

# Lecture 25

**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 25

Class Lecture 21- 4/2/2013

## CSI

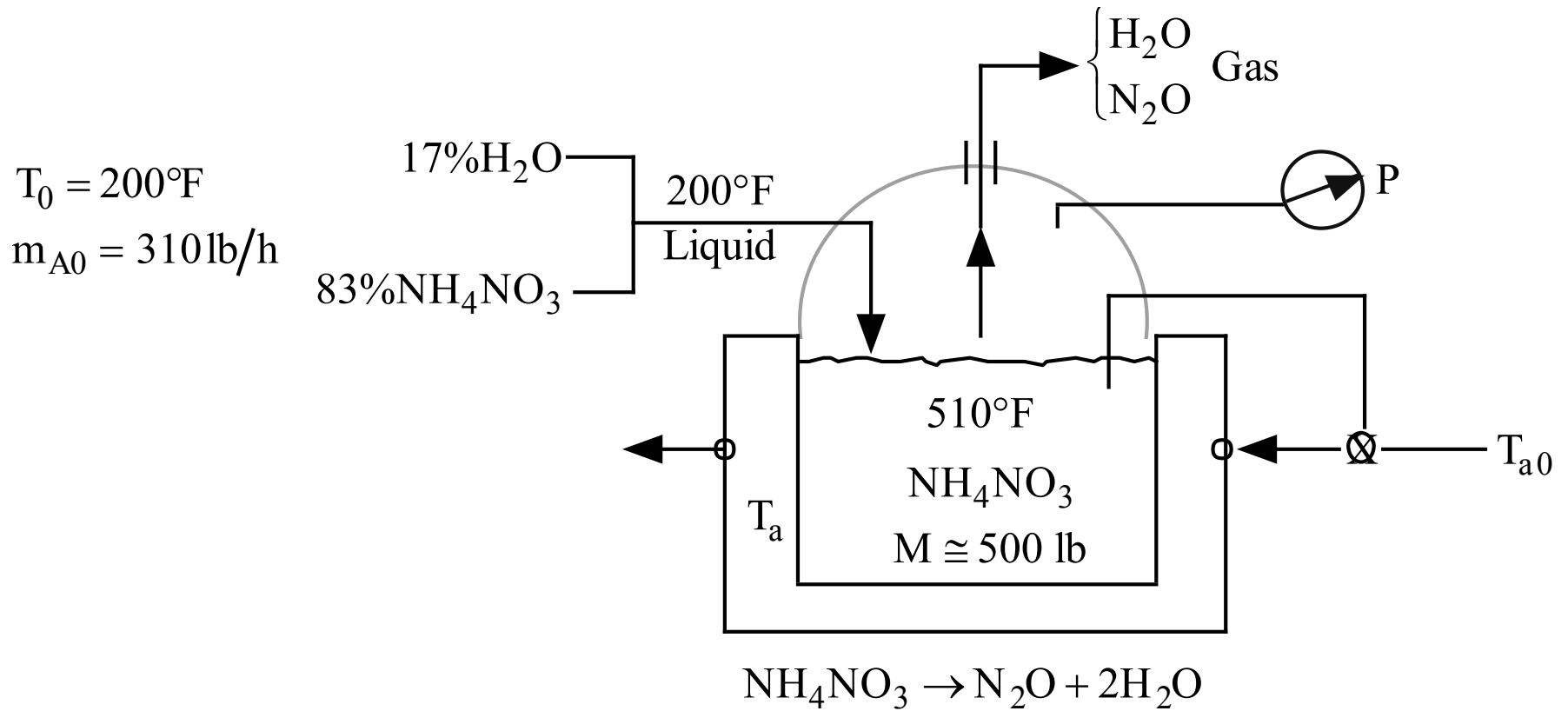
- Ammonium Nitrate Explosion
- Monsanto Explosion
- T2 Laboratories Explosion

# Case 1 – Ammonium Nitrate Explosion

Massive blast at Terra plant kills four.



# Example 1: Safety in Chemical Reactors



# 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.

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

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

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

# Unsteady State Energy Balance

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

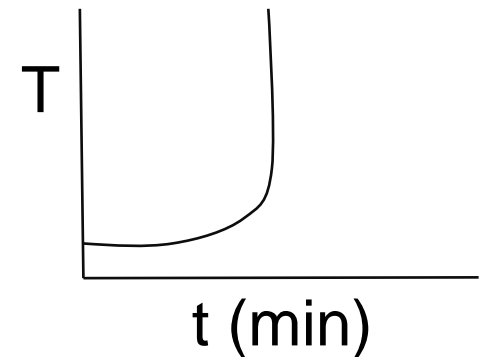
Adiabatic

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

$$F_{A0} = 0$$

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

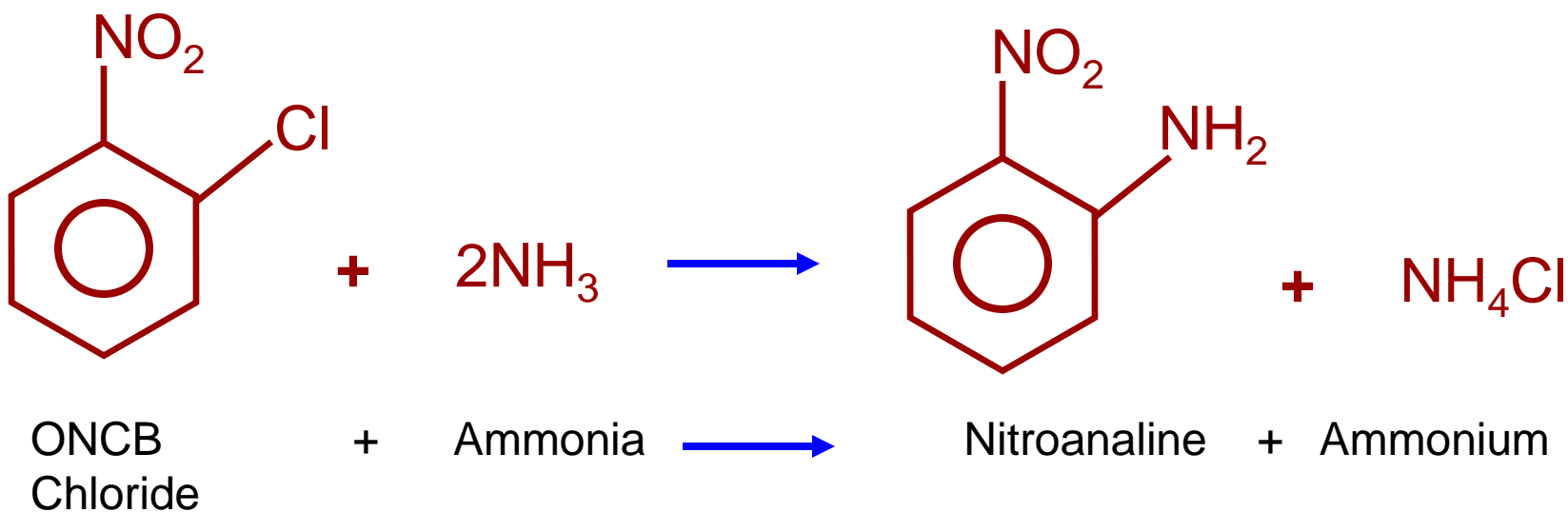
If the flow rate is shut off, the temperature will rise (possibly to point of explosion!)



# Case 2 – Monsanto Chemical Company

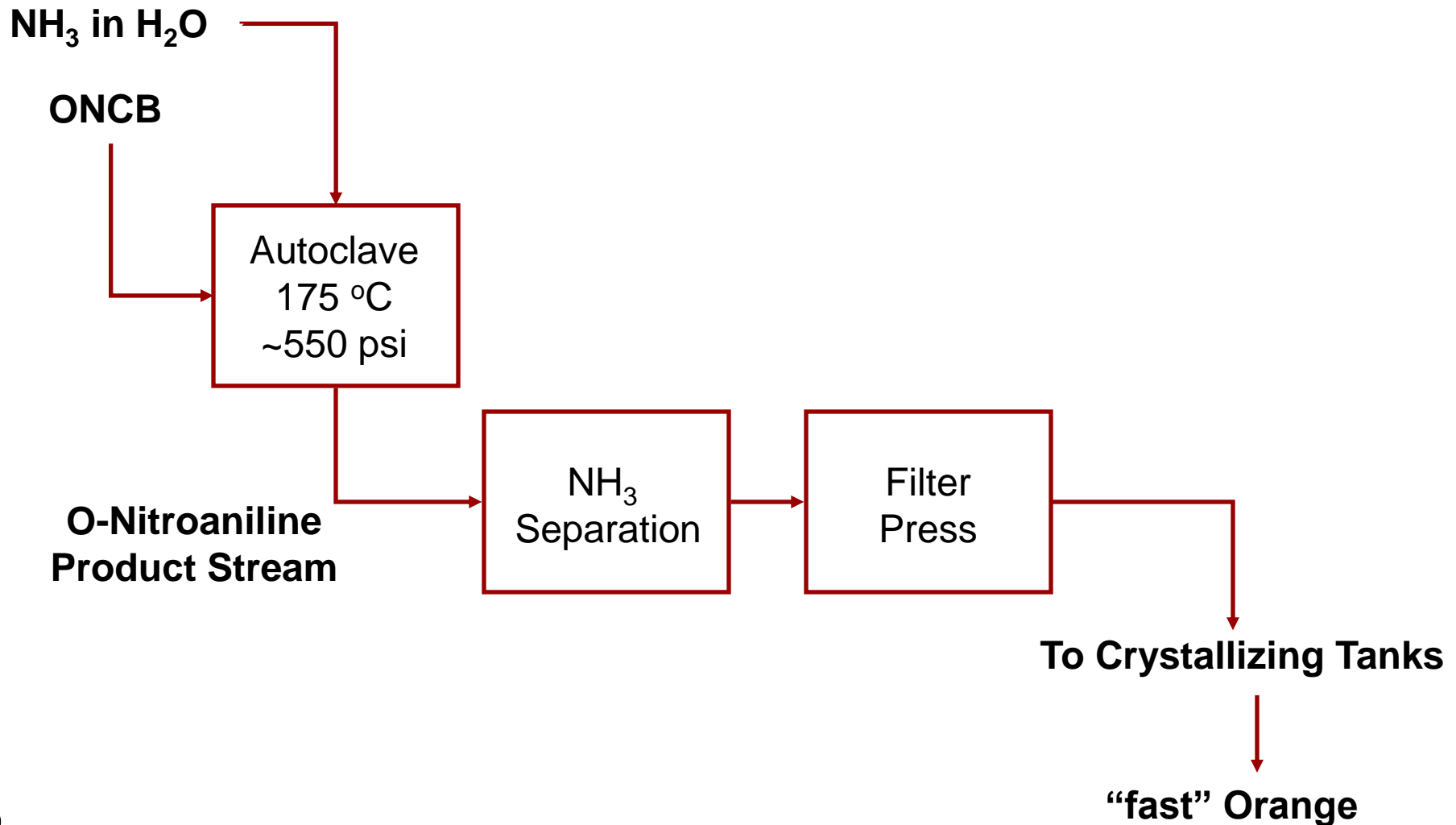
- Keeping MBAs away from Chemical Reactors
- The process worked for 19 years before “they” showed up!
- Why did they come?
- What did they want?

# Nitroaniline Synthesis Reaction

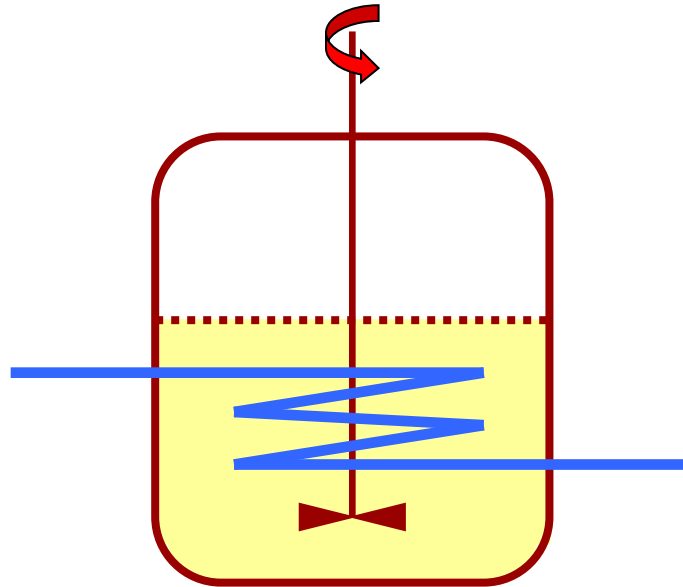




# Nitroaniline Synthesis Reaction



# Nitroanline Synthesis Reactor

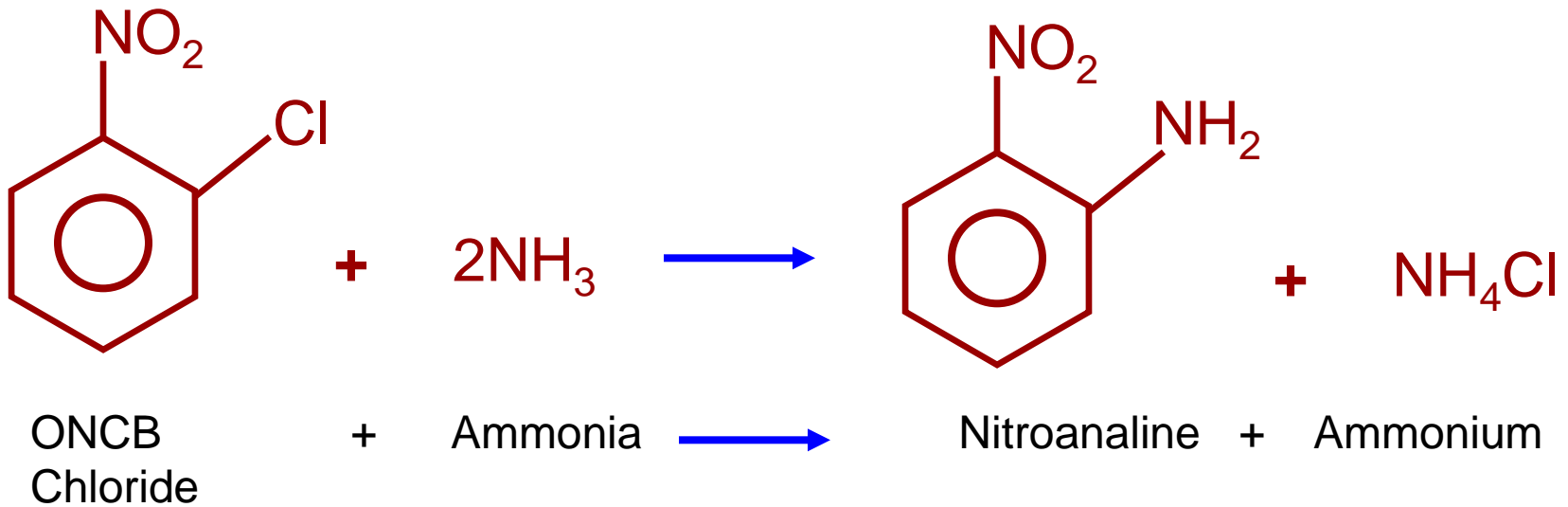


**Old**

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3 kmol ONCB  
43 kmol Ammonia  
100 kmol Water  
 $V = 3.25 \text{ m}^3$

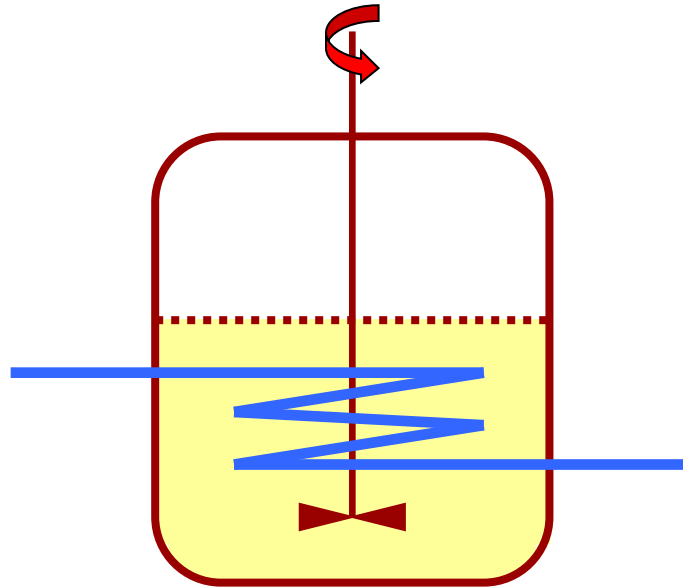
# Same Nitroaniline Synthesis Reaction



**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  
 $V = 5 \text{ m}^3$

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

For isothermal operation at  $Q_r = Q_g$ ,  $T = 448 \text{ K}$

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

$$Q_r = Q_g$$

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

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

# Isothermal Operation for 45 minutes

At the time the heat exchanger fails

$$X = 0.033, T = 448 \text{ K}$$

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

The maximum rate of removal at  $T = 448 \text{ K}$  is

$$Q_r = UA(T - T_a) = 35.85(448 - 298) = 5378 \text{ kcal / min}$$

$$Q_r > Q_g \quad \text{Everything is OK}$$



# Adiabatic Operation for 10 minutes

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

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

$$Q_g = 6591 \text{ kcal / min}$$

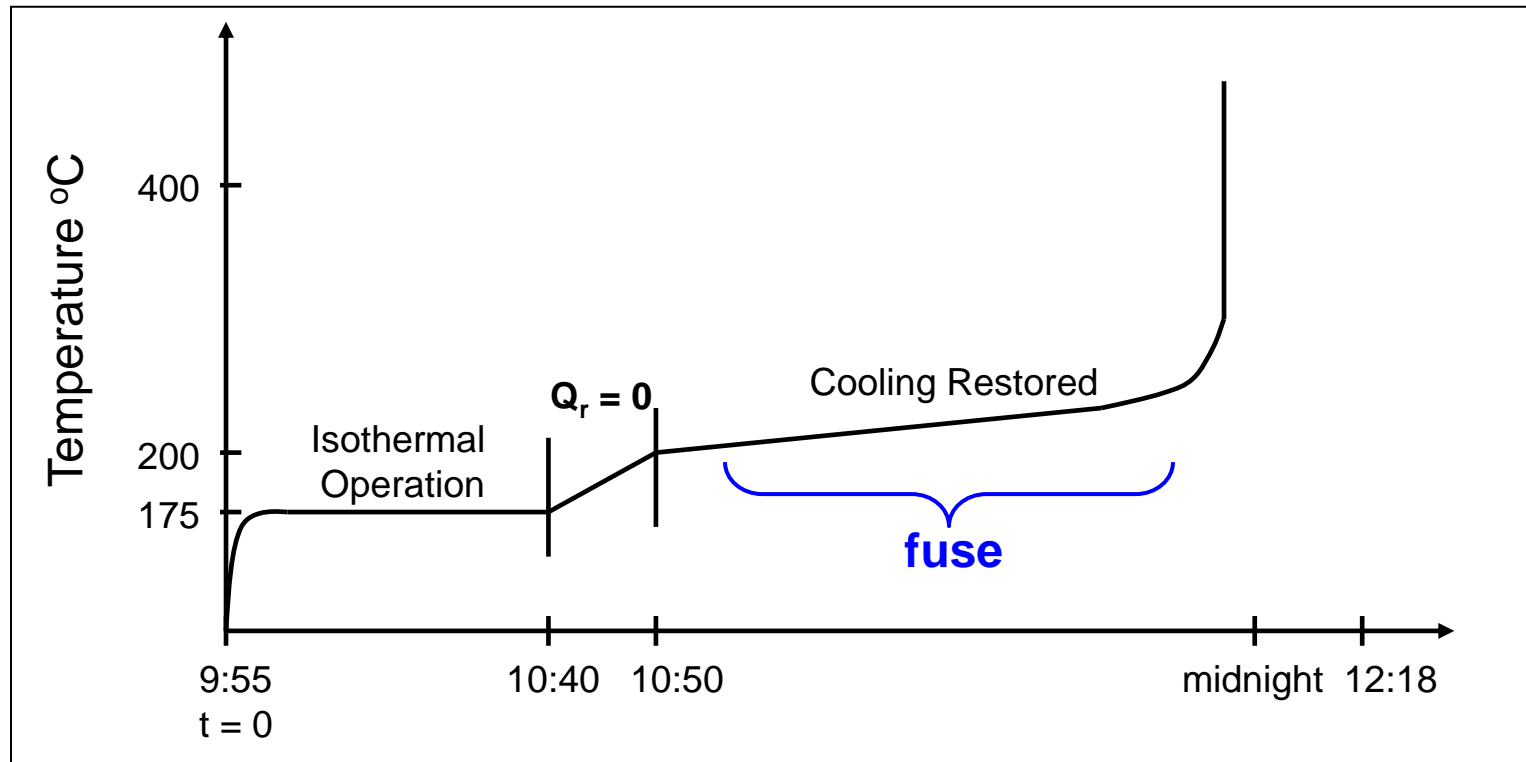
$$Q_r = 6093 \text{ kcal / min}$$

$$Q_g > Q_r$$

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

# Temperature-Time trajectory

$$\frac{dT}{dt} = \frac{Q_q - Q_r}{N C_p} = 0.2 \text{ } ^\circ\text{C} / \text{min}$$



# 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).

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

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

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

$$Q_r \gg \gg Q_g$$

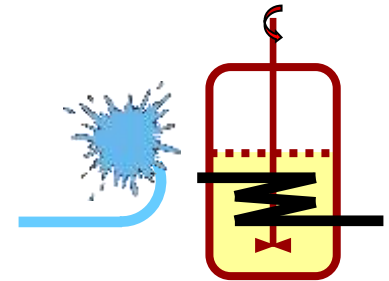
**No explosion**

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

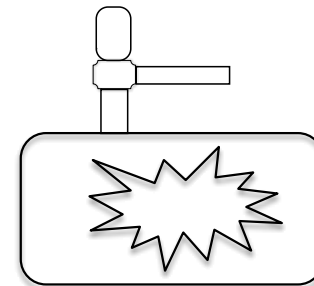
1. Tripled Production



2. Heat Exchange Failure



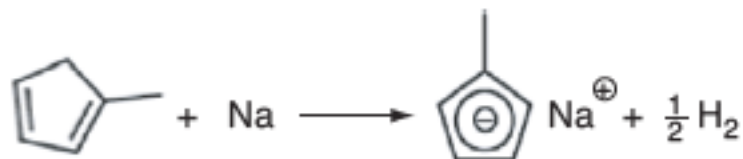
3. Relief Valve Failure



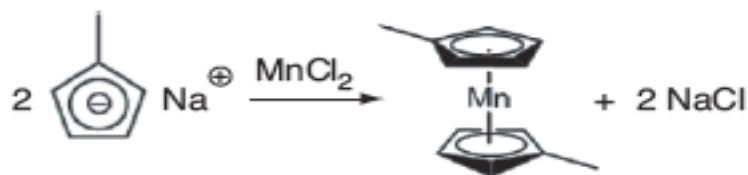
# Case 3 – Manufacture of Fuel Additive methylcyclopentadiene manganese tricarbonyl (MCMT)

## Production of methylcyclopentadienyl manganese tricarbonyl (MCMT).

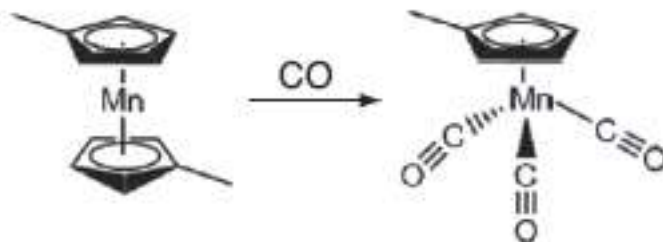
**Step 1a.** Reaction between methylcyclopentadiene (MCP) and sodium in a solvent of diethylene glycol dimethyl ether (diglyme,  $C_6H_{14}O_3$ ) to produce sodium methylcyclopentadiene and hydrogen gas:



**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:

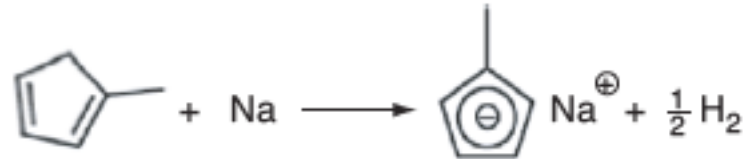


**Step 1c.** At the end of Step 1b, CO is added. The reaction between manganese dimethylcyclopentadiene and carbon monoxide produces the final product, methylcyclopentadienyl manganese tricarbonyl (MCMT), a fuel additive.



Only consider Step 1

### Desired Reaction



### Undesired Reaction of Dyglyme



### ***Simplified Model***

Let A = methycyclopentadiene, B = sodium, S = Solvent (diglyme), and D = H<sub>2</sub>.  
These reactions are:



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

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

# Case 3 – Manufacture of Fuel Additive

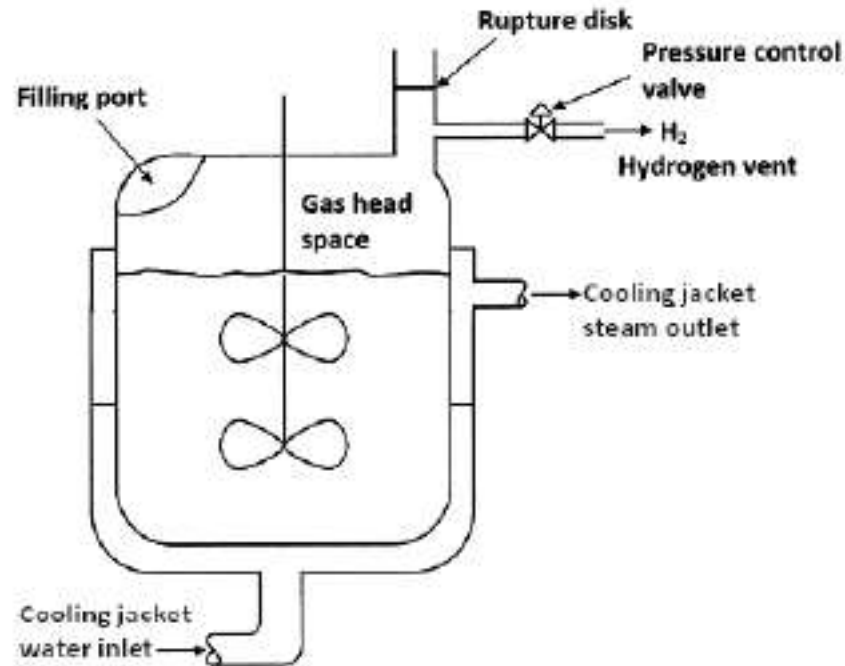


Figure E13-6.2 Reactor



# Case 3 – Manufacture of Fuel Additive

*Solution*

## (1) Reactor Mole Balances

Reactor (Assume Constant Volume Batch)

Liquid

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

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

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

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

# Case 3 – Manufacture of Fuel Additive

## (2) Rates

### Laws:

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

$$k_{1A} = A_{1A} e^{-E_{1A}/RT} \quad (\text{E13-6.12})$$

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

$$k_{2S} = A_{2S} e^{-E_{2S}/RT} \quad (\text{E13-6.14})$$

### Net Rates:

$$r_A = r_B = r_{1A} \quad (\text{E13-6.17})$$

$$r_S = r_{2S} \quad (\text{E13-6.18})$$

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

# Case 3 – Manufacture of Fuel Additive

## (4) Energy Balance:

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

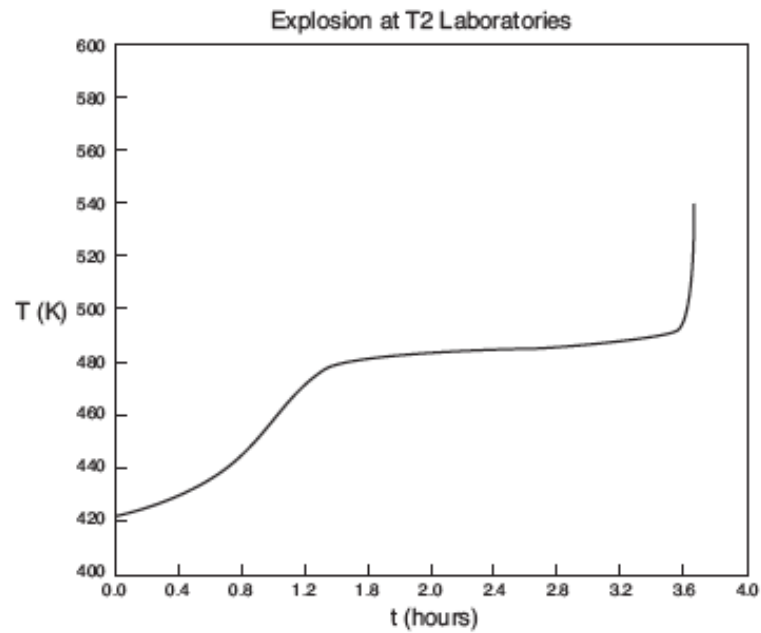
$$\frac{dT}{dt} = \frac{V_0[r_{1A}\Delta H_{Rx1A} + r_{2S}\Delta H_{Rx2S}] - UA(T - T_a)}{\sum N_j C_{P_j}} \quad (\text{E13-6.24})$$

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

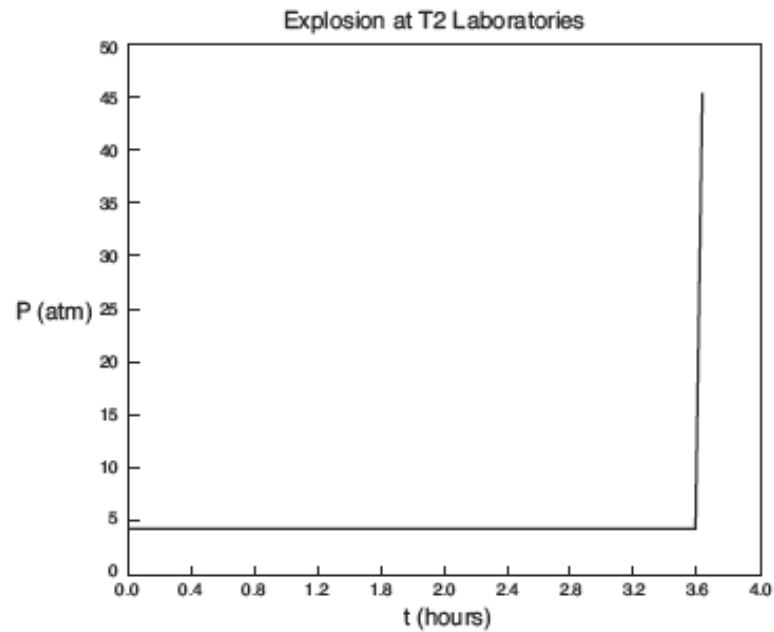
$$\frac{dT}{dt} = \frac{V_0[-k_{1A}C_A C_B \Delta H_{Rx1A} - k_{2S}C_S \Delta H_{Rx2S}] - UA(T - T_a)}{1.26 \times 10^7 (\text{J/K})} \quad (\text{E13-6.25})$$

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

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



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



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

# End of Web Lecture 25

## Class Lecture 2