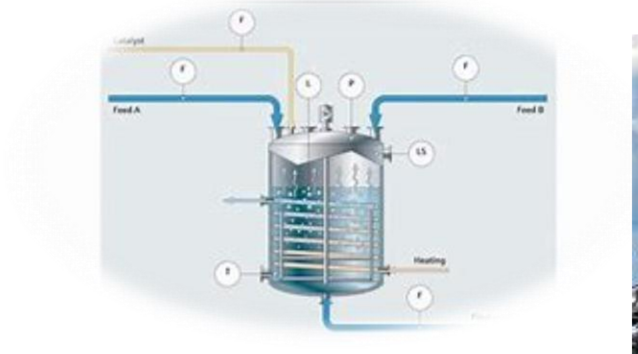
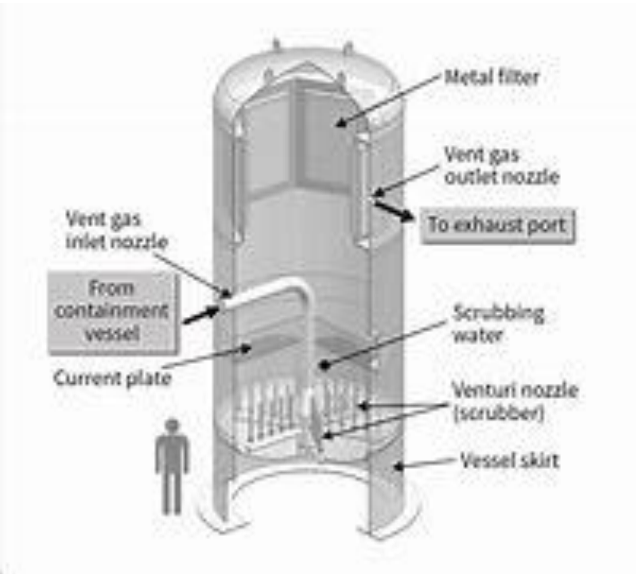
Reactor Design II





Week 10

Reactor Safety

Saba A. Gheni, Ph.D.

Chemical Engineering Department

ghenis@tu.edu.iq

Introduction

- Chemical Reaction Engineering (CRE) emphasizes safety in reactor design and operation.
- This lecture focuses on case studies of industrial accidents, exploring causes and preventive measures to ensure safety in chemical processes.

Topics to be Addressed

- \- Case Studies: Ammonium Nitrate, Monsanto, and T2 Labs Explosions
- \- Energy Balance and Heat Effects in Reactors
- \- Safety Mechanisms and Preventive Measures
- \- Lessons Learned from Industrial Accidents

Objectives

- By the end of this lecture, students will be able to:

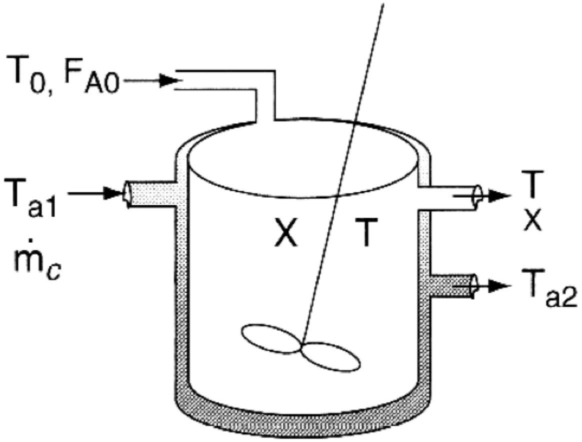
- - Understand the principles of reactor safety and energy balance.
- - Analyze causes of industrial accidents and their prevention.
- - Apply safety measures in reactor design and operation.
- - Learn from case studies to mitigate risks in chemical processes.

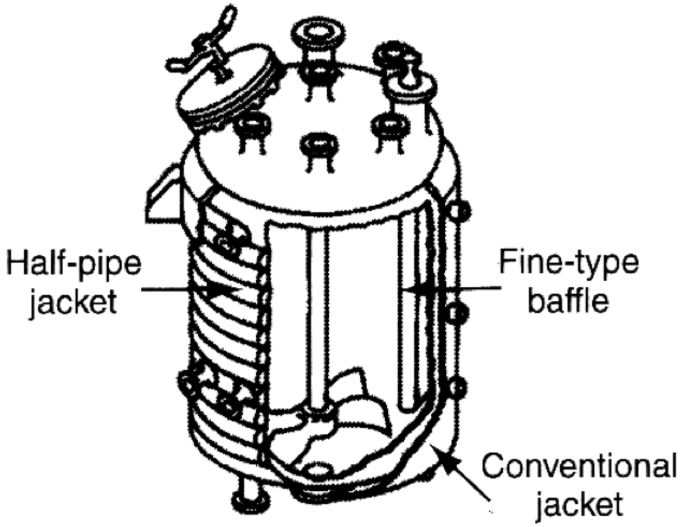
Introduction

- Understanding energy balance, heat effects, and safety mechanisms is critical for preventing disasters.

- This session covers notable accidents such as the ammonium nitrate explosion, Monsanto explosion, and T2 Laboratories explosion, and lessons learned from these events.

CSTR with Heat Effects





Energy Balance for CSTRs

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

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

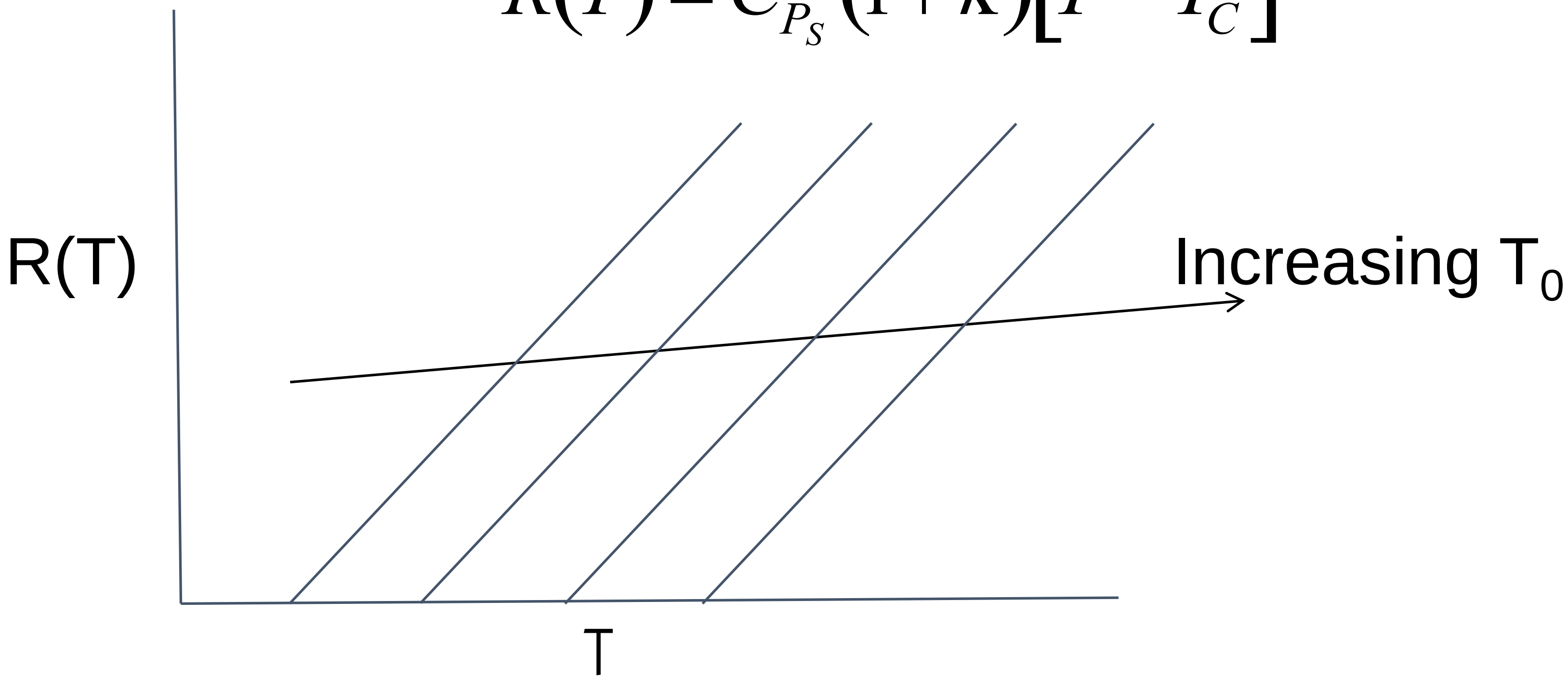
$$R(T) = C_{P_S} \left(1 + \kappa \right) \left[T - T_C \right]$$

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

Review Last Lecture

Energy Balance for CSTRs

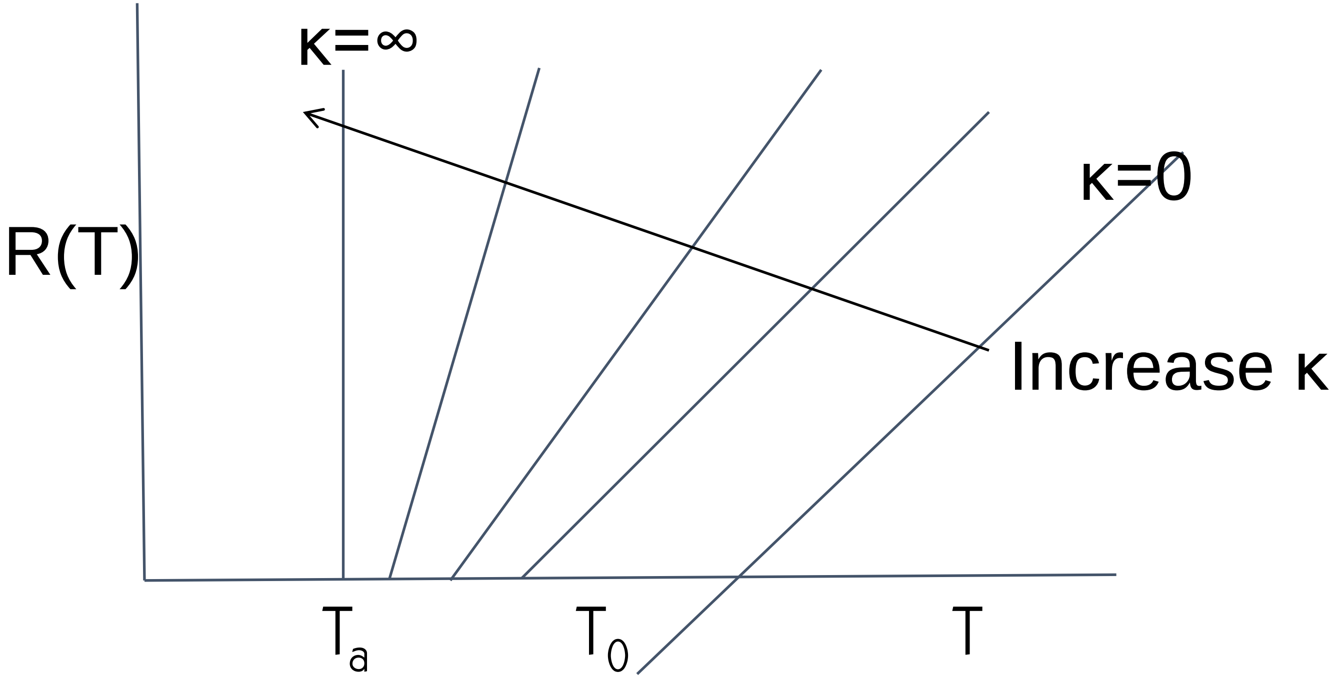
$$R(T) = C_{P_S}(1+\kappa)\left[T - T_C\right]$$



Variation of heat removal line with inlet temperature.

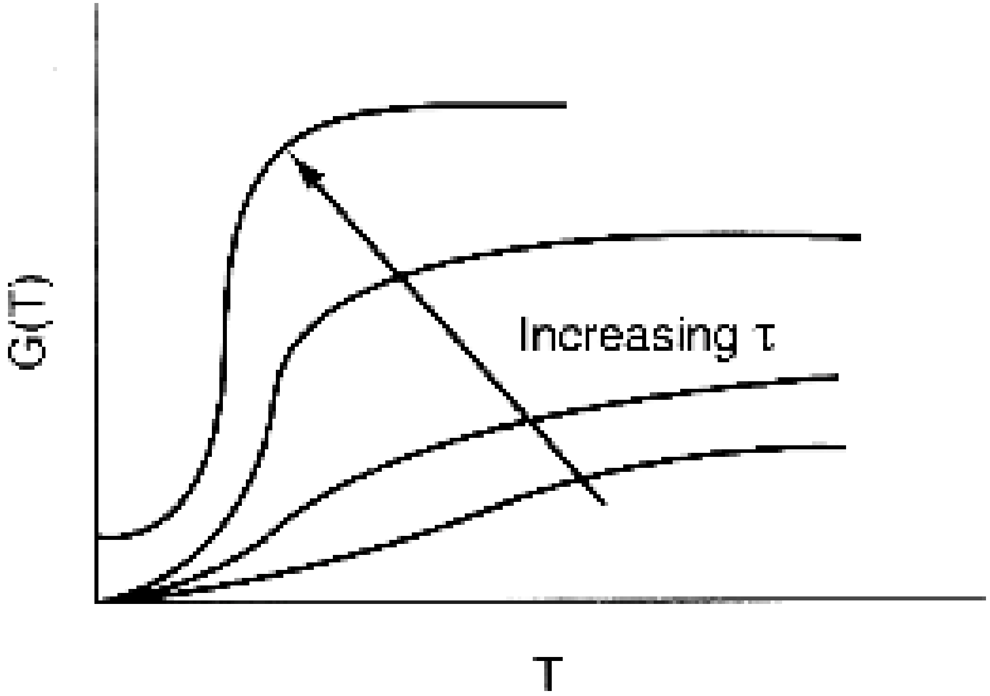
Energy Balance for CSTRs

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



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

Multiple Steady States (MSS)

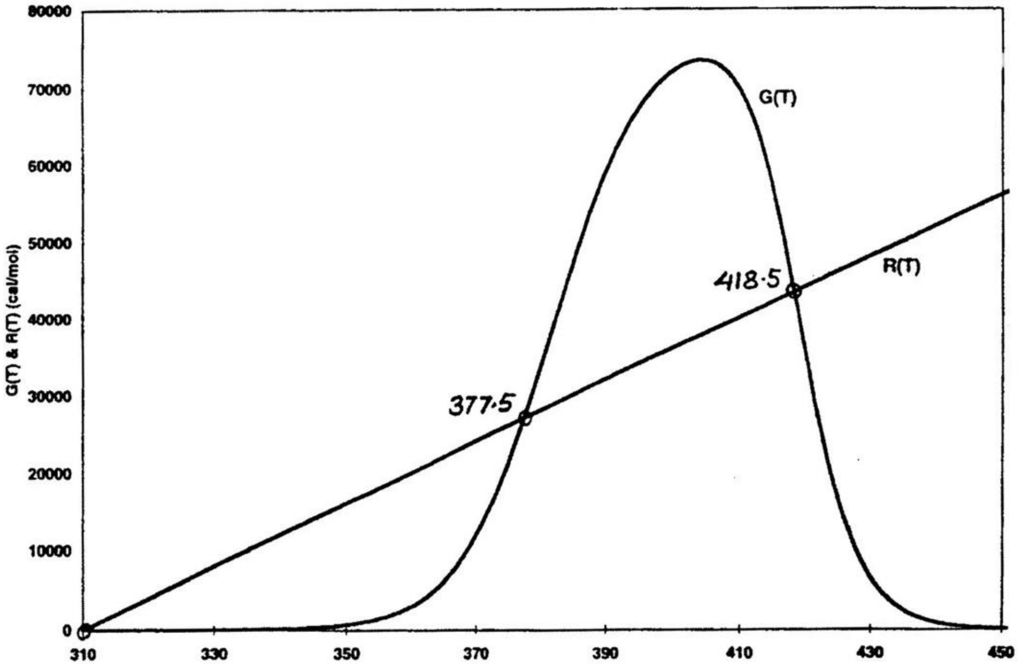


Variation of heat generation curve with space-time.

Reversible Reaction

Gas Flow in a PBR with Heat Effects

$A \leftrightarrow B$



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

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

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

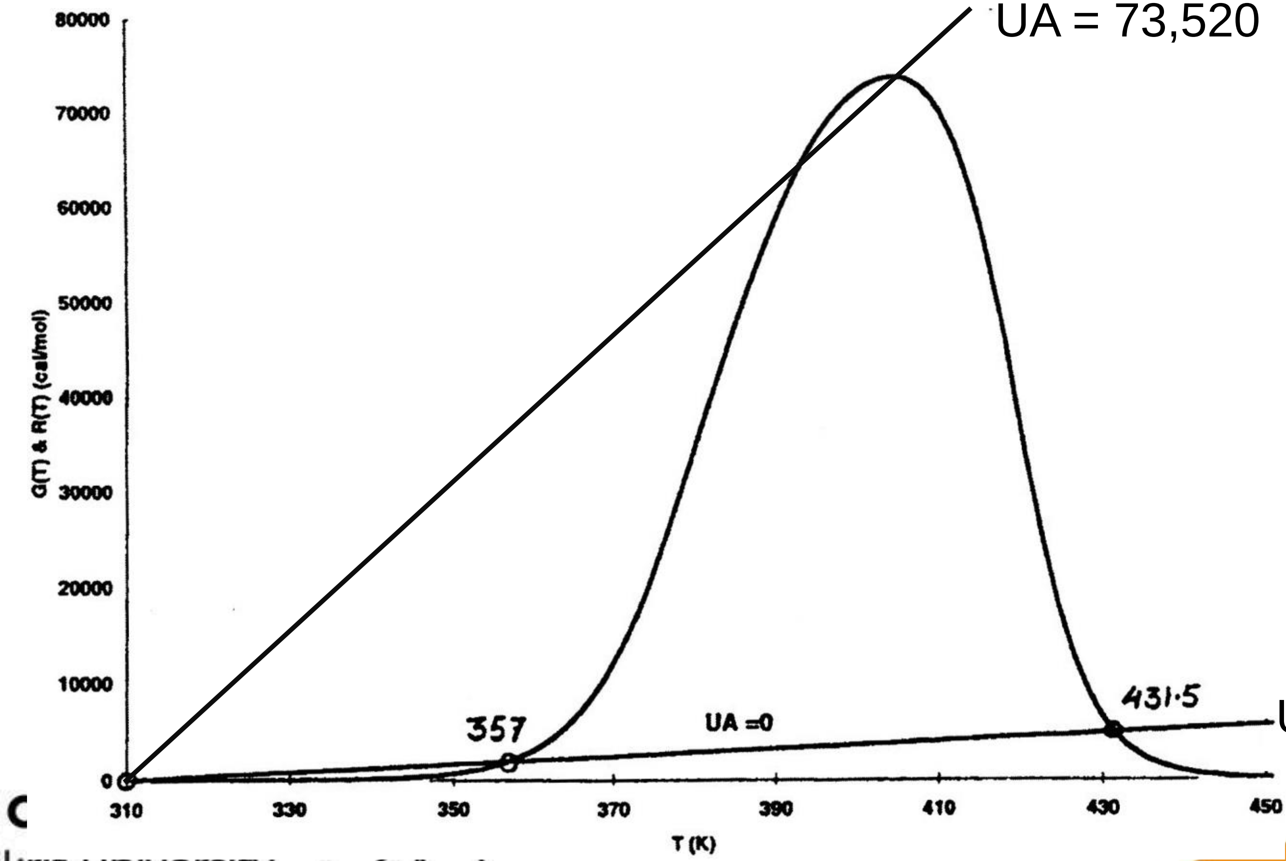
$$T_C = \frac{T_0 + \kappa T_a}{1+\kappa} = 310$$

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

Reversible Reaction

Gas Flow in a PBR with Heat Effects

$A \leftrightarrow B$



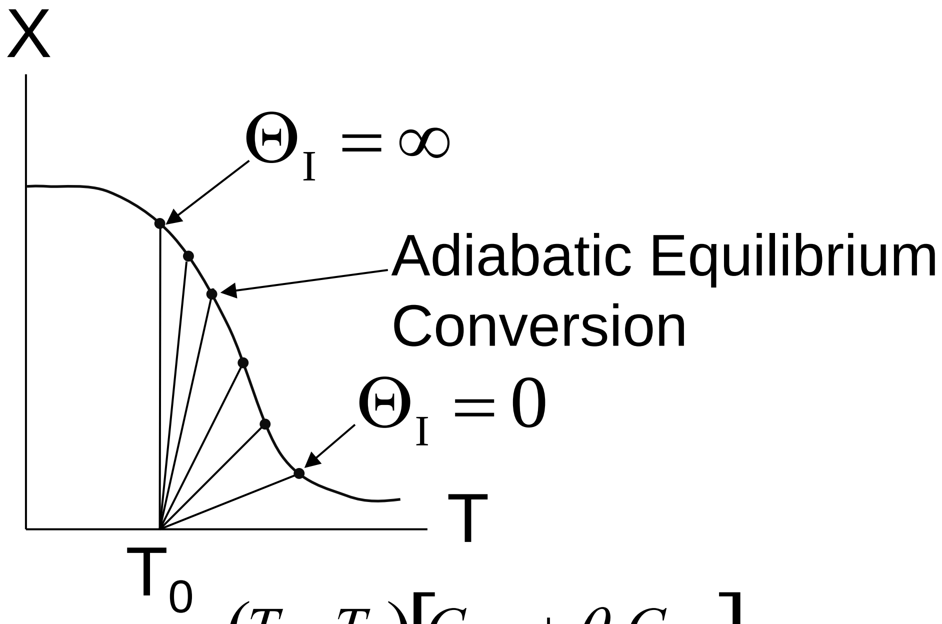
UA = 73,520

UA = 0

Gas Phase Heat Effects

Effect of adding inerts on adiabatic equilibrium conversion

Adiabatic:



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

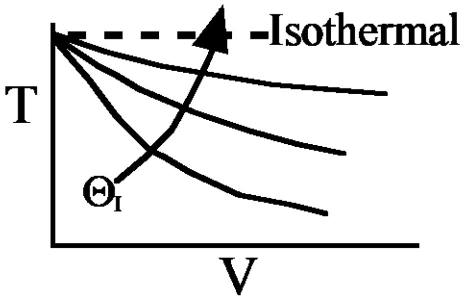
Adiabatic Exothermic Reactions

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

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

Energy Balance :

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



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

A. First Order Reaction

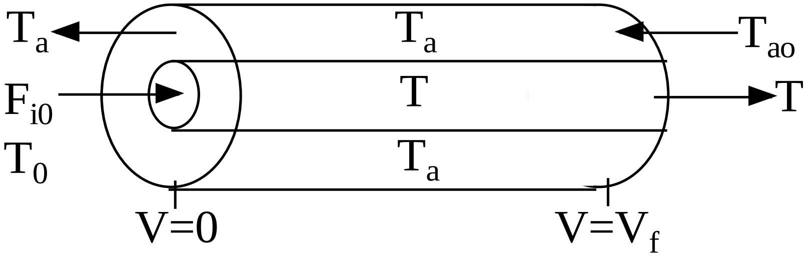
$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

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

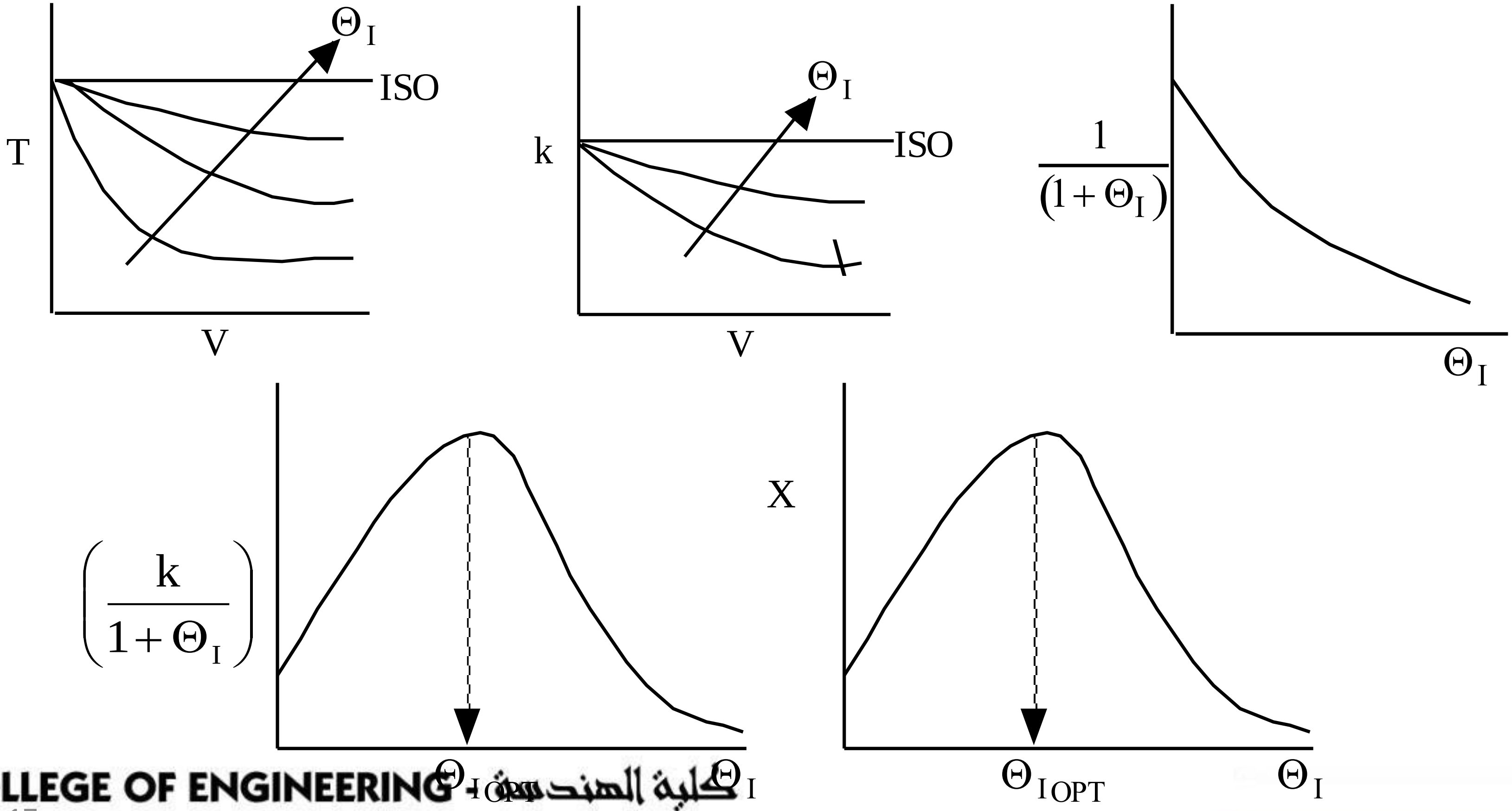


For Liquids, volumetric flow rates are additive.

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

Effect of Adding Inerts to an Endothermic Adiabatic Reaction

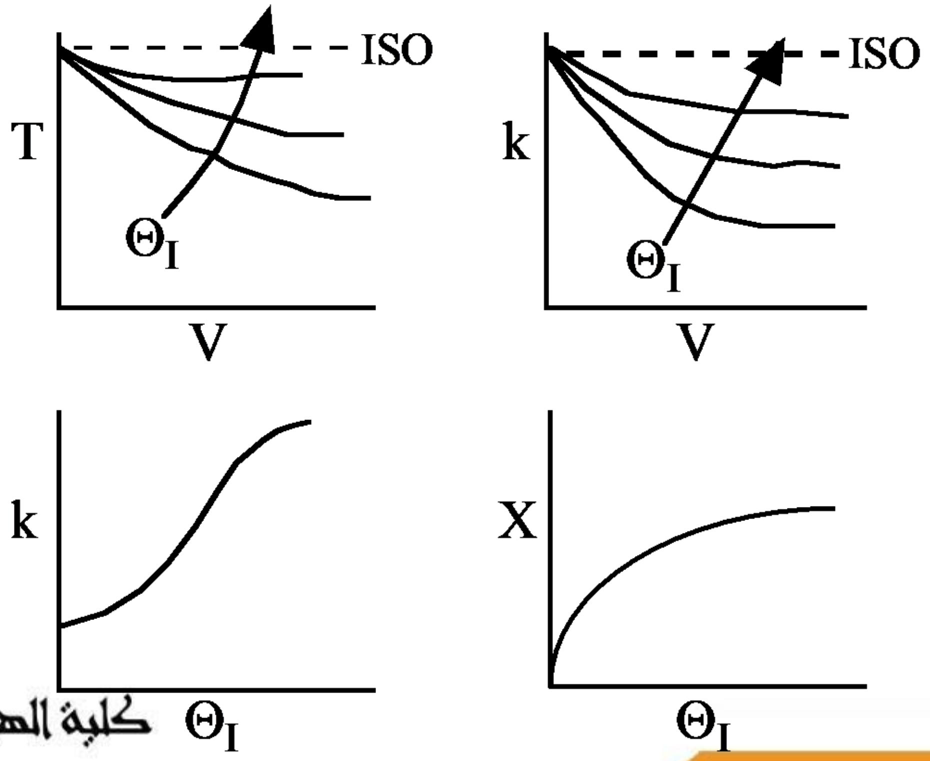
What happens when we add Inerts, i.e., vary Theta I??? It all depends what you change and what you hold constant!!!



A.1.a. Case 1. Constant υ_0

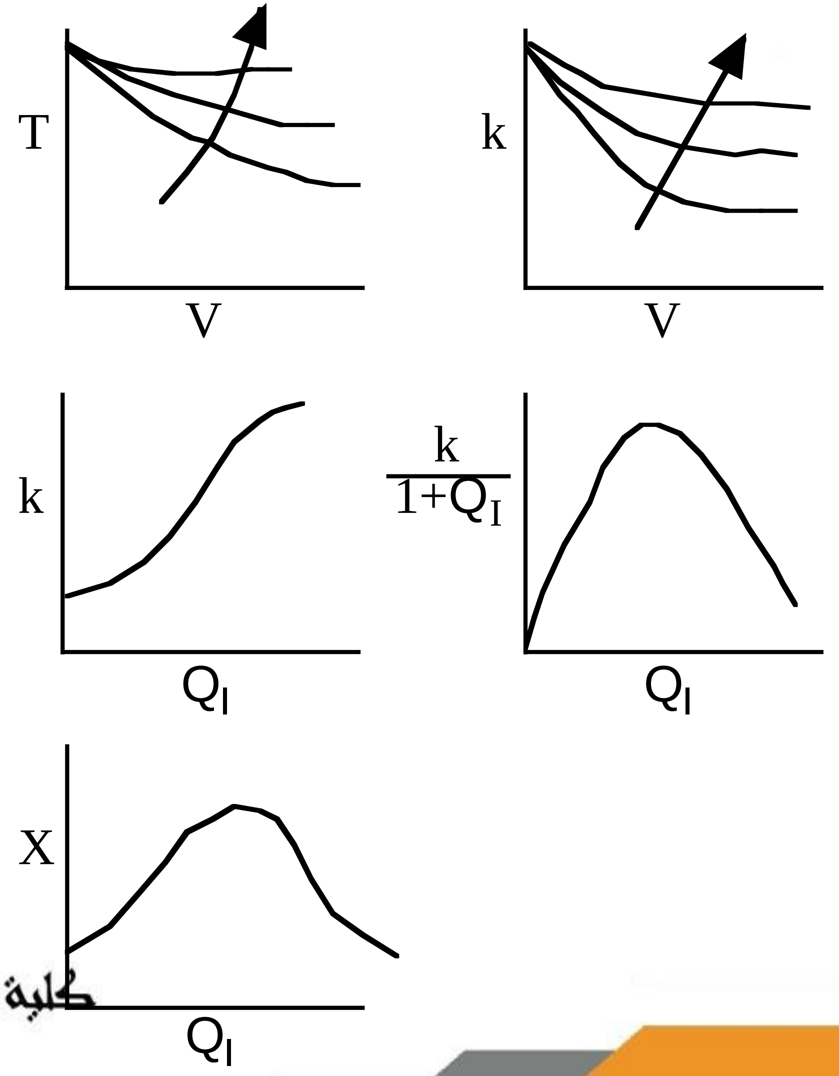
To keep υ_0 constant if we increase the amount of Inerts, i.e., increase Θ_I we will need to decrease the amount of A entering, i.e., υ_{A0}. So $\Theta_I \uparrow$ then $\upsilon_{A0} \downarrow$

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



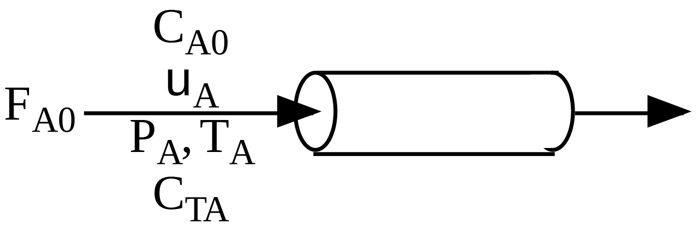
A.1.a. Case 2. Constant υ_A, Variable υ_0

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



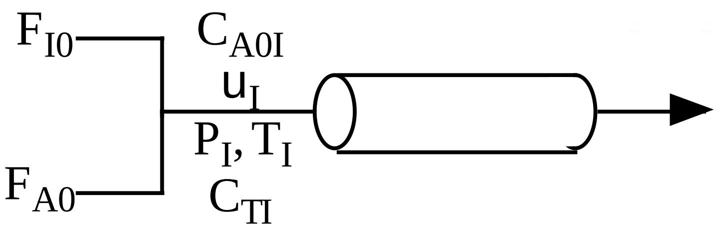
A.2. Gas Phase

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}

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

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)

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

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

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

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.

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

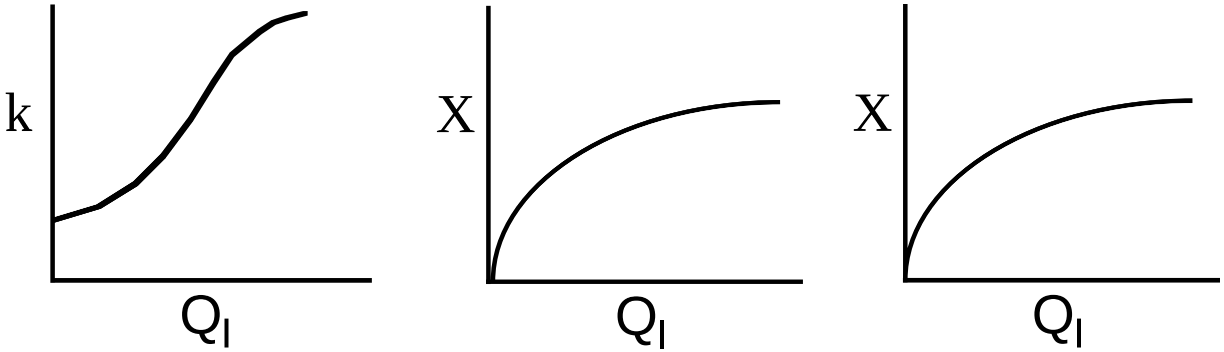
For example if $\Theta_I = 2$ then υ_I will be the same as υ_A, but we need the entering pressures P_I and P_A to be in the relationship $P_I = 3P_A$ with $T_A = T_I$

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

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

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

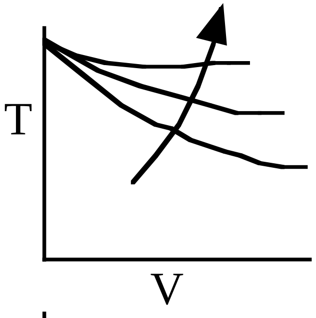


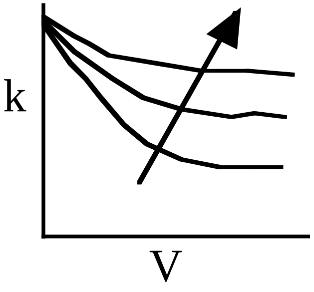
A.2.b.Case 2: Variable υ_0 Constant T, P i.e., $P_I = P_A$, $T_I = T_A$

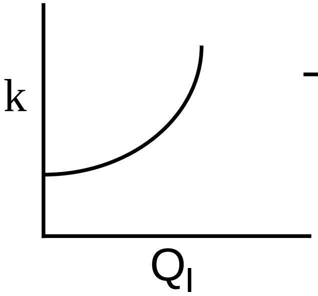
$$\upsilon_I = \upsilon_A \frac{F_{TI}}{F_{TA}} = \upsilon_A \frac{(F_{A0} + F_{I0})}{F_{A0}} = \upsilon_A (1 + \Theta_I)$$

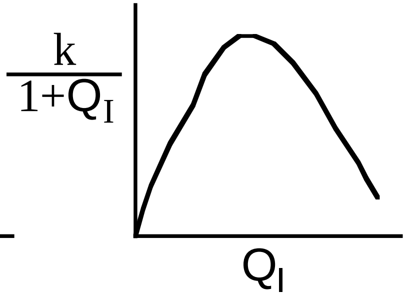
$$\upsilon_I = \upsilon_A (1 + \Theta_I)$$

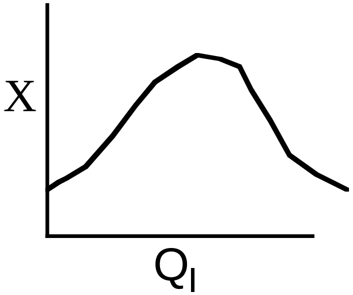
$$\frac{dX}{dV} = \frac{1}{\upsilon_A} \frac{k}{1+\Theta} (1 - X)$$





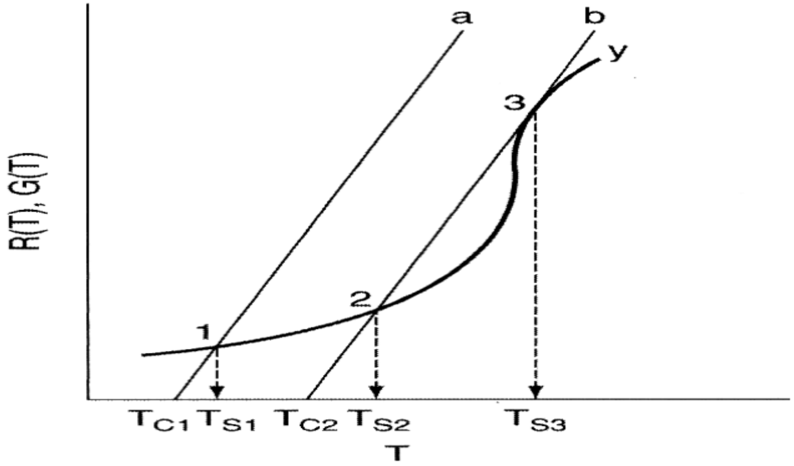






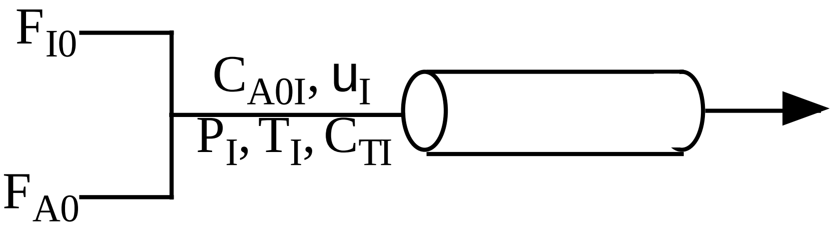
B. Gas Phase Second Order Reaction

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

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

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

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

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

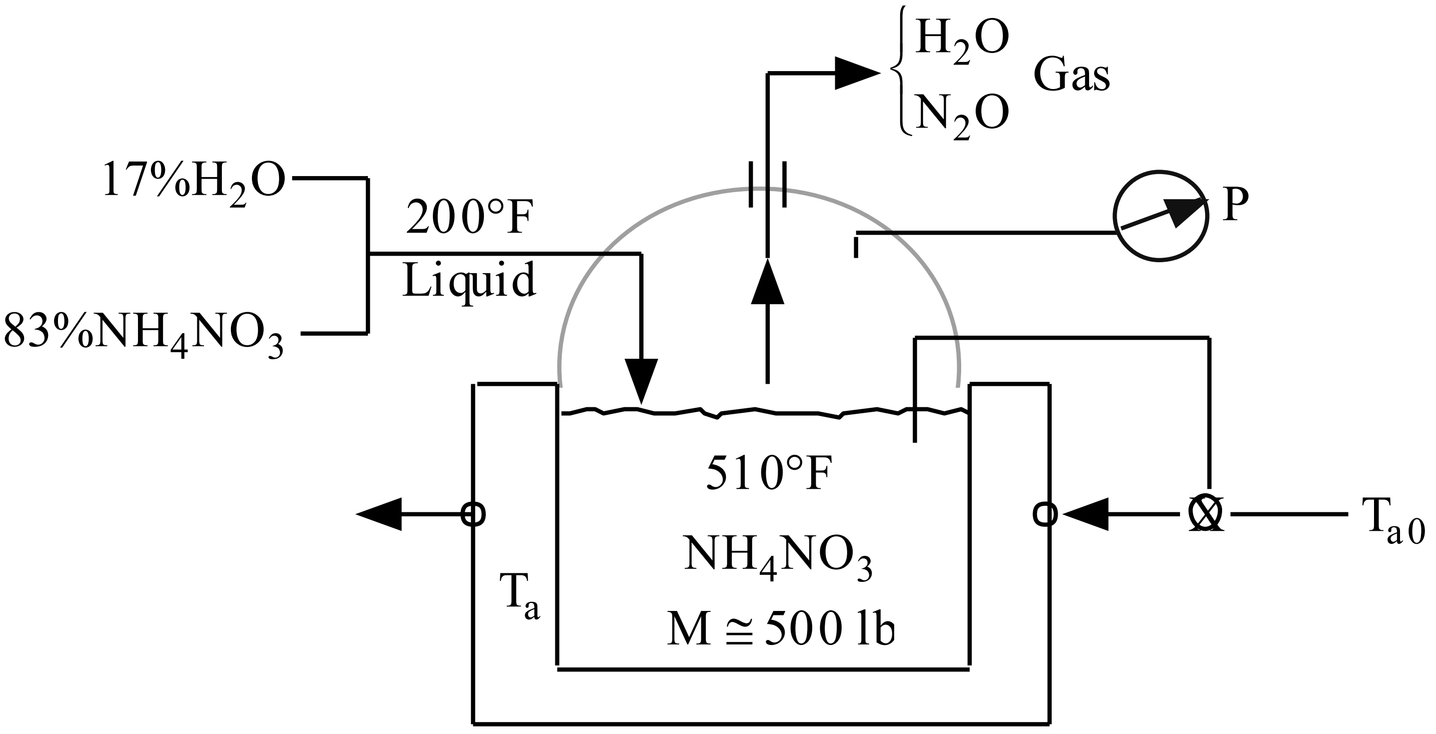
Case 1 – Ammonium Nitrate Explosion

Massive blast at Terra plant kills four.

Example 1: Safety in Chemical Reactors

$T_0 = 200°F$

$m_{A0} = 310 \text{ lb/h}$



$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Example 1: Safety in Chemical Reactors

Only liquid A in the vat as the product gases N_2O and H_2O escape immediately after being formed.

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{N_A C_{PA}}$$

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

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

Unsteady State Energy Balance

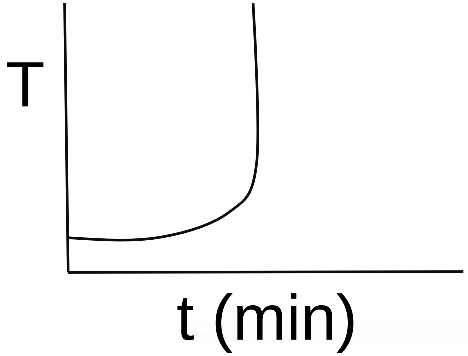
$$\frac{dT}{dt}=\frac{\overbrace{(\Delta H_{Rx})(r_A V)}^{Q_g}-\overbrace{\left[F_{A0}\sum\Theta_i C_{P_i}(T-T_0)+\left(UA(T-T_a)\right)\right]}^{Q_r}}{\sum N_i C_{P_i}}$$

Adiabatic

$$Q_r=F_{A0}\left[C_{P_A}(T-660)+\Theta_W\left(1134+C_{P_W}(T-960)\right)\right]$$

$$F_{A0}=0$$

$$\frac{dT}{dt}=\frac{(-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{P_i}}$$



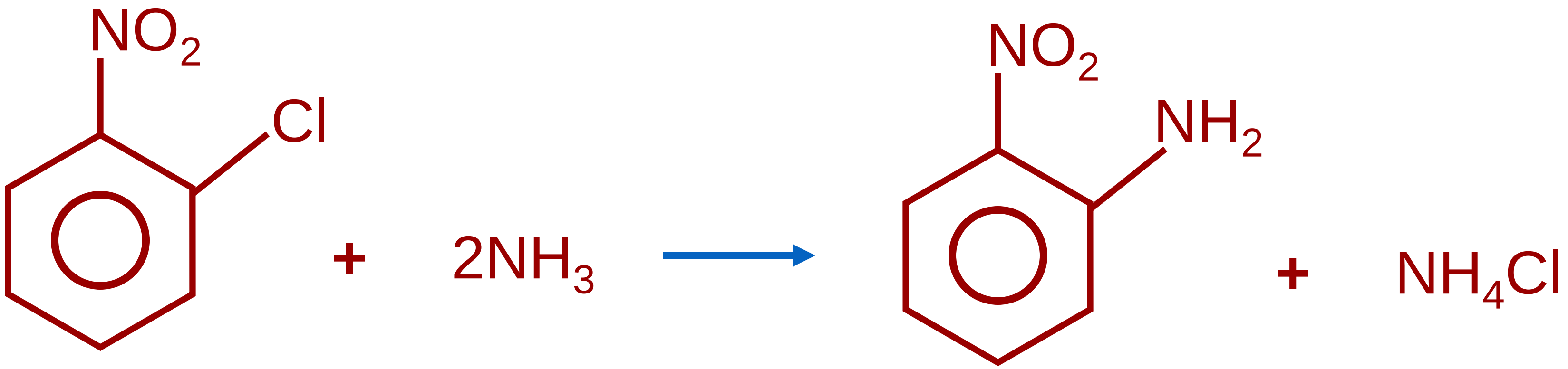
If the flow rate is shut off, the temperature will rise (possibly to point of explosion!)

Case 2 – Monsanto Chemical Company

- Keeping MBAs away from Chemical Reactors

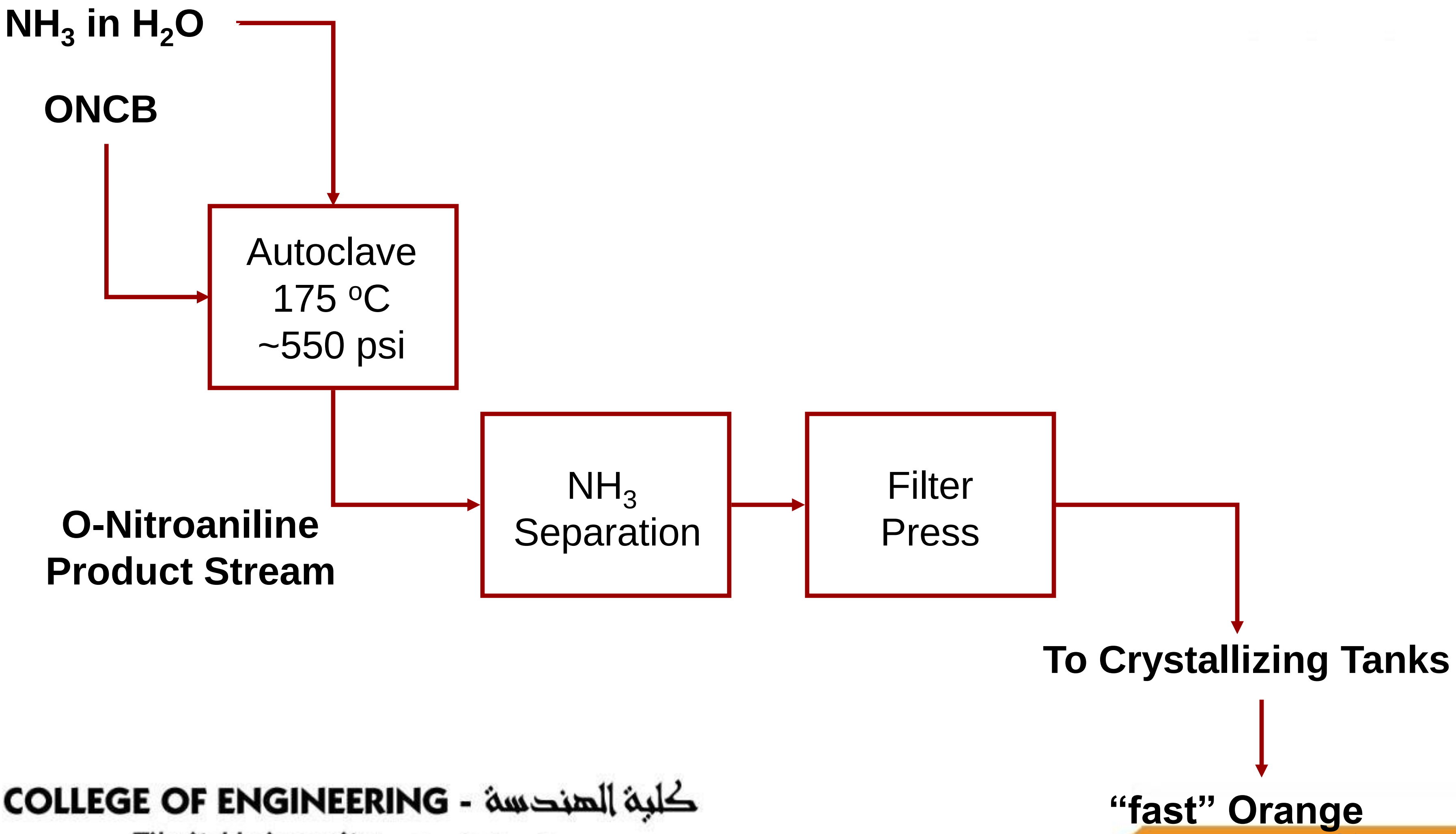
- The process worked for 19 years before “they” showed up!
- Why did they come?
- What did they want?

Nitroanline Synthesis Reaction



ONCB Chloride + Ammonia → Nitroanaline + Ammonium

Nitroanline Synthesis Reaction



NH_3 in H_2O

ONCB

Autoclave
175 ^oC
~550 psi

O-Nitroaniline Product Stream

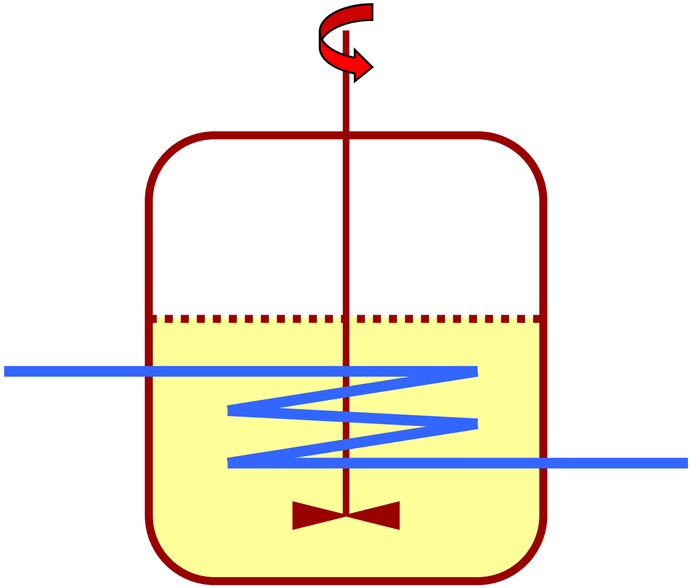
NH_3 Separation

Filter Press

To Crystallizing Tanks

“fast” Orange

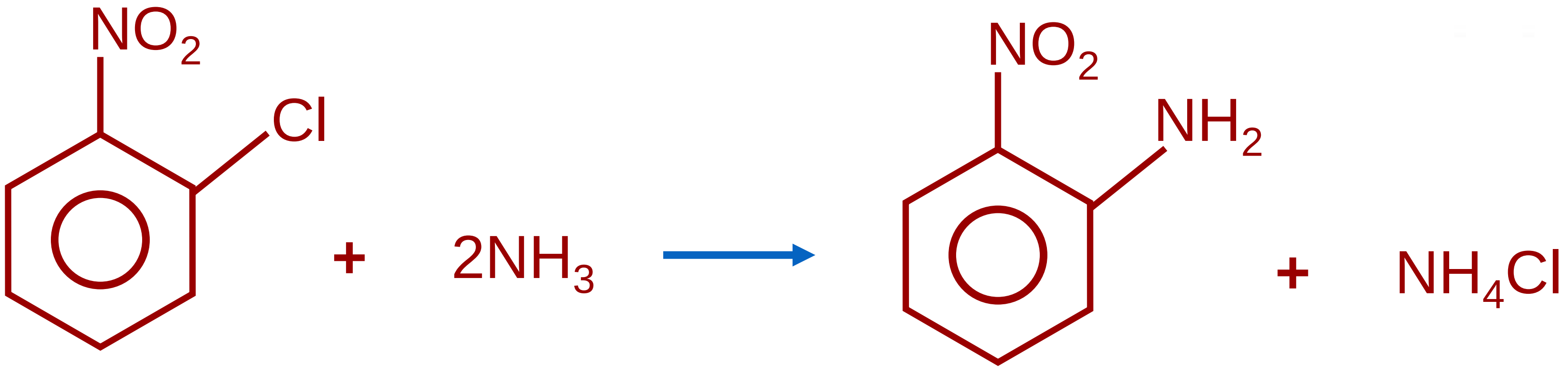
Nitroanline Synthesis Reactor



Old

3 kmol ONCB
43 kmol Ammonia
100 kmol Water
V = 3.25 m^3

Same Nitroanline Synthesis Reaction

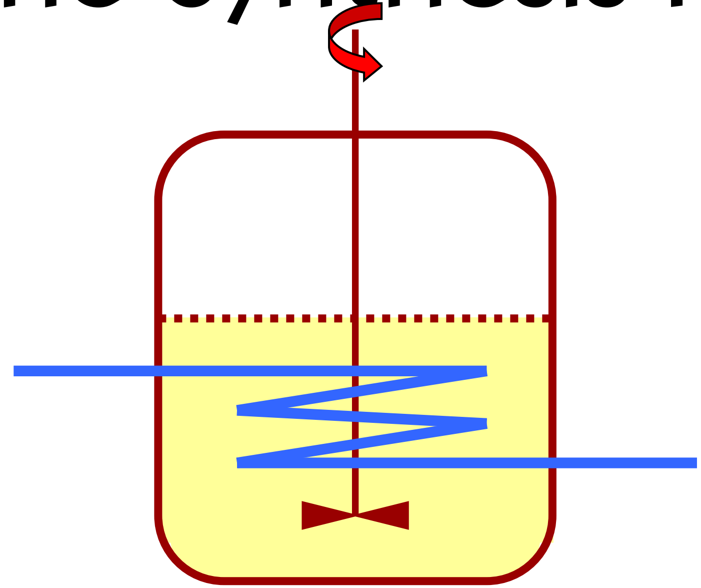


ONCB + Ammonia → Nitroanaline + Ammonium
Chloride

Batch Reactor, 24 hour reaction time

Management said: TRIPLE PRODUCTION

MBA-Style:
Nitroanline Synthesis Reactor



New

9 kmol ONCB
33 kmol Ammonia
100 kmol Water
V = 5 m^3

Batch Reactor Energy Balance

$$\frac{dT}{dt} = \frac{\overbrace{(r_A V)(\Delta H_{rx})}^{Q_g} - \overbrace{UA(T - T_0)}^{Q_r}}{N_{A0}C_{pA} + N_{B0}C_{pB} + N_W C_{pW}}$$

$$NC_P = N_{A0}C_{pA} + N_{B0}C_{pB} + N_W C_{pW}$$

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

Batch Reactor Energy Balance

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

The rate of “heat removed” is

$$Q_r = \dot{m}_c C_{P_c} \left\{ (T_{a1} - T) \left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{P_c}} \right) \right] \right\} \quad \text{Equation (12-13) p547}$$

For high coolant flow rates, $\dot{m}_c$, the maximum rate of heat removal is

$$Q_r = UA(T - T_a)$$

The rate of “heat generated” is $Q_g = (r_A V)\Delta H_{Rx} = (-r_A V)(-\Delta H_{Rx})$

$$-r_A = k_1 C_A C_B$$

$$Q_g = k_1 C_A C_B (-\Delta H_{Rx})$$

Batch Reactor Energy Balance

Recall
$$\frac{dT}{dT}=\frac{Q_r-Q_g}{NC_{P_S}}$$

For isothermal operation at Qr = Qg, T = 448 K

$$Q_g=k(448\,K)C_{A0}^2(1-X)(\Theta_B-X)(-\Delta H_{Rx})$$

$$Q_r=Q_g$$

$$\dot{m}_c C_{P_c}\left\{(T_{a1}-T)\left[1-\exp\left(\frac{-UA}{\dot{m}_c C_{P_c}}\right)\right]\right\}=(0.0001167)C_{A0}^2(1-X)$$

Vary $\dot{m}_c$ to keep “heat removed” equal to “heat generation”

Isothermal Operation for 45 minutes

At the time the heat exchanger fails

$$X = 0.033, T = 448\,K$$

$$Q_g = r_A V \Delta H_{Rx} = 3850\,kcal/\min$$

The maximum rate of removal at $T = 448\,K$ is

$$Q_r = UA\left(T - T_a\right) = 35.85(448 - 298) = 5378\,kcal/\min$$

$Q_r > Q_g$ Everything is OK

Adiabatic Operation for 10 minutes

$$t = 45\min \quad X = 0.033 \quad T = 448K$$

$$t = 55\min \quad X = 0.0424 \quad T = 468K$$

$$Q_g = 6591 kcal/\min$$

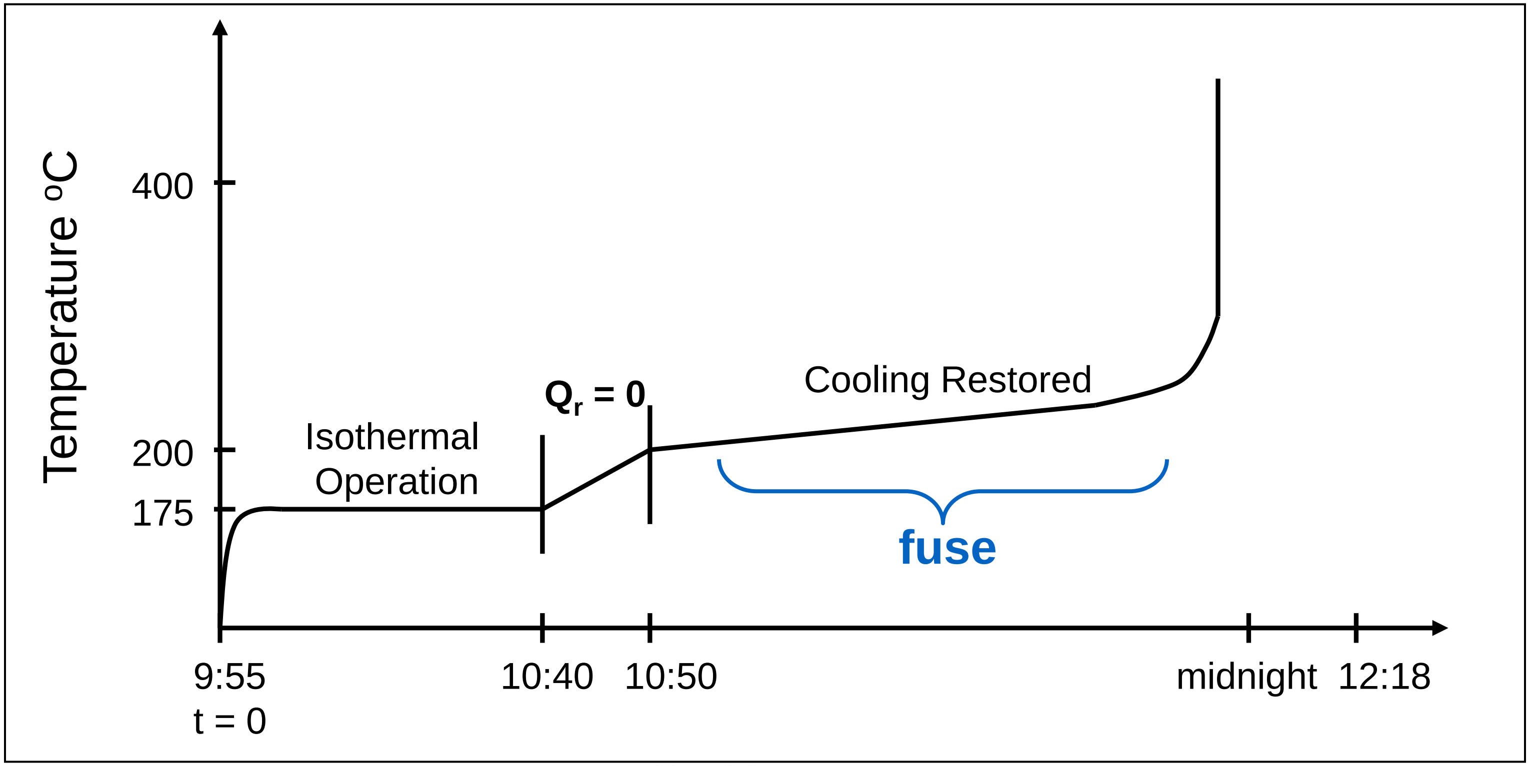
$$Q_r = 6093 kcal/\min$$

$$Q_g > Q_r$$

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{NC_p} = 0.2°C/\min$$

Temperature-Time trajectory

$$\frac{dT}{dt} = \frac{Q_q - Q_r}{N\,C_p} = 0.2\,°C/\min$$



Disk Rupture

The pressure relief disk should have ruptured when the temperature reached 265°C (ca. 700 psi) but it did not.

If the disk had ruptured, the maximum mass flow rate out of the reactor would have been 830 kg/min (2-in orifice to 1 atm).

$$Q_r = \dot{m}_{vap} \Delta H_{vap} + UA(T - T_a)$$

$$Q_r = 449{,}000 \frac{\text{kcal}}{\text{min}}$$

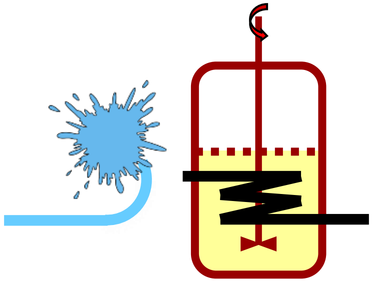
$$Q_g = 27{,}460 \frac{\text{kcal}}{\text{min}}$$

$$Q_r >>> Q_g$$

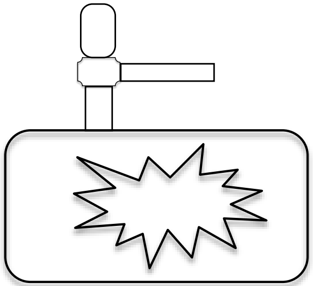
No explosion

All the following three things must have occurred for the explosion to happen

1. Tripled Production



2. Heat Exchange Failure



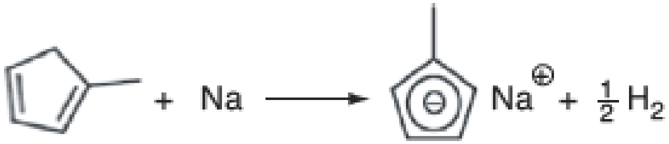
3.Relief Valve Failure

Case 3 – Manufacture of Fuel Additive

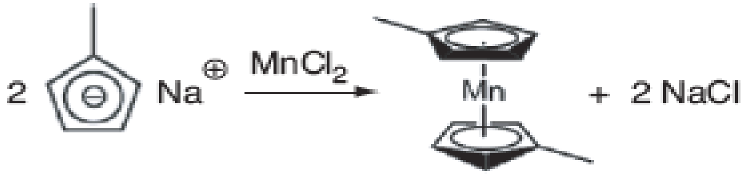
Methylcyclopentadiene Manganese Tricarbonyl (MCMT)

Production of methylcyclopentadienyl manganese tricarbonyl (MCMT).

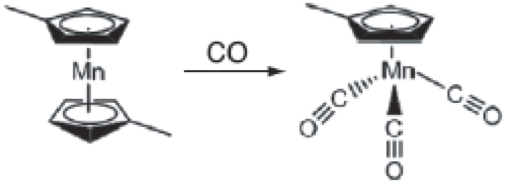
Step 1a. Reaction between methylcyclopentadiene (MCP) and sodium in a solvent of diethylene glycol dimethyl ether (diglyme, $C_6H_{14}O_3$) to produce sodium methylcyclopentadiene and hydrogen gas:



Step 1b. At the end of Step 1a, $MnCl_2$ is added to the reactor. It reacts with sodium methylcyclopentadiene to produce manganese dimethylcyclopentadiene and sodium chloride:



Step 1c. At the end of Step 1b, CO is added. The reaction between manganese dimethylcyclopentadiene and carbon monoxide produces the final product, methylcyclopentadienyl manganese tricarbonyl (MCMT), a fuel additive.



Only consider Step 1

Desired Reaction

Undesired Reaction of Dygline

$$CH_3-O-CH_2-CH_2-O-CH_2-CH_2O-CH_3 \xrightarrow[Na]{} 3H_2 + \text{misc(l)} \,\&\, (s)$$

Simplified Model

Let A = methycylcopentadiene, B = sodium, S = Solvent (diglyme), and D = H_2.
These reactions are:

(1) A + B → C + 1/2 D (gas) $-r_{1A} = -r_{1B} = k_{1A}C_AC_B$

(2) S → 3 D (gas) + miscellaneous liquid and solid products $-r_{2S} = k_{2s}C_S$

$$\Delta H_{Rx1A} = -45{,}400 \text{ J/mol}$$

$$\Delta H_{Rx2S} = -3.2\times10^5 \text{ J/mol}$$

Case 3 – Manufacture of Fuel Additive

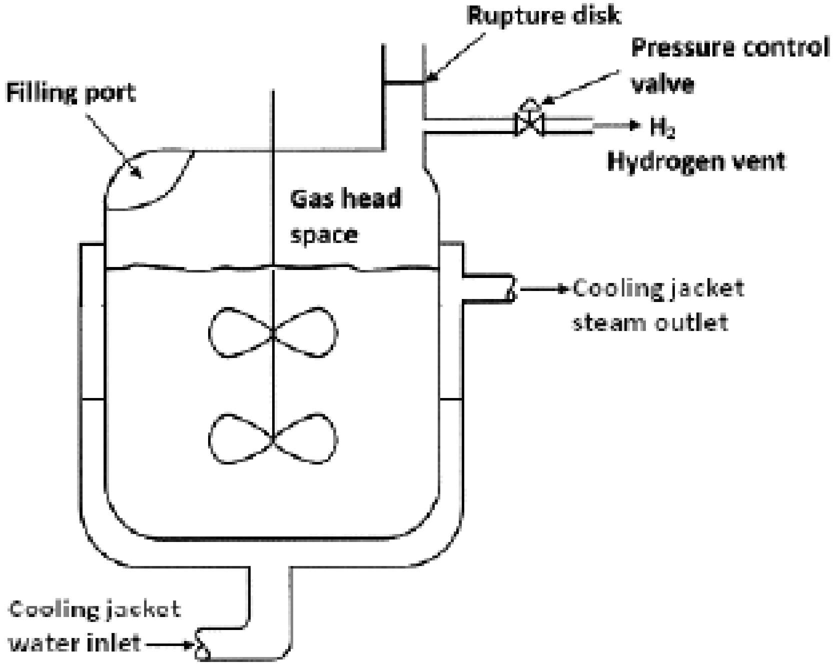


Figure E13-6.2 Reactor

Case 3 – Manufacture of Fuel Additive

Solution

(1) **Reactor Mole Balances**

Reactor (Assume Constant Volume Batch)

Liquid

$$\frac{dC_A}{dt} = r_{1A} \qquad \text{(E13-6.1)}$$

$$\frac{dC_B}{dt} = r_{1A} \qquad \text{(E13-6.2)}$$

$$\frac{dC_S}{dt} = r_{2S} \qquad \text{(E13-6.3)}$$

$$\boxed{\frac{dP}{dt} = \left(F_D - F_{vent}\right)\frac{RT_H}{V_H}}$$

Case 3 – Manufacture of Fuel Additive

(2) Rates

Laws:

$$(1)\quad -r_{1A} = k_{1A} C_A C_B \tag{E13-6.11}$$

$$k_{1A} = A_{1A} e^{-E_{1A}/RT} \tag{E13-6.12}$$

$$(2)\quad -r_{2S} = k_{2S} C_S \tag{E13-6.13}$$

$$k_{2S} = A_{2S} e^{-E_{2S}/RT} \tag{E13-6.14}$$

Net Rates:

$$r_A = r_B = r_{1A} \tag{E13-6.17}$$

$$r_S = r_{2S} \tag{E13-6.18}$$

$$r_D = -\frac{1}{2} r_{1A} + -3 r_{2S} \text{ (gas generated)} \tag{E13-6.19}$$

(3) Stoichiometry – Liquid Phase

Case 3 – Manufacture of Fuel Additive

(4) Energy Balance:

Applying Equation (E13-18) to a batch system ($F_{i0} = 0$)

$$\frac{dT}{dt} = \frac{V_0\left[r_{1A}\Delta H_{Rx1A} + r_{2S}\Delta H_{Rx2S}\right] - UA(T - T_a)}{\sum N_j C_{P_j}} \qquad \text{(E13-6.24)}$$

Substituting for the rate laws and $\sum N_j C_{P_j} = 1.26\times 10^7 \text{ J/K}$

$$\frac{dT}{dt} = \frac{V_0\left[-k_{1A}C_A C_B \Delta H_{Rx1A} - k_{2S}C_S\Delta H_{Rx2S}\right] - UA(T - T_a)}{1.26\times 10^7 (J/K)} \qquad \text{(E13-6.25)}$$

$$\Delta H_{Rx1A} = -45{,}400 \text{ J/mol}$$

$$\Delta H_{Rx2S} = -3.2\times 10^5 \text{ J/mol}$$

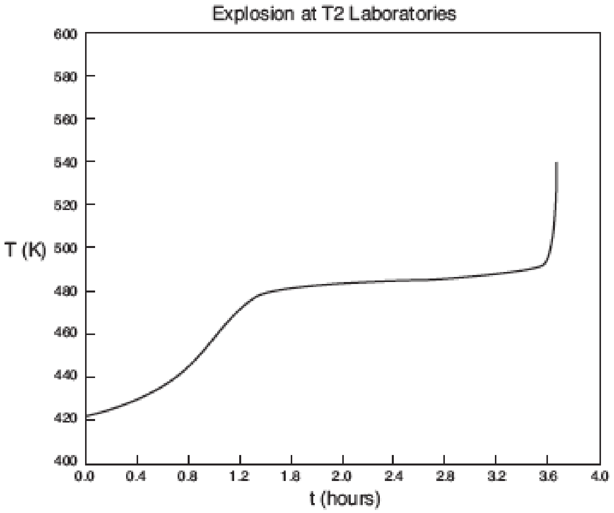


Figure E13-6.3(a) Temperature (K) versus time (h) trajectory.

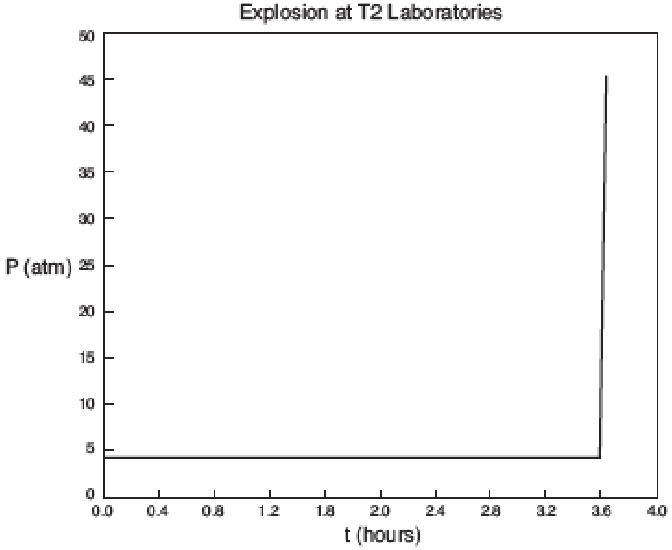


Figure E13-6.3(b) Pressure (atm) versus time (h) trajectory.

Summary

- In this lecture, we covered:

- - Case studies on industrial accidents and their causes.
- - Analysis of energy balance and heat effects in reactors.
- - Importance of safety mechanisms and preventive measures.
- - Lessons learned to improve reactor safety and reliability.

- These insights are crucial for designing safe and efficient chemical processes.