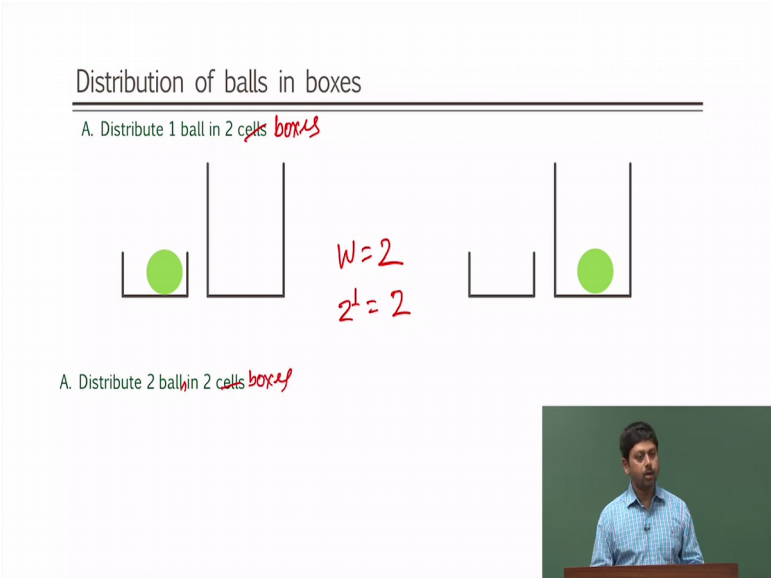

2 balls in 2 boxes. You will see what will be the answer, right? 2 balls, 2 boxes; it should be 4,

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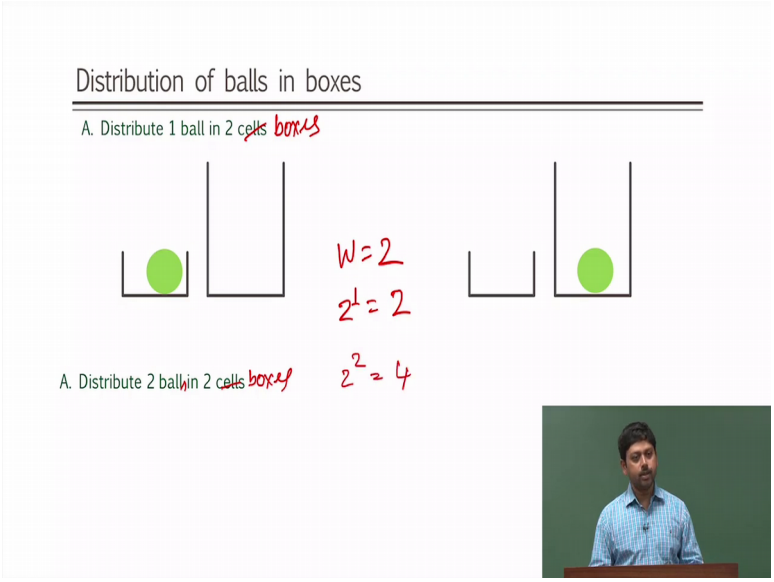

is it not? Let us see,

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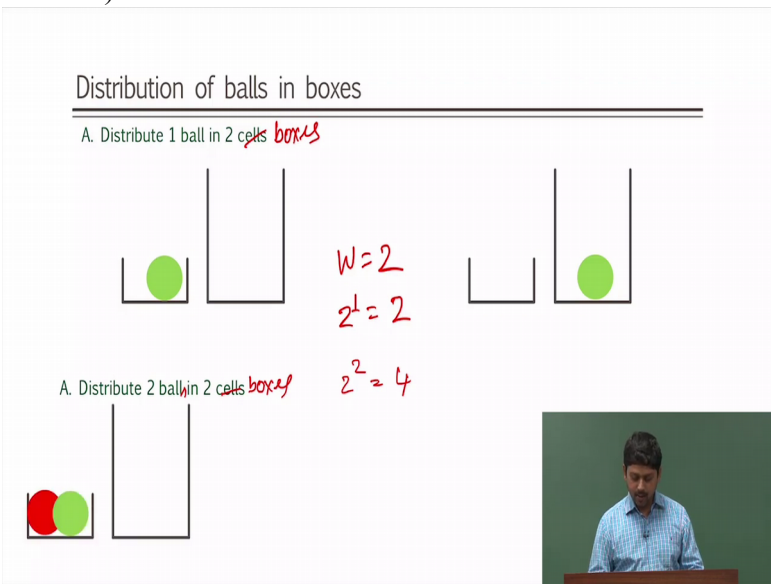

2 ball on the left box,

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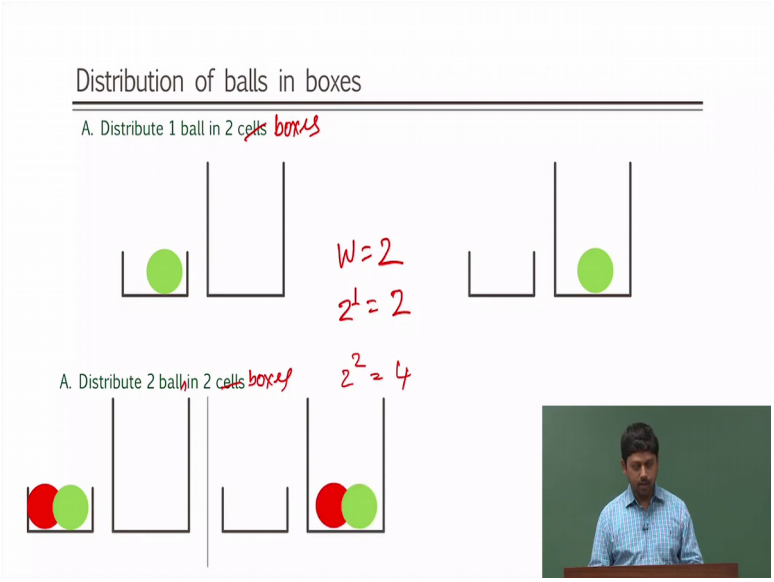

2 ball on the right box,

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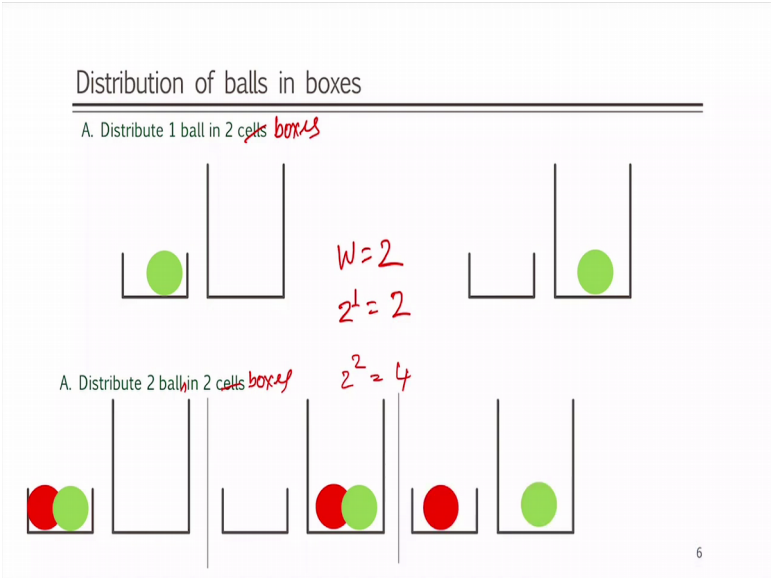

2 ball on individual boxes and

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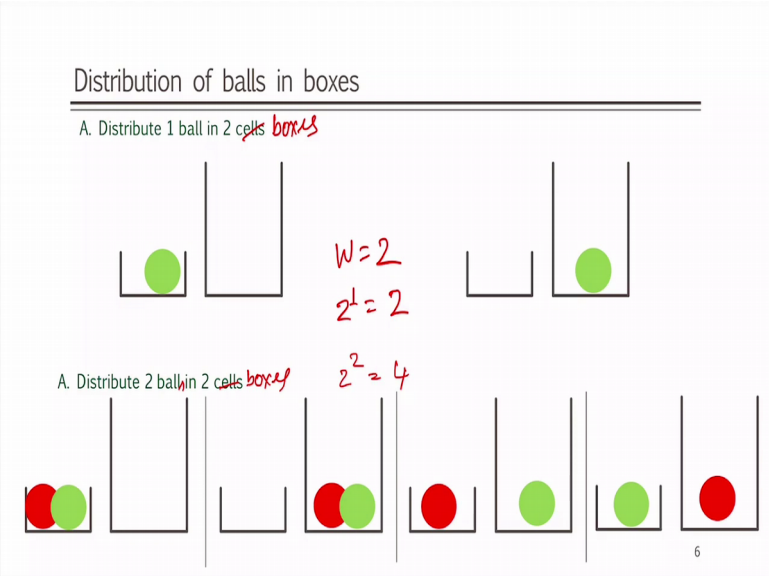

2 balls again on the individual boxes.

But sort? So you see because my boxes are distinguishable I can distinguish between this and this.

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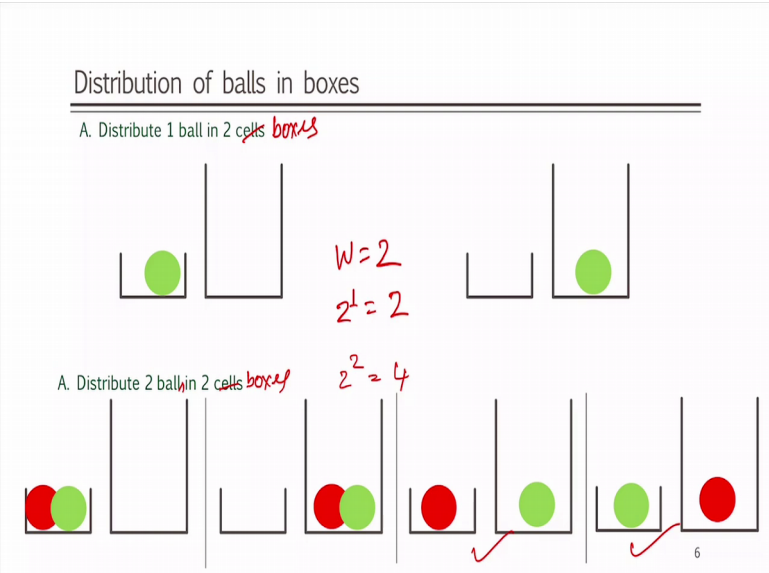

Otherwise I could not have distinguished. If my boxes were identical then this will mean the same thing.

But here boxes are also distinguishable. And therefore you can see that Ok, my green ball is in a bigger box, and here my green ball is in a smaller box. There must be 2 different configurations, not 1.

So here both the balls and the boxes are distinguishable. Otherwise we will not get all the 4 possibilities.

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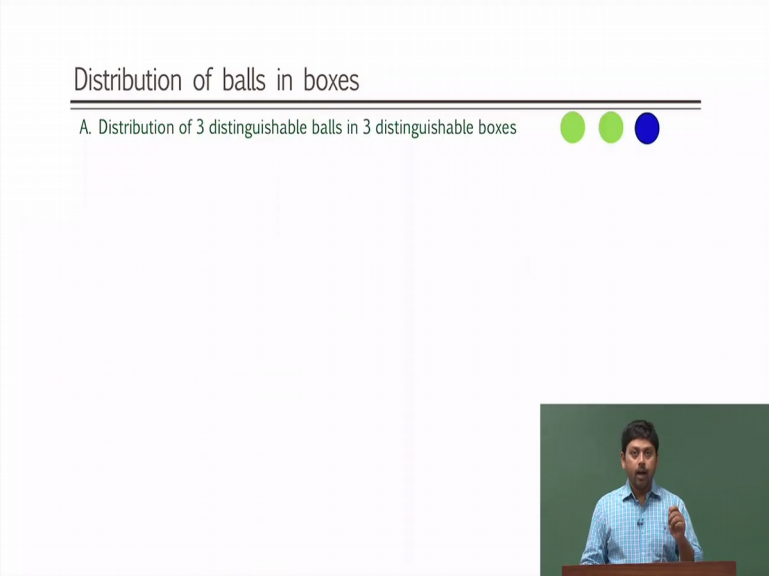

So now we are going to little more complex situations, distribution of 3 distinguishable balls in 3 distinguishable boxes.

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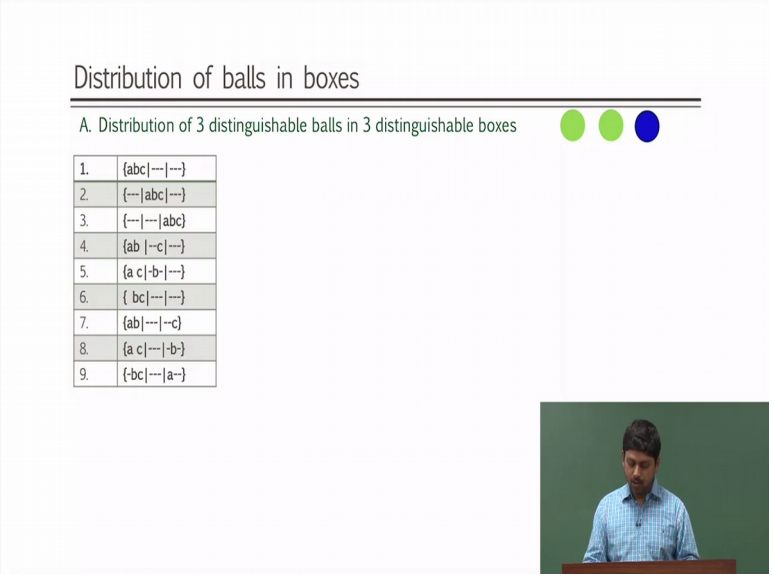

So here are 3 distinguishable balls, we will make it distinguishable, let us make it red. Now we have 3 distinguishable

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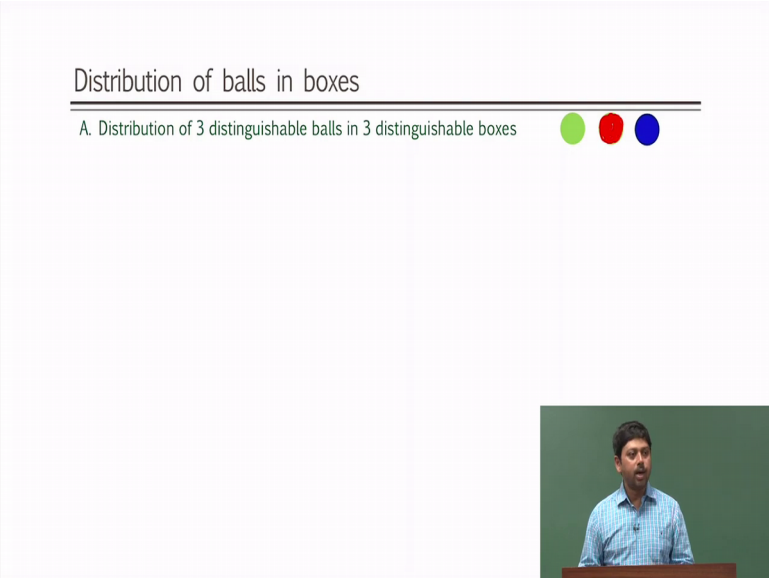

balls and I need to put it in 3

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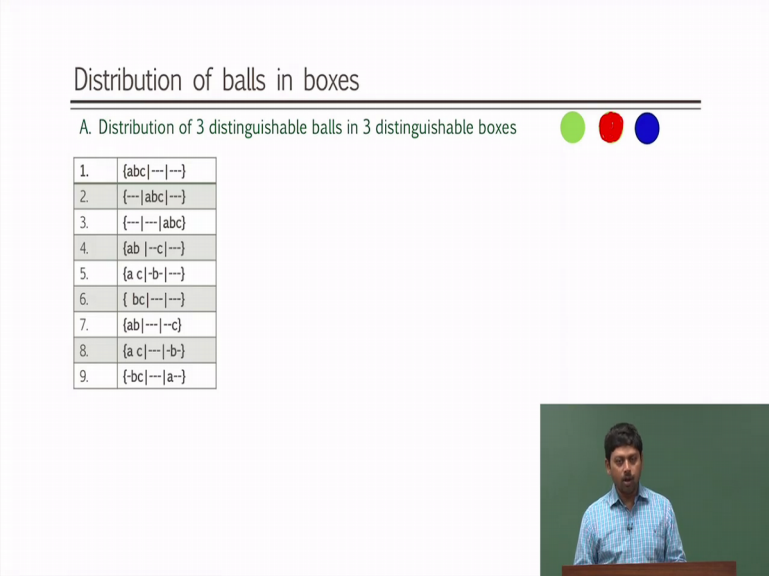

distinguishable boxes. You know the value, right. It will be n to the power r, 3 to the power 3 equal to 27.

Let us see all those 27 possibilities. I can call them also as a, b and c,

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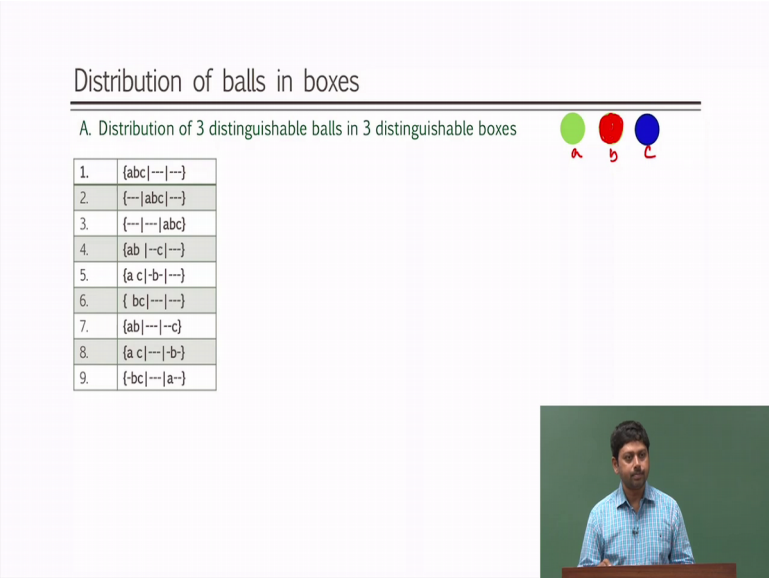

Ok. So here as you can see all a b c are put in the first box. And nothing on the second and third box.

Here all a b c are put in the second box, nothing on the first or third. Here all a b cs are put on the third box, nothing on the first or second.

And like that we get

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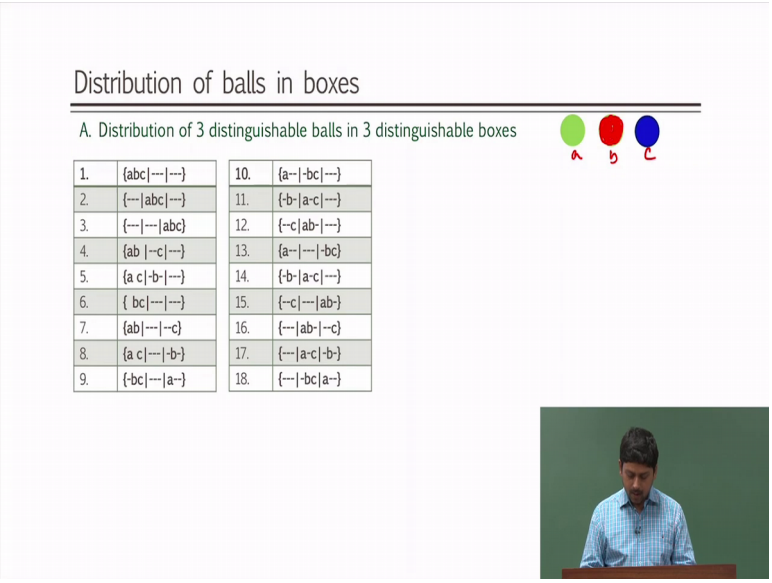
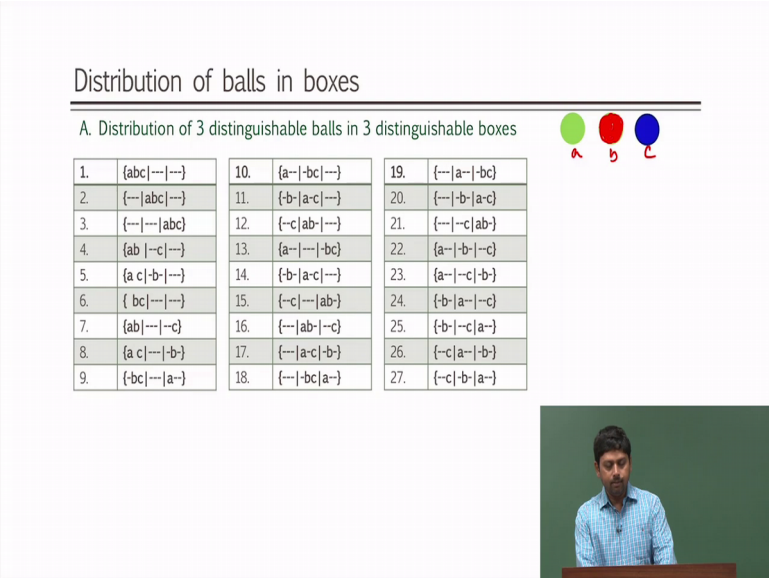


18 and

(Refer Slide Time: 29:25)



finally all 27 possibilities. Because I did not have enough, you know space here I could not really draw the boxes and balls and show the configuration.

So this is the short hand notations by which I am showing all possible combinations of putting 3 distinguishable balls in 3 distinguishable boxes. How the boxes are distinguished?

The first one, the first box is, let us say you can call it 1, box number 1, second is box number 2 and third is box number 3.

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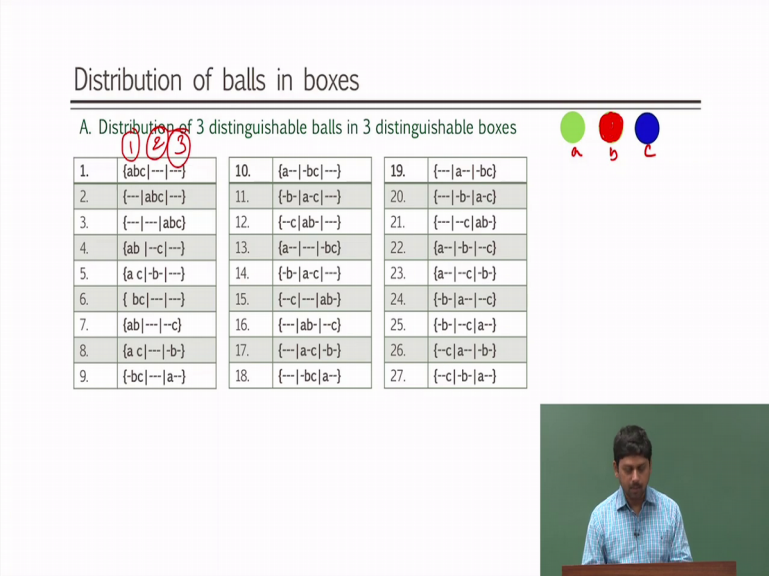

Once you distinguish the box, then you can automatically get that these should be the possibilities.

And as you see that here also I have number of, n equal to 3 and r equal to 3

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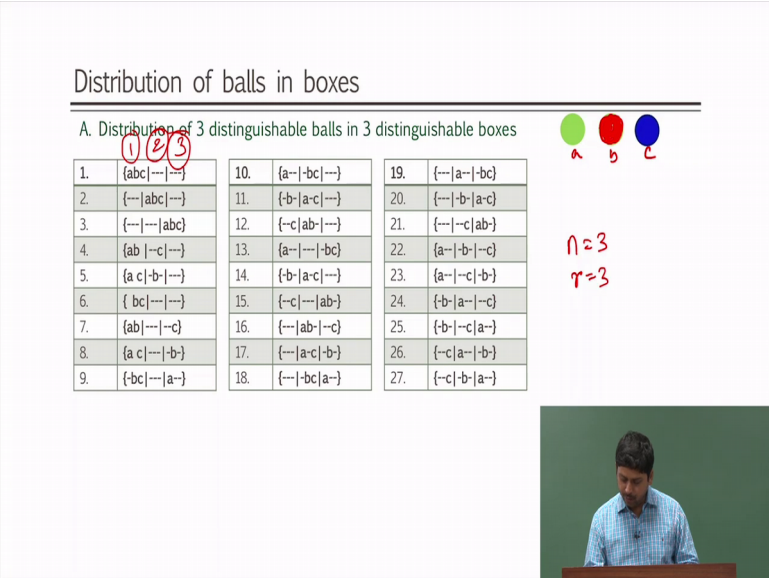

and therefore number of possibilities is, as we saw n to the power r or 3 to the power 3 are 27.

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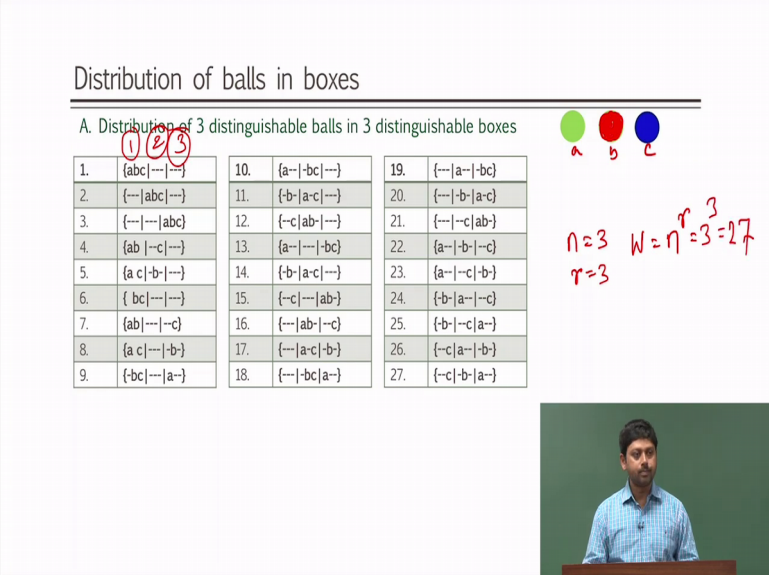

Now think of that as this way.

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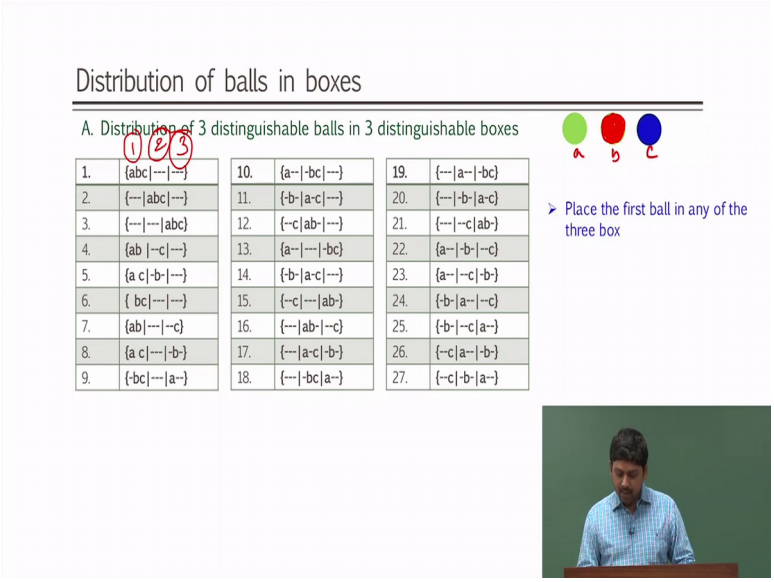

1.	{abc|---|---}	10.	{a--|-bc|---}	19.	{---|a--|-bc}
2.	{---|abc|---}	11.	{-b-|a-c|---}	20.	{---|-b-|a-c}
3.	{---|---|abc}	12.	{--c|ab-|---}	21.	{---|--c|ab-}
4.	{ab |--c|---}	13.	{a--|---|-bc}	22.	{a--|-b-|--c}
5.	{a c|-b-|---}	14.	{-b-|a-c|---}	23.	{a--|--c|-b-}
6.	{ bc|---|---}	15.	{--c|---|ab-}	24.	{-b-|a--|--c}
7.	{ab|---|--c}	16.	{---|ab-|--c}	25.	{-b-|--c|a--}
8.	{a c|---|-b-}	17.	{---|a-c|-b-}	26.	{--c|a--|-b-}
9.	{-bc|---|a--}	18.	{---|-bc|a--}	27.	{--c|-b-|a--}

Place the first ball in any of the boxes. So let us say I have 3 boxes, right. Box number 1, box number 2 and box number 3,

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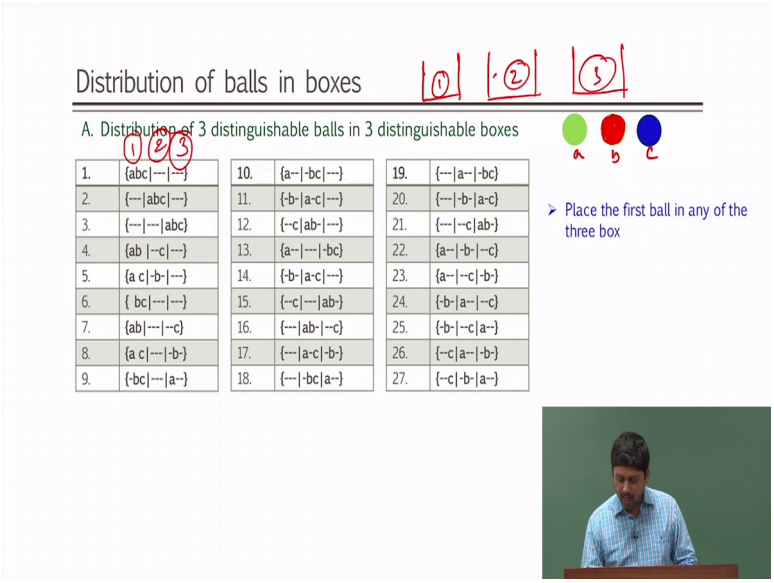

1.	{abc|---|---}	10.	{a--|-bc|---}	19.	{---|a--|-bc}
2.	{---|abc|---}	11.	{-b-|a-c|---}	20.	{---|-b-|a-c}
3.	{---|---|abc}	12.	{--c|ab-|---}	21.	{---|--c|ab-}
4.	{ab |--c|---}	13.	{a--|---|-bc}	22.	{a--|-b-|--c}
5.	{a c|-b-|---}	14.	{-b-|a-c|---}	23.	{a--|--c|-b-}
6.	{ bc|---|---}	15.	{--c|---|ab-}	24.	{-b-|a--|--c}
7.	{ab|---|--c}	16.	{---|ab-|--c}	25.	{-b-|--c|a--}
8.	{a c|---|-b-}	17.	{---|a-c|-b-}	26.	{--c|a--|-b-}
9.	{-bc|---|a--}	18.	{---|-bc|a--}	27.	{--c|-b-|a--}

I can pick up any of the a b, cs and put on the first box.

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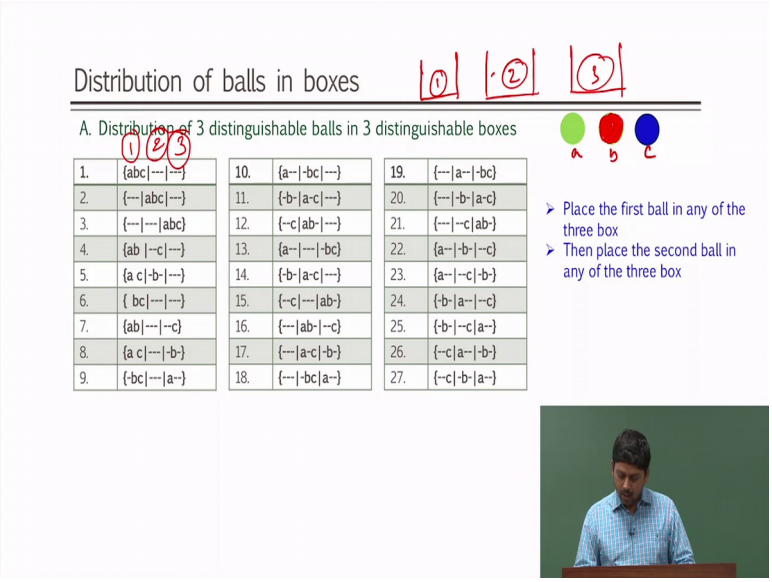

And then I can take it out. It is called placement with replacement and then place the second ball

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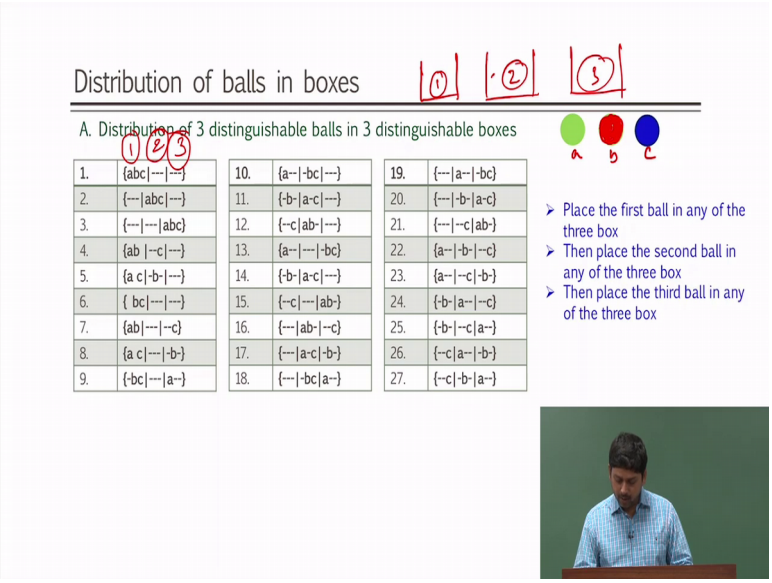

and the third ball.

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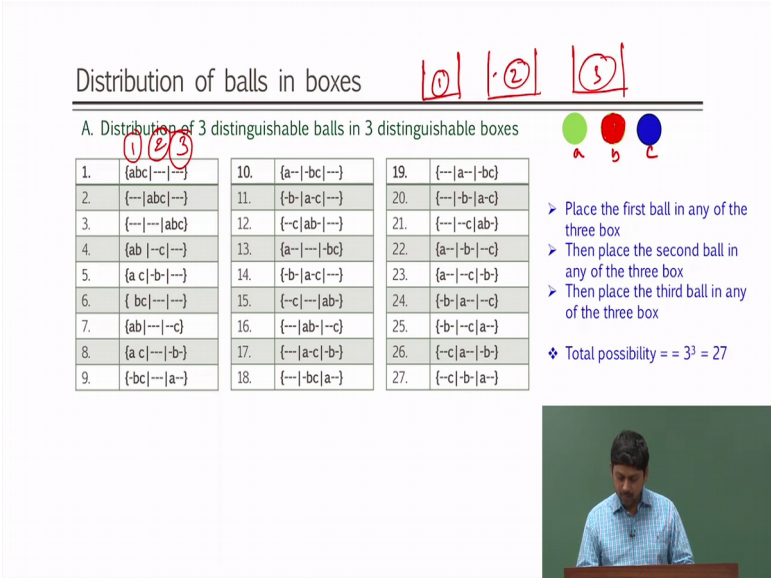

So here, place the first ball in any of the 3 boxes.

Then place, then you can take it out

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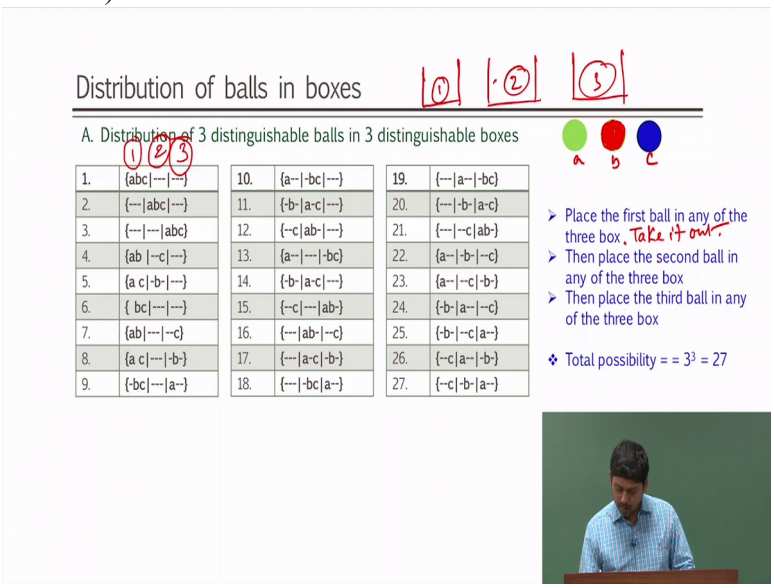

and then place the second ball in any of the, this thing and take it out,

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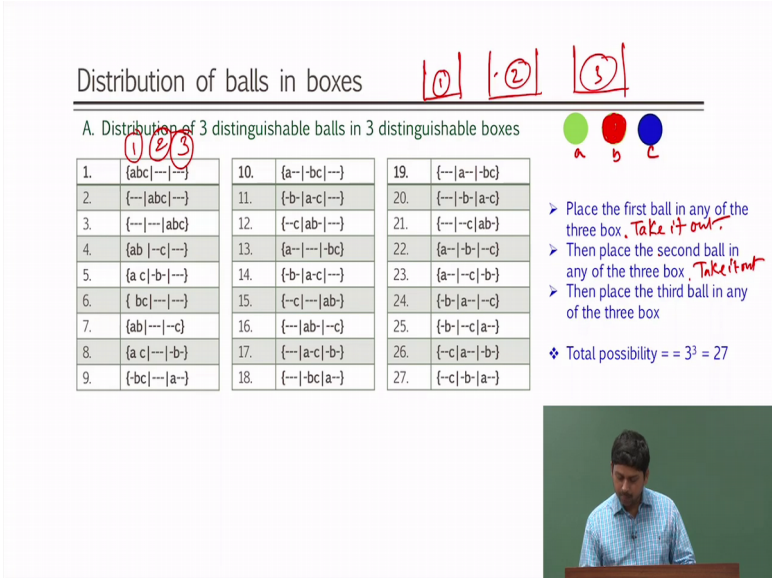

and place is a third ball in any of the boxes and take it out.

So this is called placement with replacement. Because once you placed your first ball, you will be left with only 2 more, right.

But distribution with replacement allows us to have 3 balls back again. So this particular situation of distinguishable balls in distinguishable boxes is placement with replacement. So this is called with replacement.

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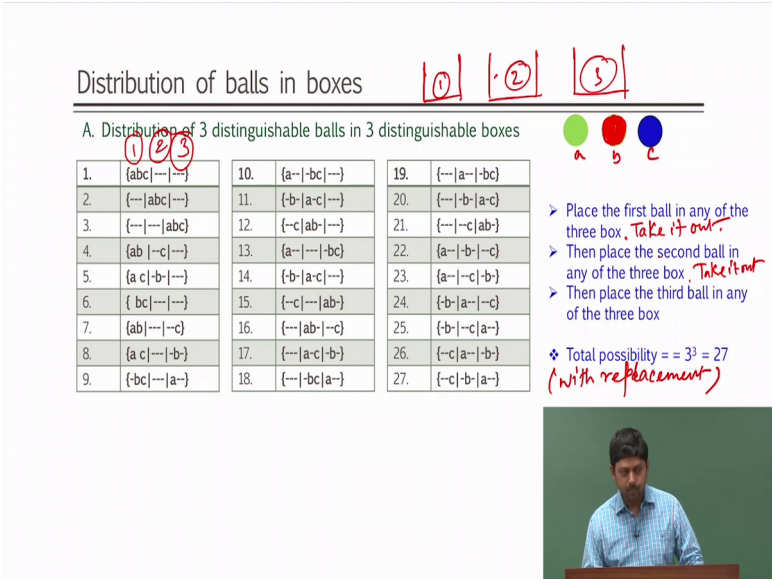

Otherwise if you put a, you do not have a. You have only b and c. But this situations I put a and then take it back again. I still have a b c. Then I can choose any of that. Again I may choose a and put it back. Again I can choose a and put it back.

So this is, this is the situation in which we call that placement with replacement. And there is some situations where we can do without replacement also. We are coming to that.

So therefore if you have r balls in n boxes

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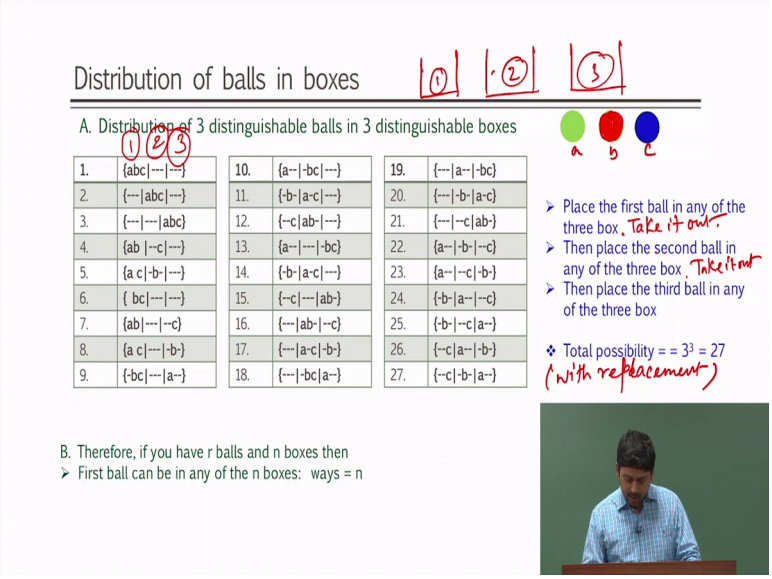

then the first ball can be any of the n boxes n ways,

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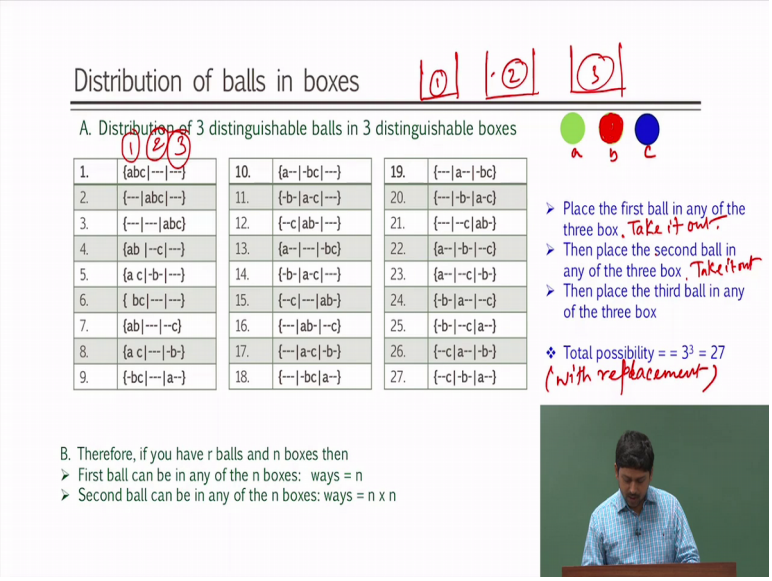

the second ball can be any of the n boxes so n into n, the third ball

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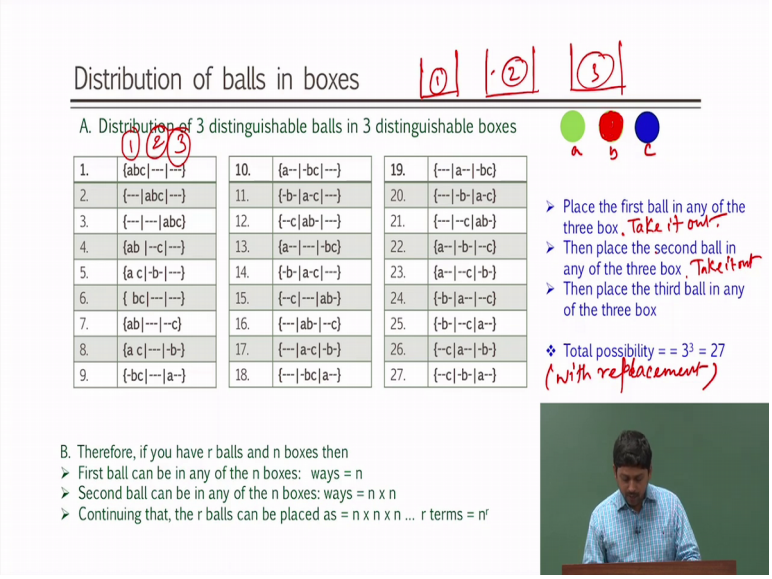

in any of the n boxes, continuing that I have r balls that can be placed in n into n into n like r times. And it would be n to the power r as we explained before.

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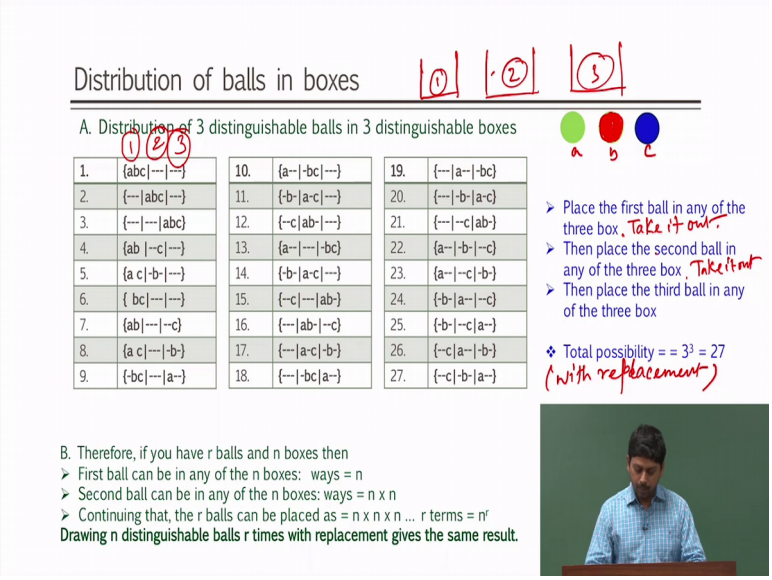

Now as I said already that drawing n distinguishable balls r times with replacement gives the same result. So let us say you have 3 color balls in a box. Now you want to pick up one of them. There are 3 ways to do that. And you put it back again.

Again you pick up, again 3 ways. You put it back again. Again you pick up. So every time you pick up you have 3 choices. So because you are replacing the ball, right, so it is called replacement distinguishable ball with, picking up r times with replacement.

So this result with replacement is very important.

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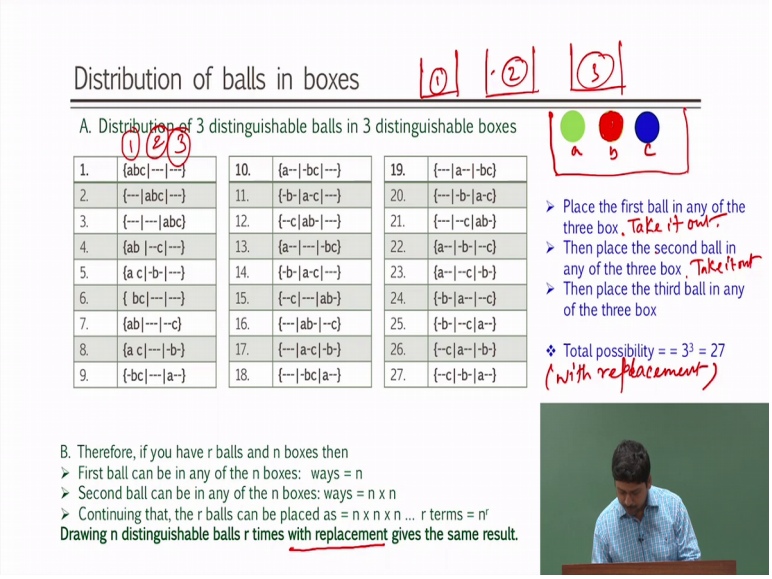

Because you are replacing the ball back again you are getting the same result, Ok. Now you will see if you do not replace it what will be the situation?

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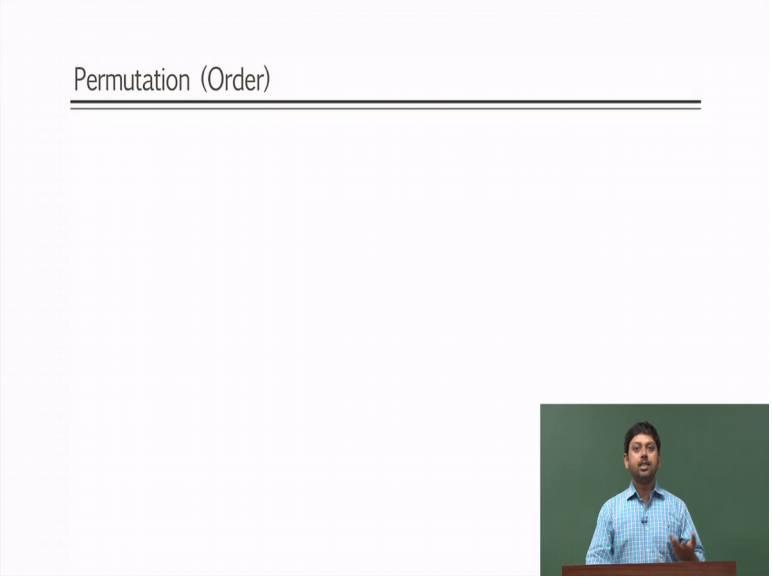

That situation is called permutation.