Polymer Reaction Engineering
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Lecture – 13
Introduction to Reactor Design - II

Welcome to this another lecture of introduction to the reactor design related to the polymer reaction engineering. Earlier we had a discussion about the different parameters associated with the reactor design. We discussed about the different type of reactors. We discussed about the different components involved in the reactor design. Now, here again we will continue this concept of reactor design with the help of a rate equation.

Now, we had a discussion about the importance of the rate equation in the previous lecture and what triggers the importance of this rate reaction into the designing factor of the reactors especially attributed to the polymer reactor. Just a brief thing which I would like to pose before you this thing is related to the sensitivity of this particular polymer products.

You see that in the previous lectures, we always emphasizing the fact that because of the sensitive approach of molecular weight distribution and in situ its influence to the property of the polymer being produced, so we need to have a very close look to the designing aspect of these reactors. A slight variation in any kind of approaches may create a severe economic loss to the industry, severe economic loss to the nation.

So, that is why these closed loop parameters whether they are catalytic or noncatalytic, whether they are homogeneous or non-homogeneous, whether they are temperature dependent, exothermic reactions, etc., so we need to give a proper importance related to these parameters. So, we will continue this rate equation approach this chapter too with the rate laws, concept of rate laws, etc.

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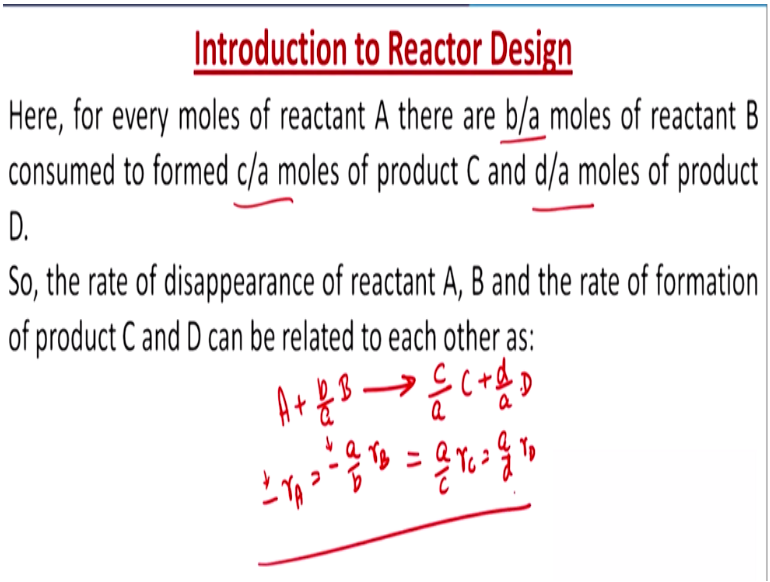

So, in addition to the previous discussion let us say that another equation for every moles of a reactant A there is b a moles of reactant B consumed to form this much of moles of a product and this much most of product D. So, the rate of disappearance of reactant A because A and B both are consumed in due course of time within the reactor. So, the rate of disappearance and that is why we put a negative sign before this.

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

So, the rate of disappearance of both reactant A and B and the rate of formation it carries the positive sign, so both C and D both are being formed in due course of time. So, let us again go back to the previous equation. So, A + b upon a B c upon a C + d upon a. Now so rate of a reaction you can always write r_B, remember negative sign we have put just because both A and B they are consuming themselves in reaction mass. This is equal to a upon c.

$$-r_A = -\frac{a}{b}r_B = \frac{a}{c}r_C = \frac{a}{d}r_D$$

So, this is the rate of equation. So, by this way we have already discussed and we have given a clue about the importance of a rate equation.

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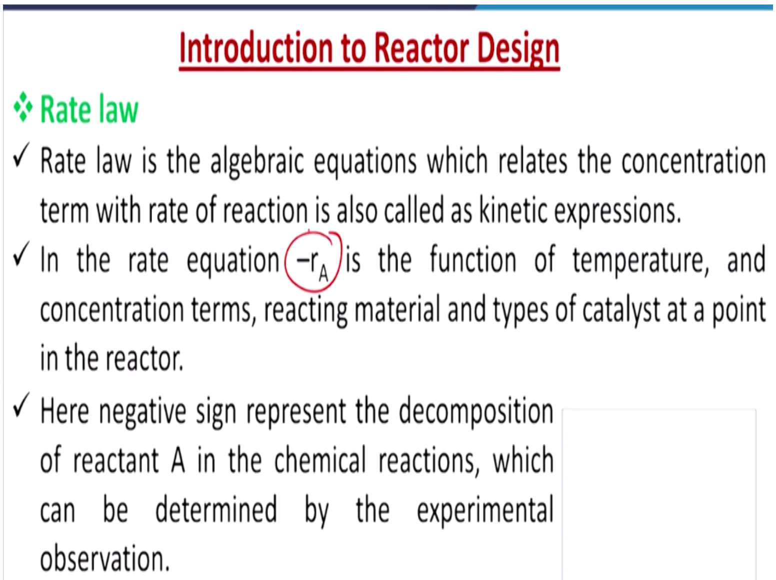

Now, come to the rate law. As I discussed that rate law is the algebraic equation which relates the concentration term with rate of reaction and sometimes it is also called the kinetic expressions. Now, in the rate equation say $-r_A$ which we are representing over here is a function of temperature and the concentration term, reacting material or type of catalyst at a point of reactor, maybe your reactor or maybe sometimes it is referred as the contacting pattern, etc.

So, here the negative sign as I told you that represents the decomposition or consumption of a reactant A in the chemical reaction which can be determined by the experimental observations.

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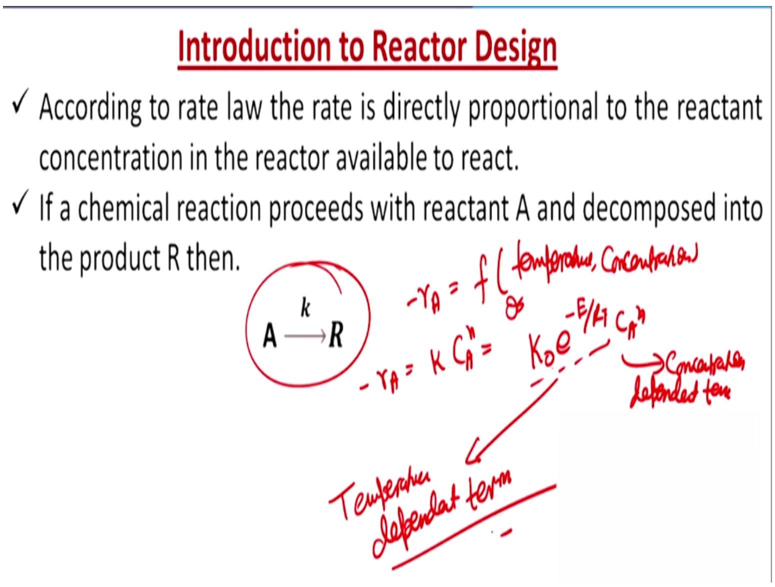

So, according to rate law, the rate is directly proportional to the reactant concentration in the reactor available to react. Now if a chemical reaction proceeds with a reactant A and decomposed into the product R, then let us say that this is my general equation. So, in that case

$-r_A$ is the function of temperature and concentration or sometimes referred as $-r_A = kC_A$ to the power n.

$$A \xrightarrow{k} R$$

$$-r_A = f\,(\text{temperature, concentration})$$

$$-r_A = kC_A{}^n = k_o e^{-E/RT} C^n{}_A$$

Or, it is represented as this is the concentration dependent term and this one is your temperature dependent term. So, this gives you a generalized equation and generalized concept of rate law.

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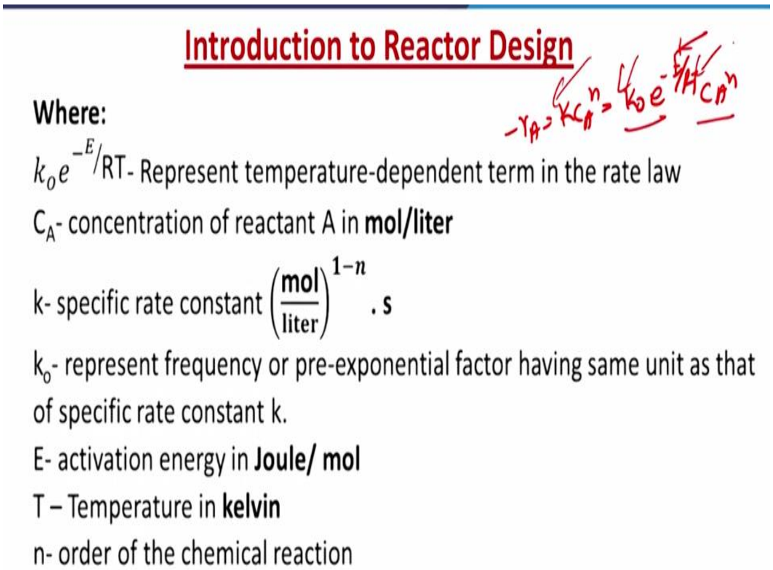

Now, here k_o in this particular equation, again I am repeating this equation over here for the convenience $-r_A = kC_A$. Now here k_o e this one represents the temperature dependent term in the rate law and this C_A concentration of reactant A and it is represented in moles per liter, k is the specific rate constant having the unit of moles per liter to the power one minus n second.

Now, k_o represents the frequency or a preexponential factor having the same unit as that of a specific rate constant k. Now E, here E is the activation energy and having the unit of joules per mole. Now here, this is the temperature usually in Kelvin and n presents the order of a chemical reaction. Now, let us have a look about the concentration dependent terms. Now, the concentration term they are used in the rate equation, it depends upon various factors.

Now, one factor is that the single or multiple reaction. So, when raw material reacts to form product, then it is easy to decide whether the single reaction or multiple reaction exists. This only after the examination of the stoichiometry at more than one temperature. So, the governing factor is your stoichiometry that is at the multiple temperature profile. There may be certain multiple reactions.

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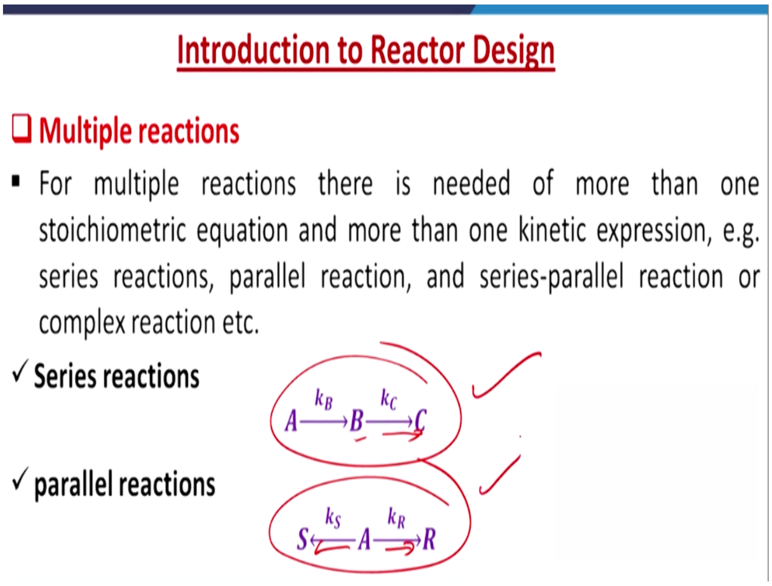

Now, for multiple reactions there is a need of more than one stoichiometric equation and more than one kinetic expression that is sometimes you may have a series of reaction, sometimes parallel reaction, sometimes series parallel reactions or sometimes a very complex reaction in nature.

Now, here you can have a look about the series reaction.

$$A \xrightarrow{k_B} B \xrightarrow{k_C} C$$

Now, here these are the parallel reactions.

$$S \xleftarrow{k_S} A \xrightarrow{k_R} R$$

Now you see that the arrow parallelly these things are moving in opposite direction. And here A is converting into the B and then subsequently C. So, this one is the series one and this one is the parallel one.

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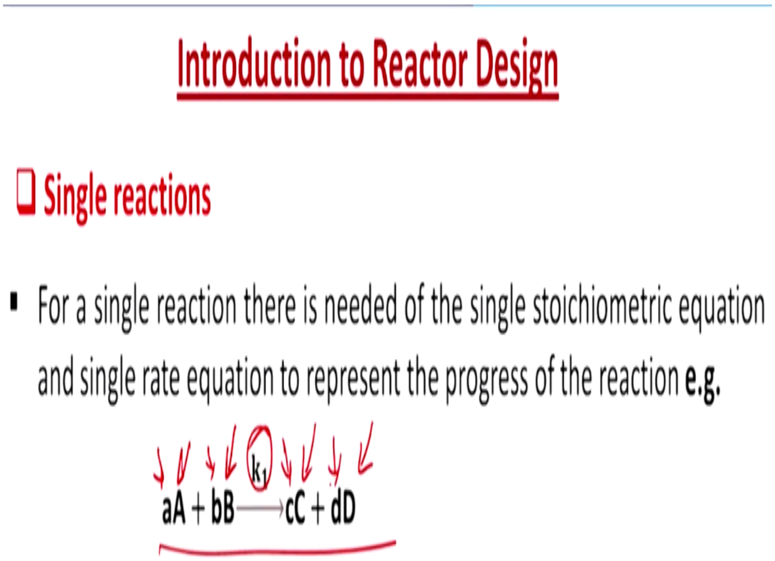

Now again come back to the single reaction. For a single reaction, there is a need of a single stoichiometric equation and single rate equation. Now, these two things they represent the progress of any kind of reaction. Now, here you can see that this particular equation this is the reactant, both A and B are the reactants and their stoichiometric numbers are correspondingly the small letters. The k_1 is the rate constant and similarly C and D both are the products, their corresponding psychometric numbers are c and d.

$$\mathrm{aA} + \mathrm{bB} \xrightarrow{k_1} \mathrm{cC} + \mathrm{dD}$$

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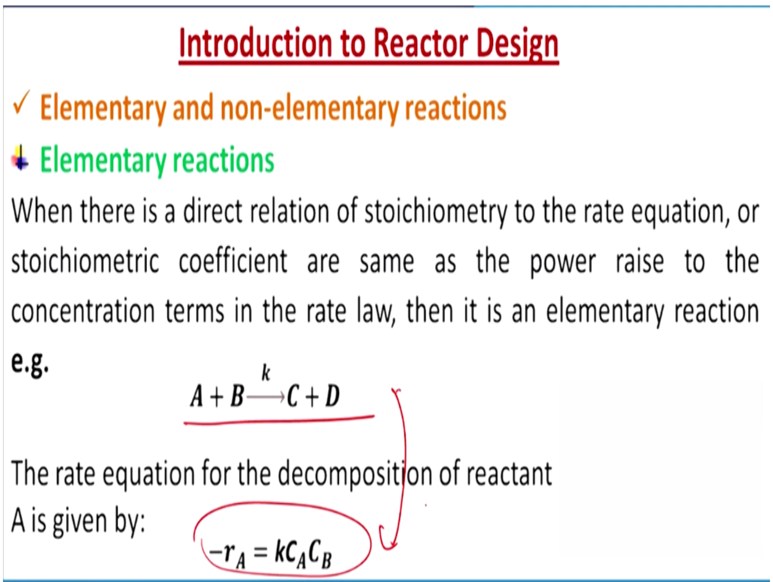

Now, let us have a look about the elementary and non-elementary reactions. Now before we go into the details, let us have a look about the elementary reaction. So, when there is a direct relation of a stoichiometry to rate equation or stoichiometric coefficients sometimes are seen as the power raised to the concentration term in the rate law, then this is termed as the elementary reaction.

$$A + B \xrightarrow{k} C + D$$

The rate equation for the decomposition of reactant A is given by

$$-r_A = kC_AC_B$$

Now just for the sake of an example, this is the example of the elementary reaction. Now the rate equation of the decomposition of reactant A is given by $-r_A = kC_AC_B$. So, this is purely based on this particular reaction.

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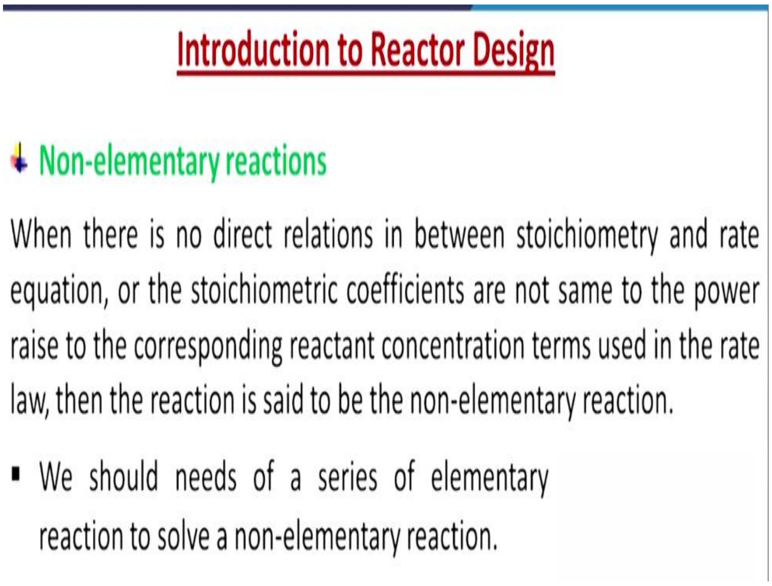

Now, the concept of nonelementary reaction is that when there is no direct relation in between the stoichiometry and the rate equation or sometimes the stoichiometric coefficients they are not same to the power raised to the corresponding reactant concentration terms used in the rate law, then the reaction is said to be the nonelementary reaction.

So, in this case we should need to have a series of elementary reaction to solve any kind of nonelementary reaction. Now, this is a very complex type of scenario when we need to solve these nonelementary reactions.

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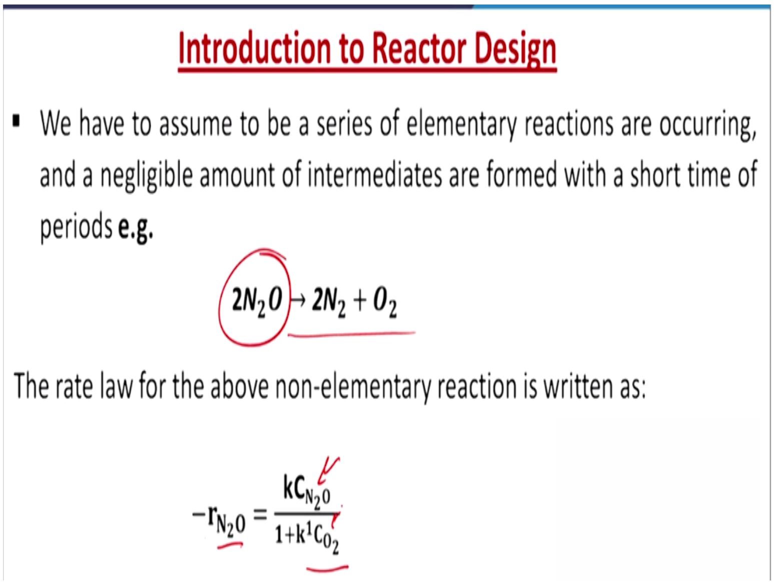

Now, in this case we need to assume to be a series of elemental reaction those who are occurring and negligible amounts of intermediates that are formed with a short time of period. So, sometimes you need to negate various aspects attributed to this particular approach. Let us have an example of twice N_2O is converting into $2N_2 + O_2$. So, the rate of above nonelementary reaction you can write as $-r_{N2O}$.

$$2N_2O \rightarrow 2N_2 + O_2$$

The rate law for the above non-elementary reaction is written as:

$$-r_{N_2O} = \frac{kC_{N_2O}}{1 + k^1 C_{O_2}}$$

Because this is being consumed in due course of time is equal to kC_{N2O} that is the concentration of this N_2O upon 1 + k to power 1 CO_2. So, this is the concentration of oxygen. Now, another important point in the reactor design is the molecularity. Now, it can be defined as the number of reactant molecules, atoms or ions those who are participating in a balanced chemical reaction.

So, these number of reactant molecules they are referred as a molecularity of the reaction. Now, this approach is based on the collision theory. Now, it is the whole number such as 1, 2 or 3 hence the reaction is said to be the monomolecular, di molecular r or termolecular that depends on that number of molecules participating in the collision. It cannot be in the fraction because it is quite obvious that partial collision not be feasible, may not be possible.

So, it cannot be in fraction as no spaces within the fractional number of molecules are used in chemical reaction. So, molecularity is only used in the elementary reaction. Sometimes people may refer as a unimolecular. Now, the arrangement of a single molecule to produce one or more molecules of product is an elementary system. For example, the decomposition of radioactive material into more than one product.

Such as a radioactive decay of say uranium 238 into thorium and helium by emission of single alpha particle, this is the unimolecular. There are certain biomolecular reactions. Now, the arrangement of two molecules in the reactant to produce the product of reaction, this may consist of two chemically different molecule or similar molecules. For example, this one $2N_2$ O is producing $2N_2 + O_2$.

$$2N_2O \rightarrow 2N_2 + O_2$$

Another arrangement is called the termolecular.

$$2NO + O_2 \rightarrow 2N_2O$$

This arrangement there are 3 different molecules in the chemical reaction to give the different products. Now, the next part is related to the order of reaction. This particular concept is again very useful for the determination of various parameters associated with the reactor design or designing of the reactor. So, here this is the sum of the power raised to the concentration term in the rate law is said to be the order of reaction.

The overall order of reaction can be a fraction say 0.5, 3 by 2, 5 by 3 up to n or sometimes it may be a whole number zeroth order reaction, first order, second order, third order so and so on.

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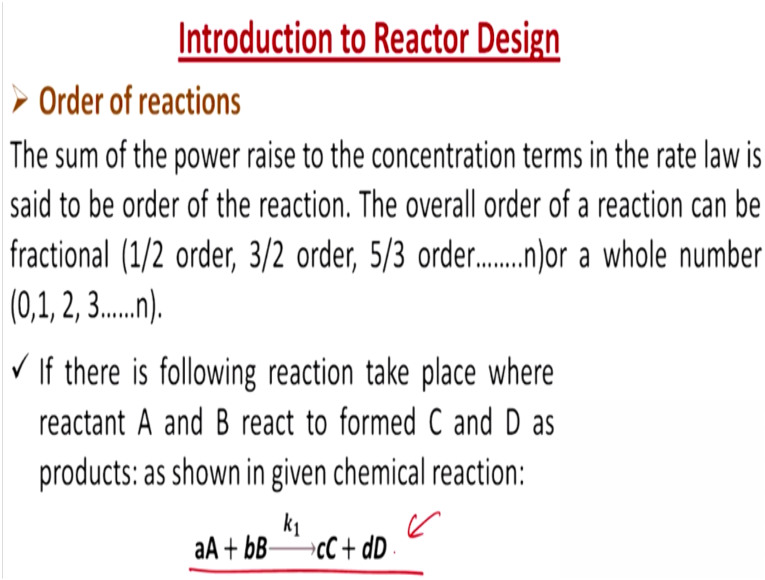

Now let us take an example. The following reaction take place where reactant A and B both are reacting together to form C and D. Now here this reaction is represented with their corresponding stoichiometric numbers.

$$\mathrm{aA + bB \xrightarrow{k_A} cC + dD}$$

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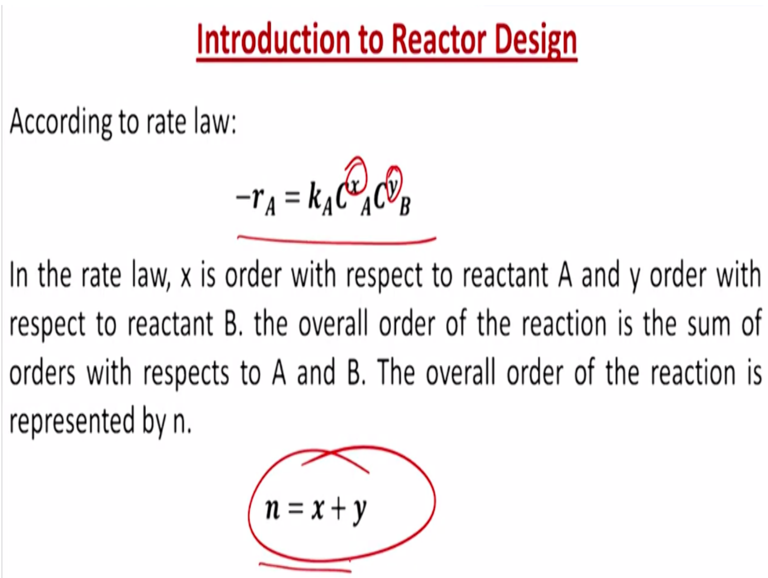

Now according to rate law, you can represent this as $-r_A = k_A C_A$ to the power x and C_B to the power y. Now in the rate law x is the order with respect to the reactant A and y is the order with respect to the reactant B and the overall order of the reactant is the sum of orders with respect to A and B.

$$-\mathrm{r_A = k_A C^x{}_A C^y{}_B}$$

So, sometimes you may refer that the overall order of that particular reaction is represented as $n = x + y$.

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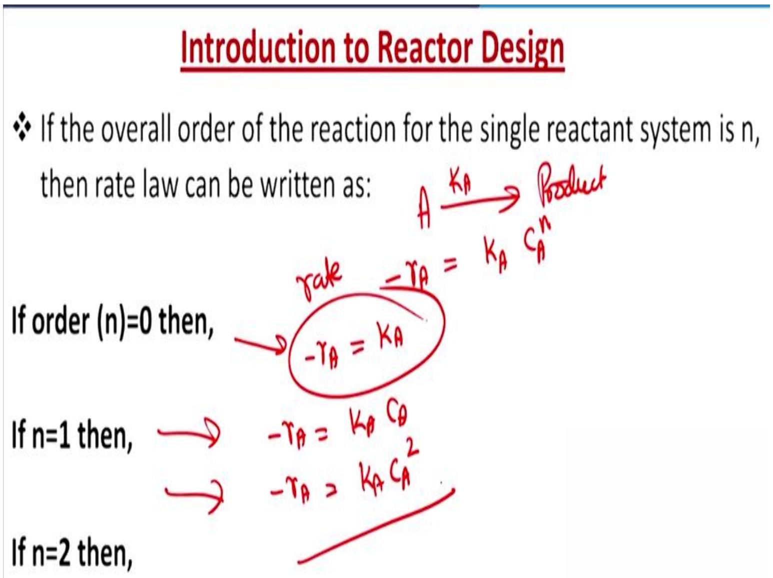

Now, the overall order of the reaction for the single reactant system is n, then you can write the rate law that is a single reactant. Now, rate law you can write $-r_A$ as a negative sign is there because A is being consumed is equal to k_AC_A to the power n. Now if order say n = 0, then in that case you can write $-r_A = k_A$, it is a zeroth order reaction. Now, if the order of the reaction is 1, then you can write $-r_A = k_AC_A$.

Now, if order is 2, then you can write $-r_A = k_AC_A^2$. So this represents the order of reaction. Now in this particular segment, we discussed about the rate law, we discussed about the rate equation, we had a brief discussion about the order of the reaction and all these parameters, all these things, all these theories are extremely important for the designing of reactor. So, we are proceeding towards the designing of reactor with the help of these different variables which are closely related to the design aspect.

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Reference

- Levenspiel, O. CHEMICAL REACTION ENGINEERING, Third Edition, John Wiley & Sons, Inc., (2006), ISBN:978-81-265-1000-9.
- Fogler, H. S. Elements of Chemical Reaction Engineering, Third Edition, Pearson Education, Inc., (2002), ISBN: 81-203-2234-7.

If you wish, you can have these references for your future reference. Thank you very much.