Chemical Kinetics and Transition State Theory

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Lecture no 01

Rate: the reaction velocity

Hello and welcome to the course on Chemical Kinetics and Transition State Theory. This course essentially, we will be focusing on how to think of kinetics and estimating rate constants. So, in terms of course outcomes we have 2 important outcomes.

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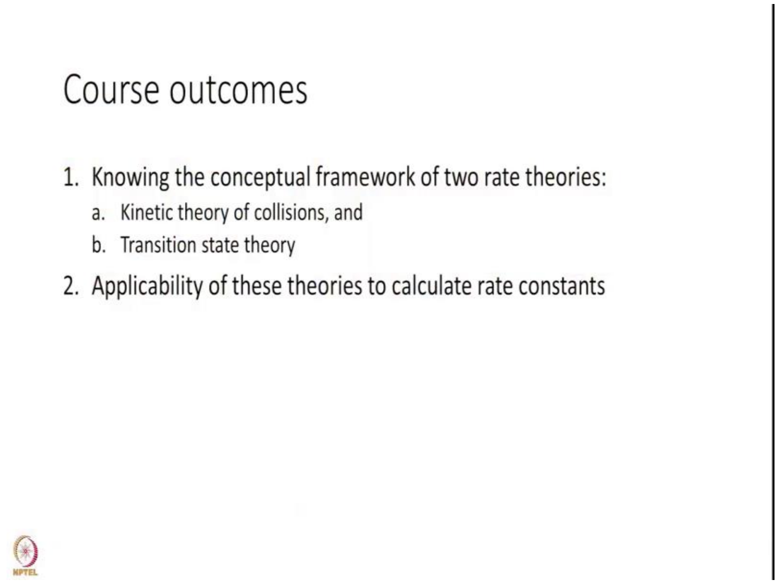

Course outcomes

1. Knowing the conceptual framework of two rate theories:
   a. Kinetic theory of collisions, and
   b. Transition state theory
2. Applicability of these theories to calculate rate constants

In this course we will be looking at 2 specific theories. The 1st one is the collision theory and the 2nd one is the transition state theory. Both these theories calculate rate constants of reactions. So, this course will cover how to calculate these rate constants under these 2 theories, so the 1st point is knowing the derivation, knowing the conceptual framework under which this theories operate, knowing when they are applicable and when they are not applicable.

And the 2nd course outcome is actually applying these 2 theories and calculating rate constants out. So, essentially at the end of this half semester course, if a reaction new reaction that you have not seen before is given to you, you should be in a position to make educated guesses on how to know about calculating the rate constant that's the main objective, that's where you will be after doing this course.

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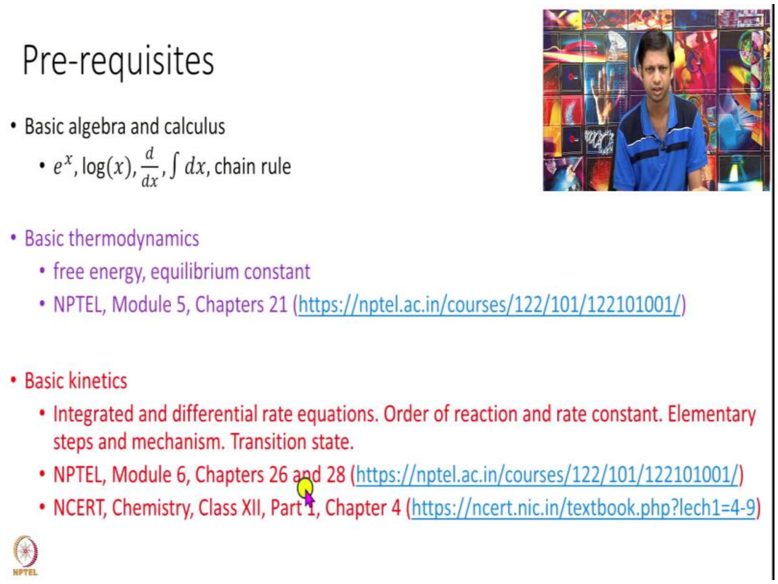

Pre-requisites

- Basic algebra and calculus
  - e^x, $\log(x)$, $\frac{d}{dx}$, $\int dx$, chain rule
- Basic thermodynamics
  - free energy, equilibrium constant
  - NPTEL, Module 5, Chapters 21 (https://nptel.ac.in/courses/122/101/122101001/)
- Basic kinetics
  - Integrated and differential rate equations. Order of reaction and rate constant. Elementary steps and mechanism. Transition state.
  - NPTEL, Module 6, Chapters 26 and 28 (https://nptel.ac.in/courses/122/101/122101001/)
  - NCERT, Chemistry, Class XII, Part 1, Chapter 4 (https://ncert.nic.in/textbook.php?lech1=4-9)

So, there are a few pre-requisites, that are, you can cover either quickly, most of it assumes 12th class knowledge. The course assumes a very minimal amount of mathematics. So, you have to know basic algebra, variables, how to add variable equations, inequalities like the most trivial of those things, nothing can see there.

You have to know basic operators like exponentials or logarithms or sin, cosine, things like that, exponentials come very very frequently in rate theories. A Minimal amount of calculus. If I give you a simple function to differentiate, if I give you e^{kx} to differentiate, you should be able to differentiate that and the same goes to for x integration, most trivial of integrations, $\int x\,dx$, $\int e^{xdx}$.

Complex integrations, for example, integrating a Gaussian function, e^{x^2} which is hard those things we will always provide, that we do not have to know for this course. Simple ideas like chain rule, so if you I ask you to differentiate x into e^x, how do I do that? So, those basic things you should know for this course.

Very fundamentals of thermodynamics, the 2nd law and the 1st law of thermodynamics as applicable to chemistry, idea of Gibbs free energy, idea of equilibrium constant and the relation of equilibrium constant with Gibbs free energy. So, there are enough resources out there where you can access these.

Here I am referring to 1 NPTEL module which you can look at which is sufficient, module 2 of chapter 21 of this course, so 1 chapter is enough. And finally, we will also assume little bit of basics of kinetics. At class 12th knowledge effectively, what is 1st order kinetics, what is the rate law itself, those kind of things, what is order of reaction okay, elementary steps in mechanism.

Again, I have provided a couple of resources, you can actually look at the NCERT book of class 12th, a 1 chapter of it is enough, the chapter 4 of part 1 of class 12th. I have also provided you an NPTEL module, these 2 chapters are suffice in understanding it.

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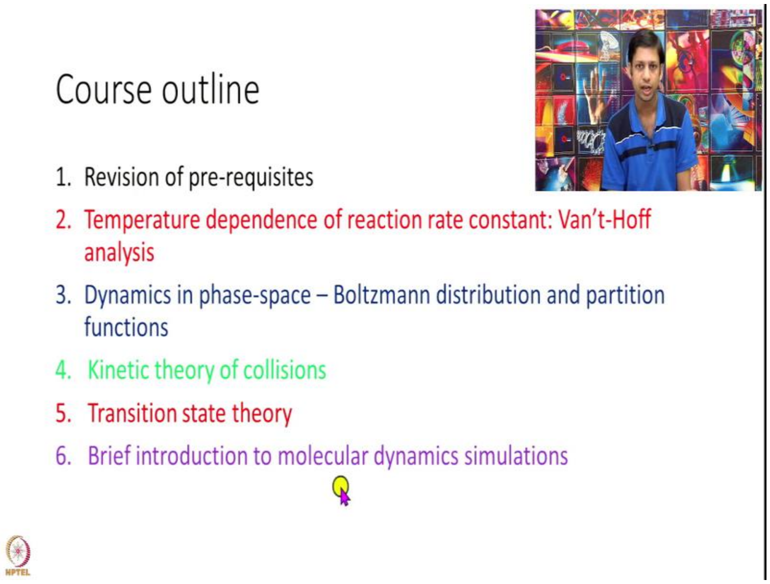

Course outline

1. Revision of pre-requisites
2. Temperature dependence of reaction rate constant: Van't-Hoff analysis
3. Dynamics in phase-space – Boltzmann distribution and partition functions
4. Kinetic theory of collisions
5. Transition state theory
6. Brief introduction to molecular dynamics simulations

So, to give you a clear cut outline, we will start with a revision of the pre-requisites particularly of chemical kinetics, we will start by defining rate formally, we will work out how to write a rate equations and all. After that we will move on to understanding how to calculate rate constant, particularly we will start with Van't Hoff and Arrhenius analysis.

These are the 2 people who really started the fields of chemical kinetics, it is late 1800, beautiful work and by then only they had written very fundamental equations on how a rate constant changes with temperature, so we will look at that analysis, it's part of this course. We will move on to build on how do we calculate these rate constants from an atomistic picture. Okay

And to understand how atoms move, the kinetics of atoms we will need to know a little bit of phase space, so we will introduce this explicitly in this course and we will introduce whatever is necessary in calculating rate constants which will be Boltzmann distribution and partition functions.

Then we will discuss the collision theory, a kinetic theory of collisions ok. So, that's the 1st theory that was given by Trots and Luis to calculate rate constant from atomistic picture and following that we will discuss the transition state theory which is one of the main focuses of this course and this transition state theory was fully developed in 1935, the equation was given and it is still used as was written in 1935, 85 years ago, we still use the equation, the same equation, it is a very powerful theory that is used across fields. So, we will look at this very very carefully in great detail. We will end with a little bit of a flavour of molecular dynamics and how this molecular dynamics is used to calculate rate constants. Ok

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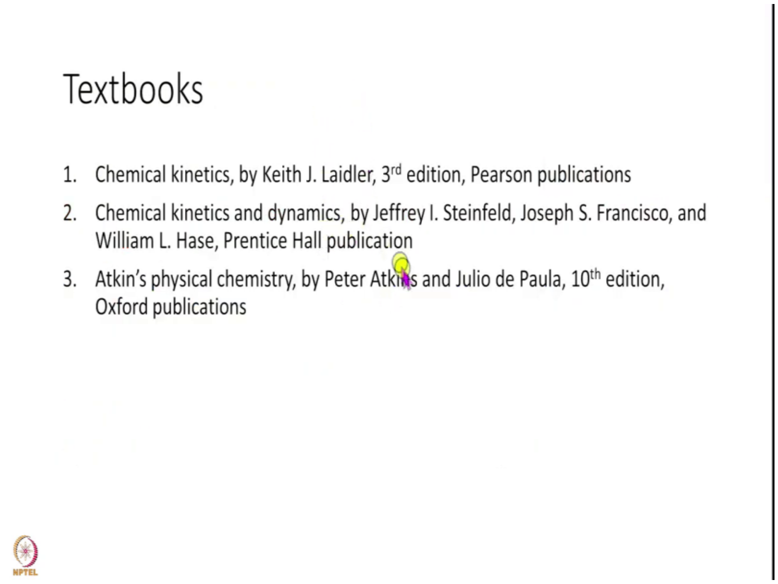

Textbooks

1. Chemical kinetics, by Keith J. Laidler, 3rd edition, Pearson publications
2. Chemical kinetics and dynamics, by Jeffrey I. Steinfeld, Joseph S. Francisco, and William L. Hase, Prentice Hall publication
3. Atkin's physical chemistry, by Peter Atkins and Julio de Paula, 10th edition, Oxford publications

So, the textbooks will be following, we will mostly be following the book by Laidler, this is a very standard textbook, very famous textbook, it's called chemical dynamic, chemical kinetics by Laidler, I will be following third edition, if you have access to any other edition please do not worry, all editions are more or less the same, you can freely whatever I am teaching will also be present in a different edition.

I will also be time and again refer to2 other books, 1 is by Steinfeld, Francisco and Hase, Chemical Kinetics and Dynamics, under the very standard textbook on kinetics, but not very often, only for a few things. And also we will be referring a little bit to Atkin's book, Atkin's physical chemistry, very popular book and once more please do not worry about edition, any other edition will do the job, the chapter number changes, not the content. Any time, by default we will be following Laidler, anytime I am following any other resource I will always mention.

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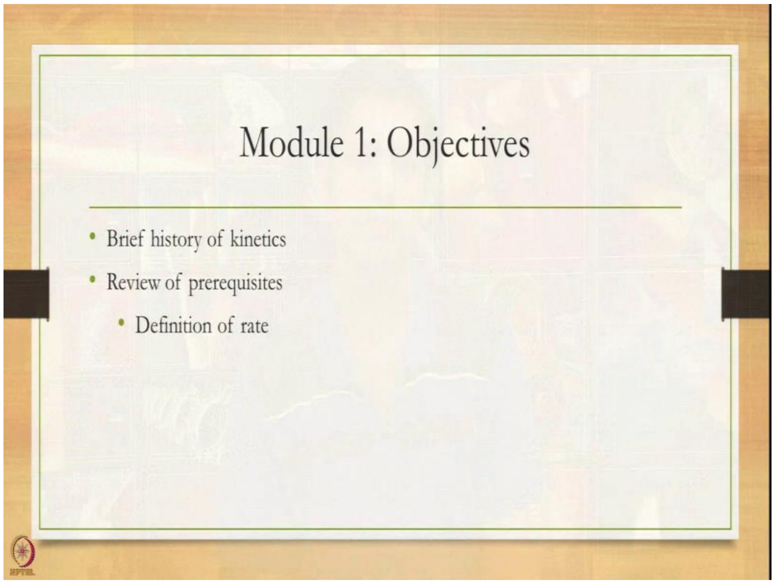

Module 1: Objectives

- Brief history of kinetics
- Review of prerequisites
  - Definition of rate

So, today we will just cover very preliminaries, we will define what is rate and before defining rate we will also cover how all this history of kinetics came about, on whose shoulders we are talk standing on.

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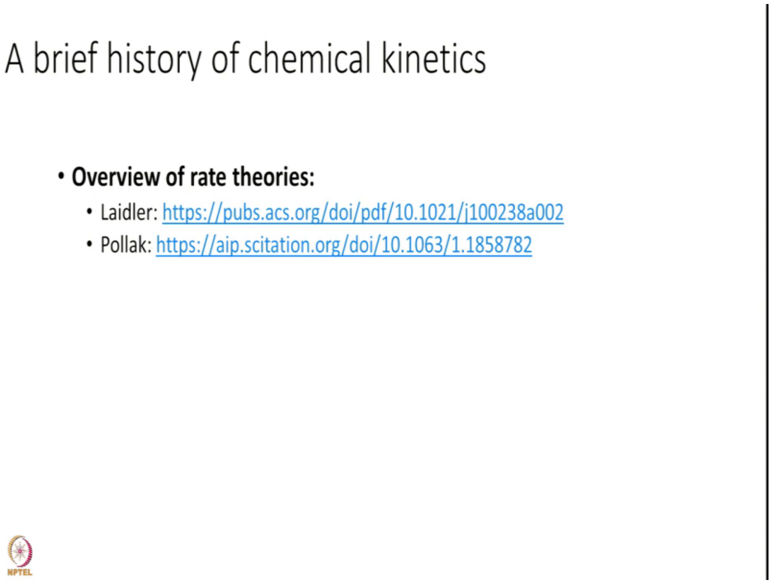

A brief history of chemical kinetics

- **Overview of rate theories:**
  - Laidler: https://pubs.acs.org/doi/pdf/10.1021/j100238a002
  - Pollak: https://aip.scitation.org/doi/10.1063/1.1858782

So, you can actually look at a very very good reviews on this point on the history of chemical kinetics in these 2 papers very very readable papers 1 by Laidler whose book we are following and by another giant called the Pollak okay. So, these references are extra, more interested students can go to this for extra knowledge. So, let us just look at a little bit of the history ok, so the history is more than 100 years old, we cannot cover every single point but the salient points, the biggest of the biggest giants in the field whose contributions are immense.

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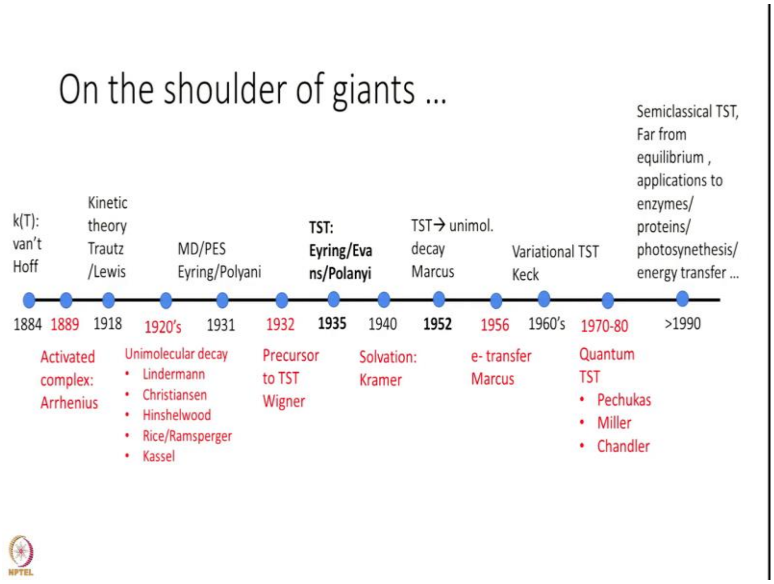

On the shoulder of giants ...

1884 k(T): van't Hoff
1889 Activated complex: Arrhenius
1918 Kinetic theory Trautz /Lewis
1920's Unimolecular decay
- Lindermann
- Christiansen
- Hinshelwood
- Rice/Ramsperger
- Kassel

1931 MD/PES Eyring/Polyani
1932 Precursor to TST Wigner
1935 **TST: Eyring/Evans/Polanyi**
1940 Solvation: Kramer
1952 TST→ unimol. decay Marcus
1956 e- transfer Marcus
1960's Variational TST Keck
1970-80 Quantum TST
- Pechukas
- Miller
- Chandler

>1990 Semiclassical TST, Far from equilibrium , applications to enzymes/ proteins/ photosynethesis/ energy transfer ...

So, the 1st 2 names are really Van't Hoff and Arrhenius, Van't Hoff essentially in 1884 did a very thorough analysis of how rate constant changes with temperature, and he actually wrote what is called Arrhenius equation today in 1884 paper, so that Arrhenius equation was written by Van't Hoff interestingly.

1889 Arrhenius wrote a similar paper, 1 and a half page paper that I will show you in the 2nd module, powerful paper and that paper is the 1st paper that postulated the idea of a transition state, pure hypothesis, pure speculation, but very powerful speculation and he gives reasons for it in a very beautiful fashion.

So, that's the reason that the Arrhenius equation is called Arrhenius equation because of that paper of 1889 of the idea of an activated complex okay. So, these people really started the field, they said ok, I want to, I have done a reaction but I am not happy enough with that, I want to know more. So, how do I calculate this rate constants?

A 1918 saw the 1st paper on calculating these rate constants from an atomistic perspective, actually getting a number out okay, then by Trots and Luis, its called kinetic theory of collisions, that we are going to cover in some detail in this course. 1920 saw lot of discussion on the some of the simplest reaction which is unimolecular okay, bimolecular is somewhat more complex, you have bonds making and forming.

So, they said ok, let us start simple, we are beginning and so a lot of focus was spent on Unimolecular reactions which turned very insightful, so that develop our intuition of chemical kinetics a lot. 1931 and 32 and 35 saw some very important works. 1931 the idea of doing dynamics occurred by Eyring and Polanyi.

Building on that idea 1932 Wigner gave a theory which is the precursor to TST and 35 2 different papers 1 by Eyring and the 2nd by Evans and Polanyi came they both came simultaneously and so the credit is given to all 3 of them. And that paper is the revolutionary paper that changed this year 1935 that laid the foundation of transition state theory.

This we are going to cover in great details in this course and the equations written in this paper are still used as there, not only that almost all development beyond 1935 take this work as the base and develop upon it, make the equations better but this is still the intuition that is still used today in even development of chemical kinetics okay, so that’s why I put this point in bold ok.

1940 saw beautiful work by Kramer on thinking of including solvent effects in transition state theory, I am moving a little bit fast now, lot of work is done. 1952 Marcus did beauty another beautiful work he essentially sold a unimolecular decay, the people, the work that was done in 1920 is Marcus entered said I cannot solve it completely and what he did it is to use transition state theory that’s the reason in 1927 were not able to solve it because transition state theory did not existed that than.

After that Marcus also solved another problem which is that of electron transfer, so a bond is not breaking and forming, only an electron is transferring from one site to another, so Marcus got a Nobel Prize for that. In 1960s Keck has a very nice work on quantifying transition state. So, remember almost 100 years later, I mean 80 years roughly, in 1889 Arrhenius had postulated the existence of a transition state. In 1960 basically Keck said I can mathematically tell you exactly what it is, I can write a mathematical description of transition state, so a lot of development.

Ideas of introducing quantum mechanical effects in transition state theory were introduced in 70s and 80s and it’s still happening till today. And essentially since then we have been developing over transition state theory, introducing if it, we cannot do full quantum mechanics, can we do semi quantum mechanics or semi classical mechanics, how do we apply it to a variety of problems I want to understand protein folding, I want to understand kinetics of enzymes of catalysis of photosynthesis of energy transfer and the list can go on, it’s a very active field, you can open any modern journal that was published let us say this year in physical chemistry. And you will find few papers at least in every public, in every journal every week that will be on this topic.

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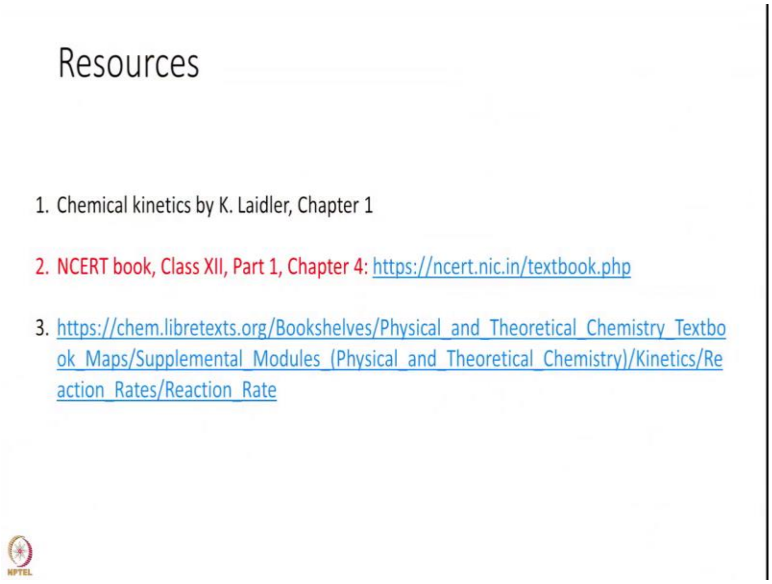

Resources

1. Chemical kinetics by K. Laidler, Chapter 1
2. NCERT book, Class XII, Part 1, Chapter 4: https://ncert.nic.in/textbook.php
3. https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Reaction_Rates/Reaction_Rate

So, what I will be covering today you can find in the chapter 1 of Laidler, or you can also read the class 12th book of NCERT, on top of that I have also given you an online resource from chem libre texts.

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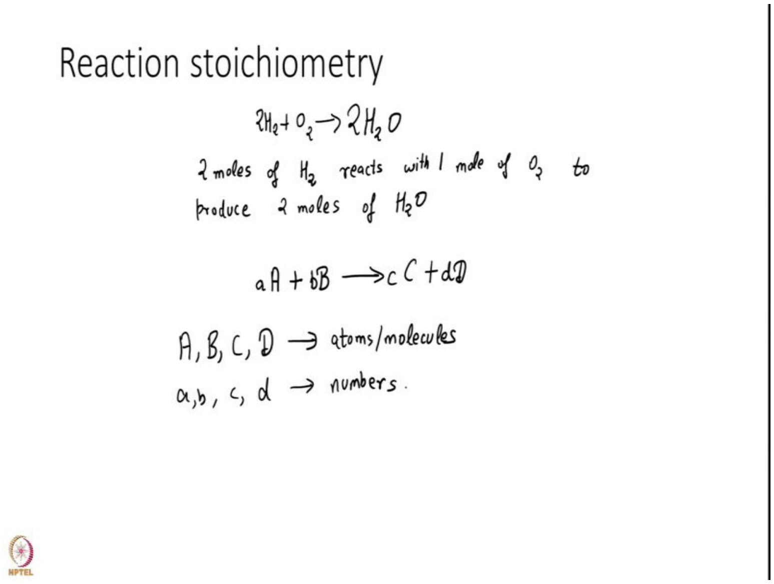

Reaction stoichiometry

$2H_2 + O_2 \rightarrow 2H_2O$

2 moles of H_2 reacts with 1 mole of O_2 to produce 2 moles of H_2O

$aA + bB \longrightarrow cC + dD$

A, B, C, D → atoms/molecules

a, b, c, d → numbers.

Ok So, let us start think formally so that everybody is on the same page and we have the same notation. The 1st we will define is what is called stoichiometry. To give you 1 example let me write a chemical reaction $2H_2$+O_2 makes $2H_2$, what I mean by this reaction? I mean 2 moles of H_2 reacts with 1 mole of O_2 to produce 2 moles of H_2O. Okay

So, in general let me write a reaction that will look like aA+bB make it some worth more general okay. So, the big letters in this course will refer to atoms or molecules and the small letters in this course will be numbers typically stoichiometric. ok

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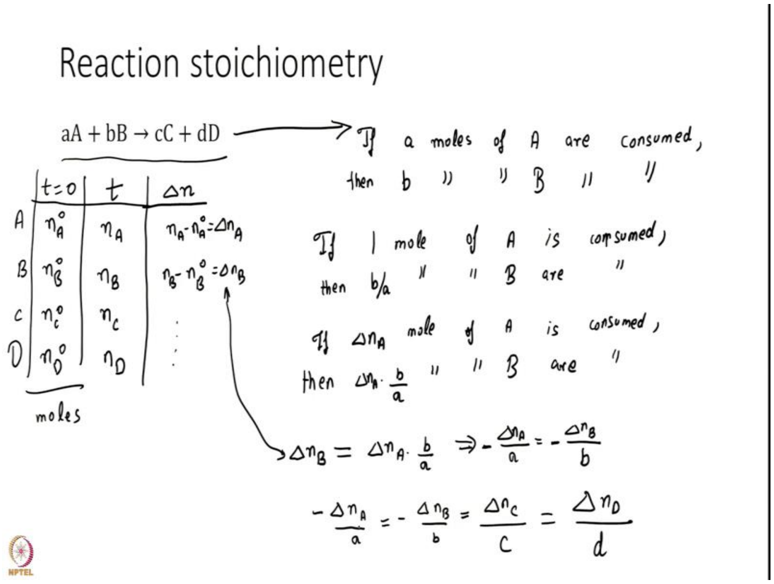

Reaction stoichiometry

$\underbrace{aA + bB \rightarrow cC + dD}$ → If a moles of A are consumed, then b " " B " "

	t=0	t	Δn
A	n_A^0	n_A	$n_A - n_A^0 = \Delta n_A$
B	n_B^0	n_B	$n_B - n_B^0 = \Delta n_B$
C	n_C^0	n_C	⋮
D	n_D^0	n_D	⋮

moles

If 1 mole of A is consumed, then b/a " " B are "

If Δn_A mole of A is consumed, then $\Delta n_A \cdot \frac{b}{a}$ " " B are "

$$\Delta n_B = \Delta n_A \cdot \frac{b}{a} \Rightarrow -\frac{\Delta n_A}{a} = -\frac{\Delta n_B}{b}$$

$$-\frac{\Delta n_A}{a} = -\frac{\Delta n_B}{b} = \frac{\Delta n_C}{c} = \frac{\Delta n_D}{d}$$

So, I have this stoichiometry, let us try to quantify what this means. So, let us just consider 1 thing let us say at time t = 0 I have moles n_A^0, n_B^0, n_C^0 and n_D^0 in general, so these are the number of moles corresponding to ABCD at some initial time t. I measure the moles at some later time t and I get nA, nB, nC and nD. Can you tell me ah relation between these n_A and n_A^0, and n_B and n_B^0 with the stoichiometry A and B, can you can you write an equation?

So, what I wanted to do is to pause the video, think about this, how do you calculate, how do you construct a relation, take your time, solve this problem and then we will solve it together, so please pause the video and solve this on your own. Hopefully, you have equation with you, you have solved the problem, if not, if you have not been able to solve, no worries, we will solve it together now.

So, the 1st thing to note is how much moles changed, so the Δn is n_A-n_A^0 = Δn_A. Well, I can write the same thing for others, I wrote an n, I will erase the n and convert it back to n_B^0, n_B, and so on and so forth. Now, we will do our analysis, ah 1st what does this stoichiometry mean, what do we understand from this?

If a moles of A are consumed then b moles of B are consumed that's the meaning of this reaction here okay by definition, this is always true, where is absolutely no exception, this is the definition. So, I want to find out how many moles of B will be consumed if Δn_A moles of A are consumed. So, we do it in a simple fashion if 1 mole of A is consumed, then b/a it's all linear moles of B are consumed, simple, if Δn_A mole of A is consumed, then Δn_A*b/a moles of B are consumed. Okay

But Δn_B is the actual moles of B that has been consumed from this. So, $\Delta n_B = \Delta n_A * b/a$. So, I simplify this as $\Delta n_A/a = \Delta n_B/b$ and as a convention we use and negative sign for consumption that's a convention. So, I will, this equation is true, so this equation is also true, I can put a negative sign that's my choosing okay. So, for consumption I choose a negative sign and for production I will choose a positive sign. So, you can work the same thing out for C and D as well.

And by convention then what we write is $\Delta n_A/a = -\Delta n_B/b$ this is $= \Delta n_C/c = \Delta n_D/d$ okay. So, I am not working of C and D part explicitly but you can easily work it out following the same logic.

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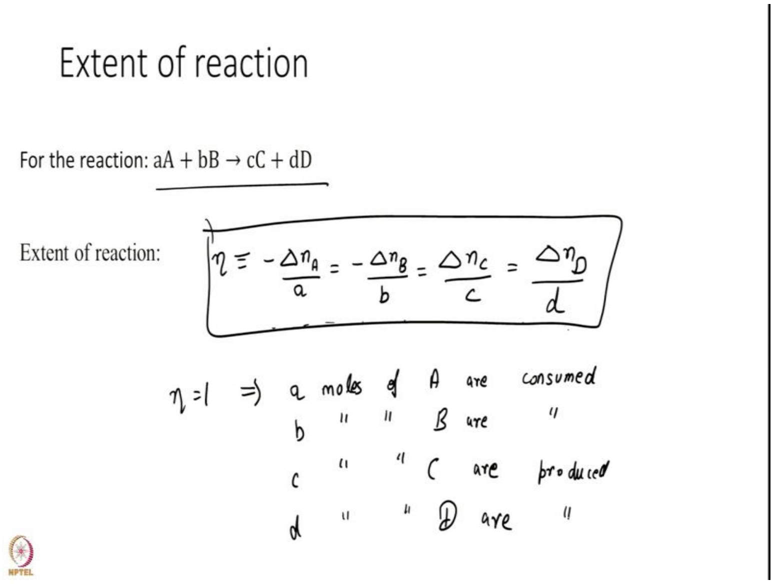

Extent of reaction

For the reaction: $\underline{aA + bB \rightarrow cC + dD}$

Extent of reaction: $\boxed{\eta \equiv -\frac{\Delta n_A}{a} = -\frac{\Delta n_B}{b} = \frac{\Delta n_C}{c} = \frac{\Delta n_D}{d}}$

$\eta = 1 \Rightarrow$ a moles of A are consumed
b " " B are "
c " " C are produced
d " " D are "

So, we define this quantity as the extent of the reaction and this equality, this is a definition but the equality here will always hold if this reaction is true, there is no exception to it, this is by definition, this is by mathematics okay. So, if this is true the whole thing will, we do not want to write again and again and we called it the extent of reaction.

And the idea is if $\Delta n_A = 0$ then the extent is 0, that means nothing has happened, you are at t = 0 and if Δn_A is 1, if Δn_A is a then η is on1. So, $\eta = 1$ implies a moles of A are consumed, b moles of B are consumed, c moles of C are produced, so it’s an easy way to think about it okay, so we quantify it in this number a dimensionless number.

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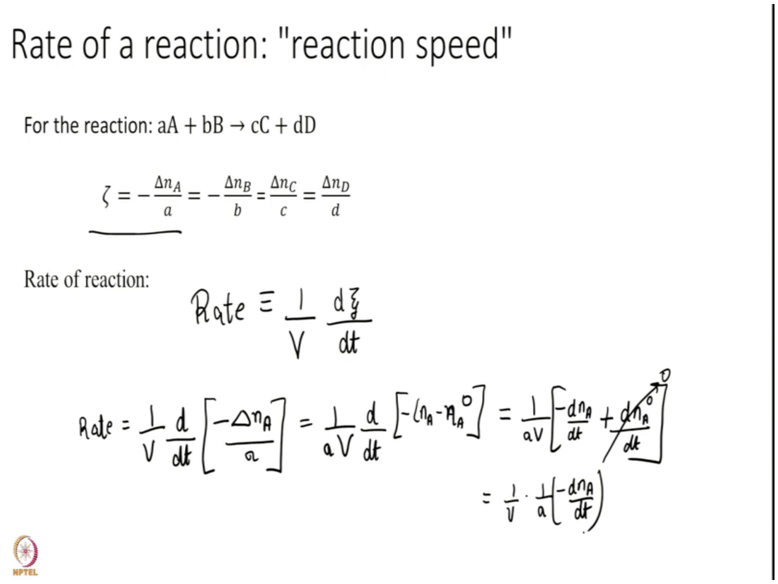

Rate of a reaction: "reaction speed"

For the reaction: aA + bB → cC + dD

$$\zeta = -\frac{\Delta n_A}{a} = -\frac{\Delta n_B}{b} = \frac{\Delta n_C}{c} = \frac{\Delta n_D}{d}$$

Rate of reaction:

$$\text{Rate} \equiv \frac{1}{V}\frac{d\xi}{dt}$$

$$\text{Rate} = \frac{1}{V}\frac{d}{dt}\left[\frac{-\Delta n_A}{a}\right] = \frac{1}{aV}\frac{d}{dt}\left[-(n_A - n_A^0)\right] = \frac{1}{aV}\left[-\frac{dn_A}{dt} + \overset{0}{\cancel{\frac{dn_A^0}{dt}}}\right]$$

$$= \frac{1}{V}\cdot\frac{1}{a}\left(-\frac{dn_A}{dt}\right)$$

Okay So, we have defined this extent of reaction. How do we define rate of reaction? So, the rate is defined to be by definition 1/V, so I use ≡ sign, these 3 arrows, these 3 lines to define that is the definition. The change of extent of reaction per unit volume that is defined to be the rate of the reaction okay. Some of you might be curious why we divide by volume, a little bit of extra information, it is just so that rate becomes an intensive variable, we do not want it to depend on the overall volume, okay none the less.

Let us just put it in this equation here, let us substitute it. So, I will substitute it for A. So, Rate = 1/V d/dt [$-\Delta n_A/a$] okay, so I have used this here. So, I will take a outside and what is the definition of Δn_A, it is n_A - n_A^0, so this is = 1/aV* [$-dn_A/dt + dn_A^0/dt$].

What you notice that this is 0 because n_A^0 is not a function of time, it is simply the number of moles at initial time, okay so that was just a number, the actual change is n_A. So, this is 0, so at the end I get 1/V* 1/a - dn_A/dt.

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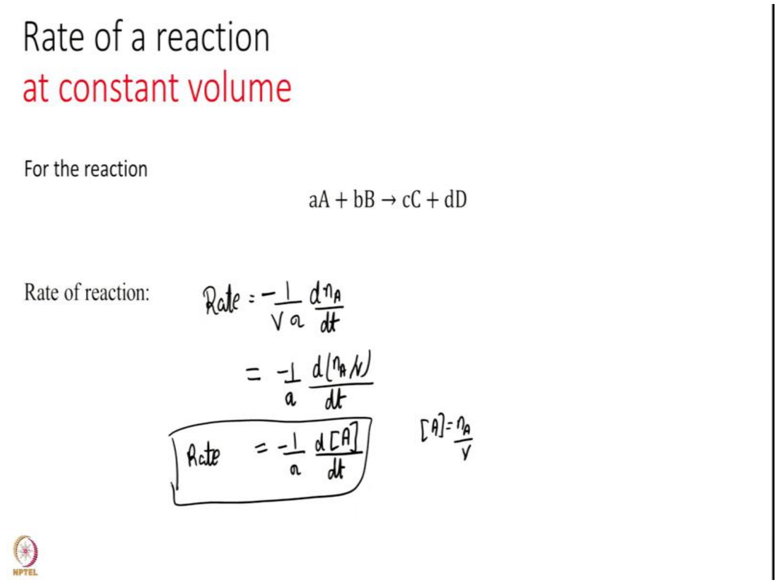

Rate of a reaction
at constant volume

For the reaction

$$aA + bB \rightarrow cC + dD$$

Rate of reaction:

$$Rate = -\frac{1}{Va}\frac{dn_A}{dt}$$

$$= -\frac{1}{a}\frac{d(n_A/V)}{dt}$$

$$\boxed{Rate = -\frac{1}{a}\frac{d[A]}{dt}} \qquad [A] = \frac{n_A}{V}$$

So, this rate that I have got -1/Va *dn_A/dt if volume is constant, there is a big if and in chemistry often deal with such reactions in solutions. So, when you mix 2 regions typically the volume is not changing by a lot but none the less if volume is constant, I can write this as dn_A/V over v/dt and so this becomes = -1/a*d[A]/dt, where concentration is defined to be n_A/V okay. So, this formula of rate holds true only for constant volumes, in this course at least we are going to stick to this definition, we are going to assume volume is constant.

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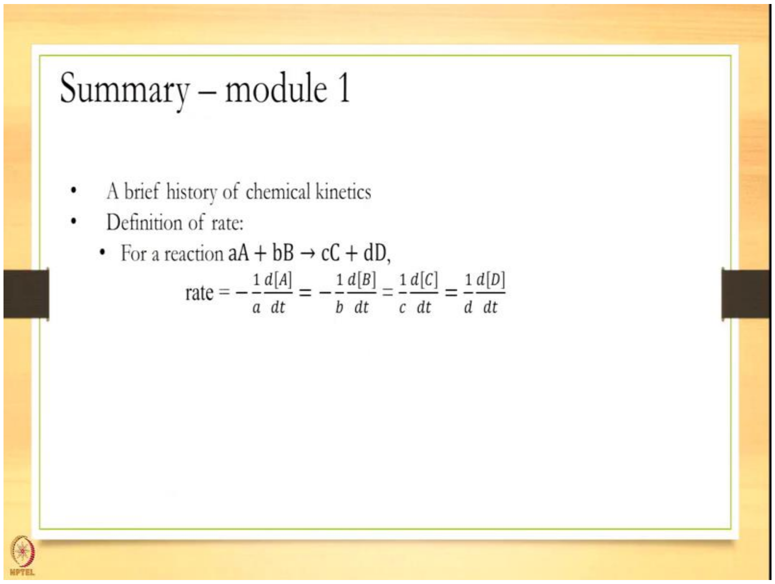

Summary – module 1

- A brief history of chemical kinetics
- Definition of rate:
  - For a reaction aA + bB → cC + dD,

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

So, in summary, today we have looked a brief history of chemical kinetics and we have looked at the very fundamental definition of rate as 1/V into d extent of reaction over dt and at constant volume we have a proven that the rate of the reaction is given by this equation, we explicitly showed it for 1 term rate = - dn_A/dt, but it is also easy to show it for these 3 other terms. In the next module we will look into what is rate constant and elementary reactions. Thank you very much.