

Chapter 11, Question 7 - Explanation

For a second-order reversible reaction the rate law reads as:

$$-r_A = k \left(c_A^2 - \frac{c_C^2}{K_C} \right) \quad (1)$$

The design equation for the PBR:

$$F_{A0} \frac{dX}{dW} = -r_A \quad (2)$$

Concentrations in the gas phase:

$$c_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)T/T_0} \quad (3)$$

$$c_C = \frac{F_{A0}X}{v_0(1+\varepsilon X)T/T_0} \quad (4)$$

Plug into the rate law (here $\varepsilon = 0$):

$$-r_A = \frac{kF_{A0}^2}{v_0^2} \left[(1-X)^2 - \frac{X^2}{K_C} \right] \left(\frac{T_0}{T} \right)^2 \quad (5)$$

Combine with the design equation and simplify:

$$\frac{dX}{dW} = \frac{kF_{A0}}{v_0^2} \left[(1-X)^2 - \frac{X^2}{K_C} \right] \left(\frac{T_0}{T} \right)^2 \quad (6)$$

$$\text{Total initial concentration: } c_{T0} = \frac{F_{T0}}{v_0} = \frac{F_{A0}+F_I}{v_0} = \frac{F_{A0}(1+\theta_I)}{v_0} \Rightarrow v_0 = \frac{F_{A0}(1+\theta_I)}{c_{T0}}$$

By eliminating unknown F_{A0} with the above we get the following design equation:

$$\frac{dX}{dW} = \frac{kC_{T0}}{v_0(1+\theta_I)} \left[(1-X)^2 - \frac{X^2}{K_C} \right] \left(\frac{T_0}{T} \right)^2 \quad (7)$$

Analysis:

For a second-order reversible reaction we see from the above equation that for large θ_I the derivative is close to zero and the conversion changes very little with W . However, the PBR is operated adiabatically and the adiabatic temperature can be expressed as:

$$T = T_0 + \frac{-\Delta H_{Rx} \cdot X}{C_{PA} + \theta_I C_{PI}}$$

The specific rate constant depends on temperature, as does the equilibrium constant.

Case A: endothermic reaction

For endothermic reaction the mixture is cooling down during the course of the reaction and the temperature decreases lowering the rate and equilibrium conversion. Now, as θ_I increases, temperature also increases and both the rate and equilibrium conversion increase - the reaction becomes virtually

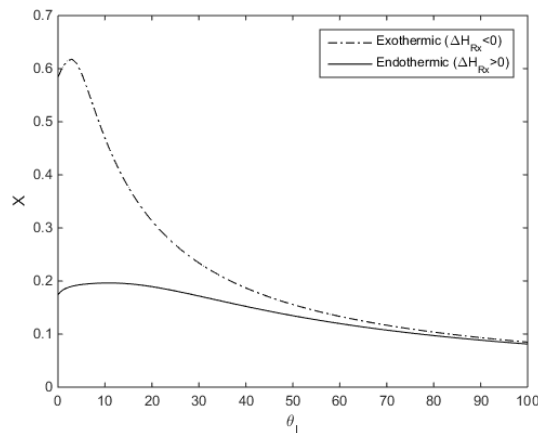
isothermal at large values of θ_I . However, as we see from Eqn. (7) that as θ_I increases, the conversion will decrease, therefore the answer is false.

Case B: exothermic reaction

As the θ_I increases, the temperature decreases while the equilibrium conversion increases. At large θ_I the reaction becomes virtually isothermal so that k and X_e remain constant but from Eqn. (7) we see that the conversion decreases with increasing θ_I .

Both X - θ_I dependences can be shown graphically on a plot which is presented below.

All in all, the cases A) and B) are false, because the curve in the question is monotonically increasing prior to reaching a plateau.



C), D) For first-order reversible reaction there is no effect of concentration on conversion, but the temperature will decrease with increasing fraction of the inerts, causing the specific reaction rate (and thus conversion) to decrease. The rate law for cases C) and D) can be expressed as follows:

$$-r_A = k \left(c_A - \frac{c_C}{K_C} \right)$$

Following the same routine as before, we arrive at the combined rate law and design equation:

$$\frac{dX}{dW} = \frac{k}{v_0} \left[(1 - X) - \frac{X}{K_C} \right] \left(\frac{T_0}{T} \right)$$

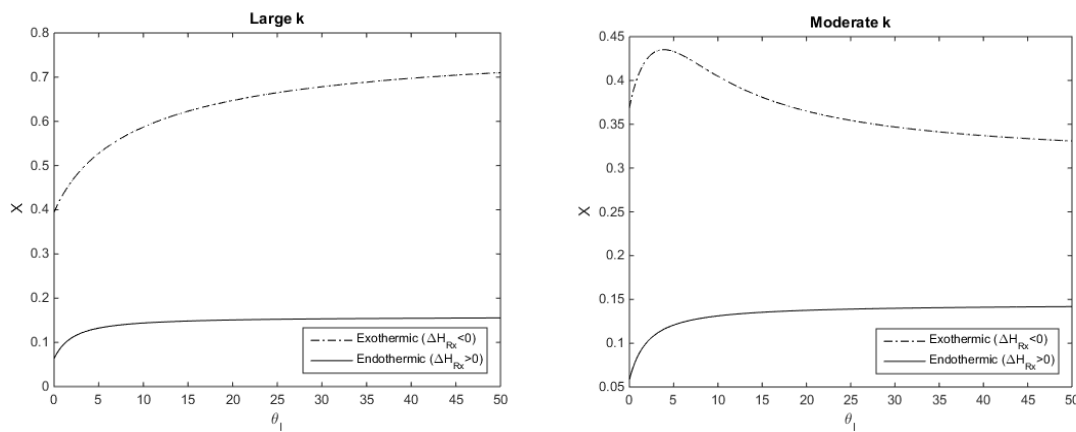
But what happened? We see that the solution does not depend on θ_I at all! Actually, this is only apparent, since we still need to couple k and K_C with the expression for adiabatic temperature:

$$T = T_0 + \frac{-\Delta H_{Rx} \cdot X}{C_{PA} + \theta_I C_{PI}}$$

We see that as θ_I increases, the temperature inside the reactor approaches T_0 . For higher values of k the system reaches equilibrium faster. Increasing θ_I makes the reaction virtually isothermal and thus k and X_e are virtually constant, so the plot proposed in the question is valid. Therefore, C) and D) are true.

For moderate k , the equilibrium is not achieved fast and the reaction might never take off. The competing effects, similar to the one for second-order reaction, appear and the maximum of X is visible on the $X-\theta_I$ plot for the exothermic reaction. Thus, answer C) is in this case false. For endothermic reaction, the curve does not exhibit extremum because the conversion has no reason to increase in an autocatalytic manner. Hence, answer D) is true. The figures obtained in a numerical simulations are presented below for comparison.

We conclude that **both C) and D) are true** even though for moderate k answer C) was false because of the keyword “The reaction **could** be a first-order reversible exothermic reaction”.



E) Finally, we arrive at the last variant, the **irreversible zero-order exothermic reaction**. The rate law is simply:

$$-r_A = k \quad (8)$$

Combined with the design equation:

$$\frac{dX}{dW} = \frac{k}{F_{A0}} \quad (9)$$

Again, substituting for F_{A0} :

$$\frac{dX}{dW} = \frac{k(1 + \theta_I)}{c_{T0}v_0} \quad (10)$$

Simple integration gives:

$$X = \frac{k(1 + \theta_I)}{c_{T0}v_0} W \quad (11)$$

In this case, as θ_I increases, we approach isothermal conditions so that k is virtually constant. We see from Eqn. (11) that X will increase linearly with increasing θ_I for constant W . X will increase and will not reach plateau for low activation energies (however, because the reaction is exothermic, the adiabatic temperature increase will enhance the reaction rate and cause deviations from linearity for moderate θ_I). This behavior is not what we see on the plot in the question, therefore E) is **false**.

For higher activation energies the conversion may however reach plateau, but we have already shown that the answer E) is **false**.

