

## PROFESSIONAL REFERENCE SHELF

## R8.3 Heat Capacities

## A Constant or Mean Heat Capacities

Heat capacities are typically expressed as a function of temperature by the quadratic

$$C_{P_i} = \alpha_i + \beta_i T + \gamma_i T^2 \quad (\text{R8.3-1})$$

We will now consider both the case of constant (or mean) heat capacities and variable heat capacities.

For the case of constant or mean heat capacities

$$\Delta H_{\text{Rx}}(T) = \Delta H_{\text{Rx}}^\circ(T_R) + \hat{\Delta C}_P(T - T_R) \quad (\text{R8.3-2})$$

The circumflex denotes that the heat capacities are evaluated at some mean temperature value between  $T_R$  and  $T$ .

$$T_R \xrightarrow{\hat{\Delta C}_P} T \quad \hat{\Delta C}_P = \frac{\int_{T_R}^T \Delta C_P dT}{T - T_R} \quad (\text{R8.3-3})$$

In a similar fashion, we can write the integral involving  $\Theta_i$  and  $C_{P_i}$  in Equation (R8.3-1) as

$$\sum \Theta_i \int_{T_{i0}}^T C_{P_i} dT = \sum \Theta_i \tilde{C}_{P_i}(T - T_{i0})$$

$\tilde{C}_{P_i}$  is the mean heat capacity of species  $i$  between  $T_{i0}$  and  $T$ :

$$T_{i0} \xrightarrow{\tilde{C}_{P_i}} T \quad \tilde{C}_{P_i} = \frac{\int_{T_{i0}}^T C_{P_i} dT}{T - T_{i0}} \quad (\text{R8.3-4})$$

Substituting the mean heat capacities into Equation (R8.3-1), the steady-state energy balance becomes

Energy balance in terms of mean or constant heat capacities

$$\dot{W}_s - F_{A0} \sum \Theta_i \tilde{C}_{P_i}(T - T_{i0}) - F_{A0} X [\Delta H_{\text{Rx}}^\circ(T_R) + \hat{\Delta C}_P(T - T_R)] = \quad (\text{8.3-5})$$

In almost all of the systems we will study, the reactants will be entering the system at the same temperature; therefore,  $T_{i0} = T_0$ .

### B Variable Heat Capacities

We next want to arrive at a form of the energy balance for the case where heat capacities are strong functions of temperature over a wide temperature range. Under these conditions, the mean values used in Equation (8-30) may not be adequate for the relationship between conversion and temperature. Combining Equation (8-23) with the quadratic form of the heat capacity, Equation (R8.3-1),

$$C_{P_i} = \alpha_i + \beta_i T + \gamma_i T^2 \quad (\text{R8.3-1})$$

we find that

$$\Delta H_{R_x}(T) = \Delta H_{R_x}^\circ(T_R) + \int_{T_R}^T (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2) dT$$

Integrating gives us

Heat capacity as a function of temperature

$$\Delta H_{R_x}(T) = \Delta H_{R_x}^\circ(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3) \quad (\text{R8.3-7})$$

where

$$\Delta\alpha = \frac{d}{a}\alpha_D + \frac{c}{a}\alpha_C - \frac{b}{a}\alpha_B - \alpha_A$$

$$\Delta\beta = \frac{d}{a}\beta_D + \frac{c}{a}\beta_C - \frac{b}{a}\beta_B - \beta_A$$

$$\Delta\gamma = \frac{d}{a}\gamma_D + \frac{c}{a}\gamma_C - \frac{b}{a}\gamma_B - \gamma_A$$

In a similar fashion, we can evaluate the heat capacity term in Equation (R8.3-1):

$$\begin{aligned} \sum_{i=1}^n \Theta_i \int_{T_0}^T C_{P_i} dT &= \int_{T_0}^T (\sum \alpha_i \Theta_i + \sum \beta_i \Theta_i T + \sum \gamma_i \Theta_i T^2) dT \\ &= \sum \alpha_i \Theta_i (T - T_0) + \frac{\sum \beta_i \Theta_i}{2} (T^2 - T_0^2) + \frac{\sum \gamma_i \Theta_i}{3} (T^3 - T_0^3) \quad (\text{R8.3-8}) \end{aligned}$$

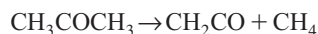
Substituting Equations (R8.3-7) and (R8.3-8) into Equation (R8.3-5), the form of the energy balance is

Energy balance for the case of highly temperature-sensitive heat capacities

$$\begin{aligned} -\dot{W}_s - F_{A0} \left[ \sum \alpha_i \Theta_i (T - T_0) + \frac{\sum \beta_i \Theta_i}{2} (T^2 - T_0^2) + \frac{\sum \gamma_i \Theta_i}{3} (T^3 - T_0^3) \right] \\ F_{A0} X \left[ \Delta H_{R_x}^\circ(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2} (T^2 - T_R^2) + \frac{\Delta\gamma}{3} (T^3 - T_R^3) \right] = (\text{R8.3-9}) \end{aligned}$$

**Example R8.3–1.1 Production of Acetic Anhydride**

Jeffreys,\* in a treatment of the design of an acetic anhydride manufacturing facility, states that one of the key steps is the vapor-phase cracking of acetone to ketene and methane:



He states further that this reaction is first-order with respect to acetone and that the specific reaction rate can be expressed by

$$\ln k = 34.34 - \frac{34,222}{T} \quad (\text{ER8.3-1.1})$$

where  $k$  is in reciprocal seconds and  $T$  is in kelvin. In this design it is desired to feed 8000 kg of acetone per hour to a tubular reactor. The reactor consists of a bank of 1000 1-inch schedule 40 tubes. We will consider two cases:

1. The reactor is operated *adiabatically*.
2. The reactor is surrounded by a *heat exchanger* where the heat-transfer coefficient is  $110 \text{ J/m}^2 \cdot \text{s} \cdot \text{K}$ , and the ambient temperature is 1150 K.

The inlet temperature and pressure are the same for both cases at 1035 K and 162 kPa (1.6 atm), respectively. Plot the conversion and temperature along the length of the reactor.

*Solution*

Let  $A = \text{CH}_3\text{COCH}_3$ ,  $B = \text{CH}_2\text{CO}$ , and  $C = \text{CH}_4$ . Rewriting the reaction symbolically gives us

1. **Mole balance:**



2. **Rate law:**

$$\frac{dX}{dV} = -r_A / F_{A0} \quad (\text{ER8.3-1.2})$$

$$-r_A = kC_A \quad (\text{ER8.3-1.3})$$

3. **Stoichiometry** (gas-phase reaction with no pressure drop):

$$v_A = \frac{C_{A0}(1-X)T_0}{(1+\epsilon X)T} \quad (\text{ER8.3-1.4})$$

$$\epsilon = y_{A0}\delta = 1(1+1-1) = 1$$

4. **Combining yields**

$$-r_A = \frac{kC_{A0}(1-X)T_0}{1+X} \frac{1}{T} \quad (\text{ER8.3-1.5})$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{k}{v_0} \left( \frac{1-X}{1+X} \right) \frac{T_0}{T} \quad (\text{ER8.3-1.6})$$

\* G. V. Jeffreys, *A Problem in Chemical Engineering Design: The Manufacture of Acetic Anhydride*, 2nd ed. (London: Institution of Chemical Engineers, 1964).

To solve the differential equation (ER8.3-1.6), it is first necessary to use the energy balance to determine  $T$  as a function of  $X$ .

### 5. Energy balance:

#### CASE I. ADIABATIC OPERATION

For no work done on the system,  $W_s = 0$ , and adiabatic operation,  $Q = 0$  (i.e.,  $U \equiv 0$ ), Equation (8-56) becomes

$$\frac{dT}{dV} = \frac{(-r_A) \left\{ - \left[ \Delta H_{R_x}^\circ(T_R) + \int_{T_R}^T (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2) dT \right] \right\}}{F_{A0} (\sum \Theta_i C_{P_i} + X \Delta C_P)} \quad (\text{ER8.3-1.7})$$

where in general

$$\Delta\alpha = \frac{d}{a} \alpha_D + \frac{c}{a} \alpha_C - \frac{b}{a} \alpha_B - \alpha_A$$

For acetone decomposition

$$\Delta\alpha = \alpha_B + \alpha_C - \alpha_A$$

Equivalent expressions exist for  $\Delta\beta$  and  $\Delta\gamma$ .

Because only A enters,

$$\sum \Theta_i C_{P_i} = C_{P_A}$$

and Equation (ER8.3-1.7) becomes

$$\frac{dT}{dV} = \frac{(-r_A) \left\{ - \left[ \Delta H_{R_x}^\circ(T_R) + \int_{T_R}^T (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2) dT \right] \right\}}{F_{A0} (C_{P_A} + X \Delta C_P)}$$

Integrating gives

$$\frac{dT}{dV} = \frac{(-r_A) \left\{ - \left[ \Delta H_{R_x}^\circ + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2} (T^2 - T_R^2) + \frac{\Delta\gamma}{3} (T^3 - T_R^3) \right] \right\}}{F_{A0} (\alpha_A + \beta_A T + \gamma_A T^2 + X \Delta C_P)} \quad (\text{ER8.3-1.8})$$

#### 6. Calculation of mole balance parameters:

$$F_{A0} = \frac{8000 \text{ kg/h}}{58 \text{ g/mol}} = 137.9 \text{ kmol/h} = 38.3 \text{ mol/s}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{162 \text{ kPa}}{8.31 \frac{\text{kPa} \cdot \text{m}^3}{\text{kmol} \cdot \text{K}} (1035 \text{ K})} = 0.0188 \frac{\text{kmol}}{\text{m}^3} = 18.8 \text{ mol/m}^3$$

$$v_0 = \frac{F_{A0}}{C_{A0}} = 2.037 \text{ m}^3/\text{s}$$

Adiabatic PFR  
with variable heat  
capacities

## 7. Calculation of energy balance parameters:

a.  $\Delta H_{R_x}^\circ(T_R)$ : At 298 K, the standard heats of formation are

$$H_{R_x}^\circ(T_R)_{\text{acetone}} = -216.67 \text{ kJ/mol}$$

$$H_{R_x}^\circ(T_R)_{\text{ketene}} = -61.09 \text{ kJ/mol}$$

$$H_{R_x}^\circ(T_R)_{\text{methane}} = -74.81 \text{ kJ/mol}$$

$$\begin{aligned}\Delta H_{R_x}^\circ(T_R) &= (-61.09) + (-74.81) - (-216.67) \\ &= 80.77 \text{ kJ/mol}\end{aligned}$$

b.  $\Delta C_p$ : The heat capacities are:

$$\text{CH}_3\text{COCH}_3: C_{PA} = 26.63 + 0.183T - 45.86 \times 10^{-6} T^2 \text{ J/mol} \cdot \text{K}$$

$$\text{CH}_2\text{CO}: C_{PB} = 20.04 + 0.0945T - 30.95 \times 10^{-6} T^2 \text{ J/mol} \cdot \text{K}$$

$$\text{CH}_4: C_{PC} = 13.39 + 0.077T - 18.71 \times 10^{-6} T^2 \text{ J/mol} \cdot \text{K}$$

$$\begin{aligned}\Delta\alpha &= \alpha_C + \alpha_B - \alpha_A = 13.39 + 20.04 - 26.63 \\ &= 6.8 \text{ J/mol} \cdot \text{K}\end{aligned}$$

$$\begin{aligned}\Delta\beta &= \beta_C + \beta_B - \beta_A = 0.077 + 0.0945 - 0.183 \\ &= -0.0115 \text{ J/mol} \cdot \text{K}^2\end{aligned}$$

$$\begin{aligned}\Delta\gamma &= \gamma_C + \gamma_B - \gamma_A = (-18.71 \times 10^{-6}) + (-30.95 \times 10^{-6}) - (-45.86 \times 10^{-6}) \\ &= -3.8 \times 10^{-6} \text{ J/mol} \cdot \text{K}^3\end{aligned}$$

$$\frac{\Delta\beta}{2} = -5.75 \times 10^{-3} \quad \frac{\Delta\gamma}{3} = -1.27 \times 10^{-6}$$

See Table ER8.3-1.1 for a summary of the calculations and Table ER8.3-1.2 and Figure ER8.3-1.1 for the POLYMATH program and its graphical output.

Note that for this adiabatic endothermic reaction, the reaction virtually *dies out* after 2.5 m<sup>3</sup>, owing to the large drop in temperature, and very little conversion is achieved beyond this point. One way to increase the conversion would be to add a diluent such as N<sub>2</sub>, which could supply the sensible heat for this endothermic reaction. However, if too much diluent is added, the concentration and rate will be quite low. On the other hand, if too little diluent is added, the temperature will drop and virtually extinguish the reaction. How much diluent to add is left as an exercise.

A bank of 1000 1-in. schedule 40 tubes 2.28 m in length corresponds to 1.27 m<sup>3</sup> and gives 20% conversion. Ketene is unstable and tends to explode, which is a good reason to keep the conversion low. However, the pipe material and schedule size should be checked to learn if they are suitable for these temperatures and pressures.

Death of a reaction

Adiabatic PFR  
with variable heat  
capacities

TABLE ER8.3-1.1. SUMMARY

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{ER8.3-1.2})$$

$$-r_A = -\frac{kC_{A0}(1-X)}{(1+X)} \frac{T_0}{T} \quad (\text{ER8.3-1.5})$$

$$\frac{dT}{dV} = \frac{(-r_A) \left\{ - \left[ \Delta H_{Rx}^{\circ}(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3) \right] \right\}}{F_{A0}(\alpha_A + \beta_A T + \gamma_A T^2 + X \Delta C_p)} \quad (\text{E8.3-1.8})$$

$$\Delta C_p = 6.8 - 11.5 \times 10^{-3} T - 3.81 \times 10^{-6} T^2$$

$$\Delta H_{Rx}^{\circ}(T_R) = 80,770$$

$$\alpha_A = 26.63$$

$$\beta_A = 0.183$$

$$\gamma_A = -45.86 \times 10^{-6}$$

$$C_{A0} = 18.8$$

$$F_{A0} = 38.3$$

$$k = 8.2 \times 10^{14} \exp\left(\frac{-34,222}{T}\right) \quad (\text{ER8.3-1.12})$$

$$\Delta\alpha = 6.8$$

$$\frac{\Delta\beta}{2} = -5.75 \times 10^{-3}$$

$$\frac{\Delta\gamma}{3} = -1.27 \times 10^{-6}$$

TABLE ER8.3-1.2. POLYMATH PROGRAM

Equations:	Initial Values:
d(T)/d(U)=-ra*(-deltaH)/(Fao*(Cpa+X*delCp))	1035
d(X)/d(U)=-ra/Fao	0
k=8.2*10**14*exp(-34222/T)	
Fao=38.3	
Cpa=26.63+1.83*T-45.86*10**(-6)*T**2	
delCp=6.8-11.5*10**(-3)*T-3.81*10**(-6)*T**2	
Cao=18.8	
To=1035	
Tr=298	
deltaH=80770+6.8*(T-Tr)-5.75*10**(-3)*(T**2-Tr**2)-1.27*10**(-6)*(T**3-Tr**3)	
ra=-k*Cao*(1-X)/(1+X)*To/T	
Uo = 0, Uf = 5	

Adiabatic  
endothermic  
reaction in a PFR

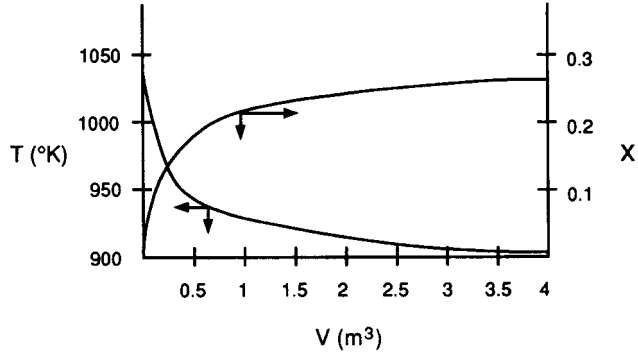


Figure ER8.3-1.1 Profits.

**CASE II. OPERATION OF A PFR WITH HEAT EXCHANGE**

See Figure ER8.3-1.2.

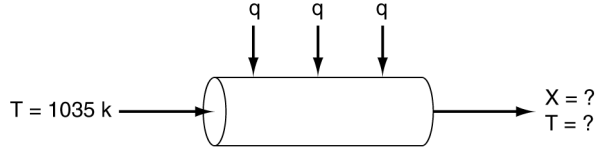


Figure ER8.3-1.2 PFR with heat exchange.

**1. The mole balance:**

$$(1) \quad \frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (ER8.3-1.2)$$

Using (2) the **rate law** (ER8.3-1.3) and (3) **stoichiometry** (ER8.3-1.4) for the adiabatic case discussed previously, we (4) **combine** to obtain the reaction rate as

$$(4) \quad -r_A = kC_{A0} \left( \frac{1-X}{1+X} \right) \frac{T_0}{T} \quad (ER8.3-1.3)$$

**5. Energy balance.**

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)[- \Delta H_{Rx}(T)]}{F_{A0}(\sum \Theta_i C_{P_i} + X \Delta C_P)} \quad (ER8.3-1.9)$$

For the acetone reaction system,

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (r_A)[\Delta H_{Rx}(T)]}{F_{A0}(C_{P_A} + X \Delta C_P)} \quad (ER8.3-1.10)$$

PFR with heat exchange

**6. Parameter evaluation:**

a. *Mole balance.* On a per tube basis,  $v_0 = 0.002 \text{ m}^3/\text{s}$ . The concentration of acetone is  $18.8 \text{ mol}/\text{m}^3$ , so the entering molar flow rate is

$$F_{A0} = C_{A0} v_0 = \left( 18.8 \frac{\text{mol}}{\text{m}^3} \right) \left( 2 \times 10^{-3} \frac{\text{m}^3}{\text{s}} \right) = 0.0376 \frac{\text{mol}}{\text{s}}$$

The value of  $k$  at 1035 K is  $3.58 \text{ s}^{-1}$ ; consequently, we have

$$k(T) = 3.58 \exp \left[ 34,222 \left( \frac{1}{1035} - \frac{1}{T} \right) \right] \quad (\text{ER8.3-1.11})$$

b. *Energy balance.* From the foregoing adiabatic case, we already have  $\Delta C_p$ ,  $C_{pA}$ ,  $\alpha_A$ ,  $\beta_A$ ,  $\gamma_A$ ,  $\Delta\alpha$ ,  $\Delta\beta$ , and  $\Delta\gamma$ . The heat-transfer area per unit volume of pipe is

$$a = \frac{\pi DL}{(\pi D^2/4)L} = \frac{4}{D} = \frac{4}{0.0266 \text{ m}} = 150 \text{ m}^{-1}$$

$$U = 110 \text{ J}/\text{m}^2 \cdot \text{s} \cdot \text{K}$$

Combining the overall heat-transfer coefficient with the area yields

$$Ua = 16,500 \text{ J}/\text{m}^3 \cdot \text{s} \cdot \text{K}$$

We now use Equations (ER8.3-1.1) through (ER8.3-1.6), and Equations (ER8.3-1.10) and (ER8.3-1.11) along with the POLYMATH program (Table ER8.3-1.3), to determine the conversion and temperature profiles shown in Figure ER8.3-1.3.

The corresponding variables in the POLYMATH program are

$$t1 = T, \quad dh = \Delta H_{R_x}(T), \quad dcp = \Delta C_p, \quad cpa = C_{pA}, \quad ua = Ua$$

TABLE ER8.3-1.3. POLYMATH PROGRAM FOR PFR WITH HEAT EXCHANGE

Equations:	Initial Values:
$d(t)/d(v) = (ua \times (ta - t) + ra \times dh) / (fa0 \times (cpa + x \times dcp))$	1035
$d(x)/d(v) = -ra / fa0$	0
fa0=0.0376	
ua=16500	
ta=1150	
cpa=26.6+.183*t-.0000459*t*t	
dcp=6.8-.0115*t-.00000381*t*t	
ca0=18.8	
t0=1035	
term=-.00000127*(t**3-298**3)	
dh=80770+6.8*(t-298)-.00575*(t**2-298**2)+term	
ra=-ca0*3.58*exp(34222*(1/t0-1/t))*(1-x)*(t0/t)/(1+x)	
$v_0 = 0, \quad v_f = 0.001$	

One notes the reactor temperature goes through a minimum along the length of the reactor. At the front of the reactor, the reaction takes place very rapidly, drawing energy from the sensible heat of the gas causing the gas temperature to drop because the heat exchanger cannot supply energy at the equal or greater rate. This drop in temperature, coupled with the consumption of reactants, slows the reaction



Living Example Problem



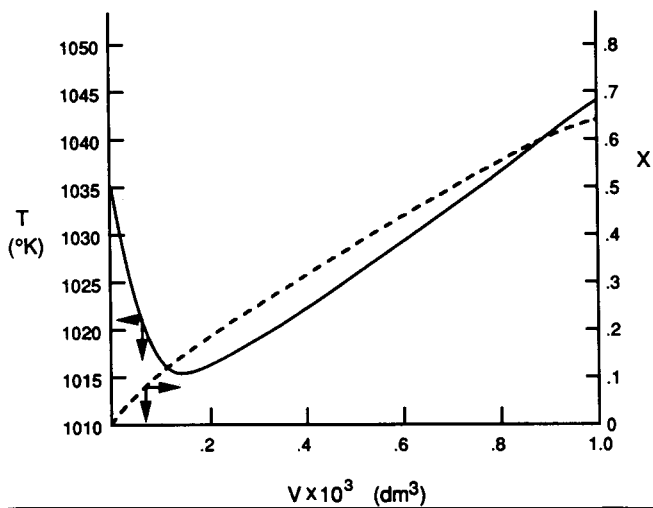


Figure ER8.3-1.3 Temperature and conversion profiles in PFR.

rate as we move down the reactor. Because of this slower reaction rate, the heat exchanger supplies energy at a rate greater than reaction draws energy from the gases and as a result the temperature increases.