Lecture 24

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Web Lecture 24
Class Lecture 20-Thursday

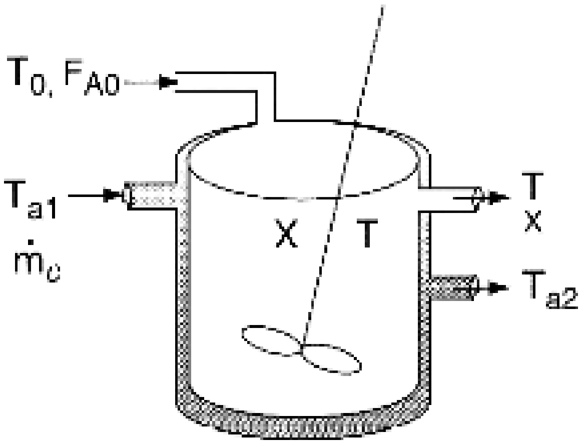
Review of Multiple Steady States (MSS)

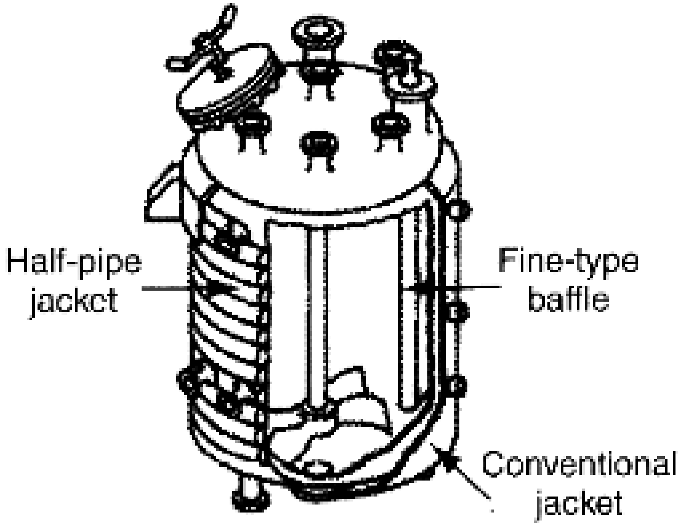
Reactor Safety (Chapter 13)

- Blowout Velocity
- CSTR Explosion
- Batch Reactor Explosion

Review Last Lecture

CSTR with Heat Effects





Review Last Lecture

Energy Balance for CSTRs

$$\frac{dT}{dt} = \frac{F_{A0}}{\sum N_i C_{P_i}} \left[\boldsymbol{G(T) - R(T)} \right]$$

$$G(T) = \left(r_A V\right)\left[\Delta H_{Rx}\right]$$

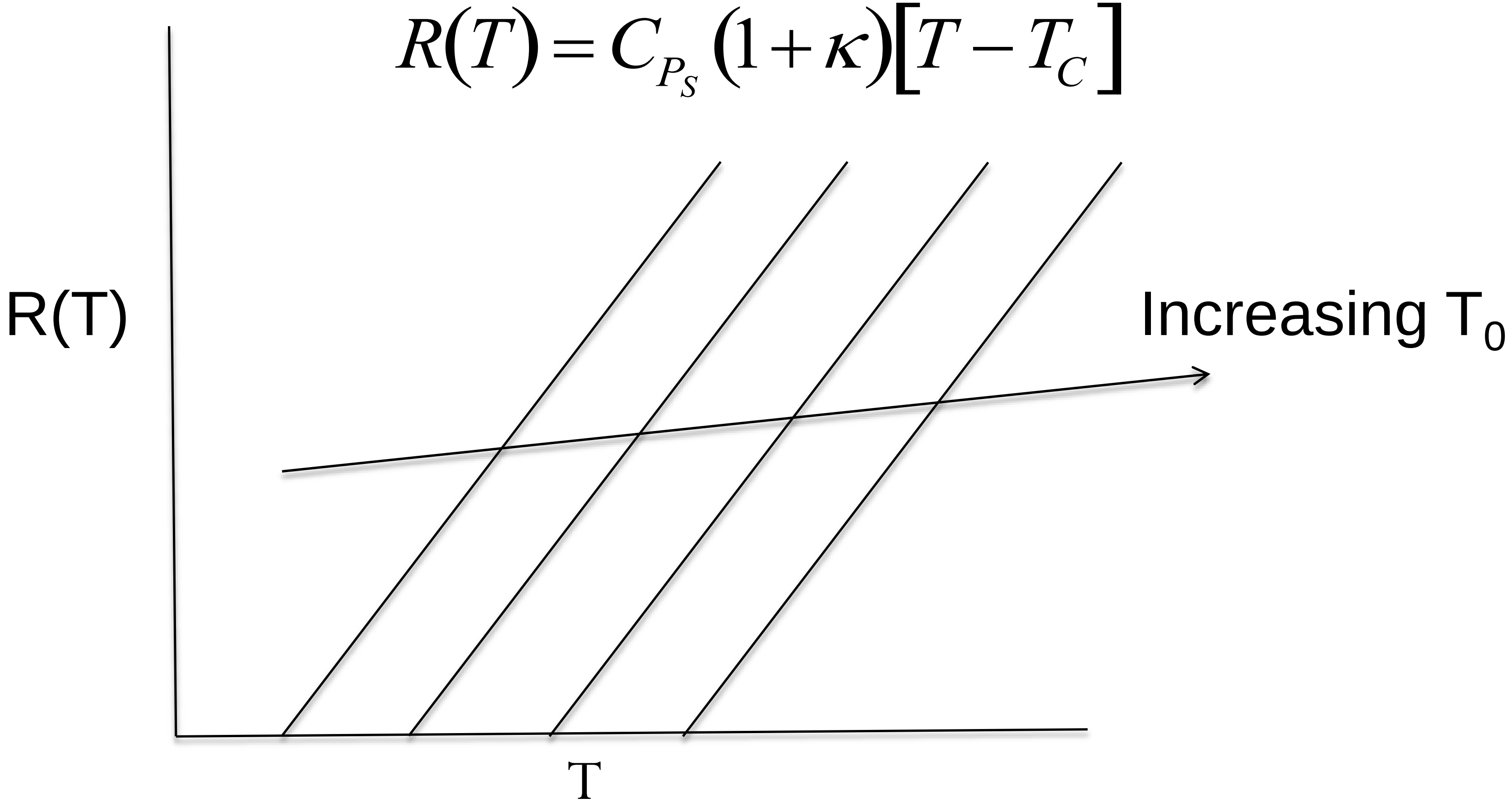
$$R(T) = C_{P_S}\left(1+\kappa\right)\left[T - T_C\right]$$

$$\kappa = \frac{UA}{F_{A0} C_{P0}} \qquad T_C = \frac{T_0 + \kappa T_a}{1+\kappa}$$

Review Last Lecture

Energy Balance for CSTRs

$$R(T) = C_{P_S}(1+\kappa)[T - T_C]$$

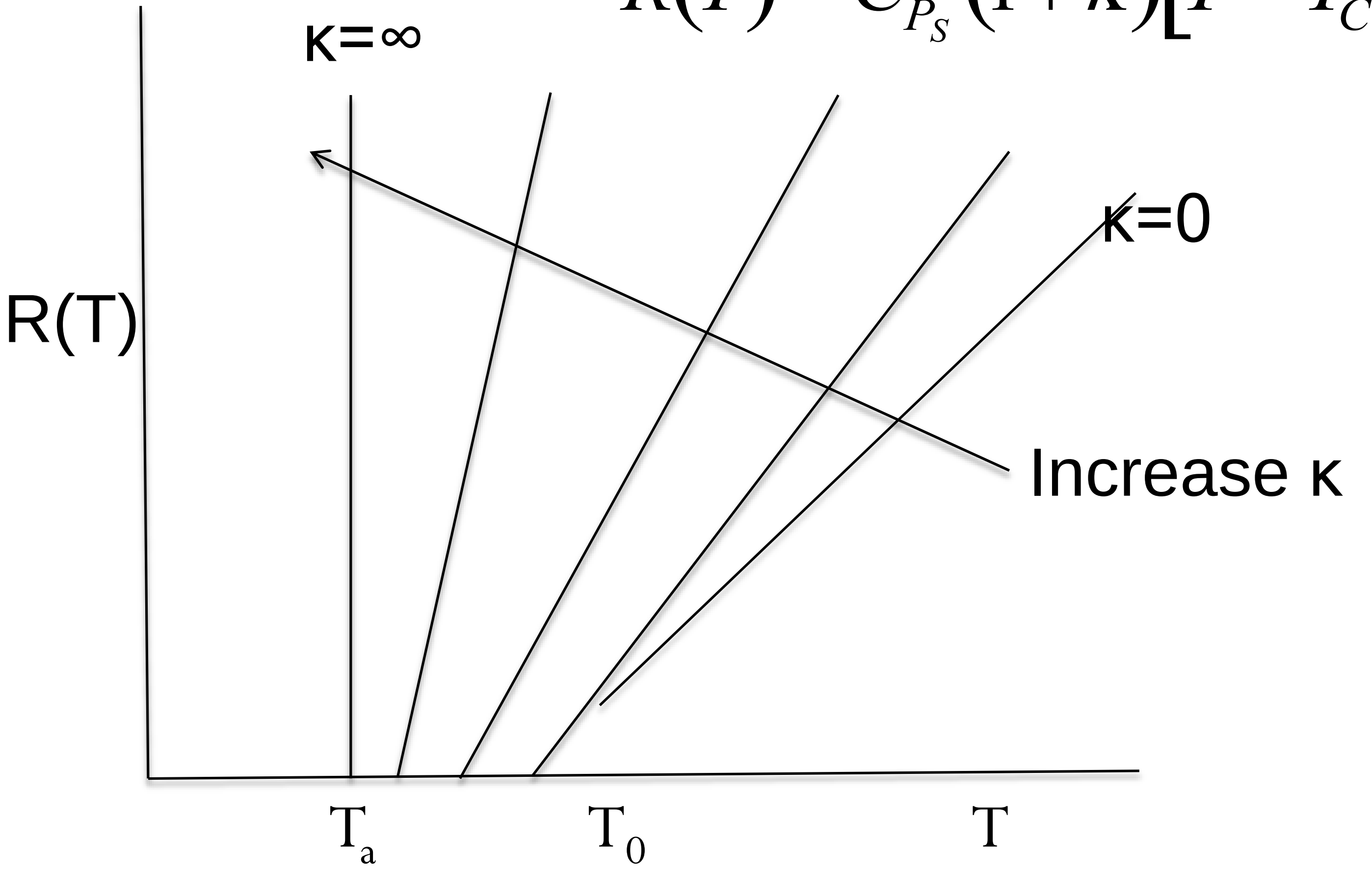


Variation of heat removal line with inlet temperature.

Review Last Lecture

Energy Balance for CSTRs

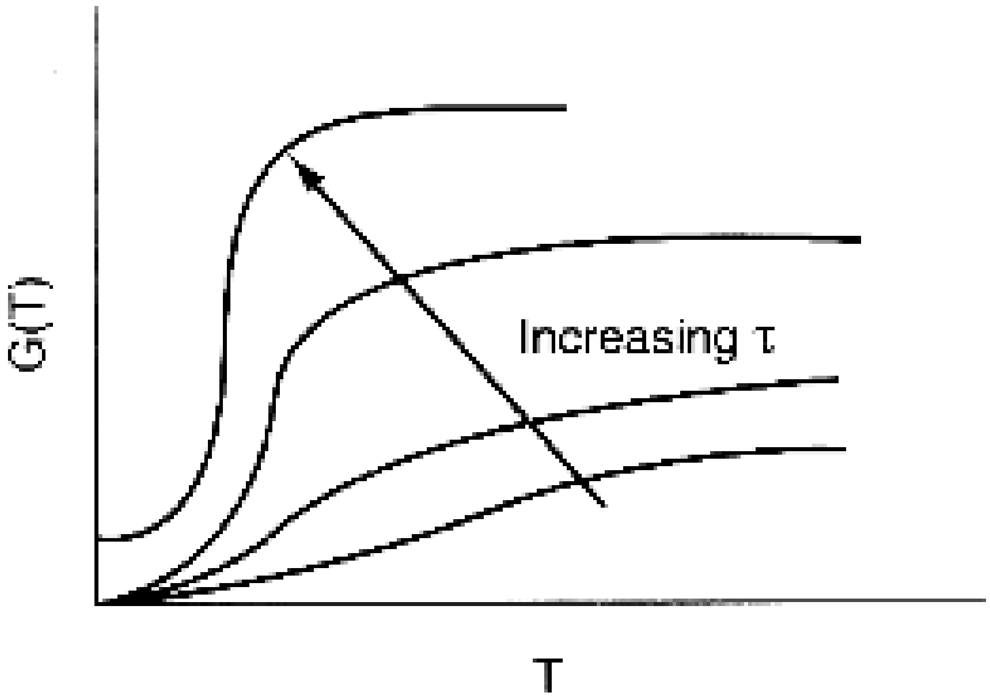
$$R(T) = C_{P_S}(1+\kappa)\left[T - T_C\right]$$



Variation of heat removal line with κ ($\kappa = UA/C_{P0}F_{A0}$)

Review Last Lecture

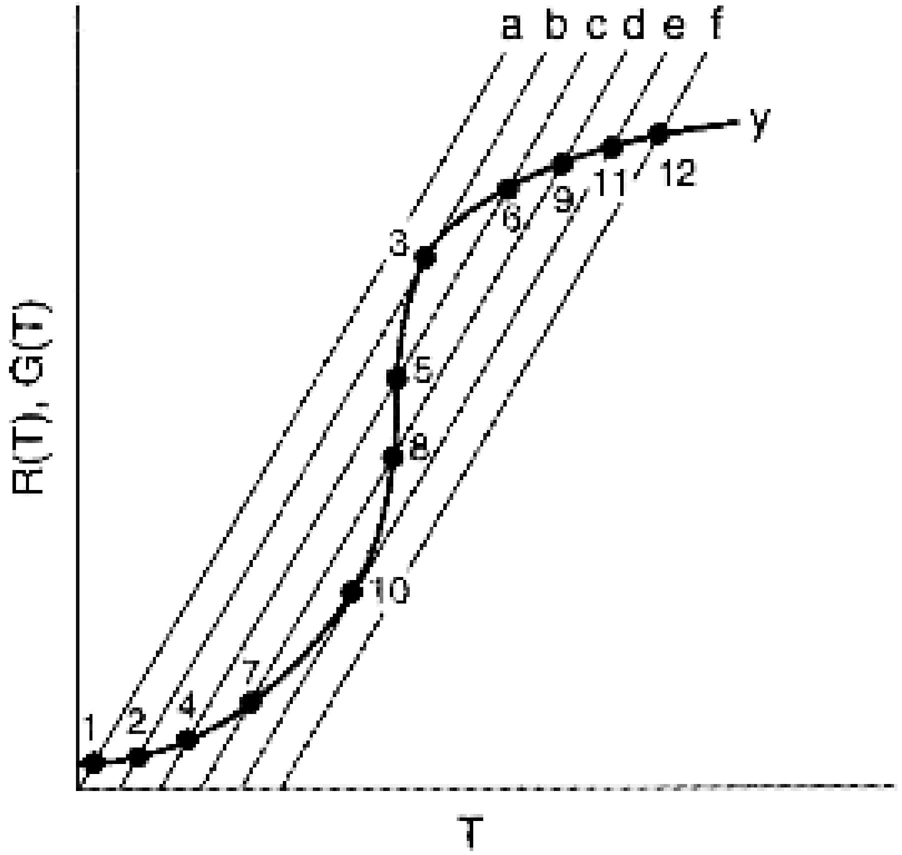
Multiple Steady States (MSS)



Variation of heat generation curve with space-time.

Review Last Lecture

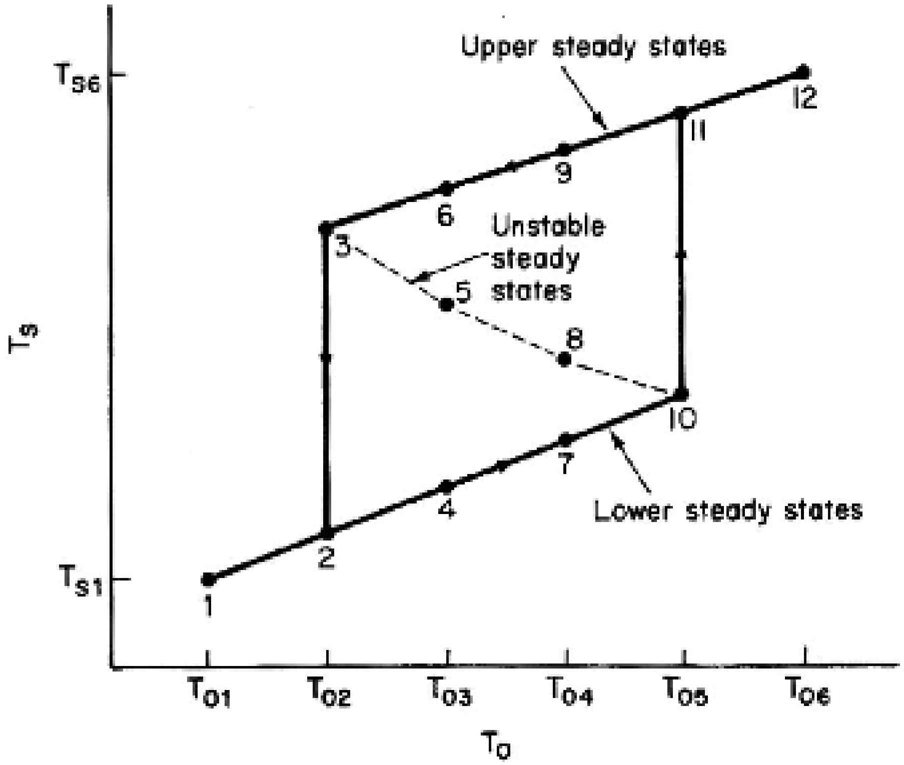
Multiple Steady States (MSS)



Finding Multiple Steady States with T_0 varied

Review Last Lecture

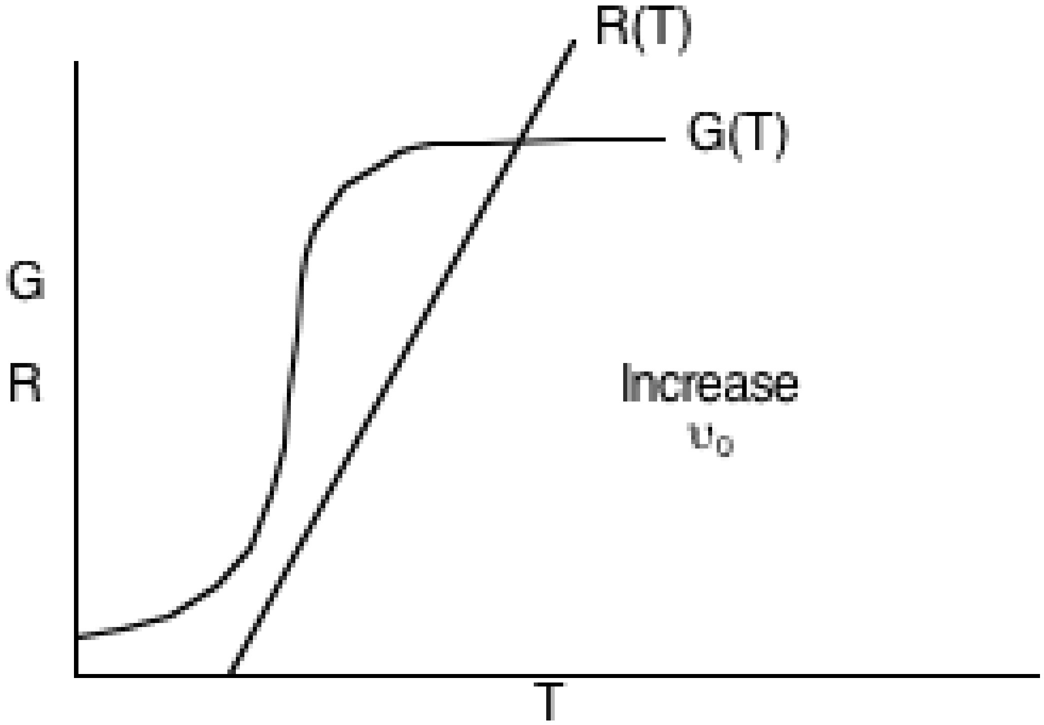
Multiple Steady States (MSS)



Temperature ignition-extinction curve

Review Last Lecture

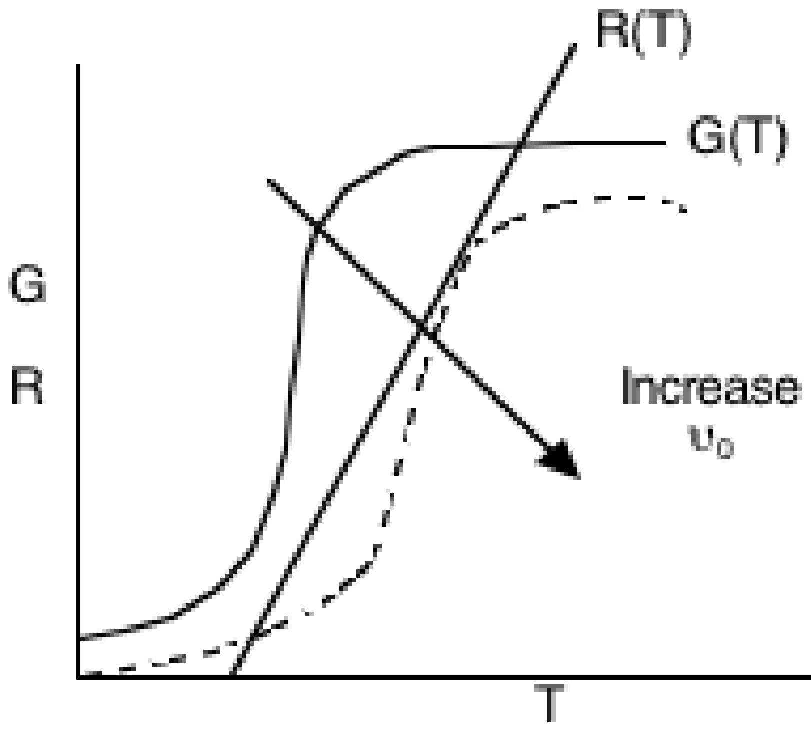
Multiple Steady States (MSS)



Bunsen Burner Effect (Blowout)

Review Last Lecture

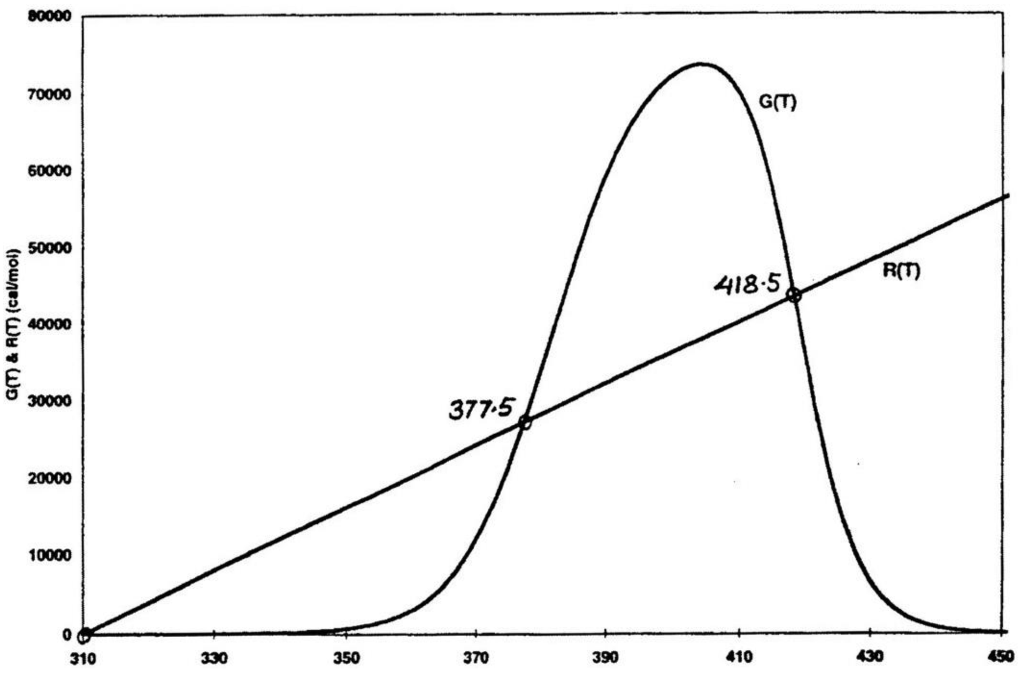
Multiple Steady States (MSS)



Bunsen Burner Effect (Blowout)

Reversible Reaction
Gas Flow in a PBR with Heat Effects

$A \leftrightarrow B$



$$V = \frac{\upsilon_0 C_{A0} X}{kC_{A0}\left(1 - X - \frac{X}{K_e}\right)}, \quad X = \frac{\tau k}{1 + \tau k\left(1 + \frac{1}{K_e}\right)}$$

$$G = -\Delta H_{Rx} X = \frac{-\Delta H_{Rx} \tau k}{1 + \tau k\left(1 + \frac{1}{K_e}\right)}$$

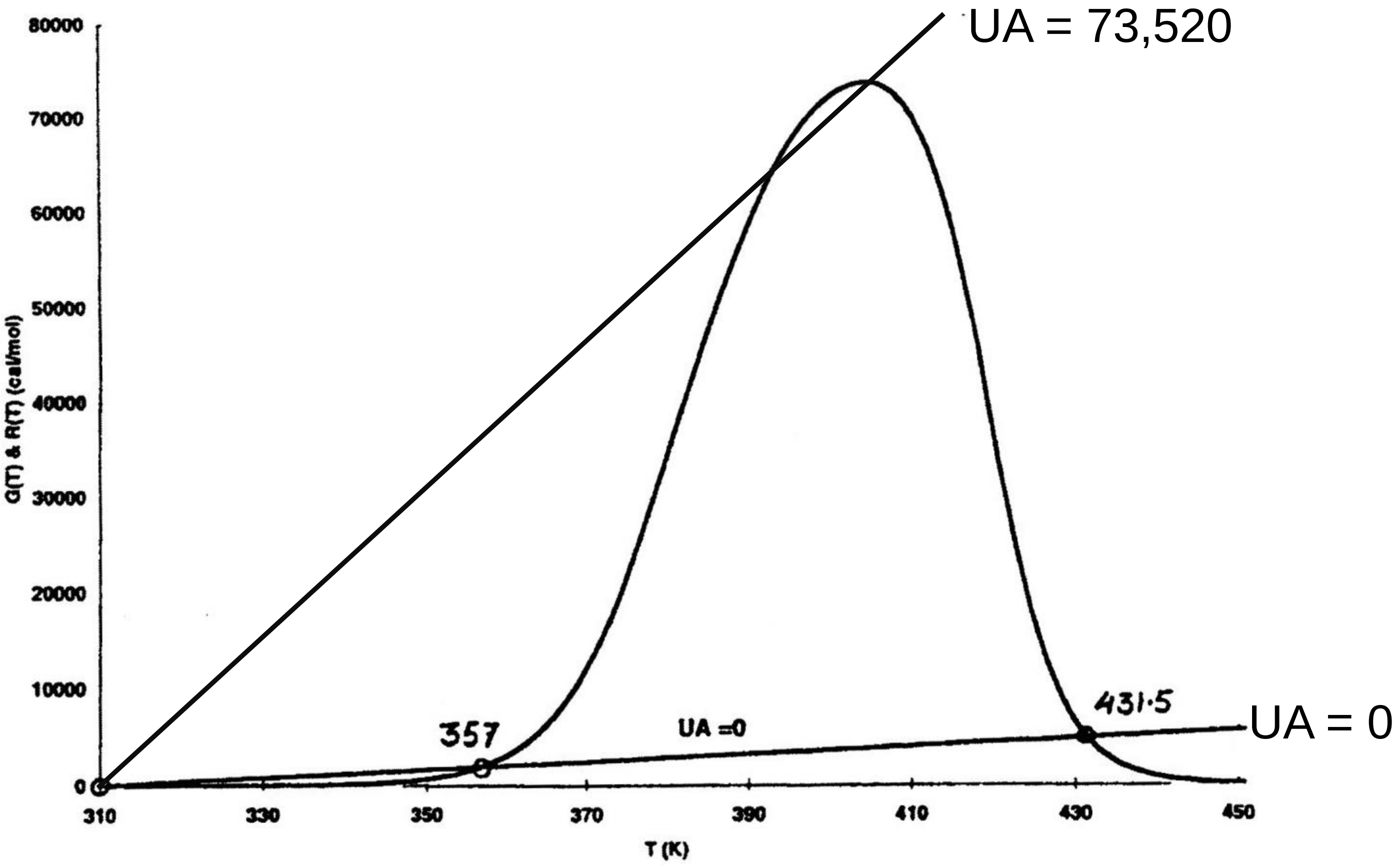
$$R(T) = C_P(1 + \kappa)[T - T_C]$$

$$T_C = \frac{T_0 + \kappa T_a}{1 + \kappa} = 310$$

$$R(T) = 400[T - 310]$$

Reversible Reaction
Gas Flow in a PBR with Heat Effects

$A \leftrightarrow B$



Reversible Reaction

Gas Flow in a PBR with Heat Effects

A ↔ B

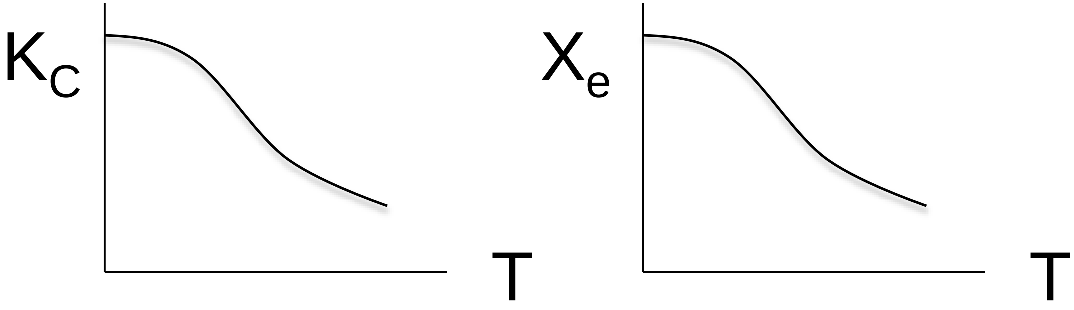
$$K_C = \frac{C_{Be}}{C_{Ae}} = \frac{C_{A0} X_e y\, T_0 / T}{C_{A0}\left(1 - X_e\right) y\, T_0 / T}$$

$$(8) \quad X_e = \frac{K_C}{1 + K_C}$$

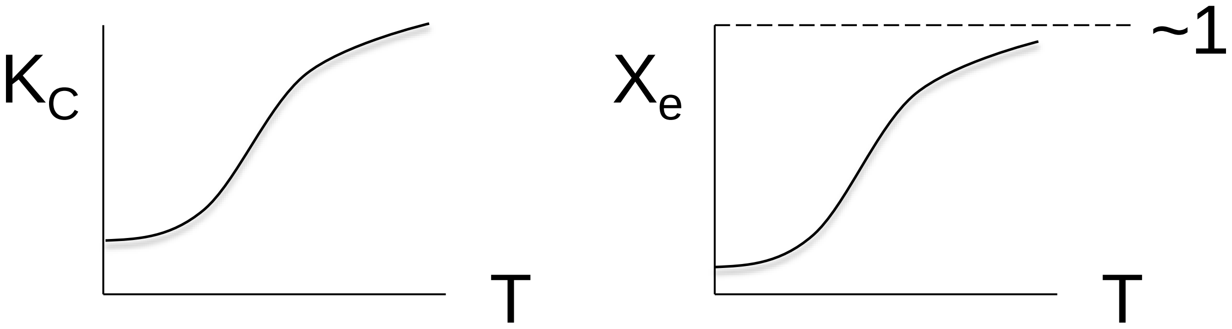
Reversible Reaction
Gas Flow in a PBR with Heat Effects

$A \leftrightarrow B$

Exothermic Case:



Endothermic Case:

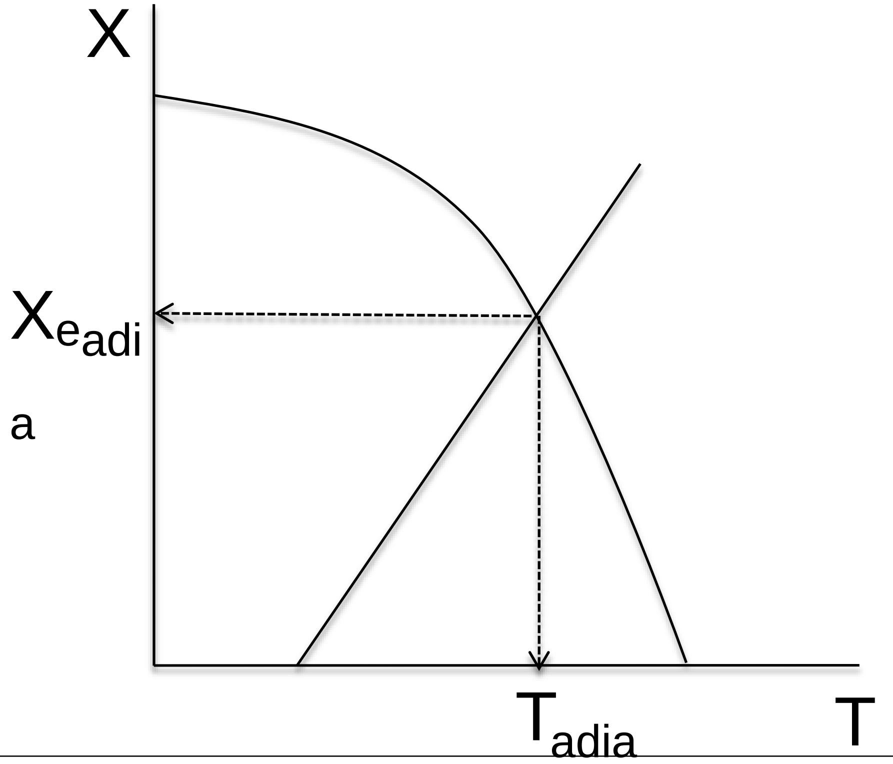


Adiabatic Equilibrium Conversion

Conversion on Temperature

Exothermic ΔH is negative

Adiabatic Equilibrium temperature (T_{adia}) and conversion ($X_{e,adia}$)



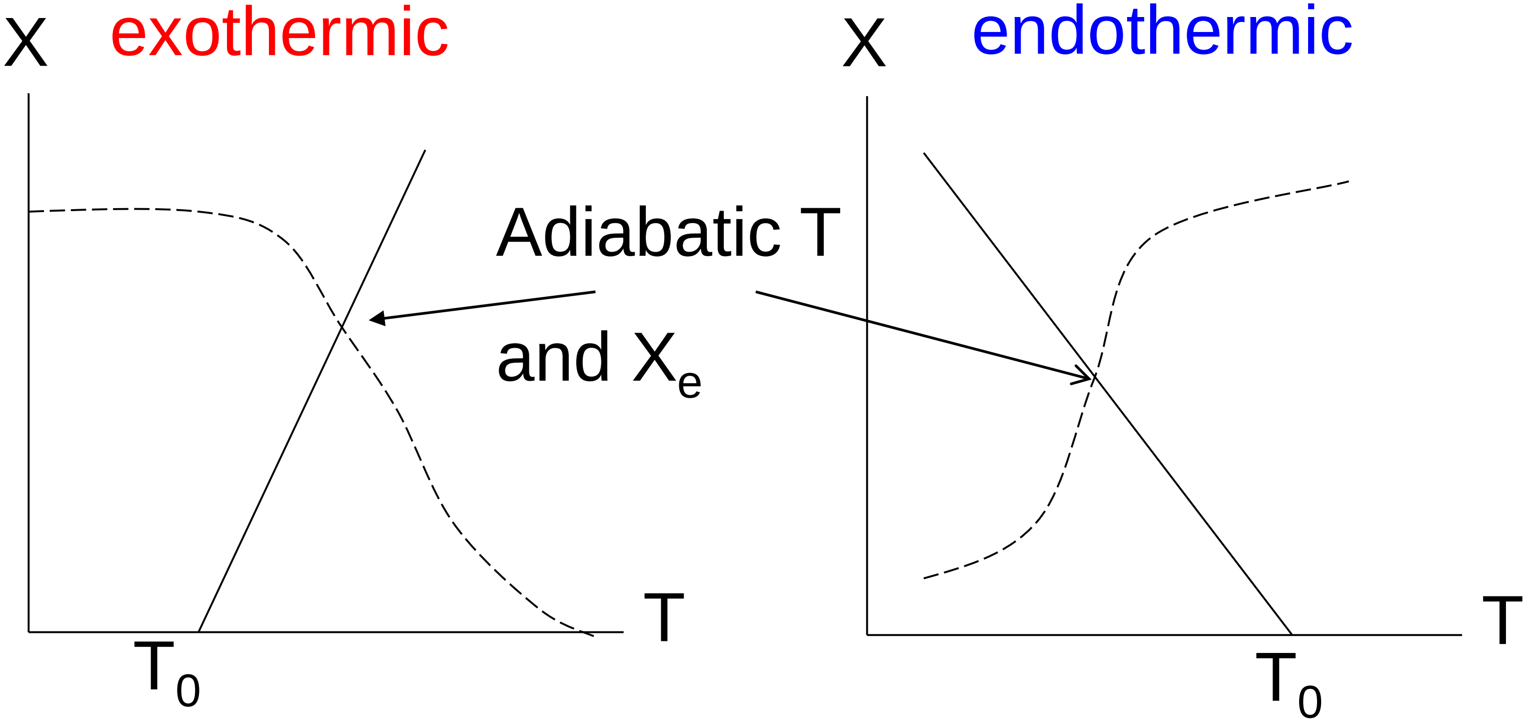
$$T = T_0 + \frac{(-\Delta H_{Rx})X}{C_{PA}}$$

$$X_e = \frac{K_C}{1+K_C}$$

Gas Phase Heat Effects

Trends:

Adiabatic:



X exothermic

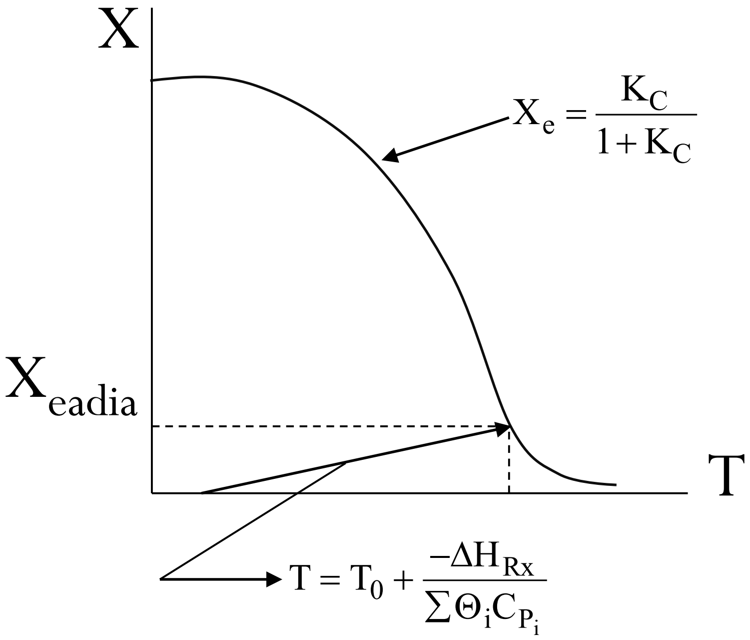
X endothermic

Adiabatic T

and X_e

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

Gas Phase Heat Effects



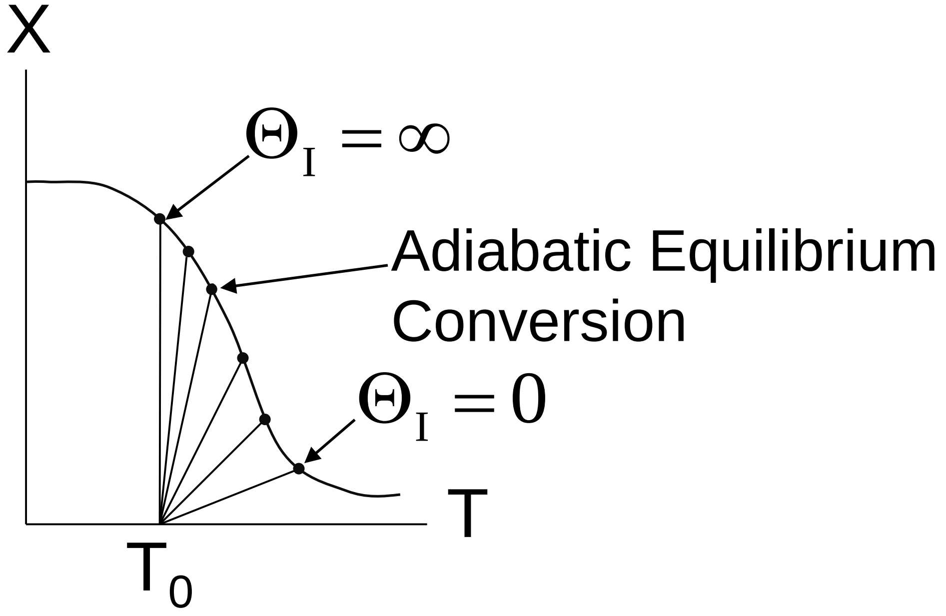
$$X_e = \frac{K_C}{1+K_C}$$

$$T = T_0 + \frac{-\Delta H_{Rx}}{\sum \Theta_i C_{P_i}}$$

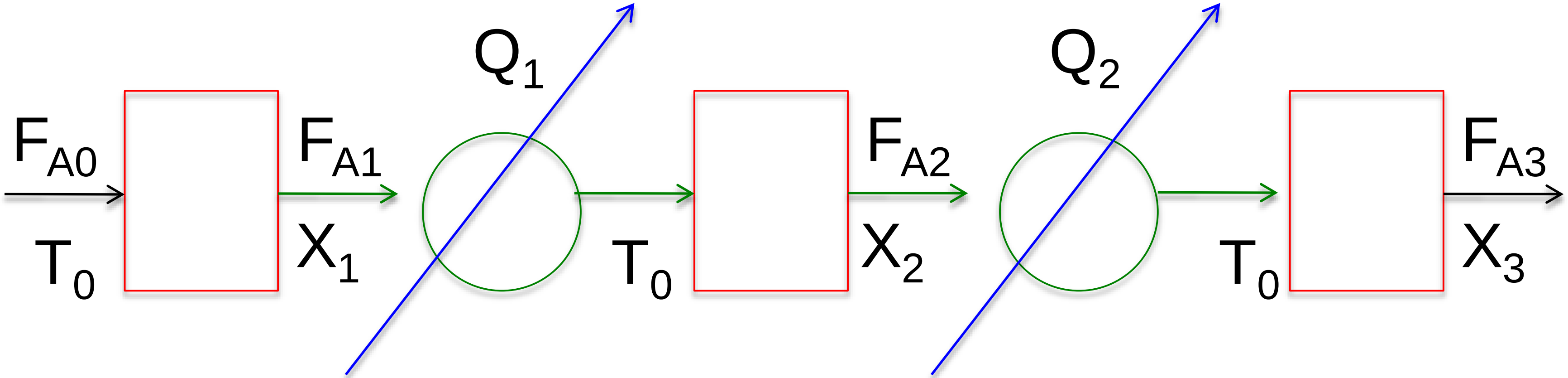
Gas Phase Heat Effects

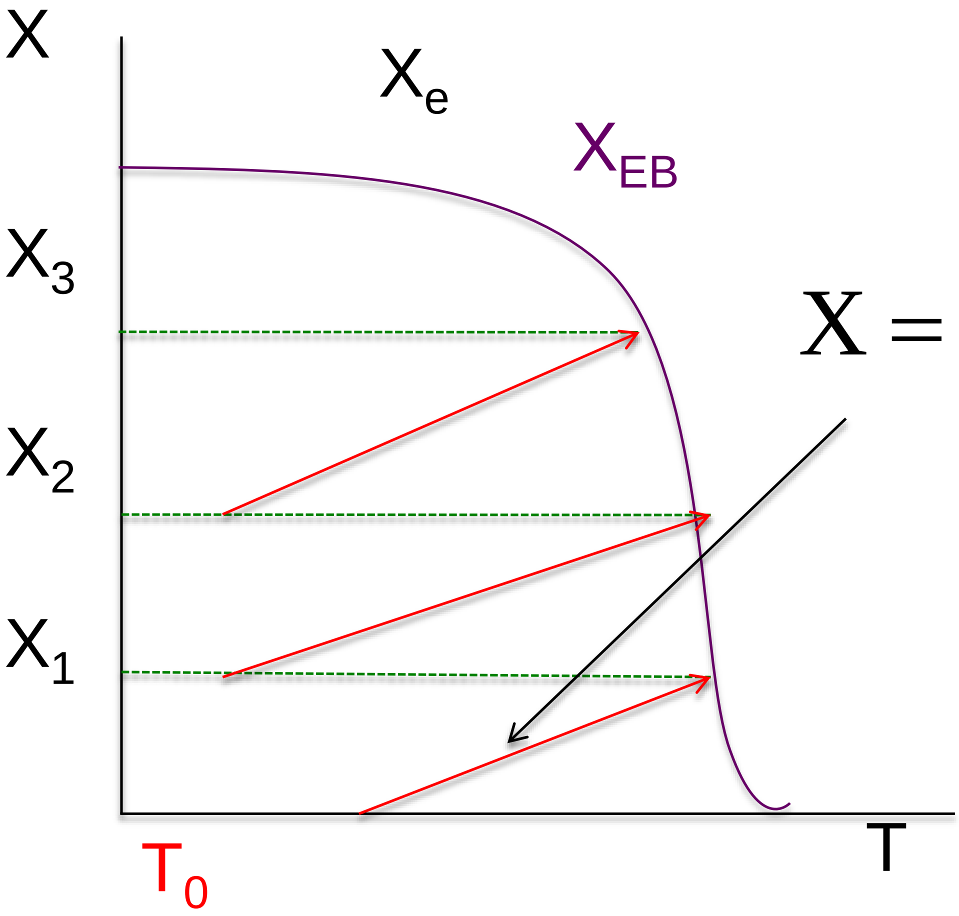
Effect of adding inerts on adiabatic equilibrium conversion

Adiabatic:



$$X = \frac{(T - T_0)\left[C_{P_A} + \theta_I C_{P_I}\right]}{-\Delta H_{Rx}}, \quad T = T_0 + \frac{(-\Delta H_{Rx})}{C_{P_A} + \theta_I C_{P_I}}$$


F_{A0}
T_0
F_{A1}
X_1
Q_1
T_0
F_{A2}
X_2
Q_2
T_0
F_{A3}
X_3



$$X = \frac{\sum \theta_i C_{Pi}\left(T - T_0\right)}{-\Delta H_{RX}}$$

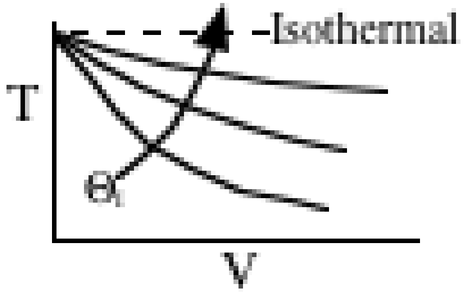
Adiabatic Exothermic Reactions

$$A \xrightarrow{\quad} B \qquad \Delta H_{Rx} = +15\frac{\text{kcal}}{\text{mol}}$$

The heat of reaction for endothermic reaction is positive, i.e.,

Energy Balance **:**

$$T = T_0 - \frac{\Delta H_{Rx} X}{C_{P_A} + \Theta_I C_{P_I}} \quad \text{and} \quad X = \frac{\left(C_{P_A} + C_{P_I}\Theta_I\right)(T_0 - T)}{\Delta H_{Rx}}$$



We want to learn the effects of adding inerts on conversion. How the conversion varies with the amount, i.e., Θ_I, depends on what you vary and what you hold constant as you change Θ_I.

A. First Order Reaction

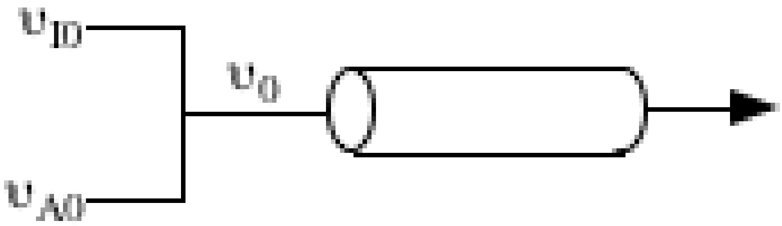
$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

Combining the **mole balance**, **rate law** and **stoichiometry**

$$\frac{dX}{dV} = \frac{kC_{A0}(1-X)}{\upsilon_0 C_{A0}} = \frac{k}{\upsilon_0}(1-X)$$

Two cases will be considered
Case 1 Constant υ_0, volumetric flow rate
Case 2: Variable υ_0, volumetric flow rate

A.1. Liquid Phase Reaction

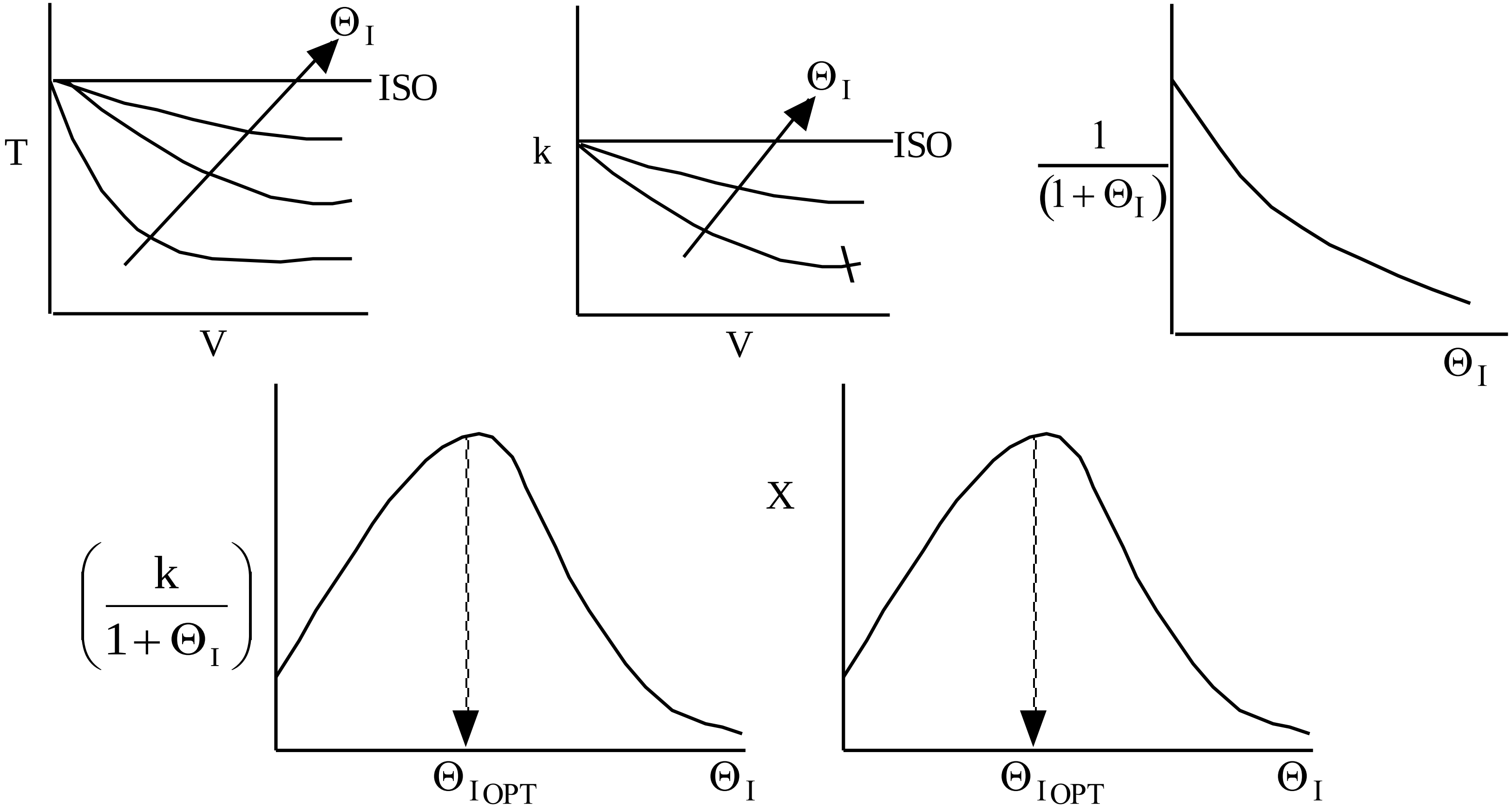


For Liquids, volumetric flow rates are additive.

$$\upsilon_0 = \upsilon_{A0} + \upsilon_{I0} = \upsilon_{A0}(1 + \Theta_I)$$

Effect of Adding Inerts to an Endothermic Adiabatic Reaction

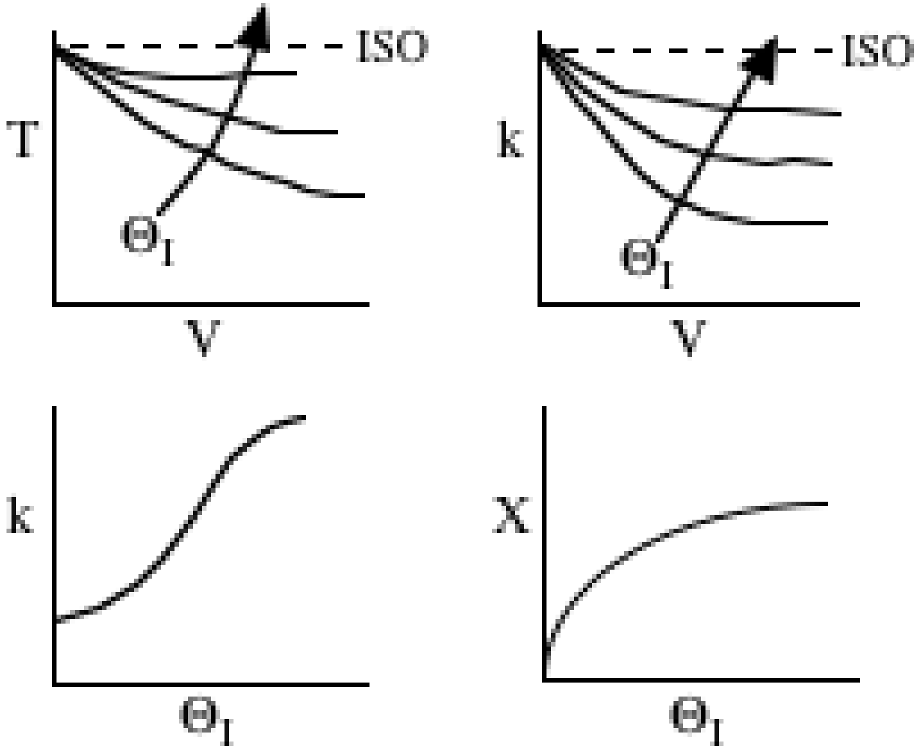
What happens when we add Inerts, i.e., vary Theta I??? It all depends what you change and what you hold constant!!!



A.1.a. Case 1. Constant υ_0

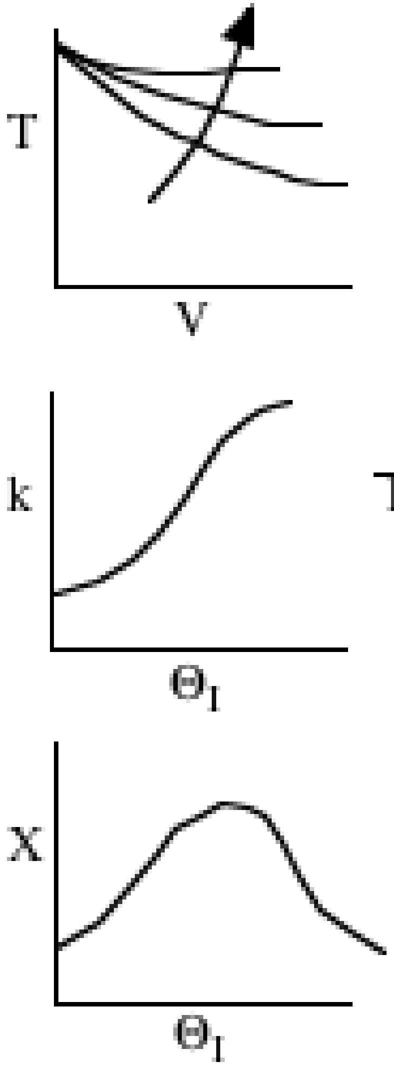
To keep υ_0 constant if we increase the amount of Inerts, i.e., increase Θ_I we will need to decrease the amount of A entering, i.e., υ_{A0}. So Θ_I ↑ then υ_{A0} ↓

$$T = T_0 - \frac{\Delta H_{Rx} X}{C_{P_A} + \Theta_I C_{P_I}}$$



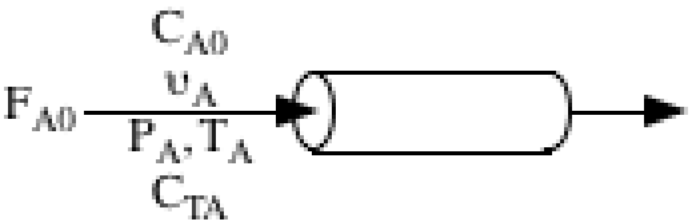
A.1.a. Case 2. Constant $\upsilon_{A,}$ Variable υ_0

$$\frac{dX}{dV}=\frac{k(1-X)}{\upsilon_0}=\frac{k(1-X)}{\upsilon_A(1+\Theta_I)}$$



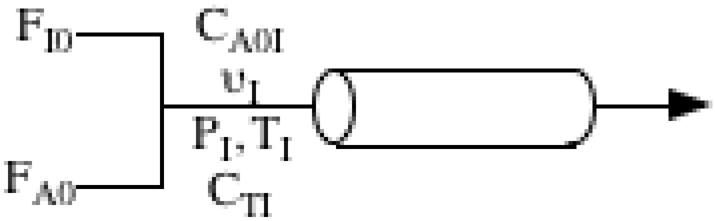
A.2. Gas Phase

Without Inerts



$$C_{TA} = \frac{F_{A0}}{\upsilon_A} = C_{A0} = \frac{P_A}{RT_A}$$

With Inerts and A



$$C_{TI} = \frac{F_{TI}}{\upsilon_I} = \frac{F_{A0} + F_{I0}}{\upsilon_I} = \frac{P_I}{RT_I}$$

Taking the ratio of C_{TA} to C_{TI}

$$\frac{C_{TI}}{C_{TA}} = \frac{\frac{F_{TI}}{\upsilon_I}}{\frac{F_{TA}}{\upsilon_A}} = \frac{\frac{P_I}{RT_I}}{\frac{P_A}{RT_A}}$$

Solving for υ_I

$$\upsilon_I = \upsilon_A \frac{F_{TI}}{F_{TA}} \frac{P_A}{P_I} \frac{T_I}{T_A}$$

We want to compare what happens when Inerts and A are fed to the case when only A is fed.

Nomenclature note: Sub I with Inerts I and reactant A fed
Sub A with only reactant A fed

F_{TI} = Total inlet molar flow rate of inert, I, plus reactant A, $F_{TI} = F_{A0} + F_{I0}$

F_{TA} = Total inlet molar flow rate when no Inerts are fed, i.e., $F_{TA} = F_{A0}$

P_I, T_I = Inlet temperature and pressure for the case when both Inerts (I) and A are fed

P_A, T_A = Inlet temperature and pressure when only A is fed

C_{A0} = Concentration of A entering when no inerts are presents $C_{A0} = \frac{F_{A0}}{\upsilon_A}$

C_{TA} = Total concentration when no inerts are present $= \frac{P_A}{RT_A}$

C_{TI} = Total concentration when both I and A are present $= \frac{P_I}{RT_I}$

C_{A0I} = Concentration of A entering when inerts A are entering $= \frac{F_{A0}}{\upsilon_I}$

υ_I = Entering volumetric flow rate with both Inerts (I) and reactant (A)

$$\frac{F_{TI}}{F_{TA}} = \frac{F_{A0} + F_{I0}}{F_{A0}} \equiv \left(1 + \Theta_I\right) = \frac{1}{\left(\dfrac{F_{A0}}{F_{I0} + F_{A0}}\right)} = \frac{1}{y_{A0}}$$

$$y_{A0} = \frac{1}{\left(1 + \Theta_I\right)}$$

$$\boxed{\upsilon_I = \upsilon_A \left[\left(1 + \Theta_I\right) \frac{P_A}{P_I} \frac{T_I}{T_A}\right]}$$

A.2.a. Case 1

Maintain constant volumetric flow, υ_0, rate as inerts are added. I.e., $\upsilon_0 = \upsilon_I = \upsilon_A$. Not a very reasonable situation, but does represent one extreme. Achieve constant υ_0 varying P, T to adjust conditions so term in brackets, [ ], is one.

$$\left[(1+\Theta_I)\frac{P_A}{P_I}\frac{T_I}{T_0}\right]=1$$

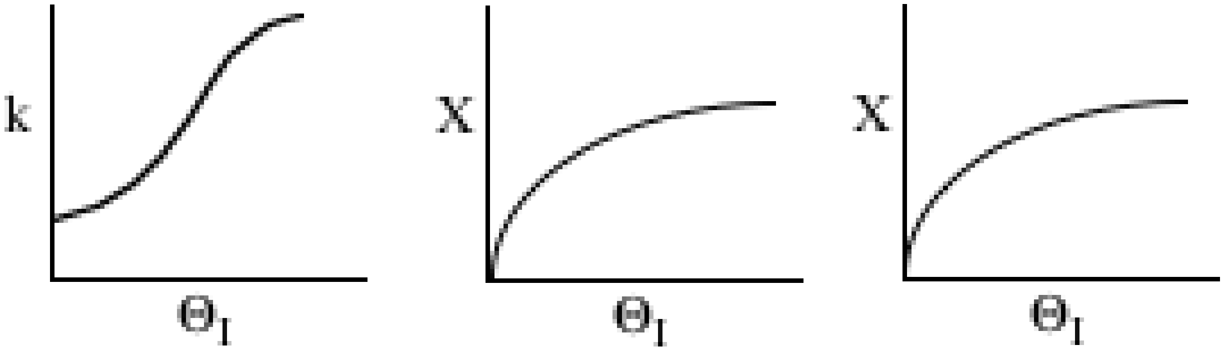
<u>For example</u> if $\Theta_I = 2$ then υ_I will be the same as υ_A, but we need the entering pressures P_I and P_A to be in the relationship $P_I = 3P_A$ with $T_A = T_I$

$$\upsilon_I = \upsilon_A\left[(1+2)\bullet\frac{P_A}{3P_A}\frac{T_A}{T_A}\right]=\upsilon_A\left[3\bullet\frac{1}{3}\right]=\upsilon_A=\upsilon_0$$

A.2.a. Case 1

That is the term in brackets, [ ], would be 1 which would keep υ_0 constant with $\upsilon_I = \upsilon_A = \upsilon_0$. Returning to our combined mole balance, rate law and stoichiometry

$$\frac{dX}{dV} = \frac{k(1-X)}{\upsilon_0}$$

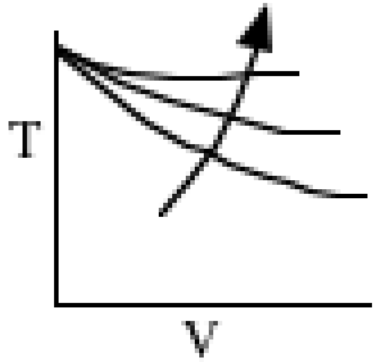


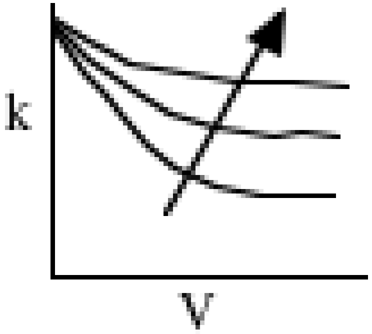
A.2.b. Case 2: Variable υ_0 Constant T, P i.e., $P_I = P_A$, $T_I = T_A$

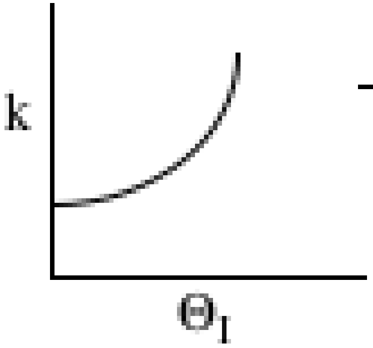
$$\upsilon_I = \upsilon_A \frac{F_{TI}}{F_{TA}} = \upsilon_A \frac{\left(F_{A0} + F_{I0}\right)}{F_{A0}} = \upsilon_A\left(1 + \Theta_I\right)$$

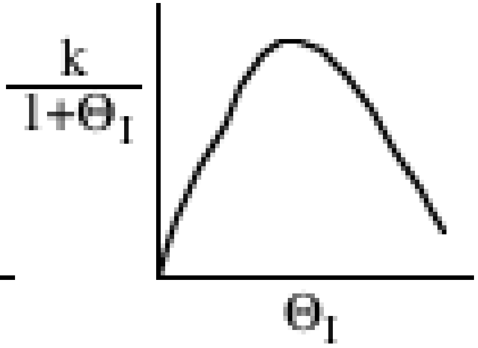
$$\upsilon_I = \upsilon_A\left(1 + \Theta_I\right)$$

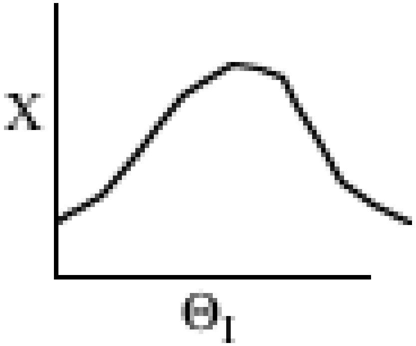
$$\frac{dX}{dV} = \frac{1}{\upsilon_A}\frac{k}{1+\Theta}\left(1 - X\right)$$





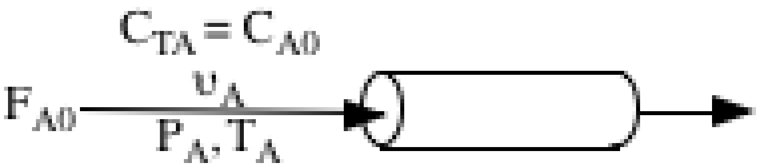






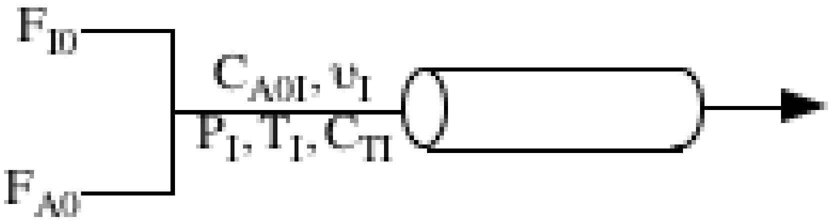
B. Gas Phase Second Order Reaction

Pure A



$$C_{A0} = \frac{P_A}{RT_A} = \frac{F_{A0}}{\upsilon_A}$$

Inerts Plus A



$$C_{TI} = \frac{F_{A0}(1+\Theta_I)}{\upsilon_I}$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{kC_{A0I}^2(1-X)^2}{F_{A0}}$$

B. Gas Phase Second Order Reaction

$$\upsilon_I = \upsilon_A (1 + \Theta_I) \frac{P_A}{P_I} \frac{T_I}{T_A}$$

$$\frac{C_{A0I}^2}{F_{A0}} = \frac{(F_{A0}/\upsilon_I)^2}{F_{A0}} = \frac{F_{A0}}{\upsilon_I^2} = \frac{F_{A0}}{\upsilon_A \cdot \upsilon_A (1 + \Theta_I)^2 \left(\frac{P_A}{P_I}\right)^2 \left(\frac{T_I}{T_A}\right)^2}$$

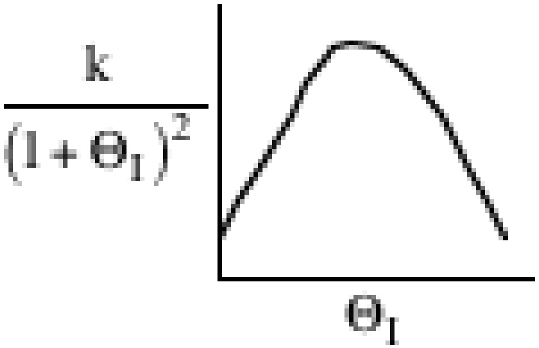
$$= \frac{C_{A0}}{\upsilon_A (1 + \Theta_I)^2} \left(\frac{P_I}{P_A} \frac{T_A}{T_I}\right)^2$$

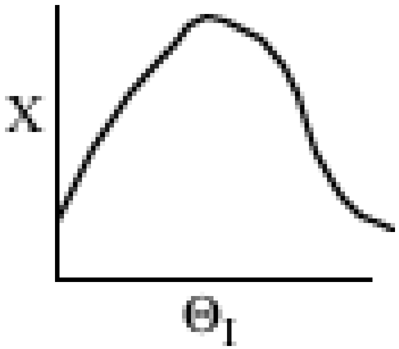
$$\frac{dX}{dV} = \frac{k}{(1 + \Theta_I)^2} \frac{C_{A0}}{\upsilon_A} \left(\frac{P_I}{P_A} \frac{T_A}{T_I}\right)^2 (1 - X)^2$$

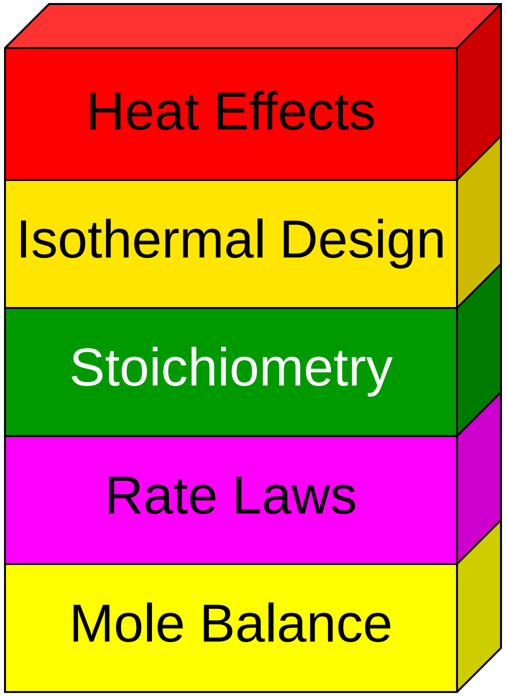
B. Gas Phase Second Order Reaction

For the same temperature and pressures for the cases with and without inerts, i.e., $P_I = P_A$ and $T_I = T_A$, then

$$\frac{dX}{dV} = \frac{k}{\left(1+\Theta_I\right)^2}\frac{C_{A0}}{\upsilon_A}\left(1-X\right)^2$$







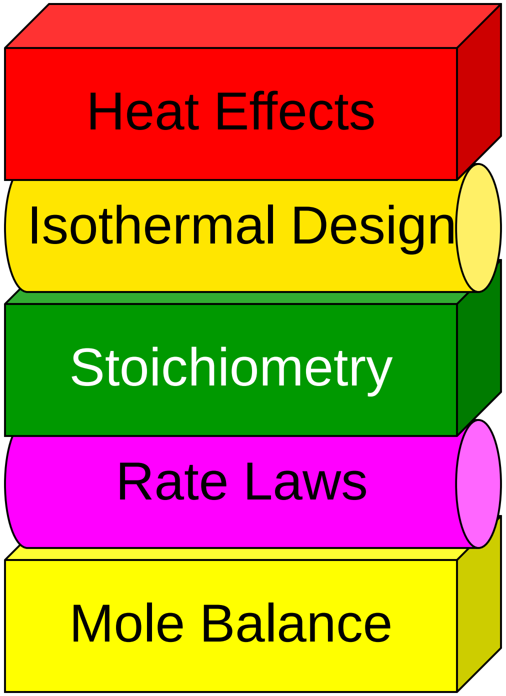
Heat Effects

Isothermal Design

Stoichiometry

Rate Laws

Mole Balance



Heat Effects

Isothermal Design

Stoichiometry

Rate Laws

Mole Balance

End of Web Lecture 24
Class Lecture 20