Wow! Five (5) multiple steady states!

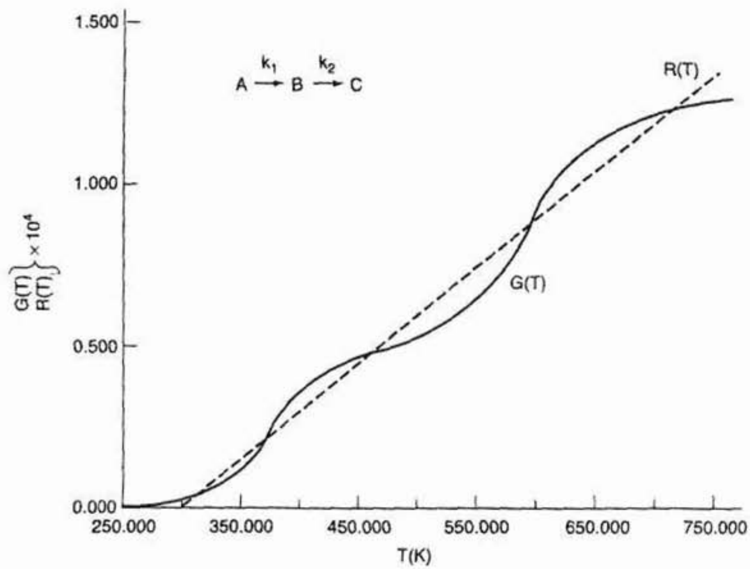


Figure E8-11.1 Heat-removed and heat-generated curves.

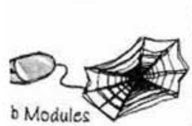
We note there are five steady states (SS) whose values are given in Table E8-11.2. What do you think of the value of tau? Is it a realistic number?

TABLE E8-11.2. EFFLUENT CONCENTRATIONS AND TEMPERATURES

SS	T	C_A	C_B	C_C
1	310	0.285	0.015	0
2	363	0.189	0.111	0.0
3	449	0.033	0.265	0.002
4	558	0.004	0.163	0.132
5	677	0.001	0.005	0.294

8.9 Radial and Axial Variations in a Tubular Reactor

FEMLAB application



In the previous sections we have assumed that there were no radial variations in velocity, concentration, temperature or reaction rate in the tubular and packed bed reactors. As a result the axial profiles could be determined using an ordinary differential equation (ODE) solver. In this section we will consider the case where we have both axial and radial variations in the system variables in which case will require a partial differential (PDE) solver. A PDE solver such as FEMLAB, will allow us to solve tubular reactor problems for both the axial and radial profiles, as shown on the web module.

We are going to carry out differential mole and energy balances on the differential cylindrical annulus shown in Figure 8-26.

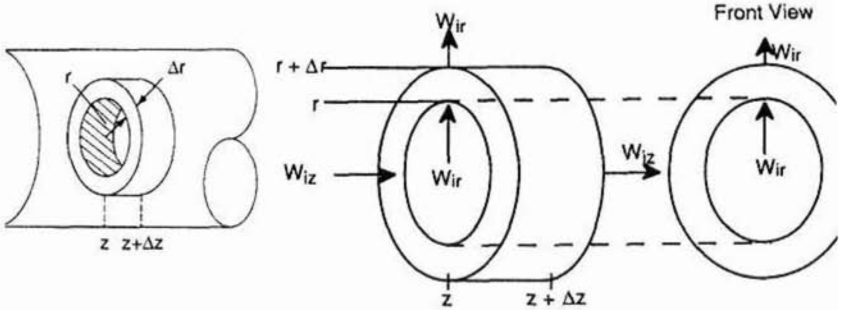


Figure 8-26 Cylindrical shell of thickness Δr, length Δz, and volume $2\pi r \Delta r \Delta z$.

Molar Flux

In order to derive the governing equations we need to define a couple of ter The first is the molar flux of species i, W_i (mol/m^2 • s). The molar flux has t components, the radial component W_{ir}, and the axial component, W_{iz}.] molar flow rates are just the product of the molar fluxes and the cross-sectio areas normal to their direction of flow A_{cz}. For example, for species i flow in the axial (i.e., z) direction

$$F_{iz} = W_{iz} A_{cz}$$

where W_{iz} is the molar flux in the z direction (mol/m^2/s), and A_{cz} (m^2) is the cross-sectional area of the tubular reactor.

In Chapter 11 we discuss the molar fluxes in some detail, but for now us just say they consist of a diffusional component, $-D_e(\partial C_i/\partial z)$, and a co vective flow component, $U_z C_i$

$$W_{iz} = -D_e \frac{\partial C_i}{\partial z} + U_z C_i \qquad \text{(8-}$$

where D_e is the effective diffusivity (or dispersion coefficient) (m^2/s), and is the axial molar average velocity (m/s). Similarly, the flux in the radial dir tion is

Radial Direction

$$W_{ir} = -D_e \frac{\partial C_i}{\partial r} + U_r C_i \qquad \text{(8-}$$

where U_r (m/s) is the average velocity in the radial direction. For now we w neglect the velocity in the radial direction, i.e., $U_r = 0$. A mole balance or cylindrical system volume of length Δz and thickness Δr as shown in Figu 8-26 gives

Mole Balances on Species A

$$\begin{pmatrix}\text{Moles of A}\\ \text{in at } r\end{pmatrix} = W_{Ar}\bullet\begin{pmatrix}\text{Cross-sectional area}\\ \text{normal to radial flux}\end{pmatrix} = W_{Ar}\bullet 2\pi r\Delta z$$

$$\begin{pmatrix}\text{Moles of A}\\ \text{in at } z\end{pmatrix} = W_{Az}\bullet\begin{pmatrix}\text{Cross-sectional area}\\ \text{normal to axial flux}\end{pmatrix} = W_{Az}\bullet 2\pi r\Delta r$$

$$\begin{pmatrix}\text{Moles of A}\\ \text{in at } r\end{pmatrix} - \begin{pmatrix}\text{Moles of A}\\ \text{out at } (r+\Delta r)\end{pmatrix} + \begin{pmatrix}\text{Moles of A}\\ \text{in at } z\end{pmatrix} - \begin{pmatrix}\text{Moles of A}\\ \text{out at } (z+\Delta z)\end{pmatrix}$$

$$+\begin{pmatrix}\text{Moles of A}\\ \text{formed}\end{pmatrix} = \begin{pmatrix}\text{Moles of A}\\ \text{Accumulated}\end{pmatrix}$$

$$W_{Ar}2\pi r\Delta z|_r - W_{Ar}2\pi r\Delta z|_{r+\Delta r} + W_{Az}2\pi r\Delta r|_z - W_{Az}2\pi r\Delta r|_{z+\Delta z}$$
$$+ r_A 2\pi r\Delta r\Delta z = \frac{\partial C_A(2\pi r\Delta r\Delta z)}{\partial t}$$

Dividing by $2\pi r\Delta r\Delta z$ and taking the limit as Δr and $\Delta z \to 0$

$$-\frac{1}{r}\frac{\partial(rW_{Ar})}{\partial r} - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t}$$

Similarly, for any species i and steady-state conditions,

$$\boxed{-\frac{1}{r}\frac{\partial(rW_{ir})}{\partial r} - \frac{\partial W_{iz}}{\partial z} + r_i = 0} \tag{8-85}$$

Using Equation (8-83) and (8-84) to substitute for W_{iz} and W_{ir} in Equation (8-85) and then setting the radial velocity to zero, $U_r = 0$, we obtain

$$-\frac{1}{r}\frac{\partial}{\partial r}\left[\left(-D_e\frac{\partial C_i}{\partial r}r\right)\right] - \frac{\partial}{\partial z}\left[-D_e\frac{\partial C_i}{\partial z} + U_z C_i\right] + r_i = 0$$

This equation will also be discussed further in Chapter 14.

For steady-state conditions and assuming U_z does not vary in the axial direction,

$$\boxed{D_e\frac{\partial^2 C_i}{\partial r^2} + \frac{D_e}{r}\frac{\partial C_i}{\partial r} + D_e\frac{\partial^2 C_i}{\partial z^2} - U_z\frac{\partial C_i}{\partial z} + r_i = 0} \tag{8-86}$$

Energy Flux

When we applied the first law of thermodynamics to a reactor to relate either temperature and conversion or molar flow rates and concentration, we arrived at Equation (8-9). Neglecting the work term we have for steady-state conditions

$$\overbrace{\dot{Q}}^{\text{Conduction}} + \overbrace{\sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1} F_iH_i}^{\text{Convection}} = 0 \tag{8-87}$$

In terms of the molar fluxes and the cross-sectional area and ($\mathbf{q} = \dot{Q}/A_c$)

$$A_c[\mathbf{q} + (\Sigma \mathbf{W}_{i0}H_{i0} - \Sigma \mathbf{W}_iH_i)] = 0 \tag{8-88}$$

The $\mathbf{q}$ term is the heat added to the system and almost always includes a conduction component of some form. We now define an **energy flux vector**, **e**, (J/m^2 · s), to include both the conduction and convection of energy.

$\mathbf{e}$ = energy flux J/s·m^2

$$\mathbf{e} = \text{Conduction} + \text{Convection}$$

$$\boxed{\mathbf{e} = \mathbf{q} + \Sigma \mathbf{W}_iH_i} \tag{8-89}$$

where the conduction term $\mathbf{q}$ (kJ/m^2 · s) is given by Fourier's law. For axial and radial conduction Fourier's laws are

$$q_z = -k_e\frac{\partial T}{\partial z} \qquad \text{and} \qquad q_r = -k_e\frac{\partial T}{\partial r}$$

where k_e is the thermal conductivity (J/m·s·K). The energy transfer (flow) is the vector flux times the cross-sectional area, A_c, normal to the energy flux

$$\text{Energy flow} = \mathbf{e} \cdot A_c$$

Energy Balance

Using the energy flux, e, to carry out an energy balance on our annulus (Figure 8-26) with system volume $2\pi r\Delta r\Delta z$, we have

$$(\text{Energy flow in at } r) = e_r A_{cr} = e_r \cdot 2\pi r\Delta z$$

$$(\text{Energy flow in at } z) = e_z A_{cz} = e_z \cdot 2\pi r\Delta r$$

$$\begin{pmatrix}\text{Energy Flow}\\ \text{in at } r\end{pmatrix} - \begin{pmatrix}\text{Energy Flow}\\ \text{out at } r+\Delta r\end{pmatrix} + \begin{pmatrix}\text{Energy Flow}\\ \text{in at } z\end{pmatrix} - \begin{pmatrix}\text{Energy Flow}\\ \text{out at } z+\Delta z\end{pmatrix} = \begin{pmatrix}\text{Accumulation}\\ \text{of Energy in}\\ \text{Volume } (2\pi r\Delta r\Delta z)\end{pmatrix}$$

$$(e_r 2\pi r\Delta z)|_r - (e_r 2\pi r\Delta z)|_{r-\Delta r} + e_z 2\pi r\Delta r|_z - e_z 2\pi r\Delta r|_{z+\Delta z} = 0 \tag{8-90}$$

Dividing by $2\pi r\Delta r\Delta z$ and taking the limit as Δr and $\Delta z \to 0$,

$$\boxed{-\frac{1}{r}\frac{\partial(re_r)}{\partial r} - \frac{\partial e_z}{\partial z} = 0} \tag{8-91}$$

The radial and axial energy fluxes are

$$e_r = q_r + \Sigma W_{ir} H_i$$

$$e_z = q_z + \Sigma W_{iz} H_i$$

Substituting for the energy fluxes, e_r and e_z,

$$-\frac{1}{r}\frac{\partial[r[q_r + \Sigma W_{ir} H_i]]}{\partial r} - \frac{\partial[q_z + \Sigma W_{iz} H_i]}{\partial z} = 0 \tag{8-92}$$

and expanding the convective energy fluxes, $\Sigma W_i H_i$,

$$\text{Radial:}\quad \frac{1}{r}\frac{\partial}{\partial r}(r\Sigma W_{ir} H_i) = \frac{1}{r}\Sigma H_i \frac{\partial(rW_{ir})}{\partial r} + \underbrace{\frac{\Sigma W_{ir}\partial H_i}{\partial r}}_{\text{Neglect}} \tag{8-93}$$

$$\text{Axial:}\quad \frac{\partial(\Sigma W_{iz} H_i)}{\partial z} = \Sigma H_i \frac{\partial W_{iz}}{\partial z} + \Sigma W_{iz}\frac{\partial H_{iz}}{\partial z} \tag{8-94}$$

Substituting Equations (8-93) and (8-94) into Equation (8-92), we obtain upon rearrangement

$$-\frac{1}{r}\frac{\partial(rq_r)}{\partial r} - \frac{\partial q_z}{\partial z} - \Sigma H_i \overbrace{\left(\frac{1}{r}\frac{\partial(rW_{ir})}{\partial r} + \frac{\partial W_{iz}}{\partial z}\right)}^{r_i} - \Sigma W_{iz}\frac{\partial H_i}{\partial z} = 0$$

Recognizing that the term in brackets is related to Equation (8-85) for steady-state conditions and is just the rate of formation of species i, r_i, we have

$$\boxed{-\frac{1}{r}\frac{\partial}{\partial r}(rq_r) - \frac{\partial q_z}{\partial z} - \Sigma H_i r_i - \Sigma W_{iz}\frac{\partial H_i}{\partial z} = 0} \tag{8-95}$$

Recalling

$$q_r = -k_e\frac{\partial T}{\partial r},\ q_z = -k_e\frac{\partial T}{\partial z},\ \frac{\partial H_i}{\partial z} = C_{P_i}\frac{\partial T}{\partial z},$$

and

$$r_i = \nu_i(-r_A)$$

$$\Sigma r_i H_i = \Sigma \nu_i H_i(-r_A) = -\Delta H_{Rx} r_A$$

we have the energy in the form

$$\frac{k_e}{r}\left[\frac{\partial}{\partial r}\left(\frac{r\partial T}{\partial r}\right)\right] + k_e\frac{\partial^2 T}{\partial z^2} + \Delta H_{\mathrm{Rx}} r_{\mathrm{A}} - (\Sigma W_{iz} C_{P_i})\frac{\partial T}{\partial z} = 0 \qquad \text{(8-}$$

Some Initial Approximations

Assumption 1. Neglect the diffusive term wrt the convective term in the exp sion involving heat capacities

$$\Sigma C_{P_i} W_{iz} = \Sigma C_{P_i}(0 + U_z C_i) = \Sigma C_{P_i} C_i U_z$$

With this assumption Equation (8-96) becomes

$$\frac{k_e}{r}\frac{\partial}{\partial r}\left(\frac{r\partial T}{\partial r}\right) + k_e\frac{\partial^2 T}{\partial z^2} + \Delta H_{\mathrm{Rx}} r_{\mathrm{A}} - (U_z \Sigma C_{P_i} C_i)\frac{\partial T}{\partial z} = 0 \qquad \text{(8-}$$

Energy balance with radial and axial gradients

Assumption 2. Assume that the sum $C_{P_m} = \Sigma C_{P_i} C_i = C_{A0}\Sigma\Theta_i C_{P_i}$ is const The energy balance now becomes

$$k_e\frac{\partial^2 T}{\partial z^2} + \frac{k_e}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \Delta H_{\mathrm{Rx}} r_{\mathrm{A}} - U_z C_{P_m}\frac{\partial T}{\partial z} = 0 \qquad \text{(8}$$

Equation (8-98) is the form we will use in our FEMLAB problem. In m instances, the term C_{P_m} is just the product of the solution density and the capacity of the solution (kJ/kg • K).

Coolant Balance

We also recall that a balance on the coolant gives the variation of coolant t perature with axial distance where U_{ht} is the overall heat transfer coeffic and R is the reactor wall radius

$$\dot{m}_c C_{P_c}\frac{\partial T_a}{\partial z} = U_{ht} 2\pi R[T(z) - T_a] \qquad \text{(8}$$

For laminar flow, the velocity profile is

$$U_z = 2U_0\left[1 - \left(\frac{r}{R}\right)^2\right] \qquad \text{(8-}$$

where U_0 is the average velocity inside the reactor.

Boundary and initial conditions

A. Initial conditions *if* other than steady state
$t = 0, \quad C_i = 0, \quad T = T_0, \quad$ for $z > 0$ all r

B. Boundary condition

1) Radial

(a) At $r = 0$, we have symmetry $\partial T / \partial r = 0$ and $\partial C_i / \partial r = 0$.

(b) At the tube wall $r = R$, the temperature flux to the wall on the reaction side equals the convective flux out of the reactor into the shell side of the heat exchanger.

$$-k_e \frac{\partial T}{\partial r}\bigg|_R = U(T_R(z) - T_a)$$

(c) There is no mass flow through the tube walls $\partial C_i / \partial r = 0$ at $r = R$.

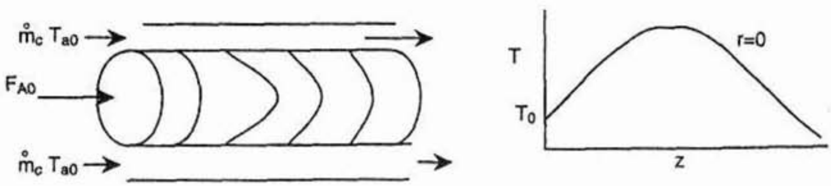
(d) At the entrance to the reactor $z = 0$,

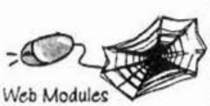
$$T = T_0 \text{ and } C_i = C_{i0}$$

(e) At the exit of the reactor $z = L$,

$$\frac{\partial T}{\partial z} = 0 \text{ and } \frac{\partial C_i}{\partial z} = 0$$

The following examples will solve the preceding equations using FEMLAB. For the exothermic reaction with cooling, the expected profiles are



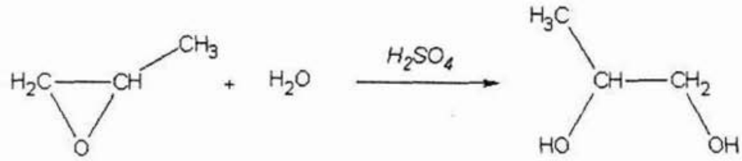


Example 8–12 Radial Effects in Tubular Reactor

This example will highlight the radial effects in a tubular reactor, which up until now have been neglected to simplify the calculations. Now, the effects of parameters such as inlet temperature and flow rate will be studied using the software program FEMLAB. Follow the step-by-step procedure in the Web Module on the CD-ROM.

We continue Example 8-8, which discussed the reaction of propylene oxide (A) with water (B) to form propylene glycol (C). The hydrolysis of propylene oxide takes place readily at room temperature when catalyzed by sulfuric acid.

$$A + B \longrightarrow C$$



This exothermic reaction is approximated as a first-order reaction given that the reaction takes place in an excess of water.

The CSTR from Example 8-8 has been replaced by a tubular reactor 1.0 m in length and 0.2 m in diameter.

The feed to the reactor consists of two streams. One stream is an equivolumetric mixture of propylene oxide and methanol, and the other stream is water containing 0.1 wt % sulfuric acid. The water is fed at a volumetric rate 2.5 times larger than the propylene oxide–methanol feed. The molar flow rate of propylene oxide fed to the tubular reactor is 0.1 mol/s.

There is an immediate temperature rise upon mixing the two feed streams caused by the heat of mixing. In these calculations, this temperature rise is already accounted for, and the inlet temperature of both streams is set to 312 K.

The reaction rate law is

$$-r_A = kC_A$$

with

$$k = Ae^{-E/RT}$$

where E = 75362 J/mol and A = 16.96×10^{12} h^{-1}, which can also be put in the form

$$k(T) = k_0(T_0)\exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

With $k_0 = 1.28$ h^{-1} at 300 K. The thermal conductivity k_e of the reaction mixture and the diffusivity D_e are 0.599 W/m/K and 10^{-9} m^2/s, respectively, and are assumed to be constant throughout the reactor. In the case where there is a heat exchange between the reactor and its surroundings, the overall heat-transfer coefficient is 1300 $W/m^2/K$ and the temperature of the cooling jacket is assumed to be constant and is set to 273 K. The other property data are shown in Table E8-12.1.

TABLE E8–12.1 PHYSICAL PROPERTY DATA

	Propylene Oxide	*Methanol*	*Water*	*Propylene Glycol*
Molar weight (g/mol)	58.095	32.042	18	76.095
Density (kg/m³)	830	791.3	1000	1040
Heat capacity (J/mol • K)	146.54	81.095	75.36	192.59
Heat of formation (J/mol)	–154911.6		–286098	–525676

Solution

Mole Balances: Recalling Equation (8-86) and applying it to species A

A:
$$D_e \frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r} D_e \frac{\partial C_A}{\partial r} + D_e \frac{\partial^2 C_A}{\partial z^2} - U_z \frac{\partial C_A}{\partial z} + r_A = 0 \tag{E8-12.1}$$

Rate Law:

$$-r_A = k(T_1) \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_A \tag{E8-12.2}$$

Stoichiometry: The conversion along a streamline (r) at a distance z

$$X(r, z) = 1 - C_A(r, z)/C_{A0} \tag{E8-12.3}$$

The overall conversion is

$$\overline{X}(z) = 1 - \frac{2\pi \int_0^R C_A(r,z) U_z r dr}{F_{A0}} \tag{E8-12.4}$$

The mean concentration at any distance z

$$\overline{C_A}(z) = \frac{2\pi \int_0^R C_A(r,z) U_z r dr}{\pi R^2 U_0} \tag{E8-12.5}$$

For plug flow the velocity profile is

$$U_z = U_0 \tag{E8-12.6}$$

The laminar flow velocity profile is

$$U_z = 2U_0 \left[1 - \left(\frac{r}{R}\right)^2\right] \tag{E8-12.7}$$

Recalling the Energy Balance

$$\boxed{k_e \frac{\partial^2 T}{\partial z^2} + \frac{k_e}{r} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) + \Delta H_{Rx} r_A - U_z C_{P_m} \frac{\partial T}{\partial z} = 0} \tag{8-98}$$

ıving Example Problem

Assumptions

1. U_r is zero.
2. Neglect axial diffusion/dispersion flux wrt convective flux when summing the heat capacity times their fluxes.
3. Steady state.

Cooling jacket

$$\dot{m}C_{P_i}\frac{\partial T_a}{\partial z} = 2\pi R U_{ht}(T_R(z) - T_a) \quad (8\text{-}99$$

Boundary conditions

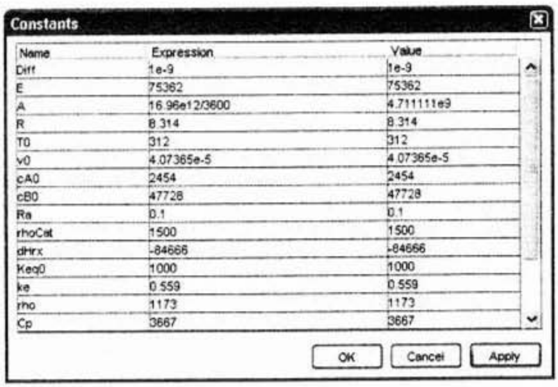
$$\text{At } r = 0, \text{ then } \frac{\partial C_i}{\partial r} = 0 \text{ and } \frac{\partial T}{\partial r} = 0 \quad (\text{E8-12.8}$$

$$\text{At } r = R, \text{ then } \frac{\partial C_i}{\partial r} = 0 \text{ and } -k_e\frac{\partial T}{\partial r} = U_{ht}(T_R(z) - T_a) \quad (\text{E8-12.9}$$

$$\text{At } z = 0, \text{ then } C_i = C_{i0} \text{ and } T = T_0 \quad (\text{E8-12.10}$$

These equations were solved using FEMLAB for a number of cases including a batic and non-adiabatic plug flow and laminar flow; they were also solved with without axial and radial dispersion. A detailed accounting on how to change parameter values in the FEMLAB program can be found in the FEMLAB Instr tions section on the web in screen shots similar to Figure E8-12.1. Figure E8- gives the data set in SI units used for the FEMLAB example on the CD-ROM.

Note: There is a step-by-step FEMLAB tutorial using screen shots for this example on the CD-ROM.


Constants

Name	Expression	Value
Diff	1e-9	1e-9
E	75362	75362
A	16.96e12/3600	4.711111e9
R	8.314	8.314
T0	312	312
v0	4.07365e-5	4.07365e-5
cA0	2454	2454
cB0	47728	47728
Ra	0.1	0.1
rhoCat	1500	1500
dHrx	-84666	-84666
Keq0	1000	1000
ke	0.559	0.559
rho	1173	1173
Cp	3667	3667

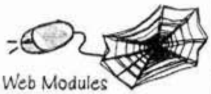
OK Cancel Apply

Define expression

Figure E8-12.1 FEMLAB screen shot of Data Set.

Color surfaces are used to show the concentration and temperature profiles, sim to the black and white figures shown in Figure E8-12.2. Use the FEMLAB prog on the CD-ROM to develop temperature concentration profiles similar to the c shown here. Read through the FEMLAB web module entitled "Radial and A Temperature Gradients" before running the program. One notes in Figure E8- that the conversion is lower near the wall because of the cooler fluid temperat These same profiles can be found in color on the web and CD-ROM in the modules. One notes the maximum and minimum in these profiles. Near the wall, temperature of the mixture is lower because of the cold wall temperature. Co quently, the rate will be lower, and thus the conversion will be lower. However, r next to the wall, the velocity through the reactor is almost zero so the react spend a long time in the reactor; therefore, a greater conversion is achieved as n by the upturn right next to the wall.

Results of the FEMLAB simulation



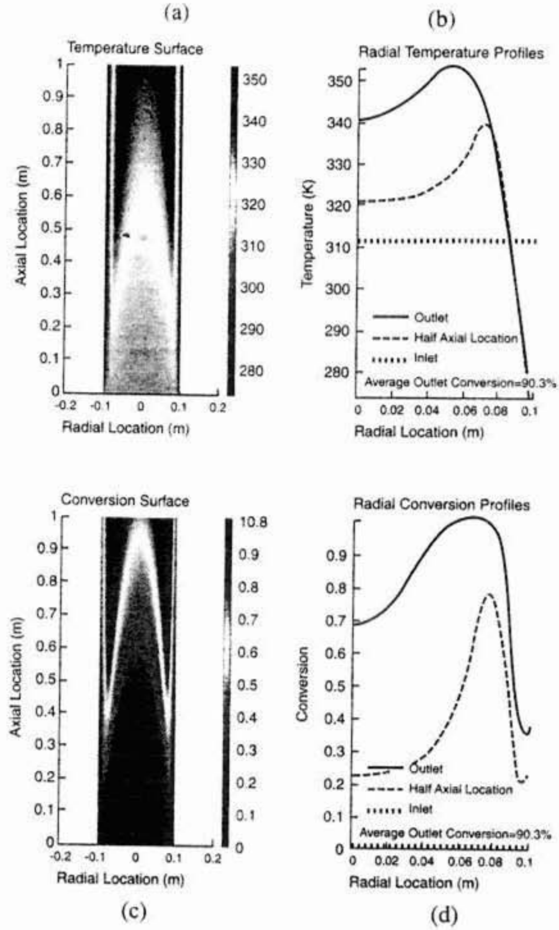


Figure E8-12.2 (a) Temperature surface, (b) temperature surface profiles, (c) conversion surface, and (d) radial conversion profile.

8.10 The Practical Side

Scaling up exothermic chemical reactions can be very tricky. Tables 8.6 and 8.7 give reactions that have resulted in accidents and their causes, respectively.[10]

[10]Courtesy of J. Singh, *Chemical Engineering*, 92 (1997) and B. Venugopal, *Chemical Engineering*, 54 (2002).

TABLE 8-6. INCIDENCE OF BATCH-PROCESS ACCIDENTS

Process Type	*Number of Incidents in U.K., 1962–1987*
Polymerization	64
Nitration	15
Sulfurization	13
Hydrolysis	10
Salt formation	8
Halogenation	8
Alkylation (Friedel-Crafts)	5
Amination	4
Diazolization	4
Oxiation	2
Esterification	1
Total:	134

[Source: U.K. Health and Safety Executive]

TABLE 8-7. CAUSES OF BATCH REACTOR ACCIDENTS IN TABLE 8.6

Cause	*Contribution, %*
Lack of knowledge of reaction chemistry	20
Problems with material quality	9
Temperature-control problems	19
Agitation problems	10
Mis-charging of reactants or catalyst	21
Poor maintenance	15
Operator error	5

Summary Notes

More information is given in the Summary Notes and Professional Reference Shelf on the web. The use of the ARSST to detect potential problems will be discussed in Chapter 9.

Closure. Virtually all reactions that are carried out in industry involve heat effects. This chapter provides the basis to design reactors that operate at steady state and involve heat effects. To model these reactors, we simply add another step to our algorithm; this step is the energy balance. Here it is important to understand how the energy balance was applied to each reaction type so that you will be able to describe what would happen if you changed some of the operating conditions (e.g., T_0). The living example problems (especially *8T-8-3*) and the ICM module will help you achieve a high level of understanding. Another major goal after studying this chapter is to be able to design reactors that have multiple reactions taking place under nonisothermal conditions. Try working Problem 8-26 to be sure you have achieved this goal. An industrial example that provides a number of practical details is included as an appendix to this chapter. The last example of the chapter considers a tubular reactor that has both axial and radial gradients. As with the other living example problems, one should vary a number of the operating parameters to get a feel of how the reactor behaves and the sensitivity of the parameters for safe operation.

SUMMARY

For the reaction

$$A+\frac{b}{a}B\rightarrow\frac{c}{a}C+\frac{d}{a}D$$

1. The heat of reaction at temperature T, per mole of A, is

$$\Delta H_{Rx}(T)=\frac{c}{a}H_C(T)+\frac{d}{a}H_D(T)-\frac{b}{a}H_B(T)-H_A(T) \quad \text{(S8-1)}$$

2. The mean heat capacity difference, ΔC_p, per mole of A is

$$\Delta C_p=\frac{c}{a}C_{pC}+\frac{d}{a}C_{pD}-\frac{b}{a}C_{pB}-C_{pA} \quad \text{(S8-2)}$$

where C_{P_i} is the mean heat capacity of species i between temperatures T_R and T.

3. When there are no phase changes, the heat of reaction at temperature T is related to the heat of reaction at the standard reference temperature T_R by

$$\Delta H_{Rx}(T)=H^\circ_{Rx}(T_R)+\Delta C_P(T-T_R) \quad \text{(S8-3)}$$

4. Neglecting changes in potential energy, kinetic energy, and viscous dissipation, and for the case of no work done on or by the system and all species entering at the same temperature, the steady state CSTR energy balance is

$$\frac{UA}{F_{A0}}(T_a-T)-X[\Delta H^\circ_{Rx}(T_R)+\Delta C_P(T-T_R)]=\Sigma\,\Theta_i C_{P_i}(T-T_{i0}) \quad \text{(S8-4)}$$

5. For adiabatic operation of a PFR, PBR, CSTR, or batch reactor, the temperature conversion relationship is

$$X=\frac{\Sigma\Theta_i C_{P_i}(T-T_0)}{\Delta H^\circ_{Rx}(T_R)+\Delta C_P(T-T_R)} \quad \text{(S8-5)}$$

Solving for the temperature, T.

$$T=\frac{X[-\Delta H^\circ_{Rx}(T_R)]+\Sigma\,\Theta_i C_{P_i}T_0+X\,\Delta C_p T_R}{[\Sigma\,\Theta_i C_{P_i}+X\,\Delta C_p]} \quad \text{(S8-6)}$$

6. The energy balance on a PFR/PBR

$$\frac{dT}{dV}=\frac{Ua(T_a-T)+(-r_A)[-\Delta H_{Rx}(T)]}{\sum_{i=1}^{m}F_iC_{P_i}} \quad \text{(S8-7)}$$

In terms of conversion,

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)[-\Delta H_{Rx}(T)]}{F_{A0}(\Sigma\,\Theta_i C_{P_i} + X\,\Delta C_P)} \qquad \text{(S}$$

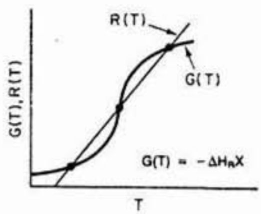
7. The temperature dependence of the specific reaction rate is given in the fo

$$k(T) = k_1(T_1)\exp\left[\frac{E}{R}\left(\frac{T - T_1}{TT_1}\right)\right] \qquad \text{(S}$$

8. The temperature dependence of the equilibrium constant is given by v Hoff's equation for $\Delta C_P = 0$,

$$K_P(T) = K_P(T_2)\exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right] \qquad \text{(S8-}$$

9. Multiple steady states:

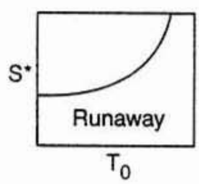


$$G(T) = (-\Delta H_{Rx})\left(\frac{-r_A V}{F_{A0}}\right) = (-\Delta H_{Rx})(X) \qquad \text{(S8-}$$

$$R(T) = C_{P0}(1 + \kappa)(T - T_c) \qquad \text{(S8-}$$

where $\kappa = \dfrac{UA}{C_{P_0} F_{A0}}$, $T_0 = \dfrac{\kappa T_a + T_0}{1 + \kappa}$

10. The criteria for *Runaway Reactions* occurs when $(T_r - T_c) > RT_r^2/E$, wh T_r is the reactor temperature and $T_c = (T_o + \kappa T_a)/(1 + \kappa)$.



$$S^* = G(T^*)\frac{E}{RT^{*2}}$$

11. When q multiple reactions are taking place and there are m species,

$$\frac{dT}{dV} = \frac{Ua(T_a - T)\sum_{i=1}^{q}(-r_{ij})[-\Delta H_{Rxij}(T)]}{\sum_{j=1}^{m} F_j C_{Pj}} \qquad \text{(S8-}$$

12. Axial or radial temperature and concentration gradients. The following coupled partial differential equations were solved using FEMLAB:

$$\boxed{D_e \frac{\partial^2 C_i}{\partial r^2} + \frac{D_e}{r}\frac{\partial C_i}{\partial r} + D_e \frac{\partial^2 C_i}{\partial z^2} - U_z \frac{\partial C_i}{\partial z} + r_i = 0} \quad \text{(S8-14)}$$

and

$$\boxed{k_e \frac{\partial^2 T}{\partial z^2} + \frac{k_e}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \Delta H_{Rx} r_A - U_z C_{P_m} \frac{\partial T}{\partial z} = 0} \quad \text{(S8-15)}$$

ODE SOLVER ALGORITHM

Packed-Bed Reactor with Heat Exchange and Pressure Drop

$$2A \rightleftarrows C$$

Pure gaseous A enters at 5 mol/min at 450 K.

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}}$$

$$\frac{dT}{dW} = \frac{UA/\rho_c(T_a - T) + (r'_A)(\Delta H^\circ_{Rx})}{C_{P_A} F_{A0}}$$

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1 - 0.5X)(T/T_0)$$

$$r'_A = -k[C_A^2 - C_C/K_C]$$

$$C_A = C_{A0}[(1 - X)/(1 - 0.5X)](T_0/T)(y)$$

$$C_C = \tfrac{1}{2} C_{A0} X (T_0/T) y/(1 - 0.5X)$$

$$k = 0.5 \exp[5032((1/450) - (1/T))]$$

$$K_C = 25{,}000 \exp\left[-10{,}065\left[\left(\frac{1}{450}\right) - \left(\frac{1}{T}\right)\right]\right]$$

$\alpha = 0.019$/kg cat.

$C_{A0} = 0.25$ mol/dm^3

$UA/\rho_b = 0.8$ J/kg cat. · s · K

$T_a = 500$ K

$\Delta H^\circ_{Rx} = -20{,}000$ J/mol

$C_{P_A} = 40$ J/mol · K

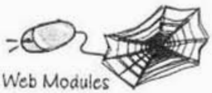
$F_{A0} = 5.0$ mol/s

$T_0 = 450$ K

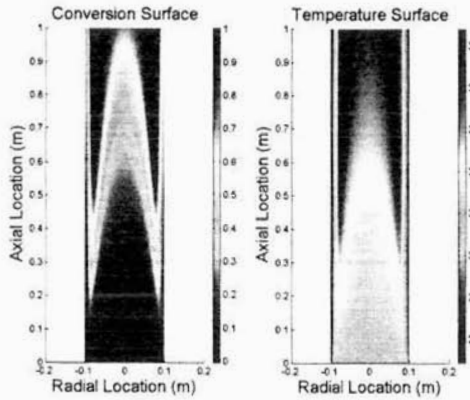
$W_f = 90$ kg cat.

CD-ROM MATERIAL


Summary Notes


Web Modules

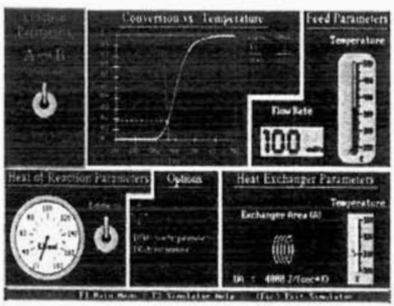
- **Learning Resources**
    1. *Summary Notes*
    2. *Web Module FEMLAB Radial and Axial Gradients*

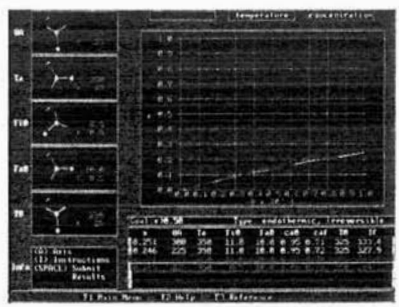


    3. *Interactive Computer Modules*
        A. Heat Effects I
        B. Heat Effects II

Interactive


Computer Modules






Solved Problems

    4. *Solved Problems*
        A. Example CD8-1 — $\Delta H_{Rx}(T)$ for Heat Capacities Expressed as Quadratic Functions of Temperature
        B. Example CD8-2 — Second-Order Reaction Carried Out Adiabatically in a CSTR
    5. *PFR/PBR Solution Procedure for a Reversible Gas-Phase Reaction*


Living Example Problem

- **Living Example Problems**
    1. *Example 8-3 Adiabatic Isomerization of Normal Butane*
    2. *Example 8-4 Isomerization of Normal Butane with Heat Exchange*
    3. *Example 8-5 Production of Acetic Anhydride*
    4. *Example 8-9 CSTR with Cooling Coil*
    5. *Example 8-10 Parallel Reaction in a PFR with Heat Effects*
    6. *Example 8-11 Multiple Reactions in a CSTR*

Living Example Problem

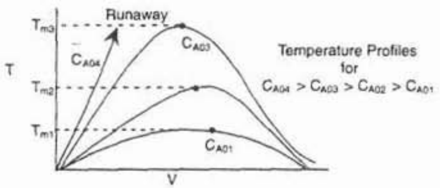
7. *Example 8-12 FEMLAB Axial and Radial Gradients*
8. *Example R8.2-1 Runaway Reactions in a PFR*
9. *Example R8.4-1 Industrial Oxidation of SO_2*
10. *Example 8-T8-3 PBR with Variable Coolant Temperature, T_a*

- **Professional Reference Shelf**

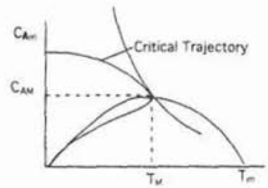
Reference Shelf

R8.1. *Runaway in Plug Flow Reactors*

Phase Plane Plots. We transform the temperature and concentration profiles into a phase plane.



Temperature profiles.



Critical trajectory on the $C_{Am} - T_m$ phase plane plot.

The trajectory going through the maximum of the "maxima curve" is considered to be *critical* and therefore is the locus of the *critical* inlet conditions for C_A and T corresponding to a given wall temperature.

R8.2. *Steady-State Bifurcation Analysis.* In reactor dynamics, it is particularly important to find out if multiple stationary points exist or if sustained oscillations can arise. We apply bifurcation analysis to learn whether or not multiple steady states are possible. Both CSTR energy and mole balances are of the form

$$F(y) = \alpha y - \beta - G(y)$$

The conditions for uniqueness are then shown to be those that satisfy the relationship

$$\max\left(\frac{\partial G}{\partial y}\right) < \alpha$$

Specifically, the conditions for which multiple steady states exist must satisfy the following set of equations:

$$\left.\frac{dF}{dy}\right|_{y^p} = 0 = \alpha - \left.\frac{dG}{dy}\right|_{y^p} \tag{1}$$

$$F(y^*) = 0 = \alpha y^* - \beta - G(y^*) \tag{2}$$

R8.3. *Variable Heat Capacities.* Next we 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 of the heat capacity may not be adequate for the relationship between conversion and temperature. Combining heat reaction with the quadratic form of the heat capacity,

$$C_{P_i} = \alpha_i + \beta_i T + \gamma_i T^2$$

Heat capacity as a function of temperature

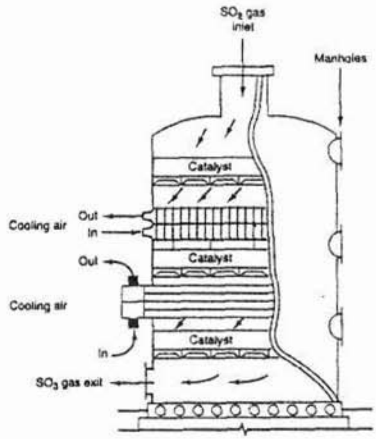
we find that

$$\Delta H_{\mathrm{Rx}}(T) = \Delta H^{\circ}_{\mathrm{Rx}}(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}T^3(-T$$

Example 8-5 is reworked for the case of variable heat capacities.

Reference Shelf

R8.4. *Manufacture of Sulfuric Acid.* The details of the industrial oxidation of are described. Here the catalys quantities reactor configuration, opera conditions, are discussed along with a model to predict the conversion temperature profiles.



QUESTIONS AND PROBLEMS

Homework Problems

The subscript to each of the problem numbers indicates the level of difficulty: A, le difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ◆◆

In each of the questions and problems, rather than just drawing a box arou your answer, write a sentence or two describing how you solved the problem, t assumptions you made, the reasonableness of your answer, what you learned, and a other facts that you want to include. See the Preface for additional generic parts (: (y), (z) to the home problems.

Creative Problems

P8-1$_A$ Read over the problems at the end of this chapter. Make up an original prc lem that uses the concepts presented in this chapter. To obtain a solution:

(a) Make up your data and reaction.

(b) Use a real reaction and real data. See Problem P4-1 for guidelines.

(c) Prepare a list of safety considerations for designing and operati chemical reactors. (See *www.siri.org/graphics.*)

Before solving the problems, state or sketch qualitatively the expected results or trends.

See R. M. Felder, *Chem. Eng. Educ.*, *19*(4), 176 (1985). The August 1985 issue of *Chemical Engineering Progress* may be useful for part (c).

(d) Choose a FAQ from Chapter 8 and say why it was most helpful.

(e) Listen to the audios on the CD and pick one and say why it could be eliminated.

(f) Read through the Self Tests and Self Assessments for Chapter 8 on the CD-ROM, and pick one that was most helpful.

(g) Which example on the CD-ROM Lecture Notes for Chapter 8 was the most helpful?

(h) What if you were asked to prepare a list of safety considerations of redesigning and operating a chemical reactor, what would be the first four items on your list?

(i) What if you were asked to give an everyday example that demonstrates the principles discussed in this chapter? (Would sipping a teaspoon of Tabasco or other hot sauce be one?)

Hall of Fame

P8-2$_A$ Load the following Polymath/MATLAB/FEMLAB programs from the CD-ROM where appropriate:

(a) **Example 8-1.** How would this example change if a CSTR were used instead of a PFR?

(b) **Example 8-2.** What would the heat of reaction be if 50% inerts (e.g., helium) were added to the system? What would be the % error if the ΔC_P term were neglected?

(c) **Example 8-3.** What if the butane reaction were carried out in a 0.8-m^3 PFR that can be pressurized to very high pressures? What inlet temperature would you recommend? Is there an optimum temperature? How would your answer change for a 2-m^3 CSTR?

(d) **Example 8-4.** (1) How would the answers change if the reactor were in a counter current exchanger where the coolant temperature was not constant along the length of the reactor? The mass flow rate and heat capacity of the coolant are 50 kg/h and 75 kJ/kg/K, respectively, and the entering coolant temperature is 310 K. Vary the coolant rate, $\dot{m}_c$, make a plot of X versus $\dot{m}_c$. (2) Repeat (1) but change the parameters K_C, E, $1{,}000 < Ua < 15{,}000 (\text{J/h/m}^3/\text{K})$, and ΔH_{Rx}. Write a paragraph describing what you find, noting any generalization.

(e) **Example 8-5.** (1) How would your answer change if the coolant flow was counter current? (2) Make a plot of conversion as a function of F_{A0} for each of the three cases. (3) Make a plot of conversion as a function of coolant rate and coolant temperature. (4) Make a plot of the exit conversion and temperature as a function of reactor diameter but for the same total volume.

(f) **Example 8-6.** How would the result change if the reaction were second order and reversible $2A \leftrightarrow 2B$ with K_C remaining the same?

(g) **Example 8-7.** How would your answers change if the heat of reaction were three times that given in the problem statement?

(h) **Example 8-8.** Describe how your answers would change if the molar flow of methanol were increased by a factor of 4.

(i) **Example 8-9.** Other data show $\Delta H_{Rx} = -58{,}700$ BTU/lbmol and $C_{P_A} = 29$ BTU/lbmol/°F. How would these values change your results? Make a plot of conversion as a function of heat exchanger area. [$0 < A < 200$ ft^2].

(j) Example 8-10. How would your results change if there is (1) a pressure drop with $\alpha = 0.08\ \text{dm}^{-3}$, (2) Reaction (1) is reversible with $K_C = 10$ at 450 K. (3) How would the selectivity change if Ua is increased? Decreased?

(k) Example 8-11. (1) How would the results (e.g., $\tilde{S}_{B/C}$) change if the UA term were varied ($3500 < UA < 4500\ J/m^3 \cdot \text{s} \cdot \text{k}$)? (2) If T_a were varied between 273 K and 400 K, make a plot of C_B versus T_a.

(l) Example P8.4-1. SO_2 oxidation. How would your results change if (1) the catalyst particle diameter were cut in half? (2) the pressure were doubled? At what particle size does pressure drop become important for the same catalyst weight assuming the porosity doesn't change? (3) you vary the initial temperature and the coolant temperature? Write a paragraph describing what you find.

(m) Example T8-3. Load the Polymath problem from the CD-ROM for this exothermic reversible reaction with a variable coolant temperature. The elementary reaction

$$A + B \rightleftarrows 2C$$

Hall of Fame

has the following parameter values for the **base case**.

$E = 25$ kcal/mol	$C_{P_A} = C_{P_B} = C_{P_C} = 20$ cal/mol/K
$\Delta H_{Rx} = -20$ kcal/mol	$C_{P_I} = 40$ cal/mol/K
$k = \dfrac{0.004\ \text{dm}^6}{\text{mol} \cdot \text{kg} \cdot \text{s}}$ @ 310 K	$\dfrac{Ua}{\rho_B} = 0.5 \dfrac{\text{cal}}{\text{kg} \cdot \text{s} \cdot K}$
$K_c = 1000$ @ 303 K	$T_a = 320$ K
$\alpha = 0.0002$ / kg	$\dot{m}_c = 1{,}000$ g/s
$F_{a0} = 5$ mol/s	$C_{P_c} = 18$ cal/g/K
$C_{T0} = 0.3$ mol/dm^3	$\Theta_I = 1$


Summary Notes

Vary the following parameters and write a paragraph describing the trends you find for each parameter variation and why they work the way they do. Use the base case for parameters not varied. *Hint:* See Selftests and Workbook in the *Summary Notes* on the CD-ROM.

(a) F_{A0}: $1 \le F_{A0} \le 8$ mol/s

(b) Θ_I: $0.5 \le \Theta_I \le 4$

*Note: The program gives $\Theta_I = 1.0$. Therefore, when you vary Θ_I, you will need to account for the corresponding increase or decrease of C_{A0} because the total concentration, C_{T0}, is constant.

(c) $\dfrac{Ua}{\rho_b}$: $0.1 \le \dfrac{Ua}{\rho_b} \le 0.8\ \dfrac{\text{cal}}{\text{kg} \cdot \text{s} \cdot \text{K}}$

(d) T_0: $310\ \text{K} \le T_0 \le 350\ \text{K}$

(e) T_a: $300\ \text{K} \le T_a \le 340\ \text{K}$