Lecture 24

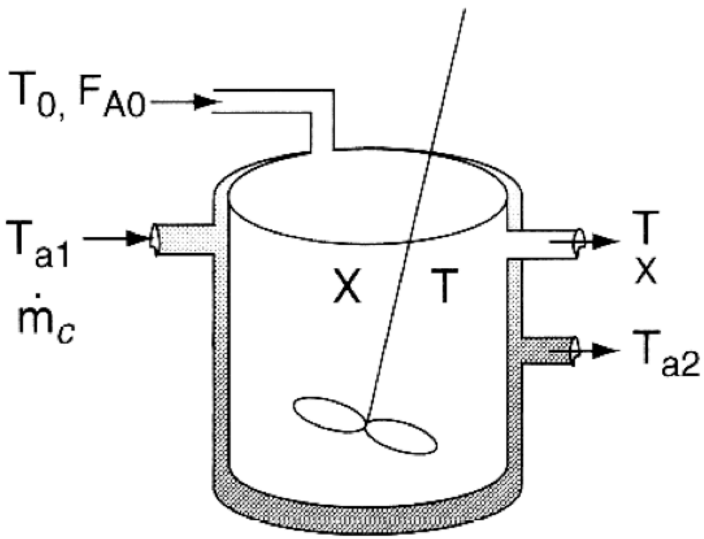
Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

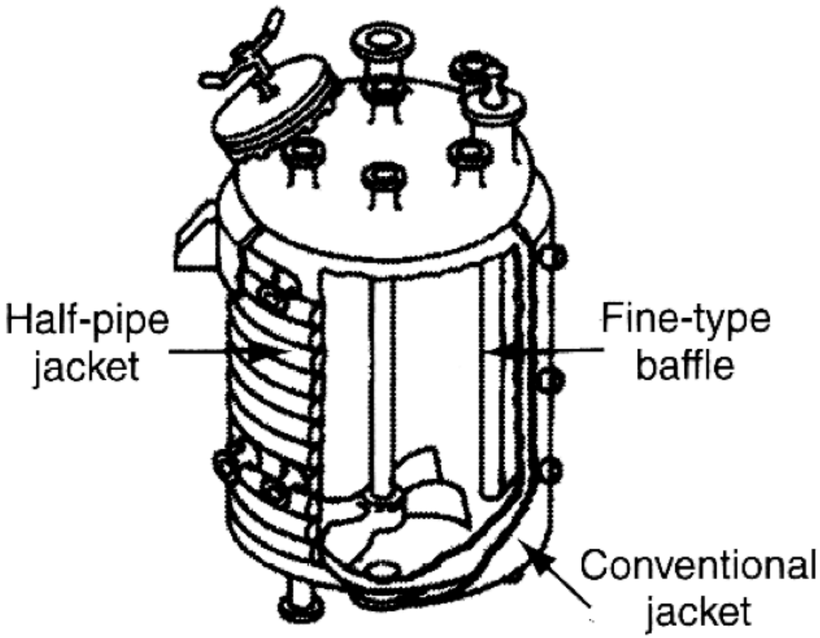
Web Lecture 24
Class Lecture 20 - Tuesday 3/26/2013

CSTR With Heat Effects

- Multiple Steady States
- Ignition and Extinction Temperatures

CSTR with Heat Effects





Courtesy of Pfaudler, Inc.

Unsteady State Energy Balance

$$\dot{Q} - \dot{W}_S + \sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i = \frac{d\hat{E}_{sys}}{dt}$$

Using $\hat{E}_{sys} = \sum N_i E_i = \sum N_i (H_i - PV_i) = \sum N_i H_i - PV$ (Neglect PV)

$$\frac{dE_{sys}}{dt} = \frac{d \sum N_i H_i}{dt} = \sum N_i \frac{dH_i}{dt} = \sum H_i \frac{dN_i}{dt}$$

$$\frac{dH_i}{dt} = C_{Pi} \frac{dT}{dt}$$

$$\frac{dN_i}{dt} = -\upsilon_i r_A V + F_{i0} - F_i$$

Unsteady State Energy Balance

We obtain after some manipulation:

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_S - \sum F_{i0} C_{Pi} \left(T - T_{i0}\right) + \left[-\Delta H_{Rx}(T)\right]\left(-r_A V\right)}{\sum N_i C_{Pi}}$$

Collecting terms with $\dot{Q} = UA\left(T_a - T\right)$ and high coolant flow rates, and $\dot{W}_S = 0$

$$F_{i0} = F_{A0}\Theta_i$$

Unsteady State Energy Balance

$$\frac{dT}{dt} = \frac{(\Delta H_{Rx})(r_A V) - \left[F_{A0} \overbrace{\sum \Theta_i C_{P_i}}^{C_{P_0}} (T - T_0) + (UA(T - T_a)) \right]}{\sum N_i C_{P_i}}$$

$$= \frac{F_{A0}}{\sum N_i C_{P_i}} \left[\overbrace{\Delta H_R \frac{r_A V}{F_{A0}}}^{\boldsymbol{G}(\boldsymbol{T})} - \overbrace{\left[C_{P_0} \left[T - T_0 + \frac{UA}{\underbrace{F_{A0} C_{P_S}}_{\kappa}} (T - T_a) \right] \right]}^{\boldsymbol{R}(\boldsymbol{T})} \right]$$

Unsteady State Energy Balance

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

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

$$R(T) = C_{P_0}\left[(1+\kappa)T - (T_0 + \kappa T_a)\right]$$

$$R(T) = C_{P_0}(1+\kappa)\left(T - \frac{T_0 + \kappa T_a}{1+\kappa}\right) = C_{P_0}(1+\kappa)(T - T_C)$$

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

Unsteady State Energy Balance

$$\frac{dT}{dt} = G(T) - R(T)$$

If G(T) > R(T) Temperature Increases

If R(T) > G(T) Temperature Decreases

Steady State Energy Balance for CSTRs

At Steady State

$$\frac{dT}{dt} = \frac{dN_A}{dt} = 0$$

$$-r_A V = F_{A0} X$$

$$\boldsymbol{G(T) - R(T) = 0}$$

$$\left(-\Delta H_{Rx}\right) F_{A0} X - F_{A0} \sum \Theta_i C_{P_i} \left(T - T_0\right) - UA\left(T - T_a\right) = 0$$

Solving for X.

Steady State Energy Balance for CSTRs

Solving for X:

$$X = \frac{\sum \Theta_i C_{P_i}\left(T - T_0\right) + \frac{UA}{F_{A0}}\left(T - T_a\right)}{-\Delta H^\circ_{Rx}} = X_{EB}$$

Solving for T:

$$T = \frac{F_{A0}X\left(-\Delta H_{Rx}\right) + UAT_a + F_{A0}\sum \Theta_i C_{P_i} T_0}{UA + F_{A0}\sum \Theta_i C_{P_i}}$$

Steady State Energy Balance for CSTRs

$$X(-\Delta H_{Rx}) = C_{P_0}\left[T - T_0 + \frac{UA}{F_{A0}C_{P_0}}(T - T_a)\right]$$

$$\text{Let } \kappa = \frac{UA}{F_{A0}C_{P_0}}$$

$$X(-\Delta H_{Rx}) = C_{P_0}(T + \kappa T - T_0 - \kappa T_a) = C_{P_0}(1+\kappa)\left(T - \frac{T_0 + \kappa T_a}{1+\kappa}\right)$$

$$= C_{P_0}(1+\kappa)(T - T_C)$$

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

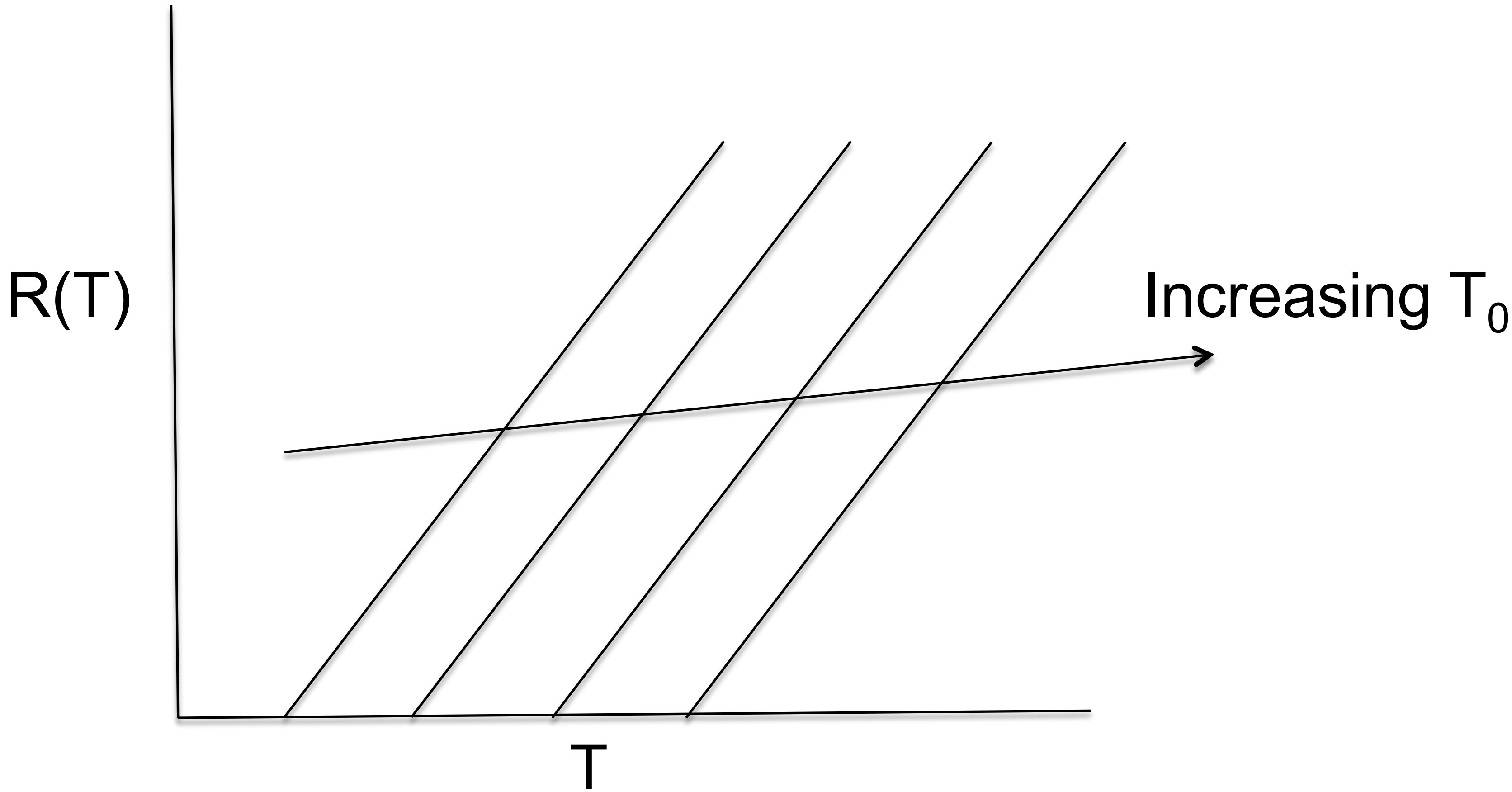
Steady State Energy Balance for CSTRs

$$\overbrace{-X\,\Delta H^{o}{}_{Rx}}^{G(T)} = \overbrace{C_{P0}(1+\kappa)(T-T_C)}^{R(T)}$$

$$X = \frac{C_{P0}(1+\kappa)(T-T_C)}{-\Delta H^{o}{}_{Rx}}$$

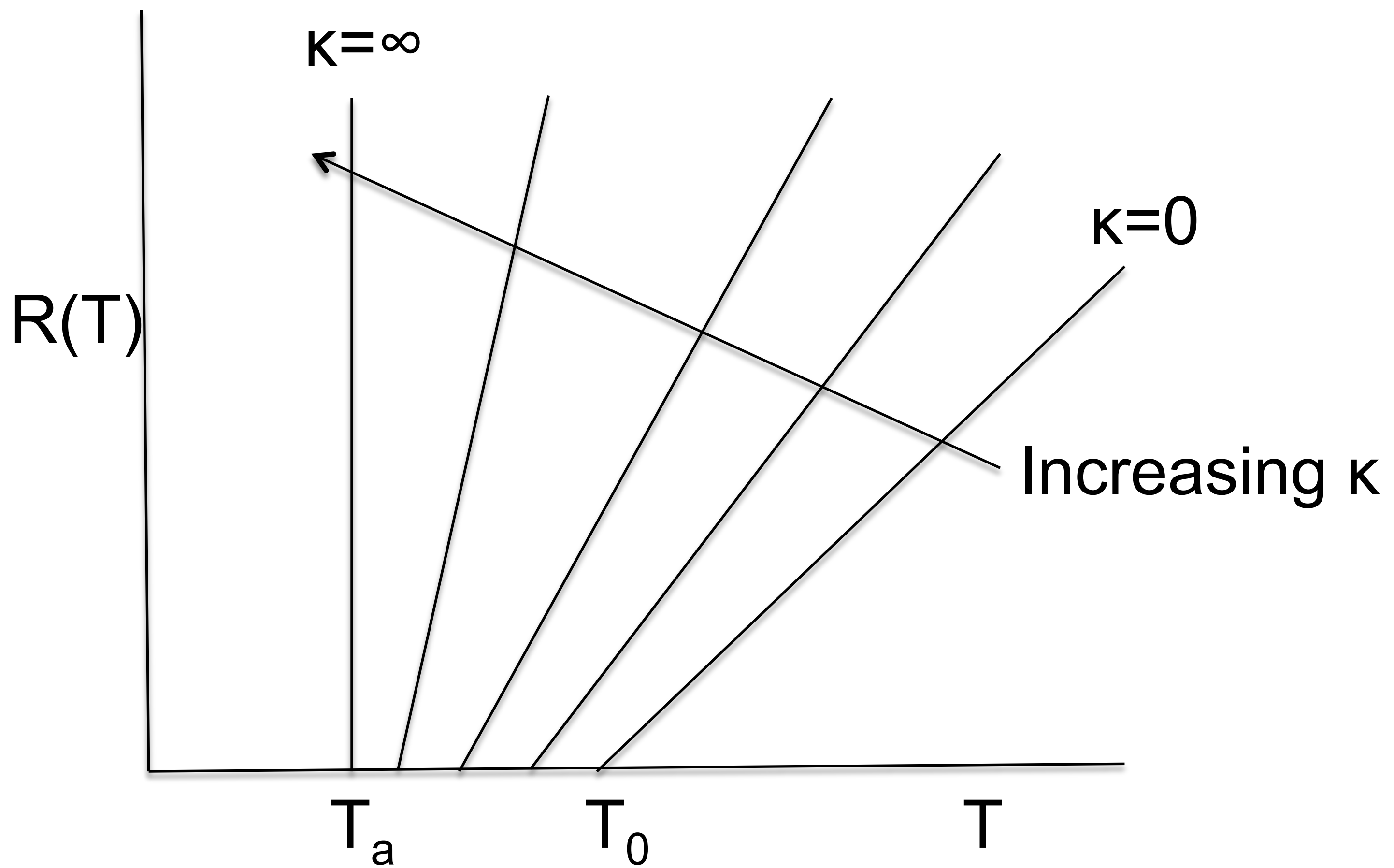
$$T = T_C + \frac{(-\Delta H^{o}{}_{Rx})(X)}{C_{P0}(1+\kappa)}$$

Steady State Energy Balance for CSTRs



Variation of heat removal line with inlet temperature.

Steady State Energy Balance for CSTRs



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

$$V = \frac{F_{A0}X}{-r_A(X,T)}$$

$$A \rightarrow B$$

1) Mole Balances:

$$V = \frac{F_{A0}X}{-r_A}$$

2) Rate Laws:

$$-r_A = kC_A$$

3) Stoichiometry: $C_A = C_{A0}(1 - X)$

4) Combine:

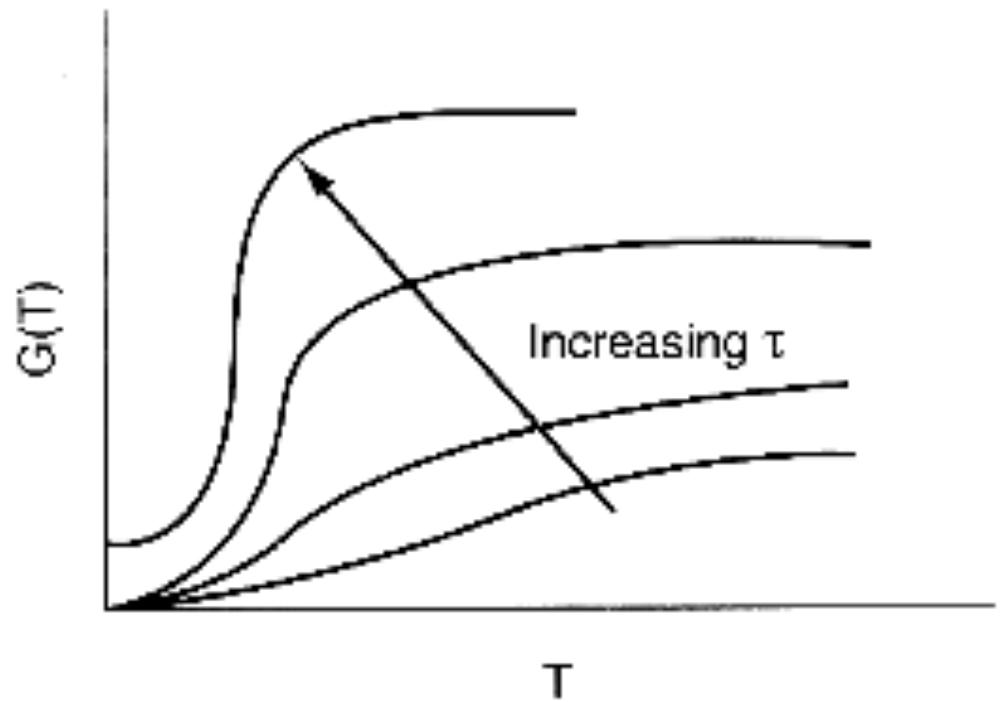
$$V = \frac{F_{A0}X}{kC_{A0}(1-X)} = \frac{C_{A0}\upsilon_0 X}{kC_{A0}(1-X)}$$

$$\tau k = \frac{X}{1-X}$$

$$X = \frac{\tau k}{1+\tau k} = \frac{\tau A e^{-E/RT}}{1+Ae^{-E/RT}}$$

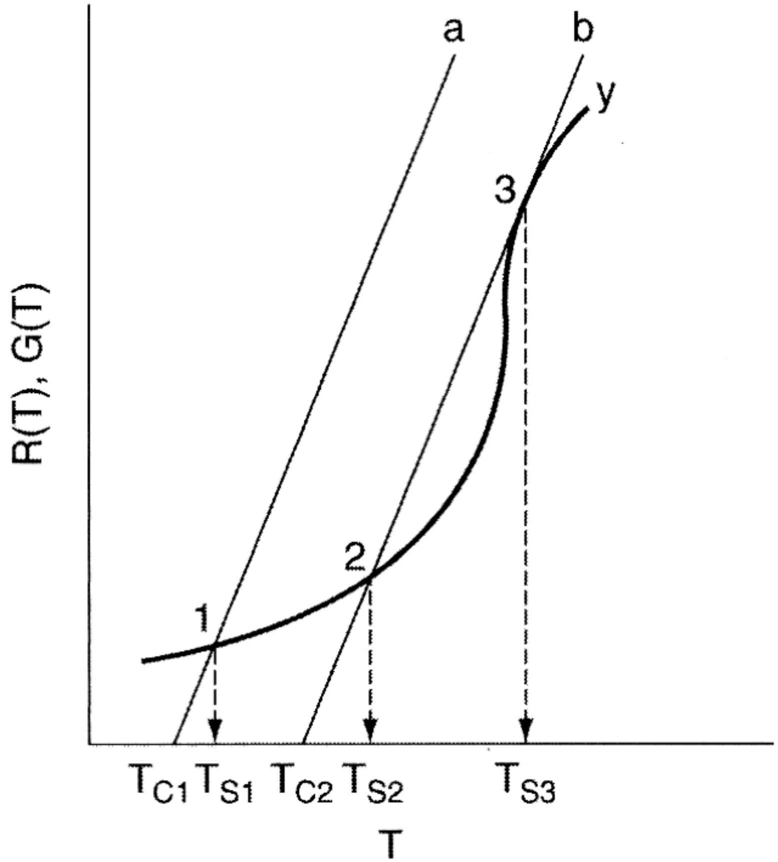
$$G(T) = X(-\Delta H_{Rx}) = \frac{\tau A e^{-E/RT}}{1+Ae^{-E/RT}}(-\Delta H_{Rx})$$

Multiple Steady States (MSS)



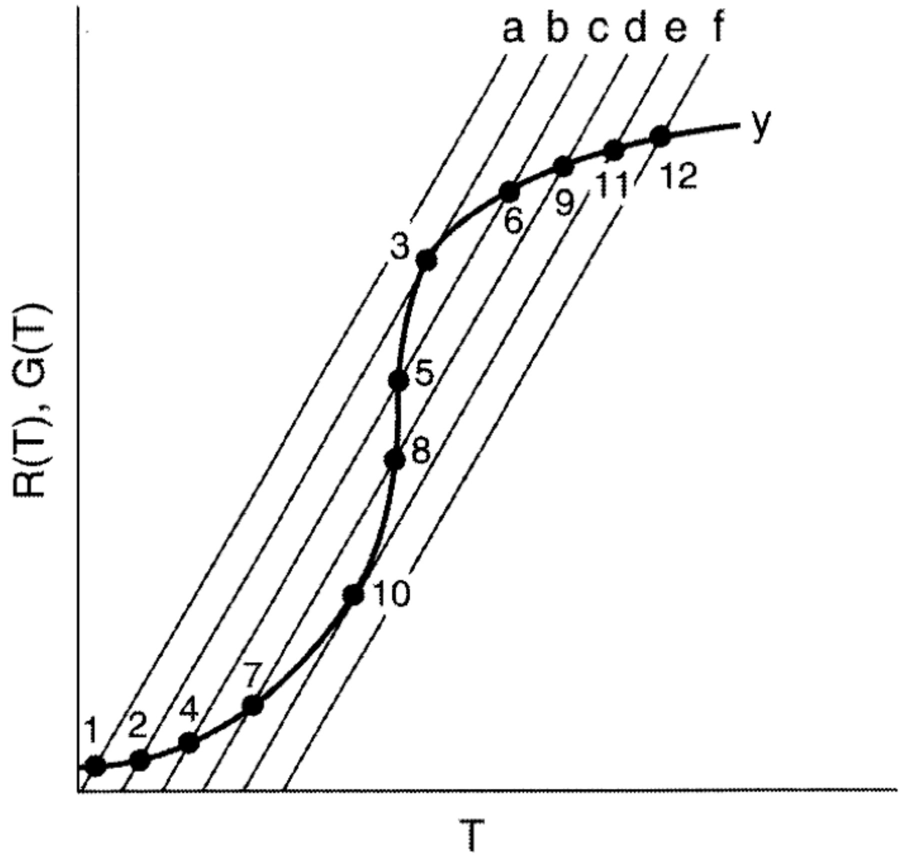
Variation of heat generation curve with space-time.

Multiple Steady States (MSS)



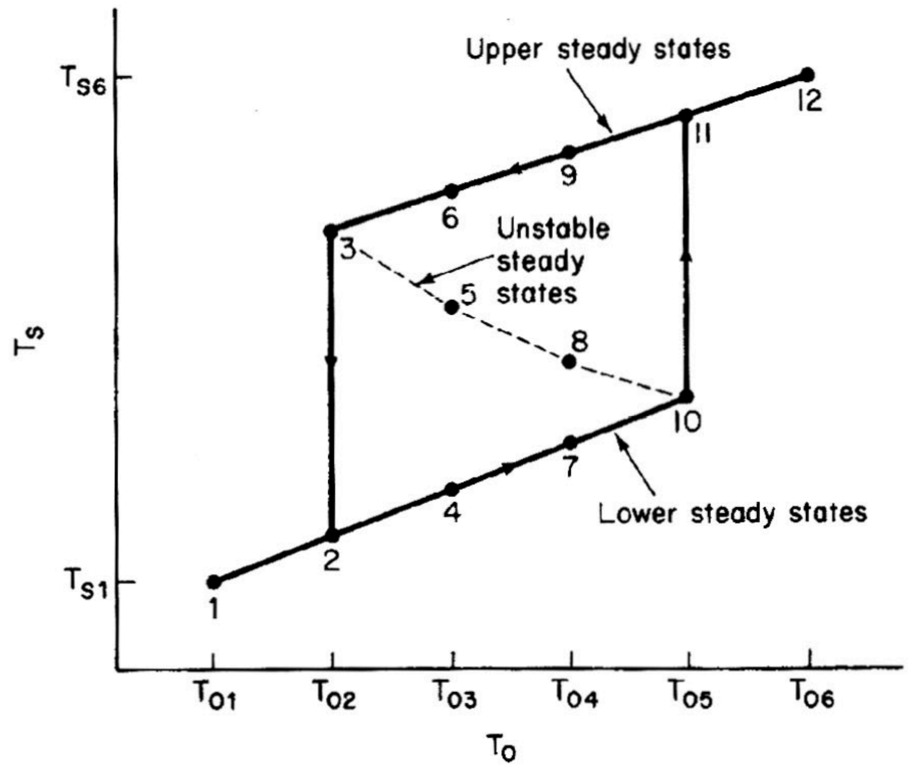
Finding Multiple Steady States with T_0 varied

Multiple Steady States (MSS)



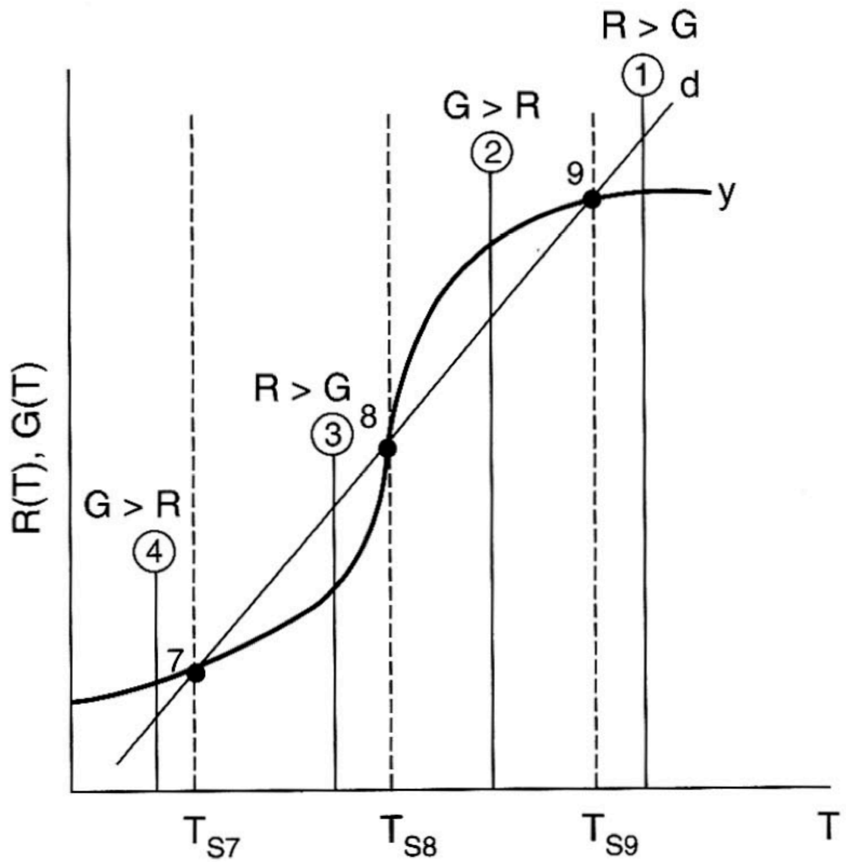
Finding Multiple Steady States with T_0 varied

Multiple Steady States (MSS)



Temperature ignition-extinction curve

Multiple Steady States (MSS)



Stability of multiple state temperatures

MSS - Generating G(T) and R(T)

$$\frac{dT}{dt} = 1$$

$$G(T) = X \cdot \left(-\Delta H_{Rx}\right)$$

$$R = C_{P_0} \cdot (1 + \kappa) \cdot (T - T_C)$$

Need to solve for X after combining **mole balance, rate law,** and **stoichiometry.**

MSS - Generating G(T) and R(T)

For a first order irreversible reaction

$$X = \frac{tau \cdot k}{(1 + tau \cdot k)}$$

$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

<u>Parameters</u>

$$Tau, (-\Delta H_{Rx}), k_1, E, R, T_1, T_C, kappa, C_{P_0}$$

Then plot G and R as a function of T.

End of Web Lecture 23
Class Lecture 19