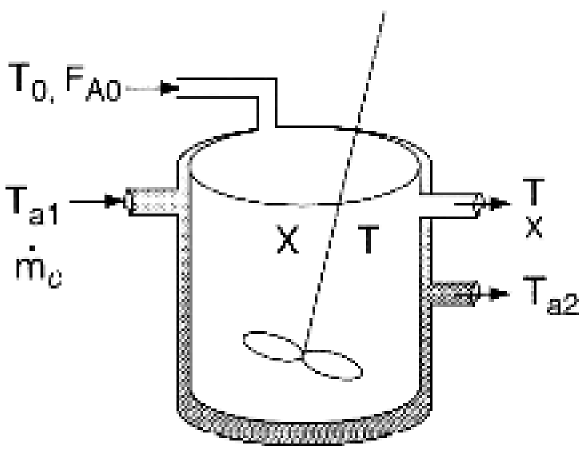
Lecture 22

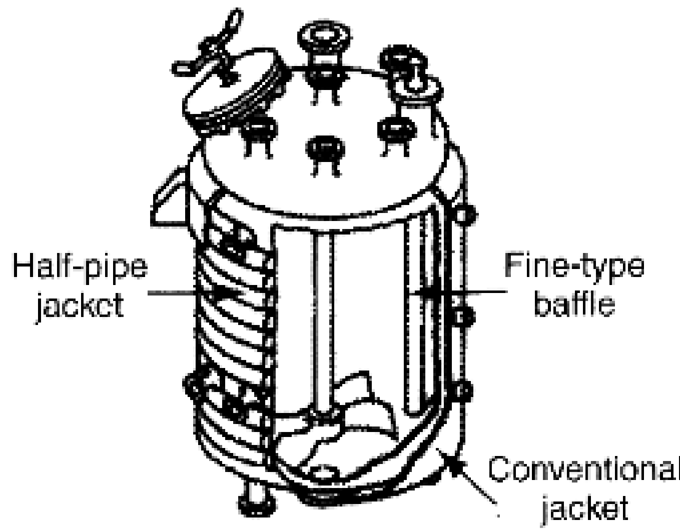
Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Today's lecture

- Blowout Velocity
- CSTR Explosion
- Batch Reactor Explosion

Last Lecture
CSTRs with Heat Effects





Energy balance for CSTRs

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

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

Energy balance for CSTRs

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

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

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

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

Steady State Energy Balance for CSTRs

At Steady State

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

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

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

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

Energy balance for CSTRs

Solving for X

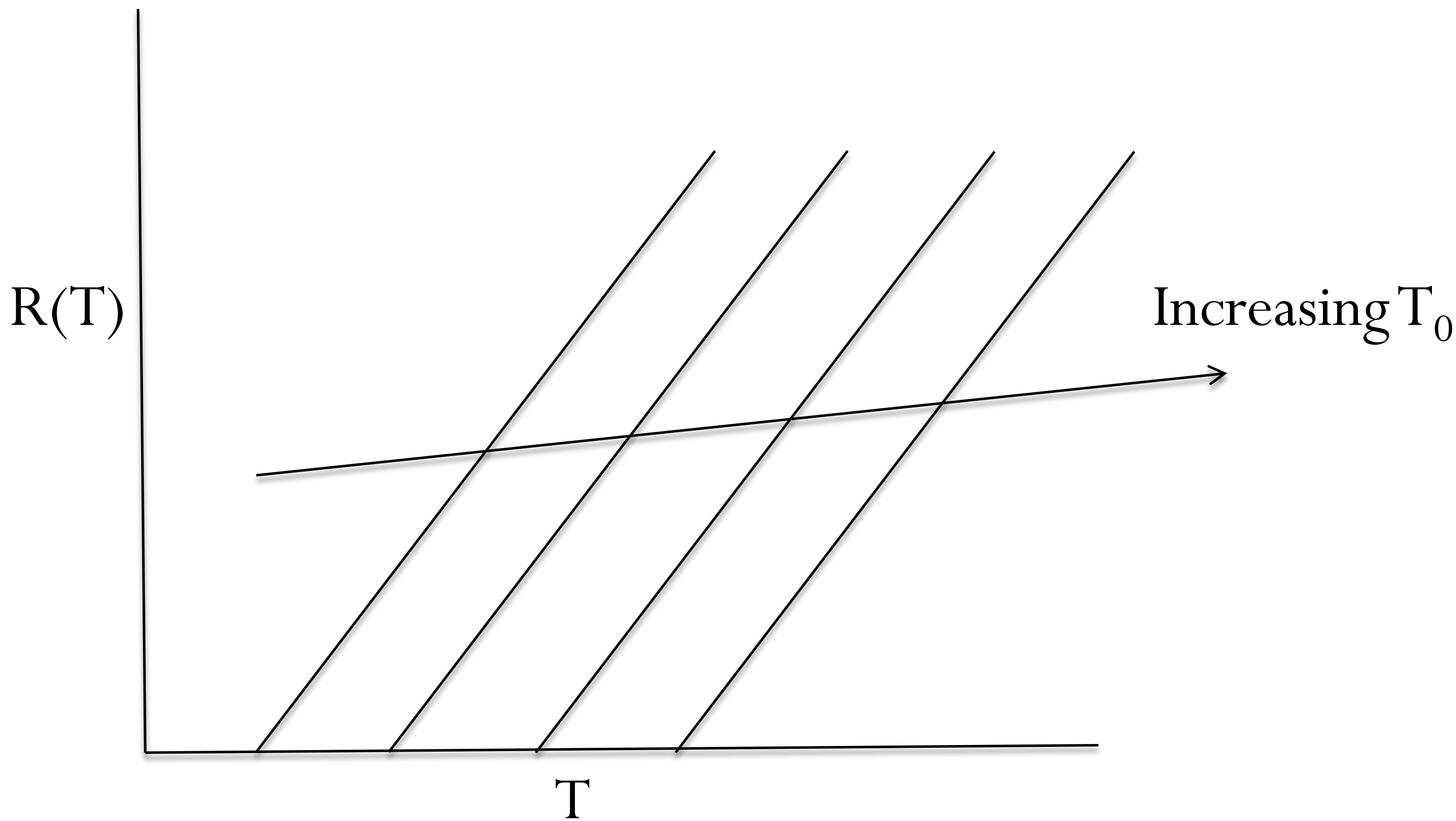
$$X = \frac{\sum \Theta_i C_{P_i}\left(T - T_0\right) + \frac{UA}{F_{A0}}\left(T - T_a\right)}{-\Delta H^{\circ}_{Rx}} = X_{EB}$$

Solving for T

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

Energy balance for CSTRs

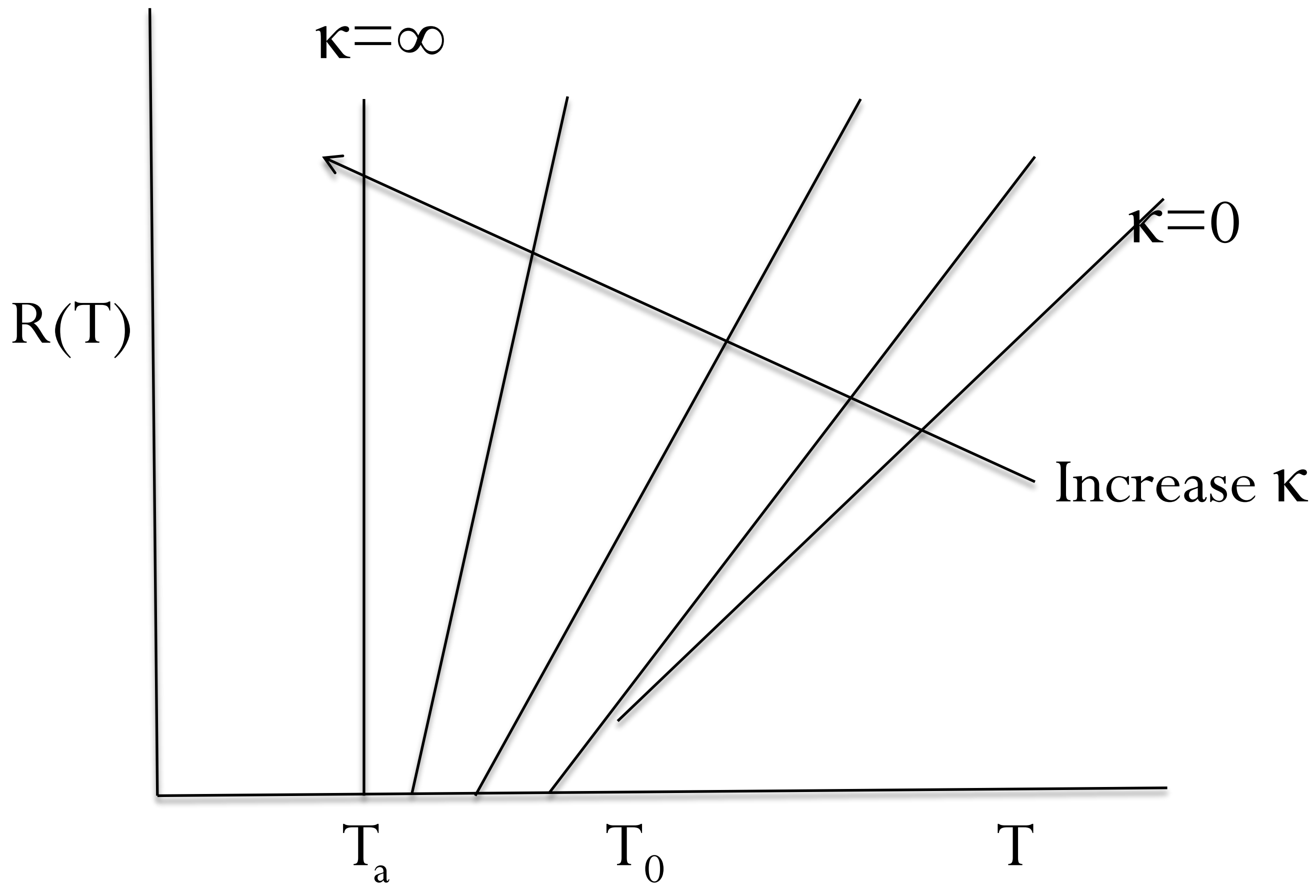
$$R(T) = C_{P_S}(1+\kappa)\left[T - T_C\right]$$



Variation of heat removal line with inlet temperature.

Energy balance for CSTRs

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



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

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

$$A \rightarrow B$$

1) Mole Balance:

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

2) Rate Law:

$$-r_A = kC_A$$

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

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

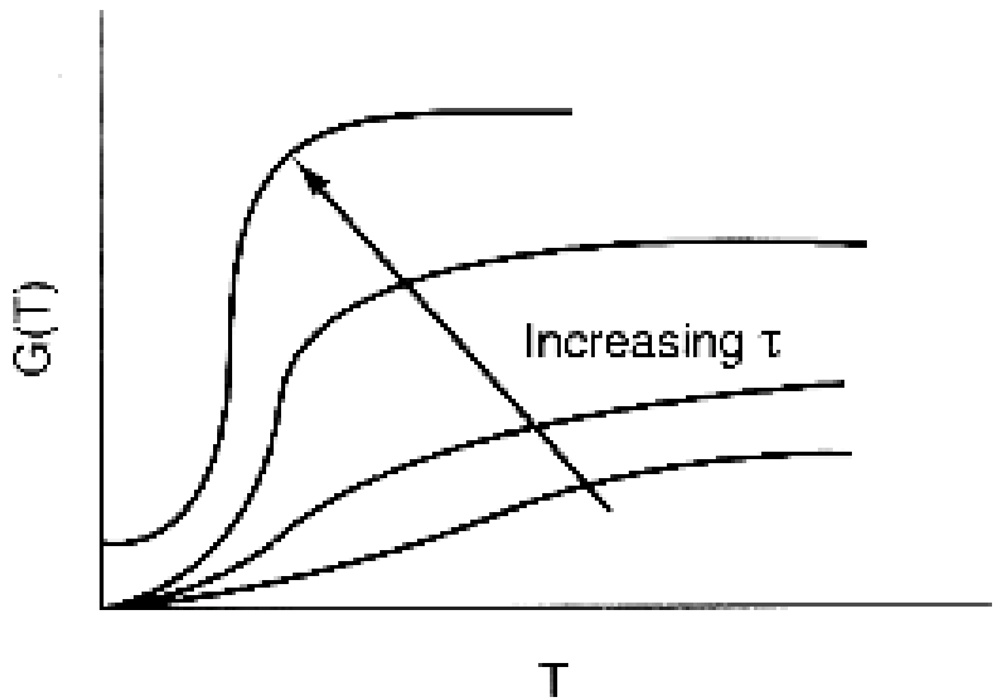
$$\tau k = \frac{X}{1-X}$$

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

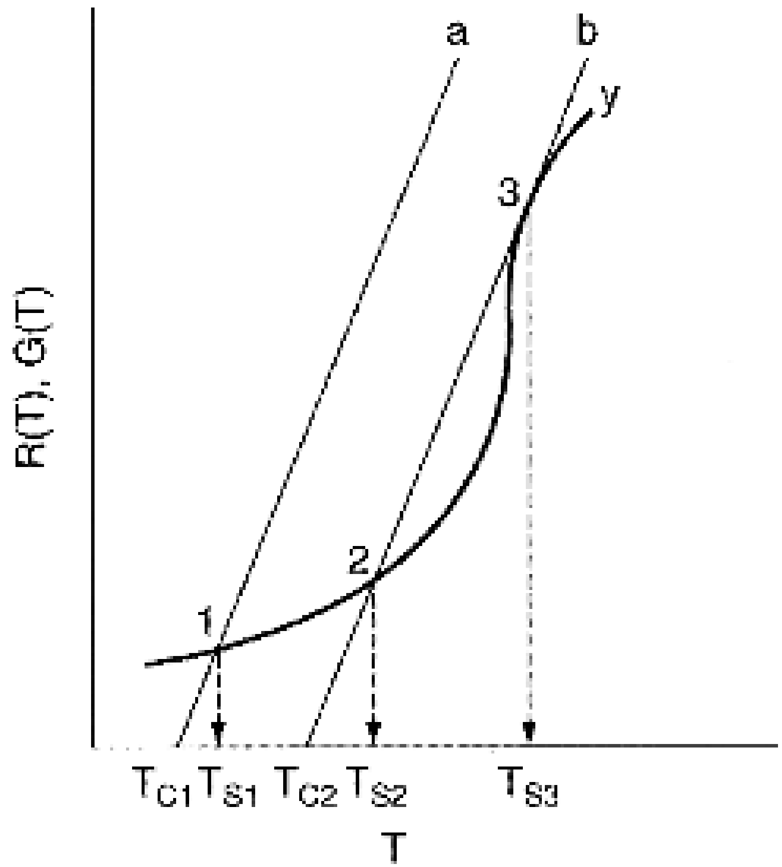
$$\tau k = \frac{X}{1-X}$$

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

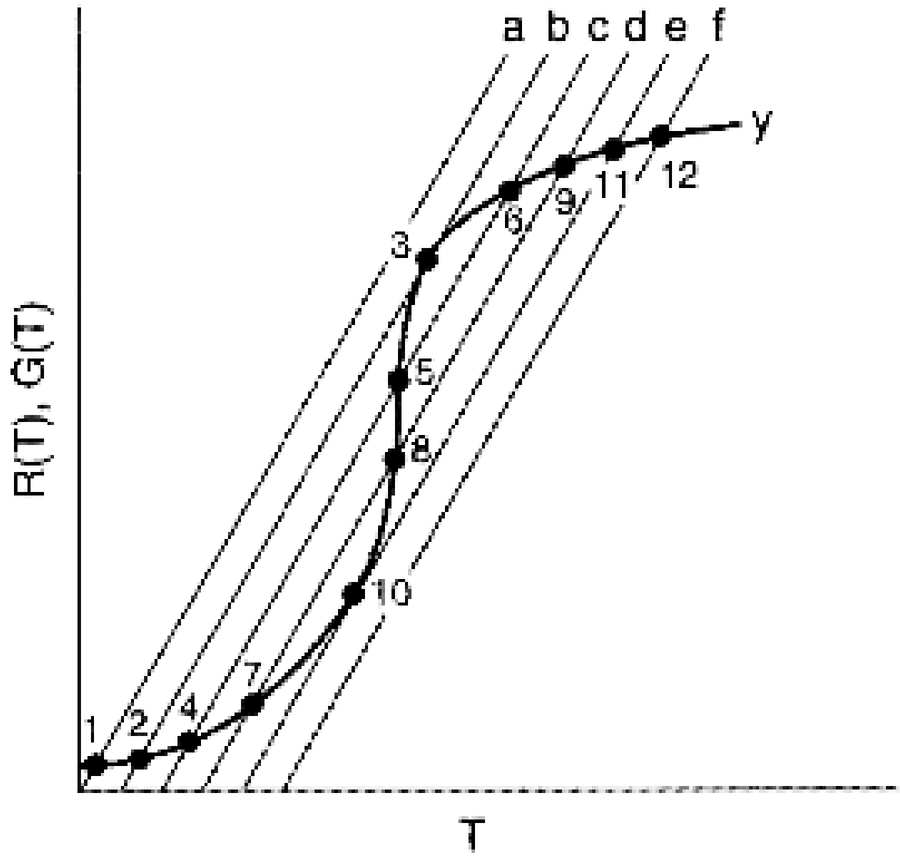
$$G(T) = X(-\Delta H_{Rx}) = \frac{\tau A e^{-E/RT}}{1+Ae^{-E/RT}}(-\Delta H_{Rx})$$



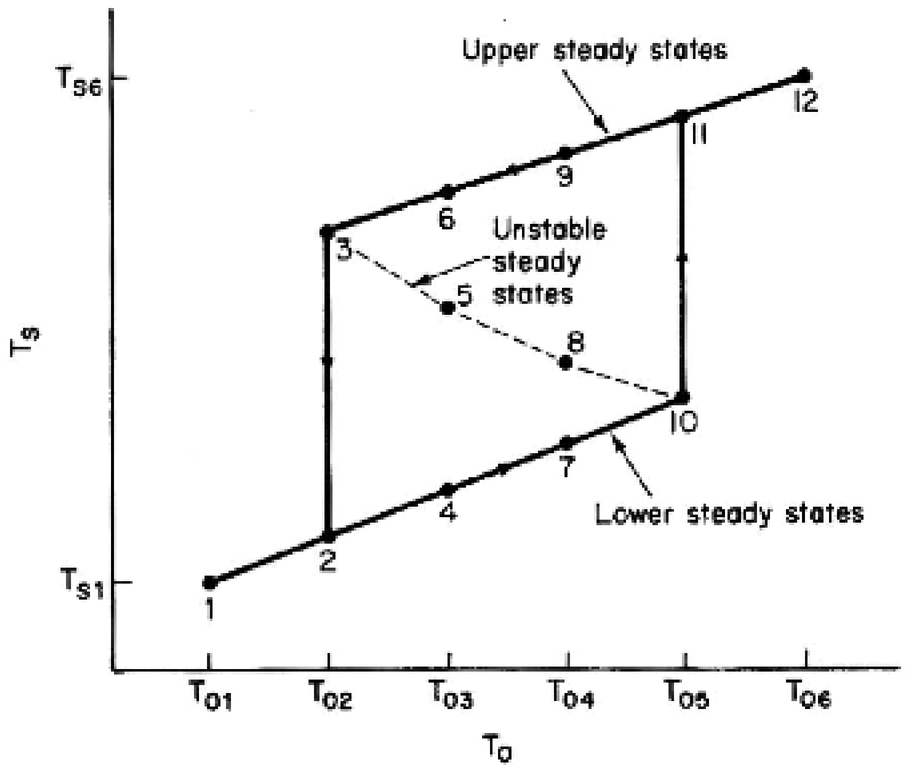
Variation of heat generation curve with space-time.



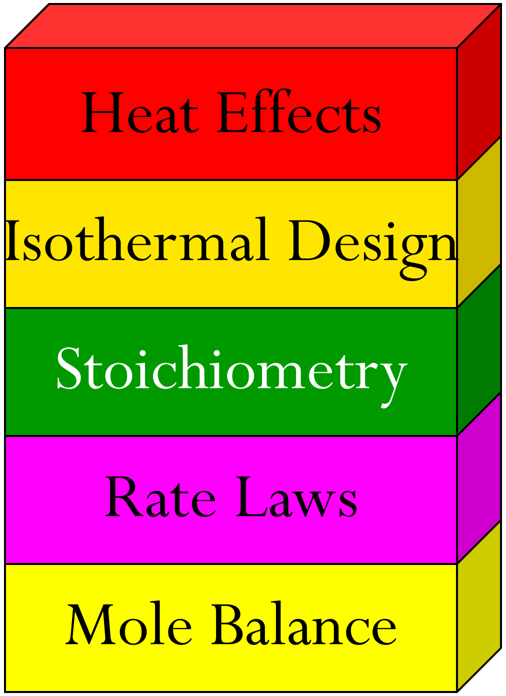
Finding Multiple Steady States with T_0 varied

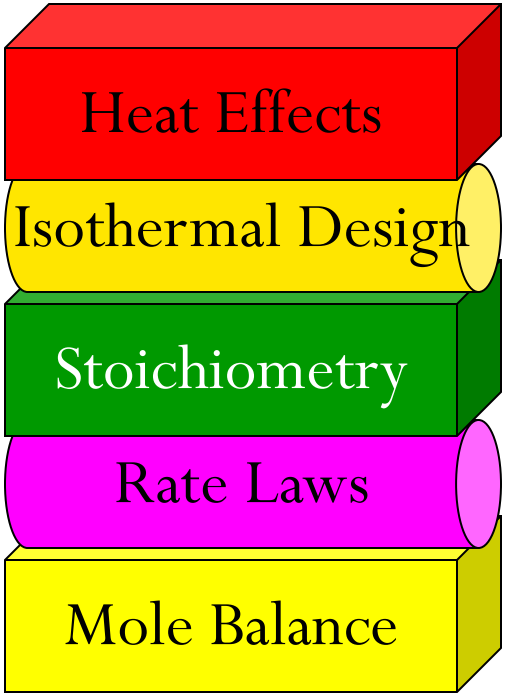


Finding Multiple Steady States with T_0 varied



Temperature ignition-extinction curve


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance

Example B: Liquid Phase CSTR

Same reactions, rate laws, and rate constants as example A

$$A + 2B \rightarrow C \, (1) \qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$3C + 2A \rightarrow D \, (2) \qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example B: Liquid Phase CSTR

The complex liquid phase reactions take place in a 2,500 dm^3 CSTR. The feed is equal molar in A and B with F_{A0}=200 mol/min, the volumetric flow rate is 100 dm^3/min and the reation volume is 50 dm^3.

Find the concentrations of A, B, C and D existing in the reactor along with the existing selectivity.

Plot F_A, F_B, F_C, F_D and $S_{C/D}$ as a function of V

Example B: Liquid Phase CSTR

Solution

Liquid CSTR

Mole Balances:

(1) $$f(C_A) = \upsilon_0 C_{A0} - \upsilon_0 C_A + r_A V$$

(2) $$f(C_B) = \upsilon_0 C_{B0} - \upsilon_0 C_B + r_B V$$

(3) $$f(C_C) = -\upsilon_0 C_C + r_C V$$

(4) $$f(C_D) = -\upsilon_0 C_D + r_D V$$

Net Rates:

(5) $$r_A = r_{1A} + r_{2A}$$

Selectivity

If one were to write $S_{C/D}=F_C/F_D$ in the Polymath program, Polymath would not execute because at V=0, F_C=0 resulting in an undefined volume (infinity) at V=0. To get around this problem we start the calculation 10^{-4} dm^3 from the reactor entrance where F_D will not be zero and use the following IF statement.

$$\tilde{S}_{C/D} = if \ (V > 0.001) \ then \left(\frac{F_C}{F_D} \right) \ else \ (0) \tag{15}$$

Selectivity

Stoichiometry:

(16) $$C_A = F_A / \upsilon_0$$

(17) $$C_B = F_B / \upsilon_0$$

(18) $$C_C = F_C / \upsilon_0$$

(19) $$C_D = F_D / \upsilon_0$$

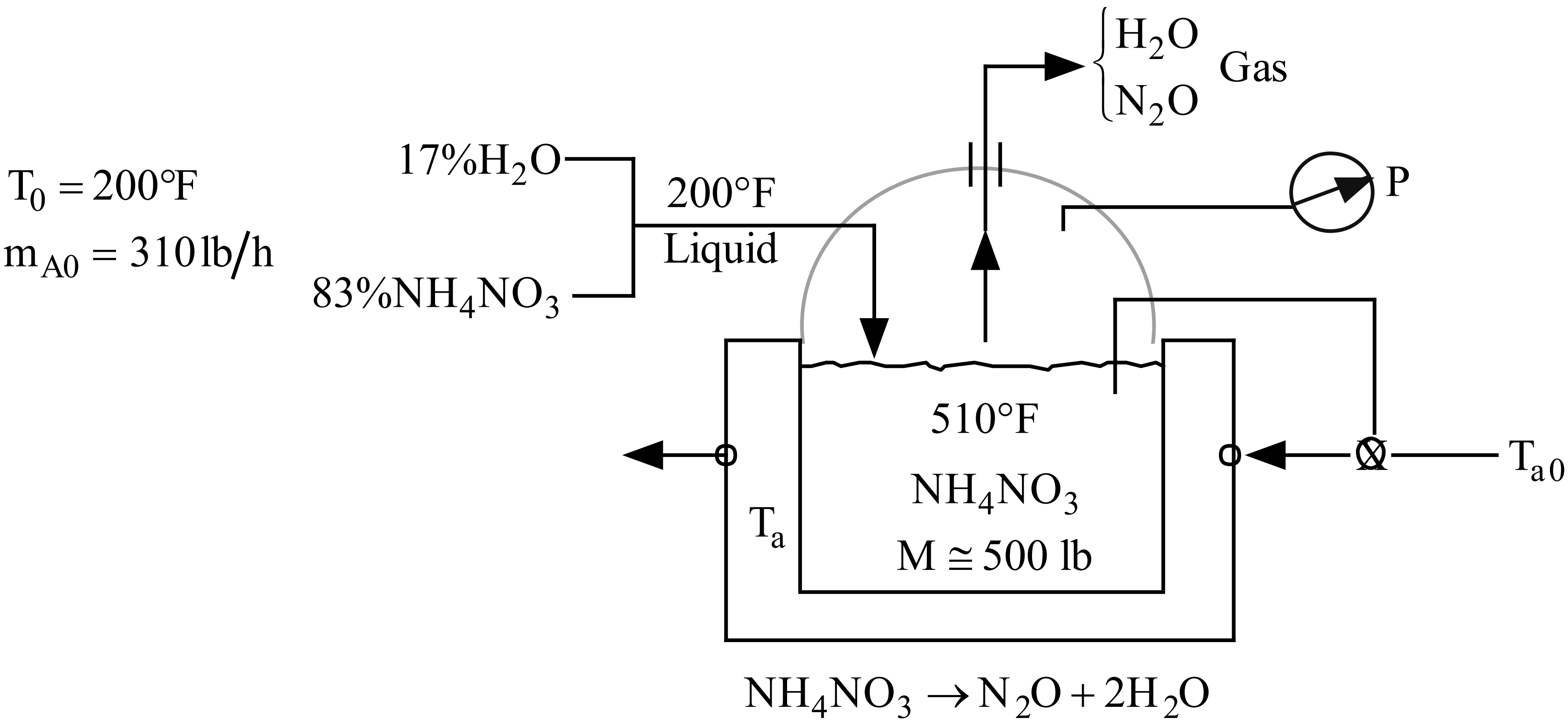
Parameters:

(20) $$\upsilon_0 = 100\ \mathrm{dm^3/min}$$

(21) $$k_{1A} = 10\left(\mathrm{dm^3/mol}\right)^2/\mathrm{min}$$

(22) $$k_{2C} = 15\left(\mathrm{dm^3/mol}\right)^4/\mathrm{min}$$

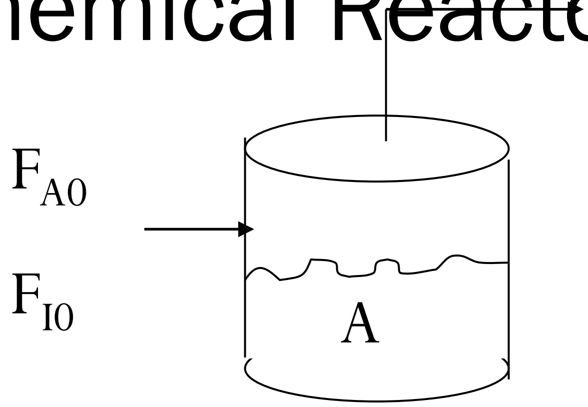
Example 1: Safety in Chemical Reactors



Example 1: Safety in Chemical Reactors

$$NH_4NO_3 \rightarrow 2H_20 + N_2O$$

$$A \rightarrow 2B + C$$



$$\frac{dN_A}{dt} = F_{A0} - F_A + r_A V$$

$$\frac{dN_B}{dt} = F_{B0} - F_B + r_B V$$

$$\frac{dN_C}{dt} = F_{C0} - F_C + r_C V$$

Example 1: Safety in Chemical Reactors

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{\sum N_i C_{Pi}} \quad \text{(only A in vat, B,C are gases)} = \frac{Q_g - Q_r}{N_A C_{PA}}$$

$$\mathrm{Q_g = (r_A V)(\Delta H_{rxA})}$$

$$\mathrm{Q_r = F_{A0}\left[C_{PA}(T - T_0) + \theta_B(H_B - H_{B0})\right] + UA(T - T_a)}$$

If the flow rate shut off, the temperature will rise (possibly to point of explosion!)

Rearranging:

$$\frac{dT}{dt} = \frac{\overbrace{(r_A V)(\Delta H_{Rx})}^{Q_g} - \overbrace{\left[F_{A0} \sum \Theta_i (H_i - H_{i0}) + UA(T - T_a)\right]}^{Q_r}}{\sum N_i C_{P_i}}$$

$$= \frac{Q_g - Q_r}{\sum N_i C_{P_i}}$$

Additional information (approximate but close to the real case):

$$\Delta H^o{}_{Rx} = -336 \text{ Btu/lb ammonium nitrate at } 500^o \text{ F (constant)}$$

$$C_P = 0.38 \text{ Btu/lb ammonium nitrate} \cdot \text{F}$$

$$C_P = 0.47 \text{ Btu/lb of steam nitrate} \cdot \text{F}$$

$$-r_A V = kC_A V = k\frac{M}{V} V = kM \text{ (lb/h)}$$

$$\dot{Q} + F_{A0}C_{P_A}(T - T_0) + F_{A0}\Theta_B[H_B(g) - H_{B0}] - r_A V\Delta H_{Rx} - F_A \Delta H_{Avap} = N_A C_{P_A} \frac{dT}{dt}$$

$$\overbrace{(r_A V)(\Delta H_{Rx})}^{Q_g} - \left[\overbrace{F_{A0}\left(C_{P_A}(T - T_0) + \Theta_B(H_B(g) - H_{B0})\right) + F_A \Delta H_{Vap}}^{Q_{r1}} + \overbrace{UA(T - T_a)}^{Q_{r2}}\right] = N_A C_{P_A} \frac{dT}{dt}$$

Complete conversion $F_A = 0$

$$Q_g - [Q_{r1} + Q_{r2}] = N_A C_{P_A} \frac{dT}{dt}$$

Batch Reactors with Heat Effects

Single Reactions $\quad Q_g = (r_A V)(\Delta H_{Rx})$

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{\sum N_i C_{P_i}}$$

Multiple Reactions $\quad Q_g = \sum r_{ij} \Delta H_{Rxij} V$

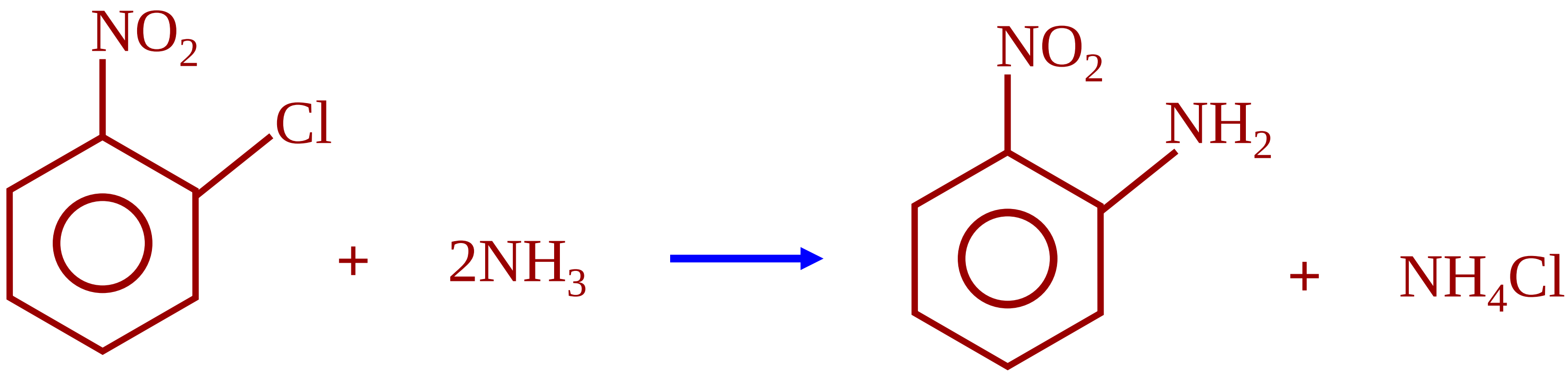
$$Q_{r1} = UA(T - T_a)$$

Risk Rupture $\quad Q_{r2} = \acute{m}\acute{Y}_{vap} \Delta H_{vap}$

Keeping MBAs Away From Chemical Reactors

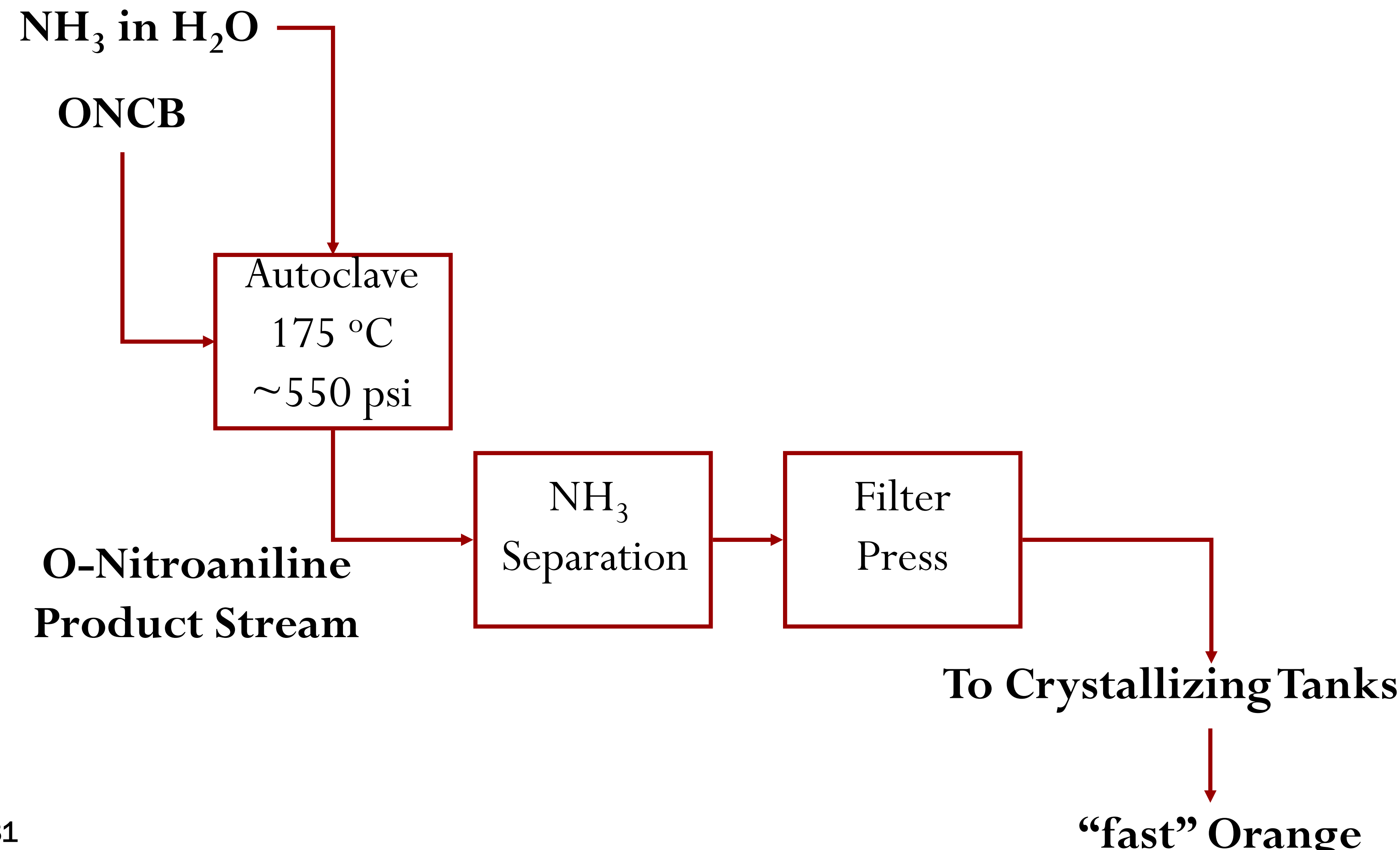
- The process worked for 19 years before they showed up!
- Why did they come?
- What did they want?

Nitroaniline Synthesis Reaction

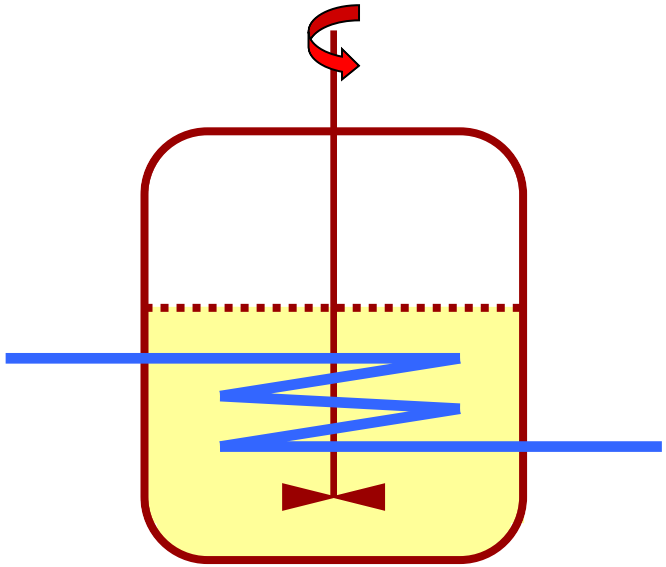


ONCB + Ammonia → Nitroanaline + Ammonium Chloride

Nitroaniline Synthesis Process



Nitroaniline Synthesis Reactor



Old

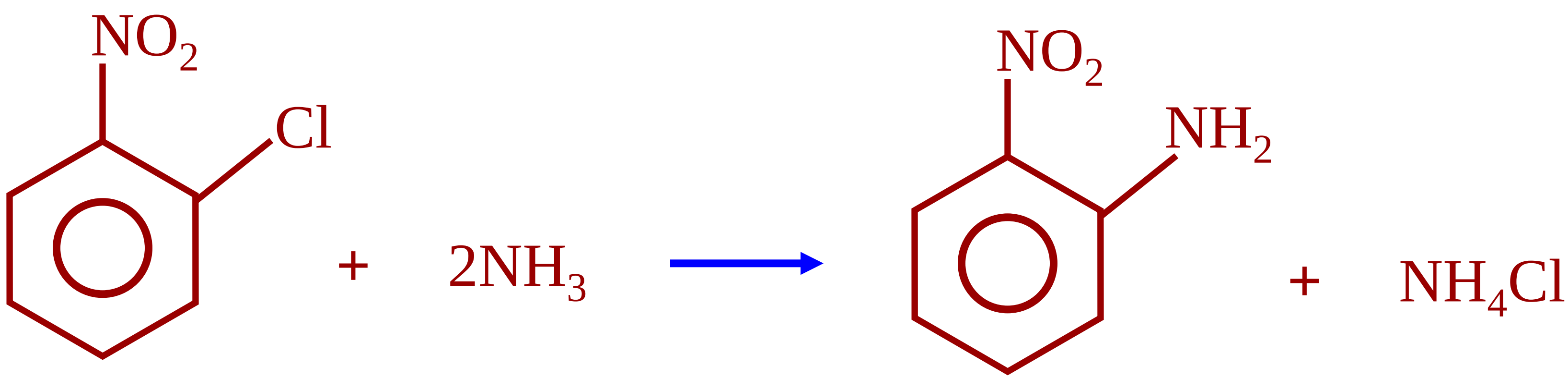
3 kmol ONCB

43 kmol Ammonia

100 kmol Water

$V = 3.25 \text{ m}^3$

Nitroaniline Synthesis Reaction

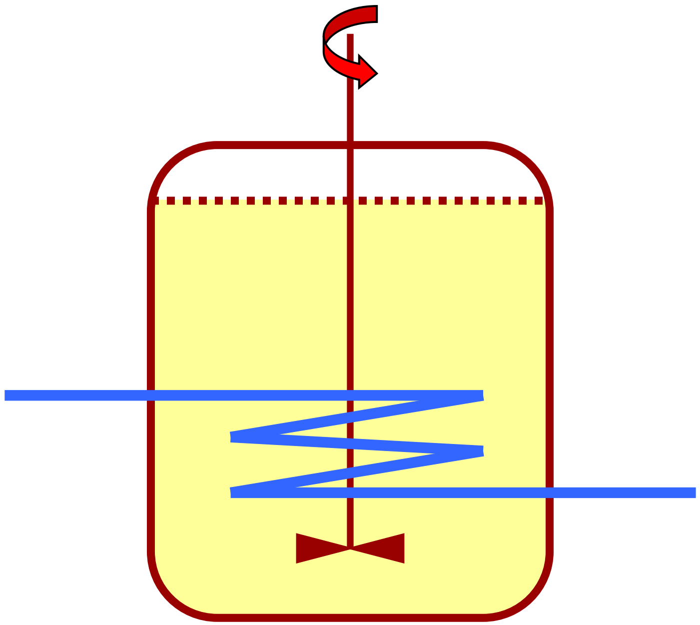


ONCB + Ammonia → Nitroanaline + Ammonium Chloride

Batch Reactor, 24 hour reaction time

Management said: TRIPLE PRODUCTION

MBA Style Nitroaniline Synthesis Reactor



New

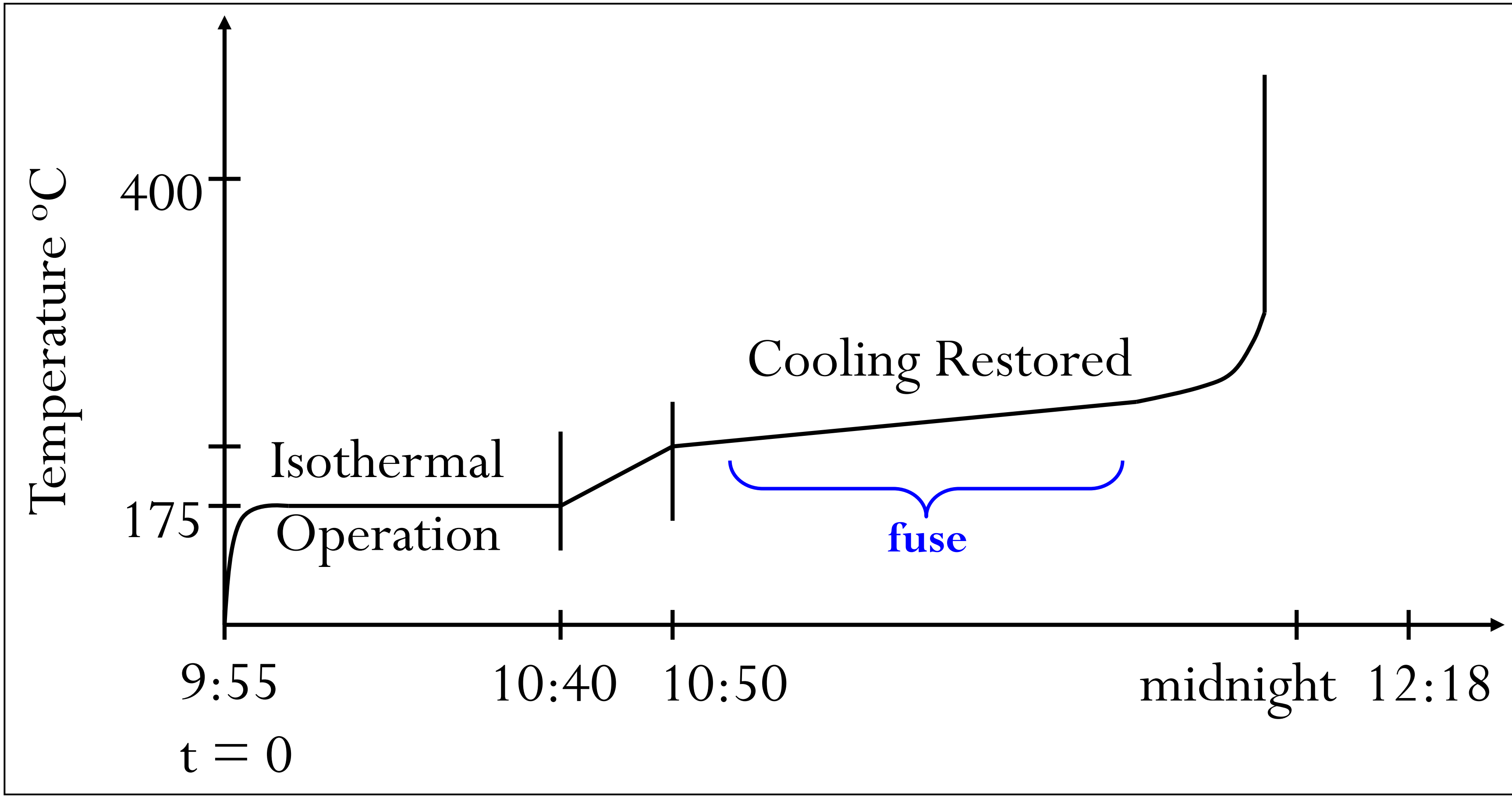
9 kmol ONCB

33 kmol Ammonia

100 kmol Water

$V = 5\ m^3$

Temperature-time trajectory



Temperature-time trajectory

$$\frac{dT}{dt} = \frac{UA(T_0 - T) + (r_A V)(DH_{rx})}{N_{A0}C_{pA} + N_{B0}C_{pB} + N_W C_{pW}}$$

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{NC_p}$$

End of Lecture 22