Chemical Kinetics and Transition State Theory
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Lecture 20
A puzzle: Cars on Highway

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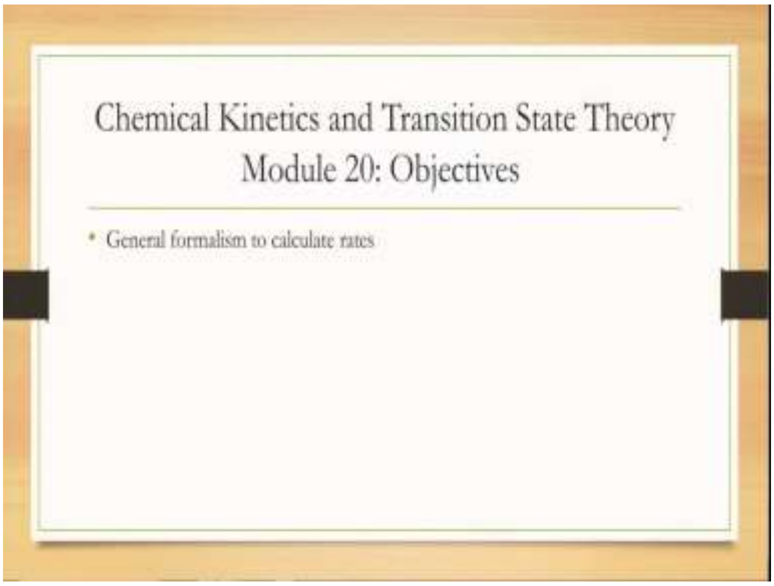

Hello and welcome to Module 20 of Chemical Kinetics and Transition State Theory. Now, we have developed some of the language of statistical mechanics specifically partition functions. Now, we want to direct our attention towards calculating rates for using these partition functions. So, before doing that, let me tell you our general prescription on how we are going to calculate the rate.

So, this is going to be a small module, but it is an important module. So, we are actually going to not think about molecules today. Let us think about something better.

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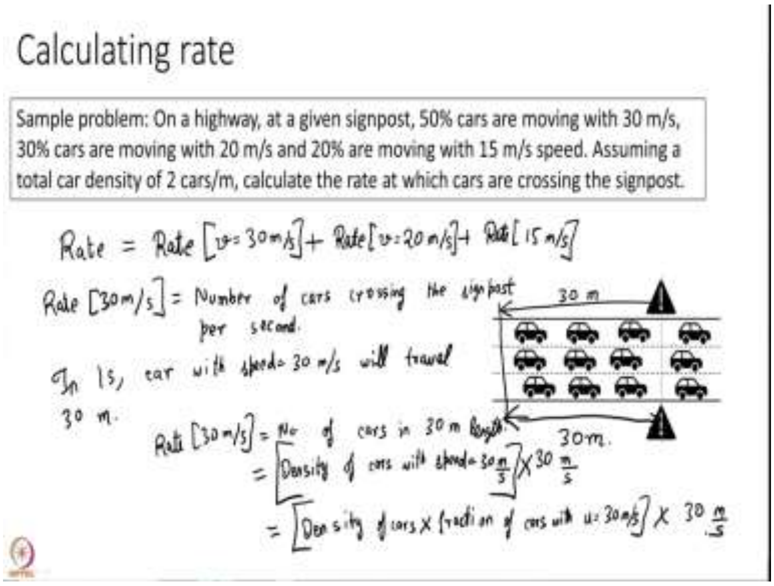

Let us think about cars. And I have a puzzle for you today. And we are going to solve this puzzle. Imagine I have a road and on this road you have a lot of vehicles that are moving. Now, do you have a distribution of speeds, just so you are really thinking of some highways many cars are moving you have different lanes.

And just for simplicity, let us assume you have cars moving at 30 metre per second, 20 metre per second and 15 metre per second only 3 speeds just as an example. And let us say 50 percent of the cars are moving with 30, 30 percent are moving with 20 and 20 percent and moving with 15 metre per second.

Now, imagine I have some signposts somewhere, just a spot on the road. And I asked you the question, what is the rate at which cars will be crossing this line, this blue line here. And we have to assume some density of the cars. And let us say that the density is some two cars per metre, that is actually a lot of cars, but fine. Every kilometre you have a 2000 cars, so a very, very busy highway, I guess. But let us assume it, whatever, it is a number.

So, this is a puzzle for you. What I want you to do is this is one of the most important things actually, if you can solve this puzzle, you understand the essence of all theories done, everything that will forward here from this point on you then understand. So, I really want you to take your time pause this video and get this answer. Most important, I want you to understand is a logic behind how to solve this problem. So, pause the video and solve this problem and do not rest until you have solved this problem. Please pause the video now.

Hopefully you are back and hopefully you have tried to solve this. If you have not please pause the video and do attempt to solve this one, this one is critically important. We are going to solve it together now. So, we are going to divide this problem, the rate, total rate will be the rate at which cars moving with speed equal to 30 metre per second plus rate of cars travelling with 20 metres per second plus rate of cars travelling with 15 metres per second. So, what I will do is to find these 3 individual rates.

So, let us focus on rate at 30 metres per second, how do I solve this problem? What is rate? So, we have to get back to our fundamentals, rate is the number of cars crossing the signpost for second. So, if I wait for one second, I have to observe how many cars passed which were travelling at 30 metres per second.

So, imagine you are sitting there at that toll booth at the signpost and every time a car travelling a 30 metre per second crosses by you have a counter and increase the counter by 1 and you find the number of cars that passed in 1 second. That is a rate by definition. So, how do I calculate this number?

Well, the idea is in 1 second cars travelling with 30 metre per second will travel, well of course, 30 metres, the speed is 30 metre per second, in 1 second you have 30 metres of distance, what it means then is, if I take a length of 30 metres here, the cars that were in this 30 metre would have crossed this blue line and any car that is outside this 30 metre line will not have crossed this blue line in 1 second.

So, in 1 second time only the cars that fall within this 30 metre range will be able to cross. So, this number, so this rate of 30 metre per second will be number of cars in 30 metre length. So, this will be equal to density of cars with speed equal to 30 metre per second into 30 metre. So, I find the density in per unit length which have this for following speed and I multiply it by 30 metres per second that will give me the rate.

So, this density is density of cars into fraction of cars with speed equal to 30 metres per second into 30 metres per second. So, the density of cars with a particular speed equal to total density of cars per unit length multiplied by the fraction of cars that were travelling with 30 metres per second. So, that is how I will find the density which are with a particular speed.

Because think about it very carefully what we are doing the total rate at 30 metres per second will be the number of cars in the 30 metre length, because those are the cars that will be able to cross this signpost in 1 second time fine, but, the number of cars in this distance is nothing but the density of the cars into this distance the density of the cars will be the total density of all kinds of cars multiplied with a fraction of this particular kind of car.

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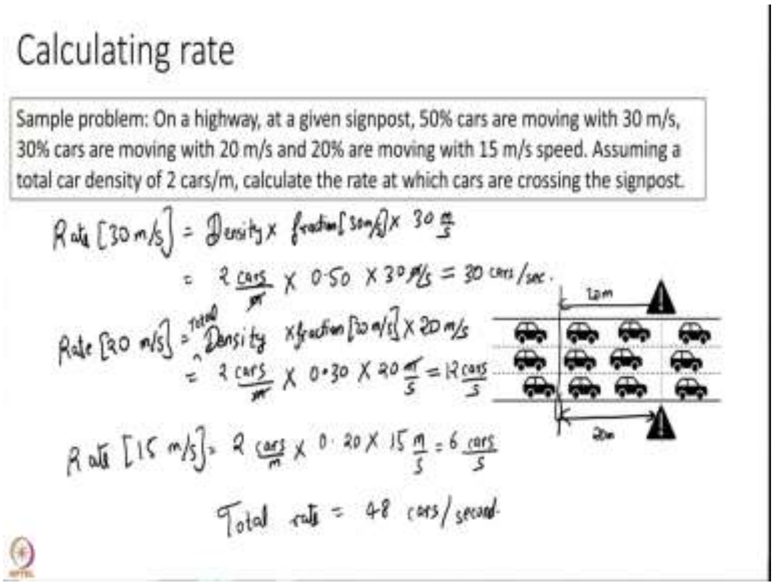

So, this rate at 30 metres per second is then density the total density into fraction of 30 metres per second into 30 metres per second the speed, the density is 2 cars per metre, that is the total density fraction for 30 metres per second is given to be half 50 percent 50 percent is nothing but half into 30 metres per second.

So, if I multiply this, I am going to get 30 yes, so I can do the same for 20 metres per second... This will be the same as the density of total cars into the fraction of cars travelling with 20 metres per second into 20 metres per second. The same logic in one second the total number of cars travelling with speed 20 metres per second. Well, those cars better be in this length of 20 metres, same logic.

So, this becomes 2 cars per metre into the fraction here is 0.30 into 20 and I can calculate this, this is equal to 12 and the corresponding rate for 15 metre per second will again the total density into the fraction of 15 metre per second which is 0.20 into 15 metres per second. So, this is equal to 6 cars per second. So, the total rate is then equal to the sum of these 3, which is nothing but 48 cars per second. So, if you sit at that signpost you will observe 48 total cars passing.

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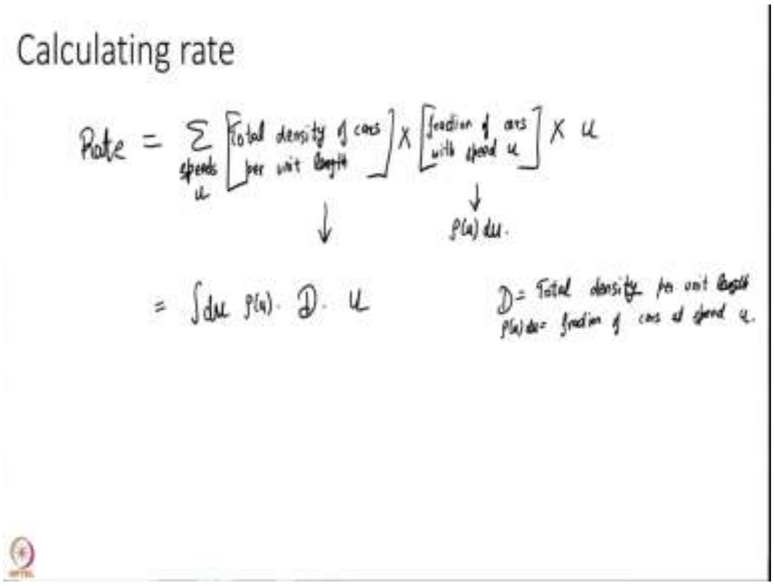

So, we want to generalise this a little bit. The total rate if I have in general some number of cars with some number of speeds will then be equal to sum over all speeds at which the cars are moving the total density of cars per unit length into fraction of cars with speed u into u. So, if you are travelling with some speed u in each second the cars have to be within the length u metres.

So, I have to find the number of cars in this u meter length, but the number of cars in this u metre length is nothing but the density of cars or total density of cars into the fraction of density which are moving at speed u multiplied by u metres, so that will give me the rate in per second. I can generalise this a little bit, if I have a distribution of speeds rather than summation this summation will become an integral.

So, imagine you have a cars at all possible speeds travelling not only at 30 but you also have a 30.001 30.002 at every speed there is a distribution that is how molecules behave. So, I am trying to get to the molecules from cars. So, the fraction basically replaced gets replaced by some density, into density into u where D is total density per unit length rho of u du is fraction of cars at speed u.

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So, this is the expression I get rate is equal to integral and I had forgotten to do one very important thing which is the limits. So, we are only looking at positive speeds for integral goes from 0 to infinity all cars at a moving with positive speeds. So, these limits are very important. So, in writing this expression, we have made 2 important assumption one is only forward speeds that is that these cars are later on not turning around and coming back then your rate decreases the forward rate decreases.

So, we are assuming the all the cars even say both through this goalpost keep on going forward. And the second is importantly we are treating cars classically, obviously, this becomes a bit more tricky when you think of atoms and molecules. Cars are of course described by Newton's laws very well. Atoms molecules most likely they are but you can have exceptions.

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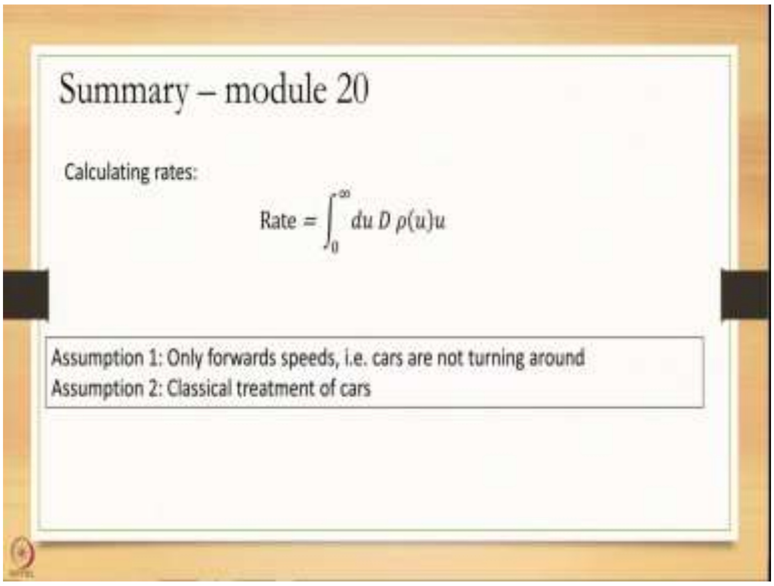

So, today I just want to give you this important expression for the rate. Anytime you calculate rate actually this fundamental expression is used rate is an integral over speeds. The density multiplied by the probability that I might given speed u and multiplied by u. So, this u is called the flux. So, I met a given goalpost what is the flux multiplied by its density. That is how you calculate later it.

And in doing that we have written two assumptions here we are we are really thinking of a speed, and they did not even use the word speed it is somewhat classical. In quantum mechanics, you have to be very careful when using the word speed. So, we will just end here and in the next module, we will actually derive transition state theory. Thank you very much.