Chemical Reaction Engineering 1
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Lecture 22
General Graphical Reactor Design Procedure

Welcome to the 12th lecture of module four. In this module, we are discussing reactor design, before going to this lecture let us have brief recap on the lecture which we have covered in this module so far.

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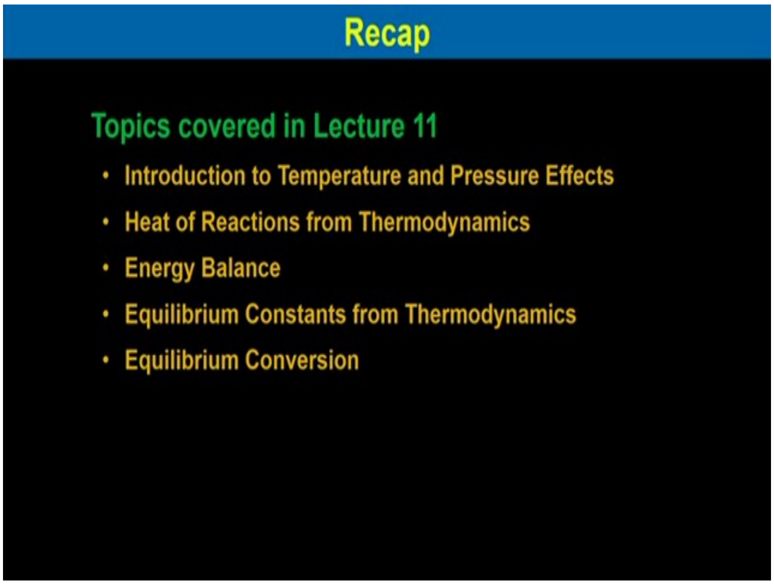

Recap

Topics covered in Lecture 11

- Introduction to Temperature and Pressure Effects
- Heat of Reactions from Thermodynamics
- Energy Balance
- Equilibrium Constants from Thermodynamics
- Equilibrium Conversion

In our last lecture, we have covered introduction to temperature and pressure effects. Then we have considered heat of reaction from thermodynamics and energy balance, equilibrium constant from thermodynamics and how to calculate the equilibrium conversion.

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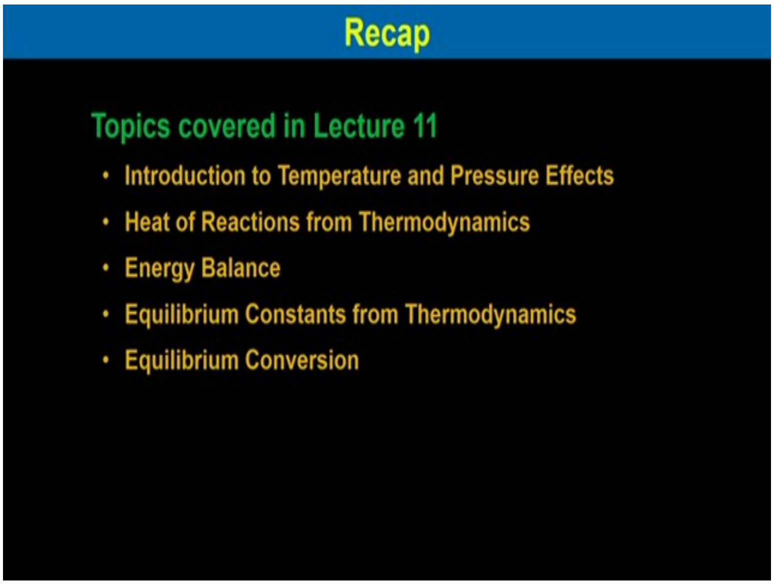

Recap

Topics covered in Lecture 11

- Introduction to Temperature and Pressure Effects
- Heat of Reactions from Thermodynamics
- Energy Balance
- Equilibrium Constants from Thermodynamics
- Equilibrium Conversion

In this lecture, we will consider general graphical reactor design procedure. Mainly we will consider first the outline of general graphical design. Then we will construct the rate conversion and temperature chart. So, this we will done with an example.

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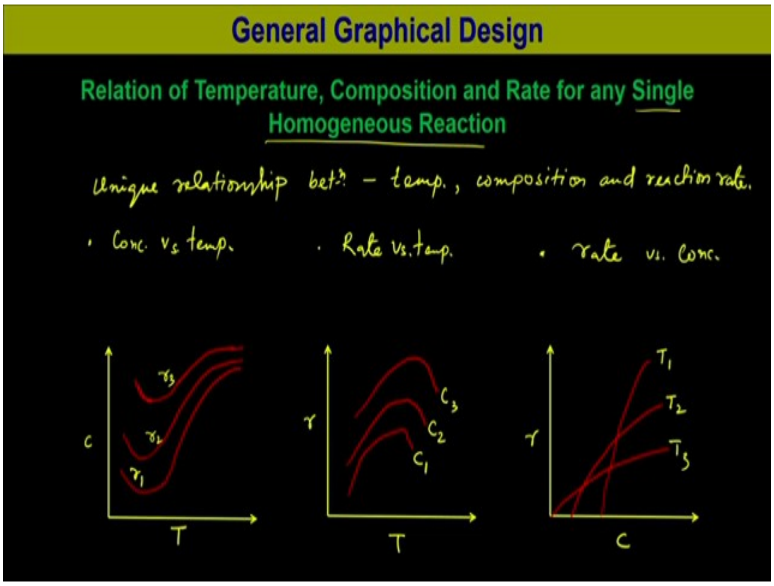

General Graphical Design

Relation of Temperature, Composition and Rate for any Single Homogeneous Reaction

Unique relationship betn – temp., composition and reaction rate.

- Conc. vs temp.
- Rate vs. temp.
- rate vs. conc.

So, let us start with general graphical design for a single reaction, there is a unique curve which we can obtain between the temperature, composition and reaction rates. They are very uniquely related to each other. So, for single reaction, relation of temperature, composition and rate for any single homogeneous reactions. As we said they are very uniquely related to each other when there is a single homogeneous reaction.

So, unique relationship temperature, composition and reaction rate in three different ways they can related. One of them is concentration versus temperature, and the typical plot looks like this, say this is r_1, this is r_2 and this is r_3. So, three different rates, there if we plot concentration versus time they look like this for any single reaction. So this is for single reaction, concentration versus temperature.

And we will use this curve in many occasions to describe the system or to design a reactor. And the second one is the rate versus temperature, so we can plot rate versus temperature and this can be like this. So, this is for say concentration C_1, this is C_2 and this is C_3. So, the rate versus temperature curve look like this and the other variation of it is the rate versus concentration. So, if we plot reaction rate versus concentration then we can obtain the curve at different temperature.

Say this is at temperature T_1, this is at temperature T_2 and this is at temperature T_3. So, the relations between temperature, composition and reaction rate for any single homogeneous reaction we can represent in three different ways. One is concentration versus temperature, second one is rate versus temperature and the third one is rate versus concentration. So, any three-ways we can represent the relationships among them.

But we will extensively use and analyze the concentration and temperature diagram at different temperatures. And we will see that a how to navigate the Contour plot. So, when we plot three different variables in two dimensions we call Contour plot. So we will extensively use these concentrations versus time graph different rates to compare among the different sizes as well as the other design aspects.

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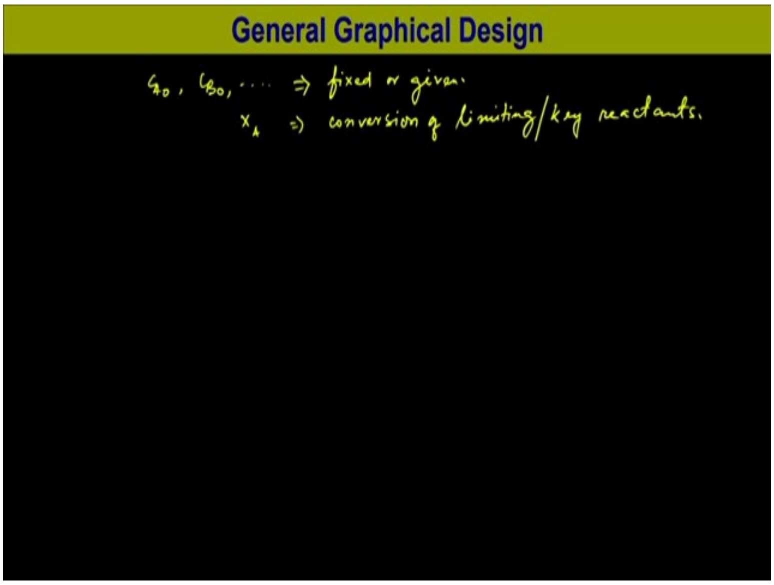
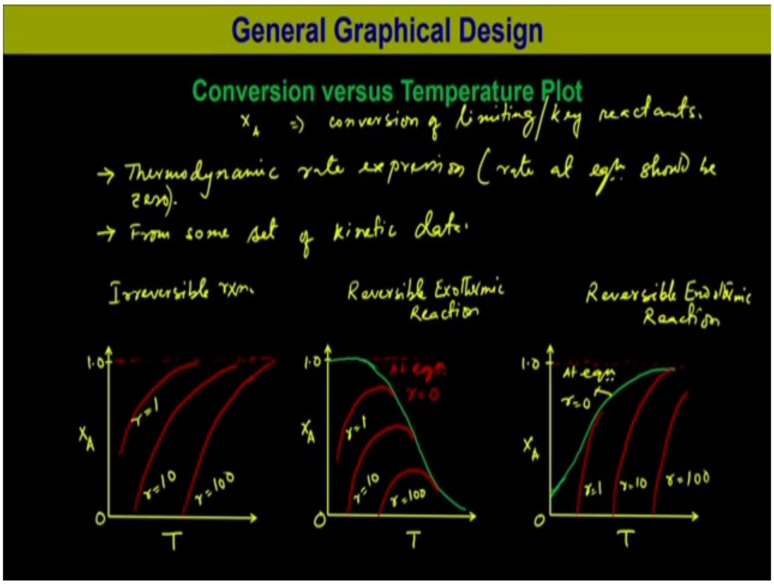


General Graphical Design

C_{A0}, C_{B0}, ... ⇒ fixed or given.

X_A ⇒ conversion of limiting/key reactants.



General Graphical Design

Conversion versus Temperature Plot

X_A ⇒ conversion of limiting/key reactants.

→ Thermodynamic rate expression (rate at eqm. should be zero).

→ From some set of kinetic data.

Irreversible rxn.

Reversible Exothermic Reaction

Reversible Endothermic Reaction

Now, for a given concentration at this concentration is a concentration say C_{A0}, C_{B0} and so on, these are fixed. Now we can consider any key components or the limiting reactants say X_0 is the conversion of limiting reactants. We can plot conversion versus temperature, so we can obtain conversion versus temperature plot. And say, let us consider a case of irreversible reaction and this is X_A which is from 0 to 1 and at temperature T.

Now, if we plot different rates for irreversible reaction say, so these are at different rates. So, this is for rate is equal to 1, this is for rate is equal to 10 and this is for rate is equal to 100. So, we can see the how for irreversible reaction, conversion versus temperature plot at different rates looks like. Similarly, if we consider reversible reaction there will be two cases of reversible reaction. One is exothermic reversible reaction and endothermic reversible reaction.

So, when it is exothermic reversible reaction, the conversion will be limited by the equilibrium relationship. So, for reversible exothermic reaction and this is X_A, this is T, this is 0 and this is what is conversion maximum one. Now if we plot, so this is the equilibrium conversion which is shown in the green line where the rate for reversible reactions would be zero. So, at equilibrium r should be 0. So, in that case, the rate at different values would be like this. So this is the rate at r is equal to one, this is at r is equal to 10 and this is at r is equal to 100.

So, and this is for reversible exothermic reactions and at for reversible exothermic reactions the conversion will be limited by the equilibrium relationships. And at equilibrium the rate should be zero. So, for another case, is the reversible endothermic reaction, so this is X_A, this is T, this is 0. So this is 1.0, so this is the maximum conversion line at different temperature. And at equilibrium for exothermic reaction it would be like this and then the rate at, so this would be the rate at r is equal to one, this is at r is equal to 10 and this is at r is equal to 100.

So, this is the rate at equilibrium, r is equal to 0 at equilibrium. So these are the general shape of the conversion versus temperature at different rates and for different reaction types, irreversible, reversible exothermic and reversible endothermic reaction. This plot can be prepared from the thermodynamic rate expression.

Rate at equilibrium should be 0 or we can plot from some set of kinetic data. So this can be either to H, we can plot this either we have thermodynamic consistent rate expression which is from where we can see that rate at equilibrium should be 0. Or we can plot from the set of kinetic data which are available but the accuracy of the data is very important to get a meaningful results. So the very accurate data should be generated to plot this curves.

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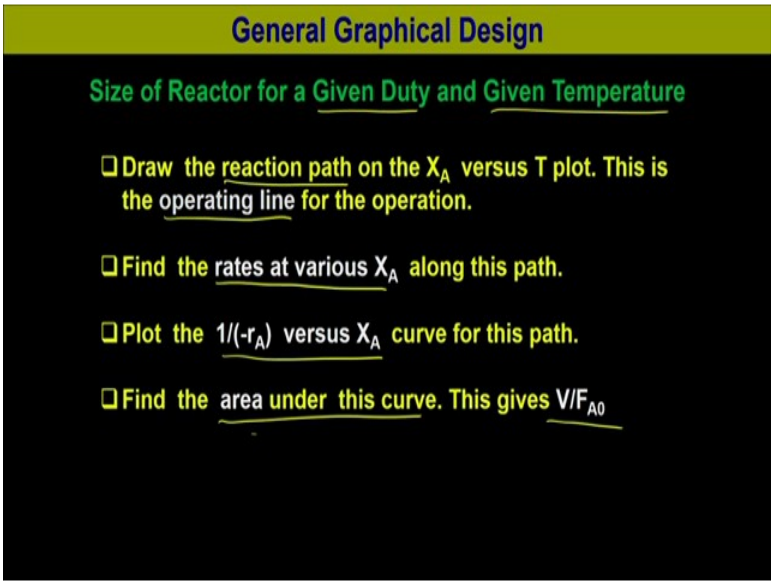

General Graphical Design

Size of Reactor for a Given Duty and Given Temperature

- ❑ Draw the reaction path on the X_A versus T plot. This is the operating line for the operation.
- ❑ Find the rates at various X_A along this path.
- ❑ Plot the $1/(-r_A)$ versus X_A curve for this path.
- ❑ Find the area under this curve. This gives V/F_{A0}

Now, let us see, how we can find out size of a reactor for a given duty and given temperature? The general procedure to calculate the size of the reactor for a given duty and given temperature can be as follows. First we need to draw the reaction path on X_A versus T the plot. We have seen X_A versus T plot and we need to draw the reaction path on this X_A versus T plot. And this would be the operating line for the operation.

So, once we get this operating line from the reaction path from the figure X_A versus T, we can calculate the rates at various X_A along this path. And then, once rate is known to us we can calculate one by $-r_A$ versus X_A curve from this path. And then the area under this curve gives the V by F_{A0}. So, once we get the area that would be the V by F_{A0}.

. So that way we can calculate the size for a given duty and at a given temperature.

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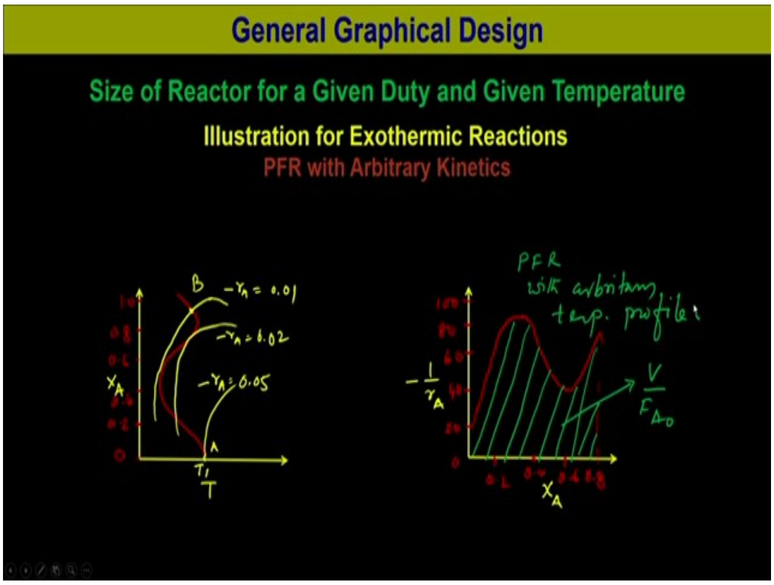

General Graphical Design

Size of Reactor for a Given Duty and Given Temperature

Illustration for Exothermic Reactions

PFR with Arbitrary Kinetics

So, let us illustrate for an exothermic reactions how it look like? And first we will consider PFR plug flow reactor with the arbitrary kinetics. Say this is X_A and this is temperature and let the reactions start with a inlet temperature T_1. So, the consider any arbitrary path for this, so this point, say this is point A and have the rate is 0.05. And then say this is rate, say $-r_A$, here $-r_A$ is equal to 0.02 and say this is a rate at B and rate is $-r_A$ is equal to 0.01.

So, at different locations of this arbitrary path, which is the operating line for this reactions to happen in plug flow reactor? So, we can calculate the rate at different locations. So, we can plot $-r_A$ versus conversion and we can obtain this say this is 0, this is 20, this 40, this is 60, 80, 100. And this is a path you will get where the conversion here is 0.8, say this is 0.4, 0.6, 0.2, 0. So, the area under this, this will give the V by F_{A0} and this is for PFR with arbitrary temperature profile.

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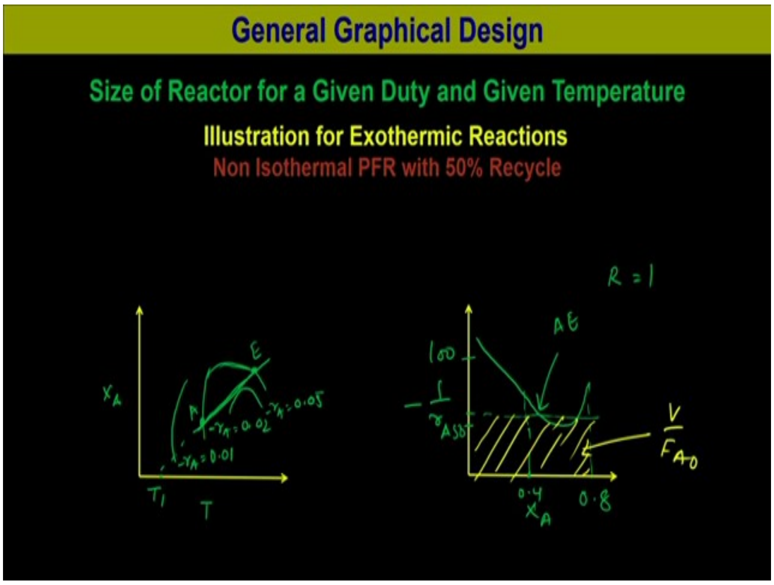

General Graphical Design

Size of Reactor for a Given Duty and Given Temperature

Illustration for Exothermic Reactions

Non Isothermal PFR with 50% Recycle

Now, let us consider another case similar to this is non-isothermal PFR with 50 percent recycle. And in this case, we can plot X_A versus T and say the reaction the starts at T_1 and this so this is the path and at different rates. This is for r minus r A is equal to 0.01 and this is for say point minus r A is equal to 0.02. And this is $-r_A$ is equal to 0.05 and so on. So this is the profile for the recycle reactor say this is A and this is E.

So, if we plot this recycle reactor with a recycle ratio R=1, we can get the curve like this. This is $-r_A$ versus X_A plot and say this is 50, this is 100 and in this case the, say this is 0.4, so this is the location or the arbitrary kinetics is look like this. This is along the path AE and the average area is about this. So this gives V by F_{A0}, so this is for non-isothermal PFR with 50 percent recycle.

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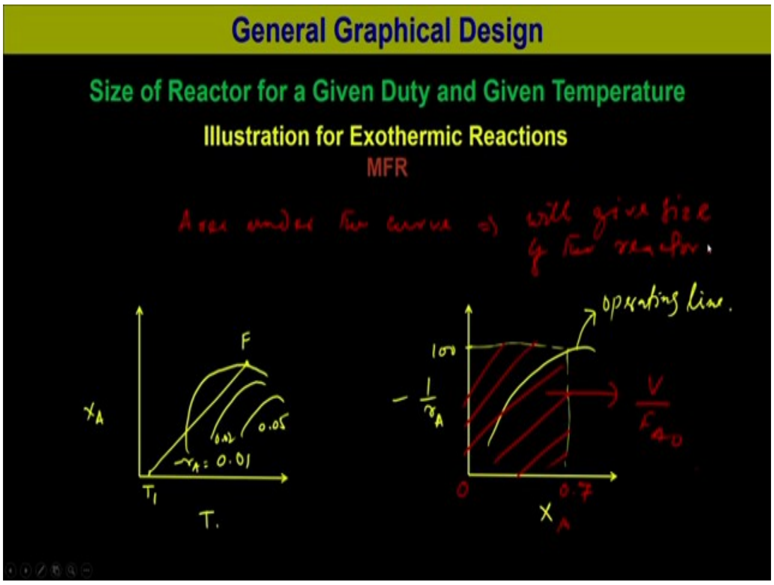

General Graphical Design

Size of Reactor for a Given Duty and Given Temperature

Illustration for Exothermic Reactions

MFR

Area under the curve ⇒ will give size of the reactor.

Similarly, for mix flow reactor if we consider mix flow reactor the operating line will reached to a point. Because this is well mixed and the concentration at the entrance at the inside the reactor as well as the exit are same at you know at a particular time. So if we plot for this say this is X_A and this is T and reaction start at any T, T_1 and it will reach to a point say the rate curve say point F.

So this is $-r_A$ is equal to 0.01 then you have other rate curves, so which is 0.02 and 0.05. So if we plot for this we would obtain $-r_A$ versus X_A it would be say this is 100. So this is the operating line and the area under this is the V by F_{A0}, say this is zero and this is say 0.7.

So, this way, we can determine the size of the reactor when, you know, the temperature is given and for a particular duty we can plot in a stepwise manner. First we need to obtain the operating line and then we can calculate the rate versus conversion. And then we can plot $-r_A$ versus conversion and from that the area under the curve will give the volume or size of the reactor.

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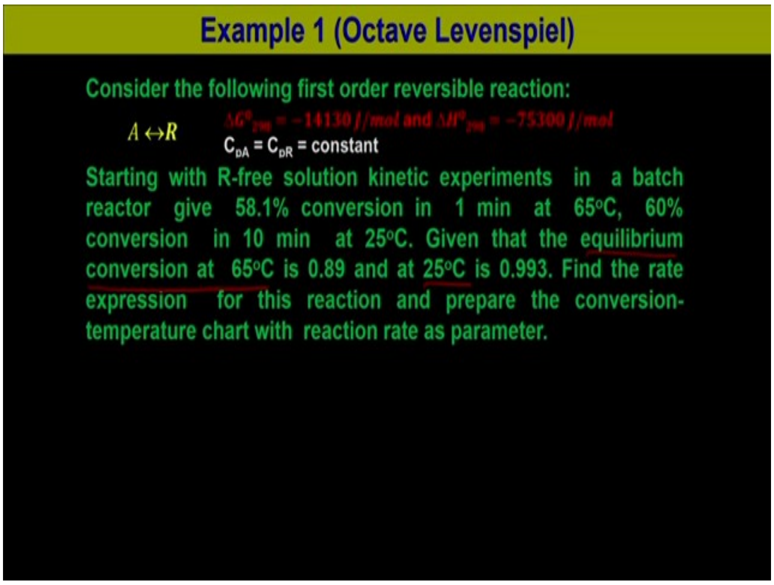

Example 1 (Octave Levenspiel)

Consider the following first order reversible reaction:

$A \leftrightarrow R$ $\Delta G^0_{298} = -14130\ J/mol$ and $\Delta H^0_{298} = -75300\ J/mol$

$C_{pA} = C_{pR}$ = constant

Starting with R-free solution kinetic experiments in a batch reactor give 58.1% conversion in 1 min at 65°C, 60% conversion in 10 min at 25°C. Given that the equilibrium conversion at 65°C is 0.89 and at 25°C is 0.993. Find the rate expression for this reaction and prepare the conversion-temperature chart with reaction rate as parameter.

Now, let us consider an example to see how we can calculate the rate concentration and temperature diagram. So we will consider the same example which is given in octave levenspiel, so consider the following. First order reversible reaction where A to R, this is first order reversible reaction and this is the values which we have considered in the last lecture. These are the Gibbs you know free energy standard Gibbs free energy change values, ΔH^0 is also given.

And C D A is equal to C D R is equal to constant and we from this, we have obtained the equilibrium relationship. Now, if we start with R free that is initially you now R H present. So C_A are not equal to 0 and the kinetic experiment in a batch reactor give 58.1 percent conversion in one minute at 65 ^0C , 60 percent conversion in 10 minutes at 25 ^0C . Given that the equilibrium conversion at 65 ^0C is 0.89 and at 25 ^0C is 0.993.

Find the rate expression for this reaction and prepare the conversion temperature chart with reaction rate as parameter. This equilibrium conversion values at 65 and at 25 which is we have calculated in the example, we considered in the last you know lecture from there we have taken this values. And we can consider the same equilibrium relationship which we have developed would be applicable here. So let us start with this problem.

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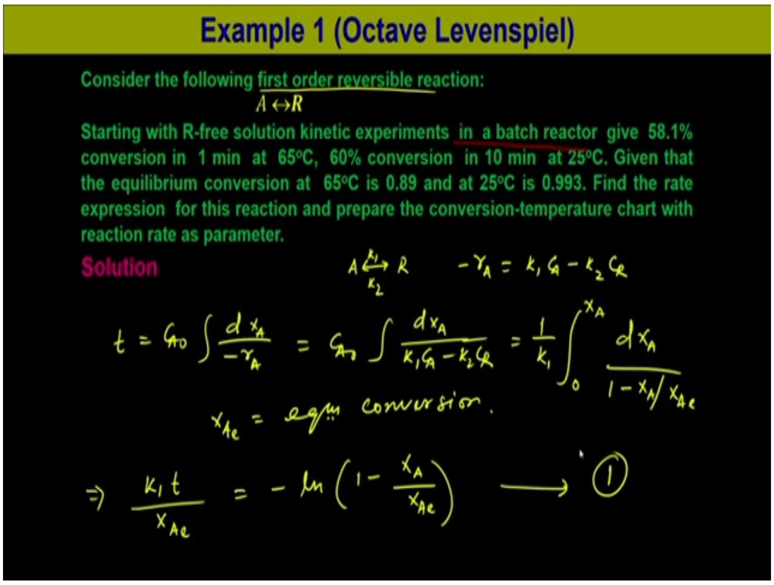

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Solution

$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R \qquad -r_A = k_1 C_A - k_2 C_R$

$$t = C_{A0} \int \frac{dX_A}{-r_A} = C_{A0} \int \frac{dX_A}{k_1 C_A - k_2 C_R} = \frac{1}{k_1} \int_0^{X_A} \frac{dX_A}{1 - X_A/X_{Ae}}$$

X_{Ae} = eqm conversion.

$$\Rightarrow \frac{k_1 t}{X_{Ae}} = -\ln\left(1 - \frac{X_A}{X_{Ae}}\right) \longrightarrow ①$$

So, now we have to considered the performance equation in a batch reactor. So, let us consider the performance equation for reversible first order reaction first order reversible reaction, the performance equation we have to derive. So A to R the rate $-r_A = k_1 C_A - k_2 C_R$.

Now for batch reactor, the performance equation $t = C_{A0} \int \frac{dX_A}{-r_A}$.

Now, if you substitute $-r_A$ over here it would be $t = C_{A0} \int \frac{dX_A}{k_1 C_A - k_2 C_R}$. So we can write this one as equal $\frac{1}{k_1} \int_0^{X_A} \frac{dX_A}{1 - \frac{X_A}{X_{Ae}}}$. Here X_{Ae} is the equilibrium conversion and all other terms have there usual meaning as we have discussed earlier.

C_A is the concentration of competent of A, C_R is the concentration of competent R and k_1 is the forward rate constant and k_2 is the reversed rate constant, so t is the time and C_{A0} is the initial concentration, X_A is the conversion. So, now, as we have discussed earlier in module 2 for the interpretation of the batch reactor data, we have done the integration of this, if we follow the same procedure. If we integrate it, we would obtain $\frac{k_1 t}{X_{Ae}} = -\ln(1 - \frac{X_A}{X_{Ae}}) \to (1)$.

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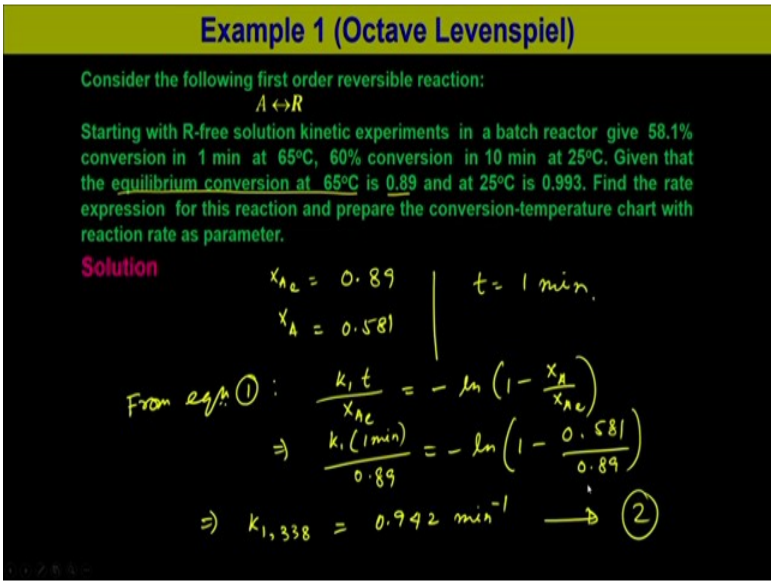

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Solution

$X_{Ae} = 0.89$ | $t = 1$ min

$X_A = 0.581$

From eqn ①: $\frac{k_1 t}{X_{Ae}} = -\ln\left(1 - \frac{X_A}{X_{Ae}}\right)$

$\Rightarrow \frac{k_1 (1\,\text{min})}{0.89} = -\ln\left(1 - \frac{0.581}{0.89}\right)$

$\Rightarrow k_{1,338} = 0.942\ \text{min}^{-1} \longrightarrow$ ②

Now, we will calculate the forward rate constant which is not given over here. So as it is given here that the equilibrium conversion at 65 ^0C is 0.89. So X_{Ae}= 0.89 and at 65 ^0C temperature, the conversion X_A= 0.581, time t=1 min. So if we apply this equation, equation one, so the equation one is $\frac{k_1 t}{X_{Ae}} = -\ln(1 - \frac{X_A}{X_{Ae}})$.

Now, this would be equal to $\frac{k_1(1\,\text{min})}{0.89} = -\ln(1 - \frac{0.581}{0.89})$. And if we solve it, we would obtain k_1 at 65 ^0C , $k_{1,338} = 0.942\,\text{min}^{-1} \rightarrow (2)$.

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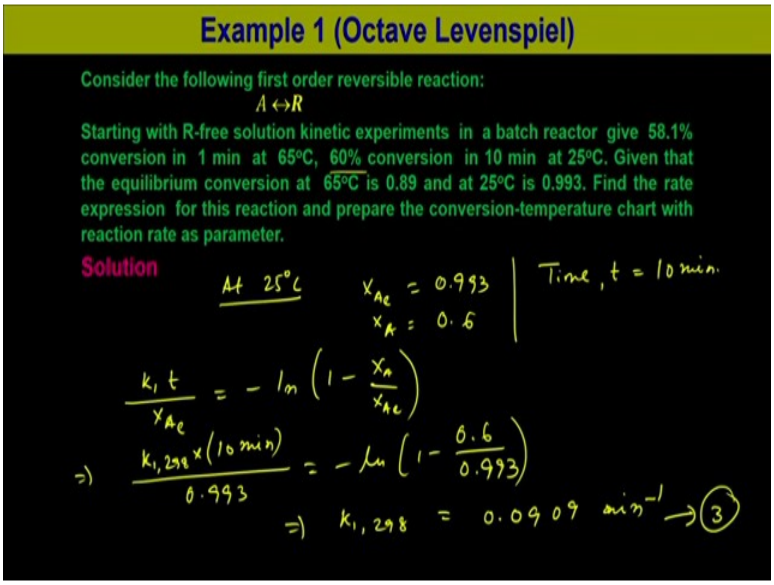

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Solution

At 25°C

$X_{Ae} = 0.993$

$X_A = 0.6$

Time, $t = 10$ min.

$$\frac{k_1 t}{X_{Ae}} = -\ln\left(1 - \frac{X_A}{X_{Ae}}\right)$$

$$\Rightarrow \frac{k_{1,298} \times (10\,\text{min})}{0.993} = -\ln\left(1 - \frac{0.6}{0.993}\right)$$

$$\Rightarrow k_{1,298} = 0.0909\ \text{min}^{-1} \rightarrow ③$$

Now, similarly, at 25 ^0C temperature $X_{Ae} = 0.993$ is the conversion that is at 60 percent 0.6, time $t = 10$ min. So, now if we substitute $\frac{k_1 t}{X_{Ae}} = -\ln(1 - \frac{X_A}{X_{Ae}}) \rightarrow (1)$. So, if we substitute here at 25 ^0C. So, this would be $\frac{k_{1,298}(10\,\text{min})}{0.993} = -\ln(1 - \frac{0.600}{0.993})$.

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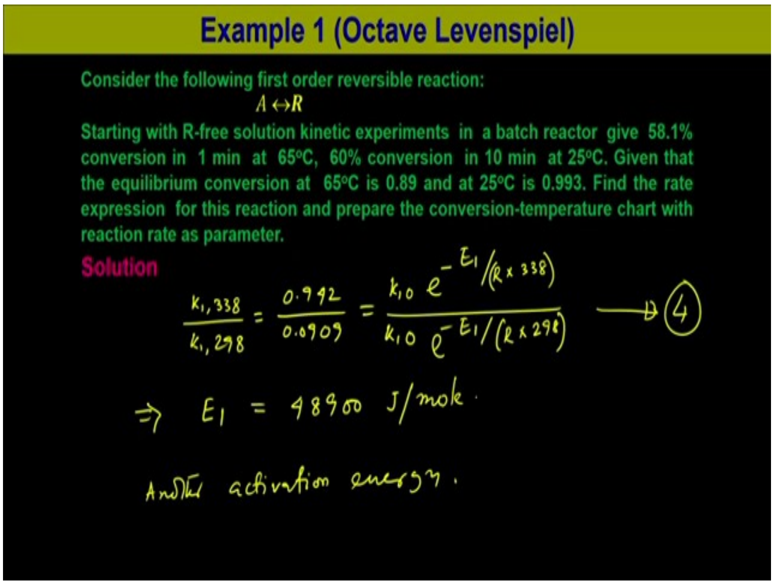

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Solution

$$\frac{k_{1,338}}{k_{1,298}} = \frac{0.942}{0.0909} = \frac{k_{1,0}\, e^{-E_1/(R \times 338)}}{k_{1,0}\, e^{-E_1/(R \times 298)}} \longrightarrow ④$$

$$\Rightarrow E_1 = 48900\ \text{J/mole}.$$

Another activation energy.

And from here we can obtain $k_{1,298} = 0.0909\,\text{min}^{-1} \rightarrow (3)$. So, we have calculated the forward rate constant at different temperature and also we have obtained the integral form of the performance equation. Now, if we assume the Arrhenius dependency of the Arrhenius temperature dependency of the ratio of the forward rate constants. Then at these two temperature we can write $\frac{k_{1,338}}{k_{1,298}} = \frac{0.942}{0.0909} = \frac{k_{10}\exp(-\frac{E_1}{(R*338)})}{k_{10}\exp(-\frac{E_1}{(R*298)})} \rightarrow (4)$.

So, from this if we solve, we can calculate $E_1 = 48900 J/mole$. So, similar to this since it is reversible reaction, so we have two activation energies. One is for the forward reaction and another is for the reverse reaction. So, we will calculate the another activation energy, say this is equation four. Now, from once we know E_1, we can calculate the relationship at different temperature, we can obtain the relationship at different temperature for the forward reaction.

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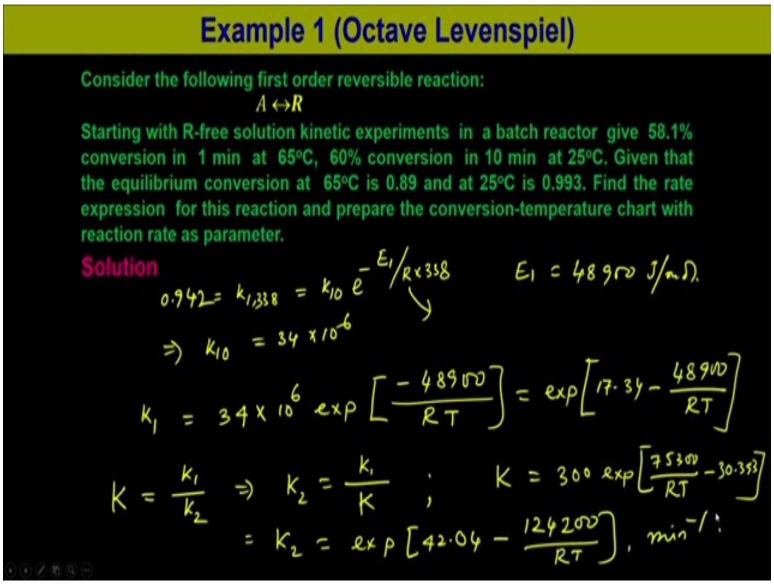

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Solution

$$0.942 = k_{1,338} = k_{10}\, e^{-E_1/R \times 338} \qquad E_1 = 48900\ J/mol.$$

$$\Rightarrow k_{10} = 34 \times 10^{-6}$$

$$k_1 = 34 \times 10^{6} \exp\left[\frac{-48900}{RT}\right] = \exp\left[17.34 - \frac{48900}{RT}\right]$$

$$K = \frac{k_1}{k_2} \Rightarrow k_2 = \frac{k_1}{K} \quad ; \quad K = 300 \exp\left[\frac{75300}{RT} - 30.353\right]$$

$$= k_2 = \exp\left[42.04 - \frac{124200}{RT}\right],\ min^{-1}$$

So, we can write from this we can evaluate $0.942 = k_{1,338} = k_{10} \exp(-\frac{E_1}{(R*338)})$. So, we know the values of , we have calculated which is 48900 joule per mole. And R is the universal gas constant, so and the value of $k_{1,338}$=0.942. So from here we can calculate k_{10} that is the free exponential factor $k_{10} = 34*10^{-6}$.

So, now, if we substitute in this relation we would get at any temperature $k_1 = 34*10^{-6} \exp(-\frac{48900}{RT}) = \exp(17.34 - \frac{48900}{RT})$. Now, we know equilibrium constant $K = \frac{k_1}{k_2}$. So from here we can write $k_2 = \frac{k_1}{K}$, capital K is the equilibrium constant. So, K already we have discussed in the last example, $K = 300 \exp(\frac{75300}{RT} - 30.393)$.

So, if we substitute these values over here and K 1 over here, we can calculate k_2. So, $k_2 = \exp(42.04 - \frac{124200}{RT}) \min^{-1}$.

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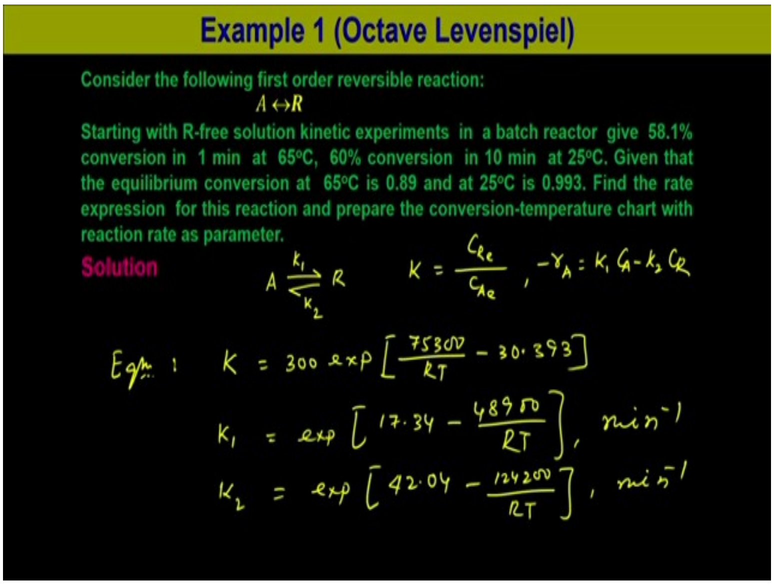

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Solution

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R \qquad K = \frac{C_{Re}}{C_{Ae}}, \; -r_A : K_1 C_A - K_2 C_R$$

Eqm : $K = 300 \exp\left[\frac{75300}{RT} - 30.393\right]$

$$K_1 = \exp\left[17.34 - \frac{48900}{RT}\right], \; min^{-1}$$

$$K_2 = \exp\left[42.04 - \frac{124200}{RT}\right], \; min^{-1}$$

So, now if we summarize what we have obtained for this reversible first order reaction, say our reaction is $A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R$, $K = \frac{C_{\mathrm{Re}}}{C_{Ae}}$, rate of reactions $-r_A = k_1 C_A - k_2 C_R$. Equilibrium relationship $K = 300\exp(\frac{75300}{RT} - 30.393)$. Rate constants $k_1 = \exp(17.34 - \frac{48900}{RT})\min^{-1}$, $k_2 = \exp(42.04 - \frac{124200}{RT})\min^{-1}$. So, with this specific information we can obtain the plot of conversion, temperature. So for any specific values of C_{A0} we can plot the conversion versus temperature.

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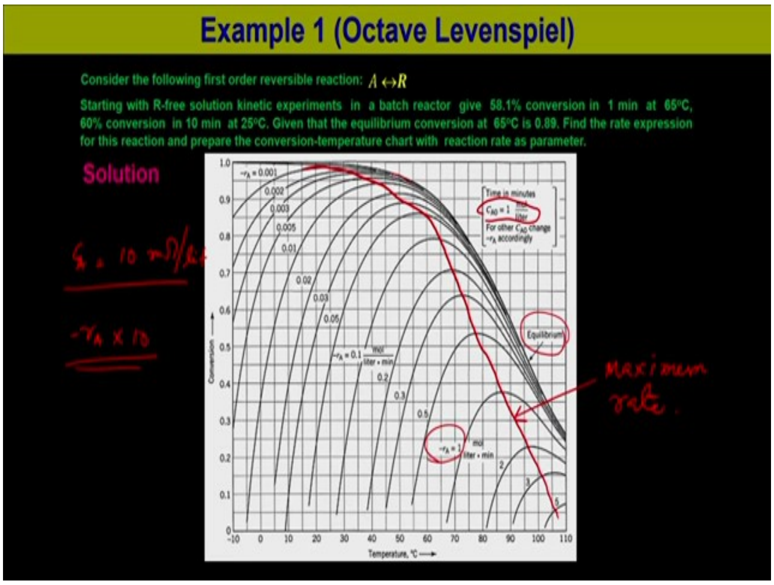

Example 1 (Octave Levenspiel)

Consider the following first order reversible reaction: $A \leftrightarrow R$

Starting with R-free solution kinetic experiments in a batch reactor give 58.1% conversion in 1 min at 65°C, 60% conversion in 10 min at 25°C. Given that the equilibrium conversion at 65°C is 0.89. Find the rate expression for this reaction and prepare the conversion-temperature chart with reaction rate as parameter.

Solution

C_{A0} = 10 mol/lit

$-r_A \times 10$

And the plot from levenspiel is look like this which is you know generated at different conversion versus temperature at a C_{A0}. So, C_{A0} is basically one mole per liter and time in minutes, so conversion versus temperature at different rate. And this is the line the black line represents over here is basically the equilibrium line and the rate you can see this is the maximum rate line.

So this line represents maximum rate. And this plot can be you know used for any other initial concentrations with only we need to multiply another rate with that you know concentration. Suppose we have concentration C_{A0} is 10 mole per liter. The, all the rates must be multiplied with minus r A into 10, so that we can use this plot for any initial concentration of the reactant.

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THANK YOU

So, thank you very much for attending this lecture and we will continue our discussion of reactor design where we were discussing the temperature and pressure effect. And that we will continue with different optimum design conditions in the next lecture.