

Figure S-1 Startup of a CSTR.

4. Multiple reactions (q reactions and n species)

$$\frac{dT}{dt} = \frac{\dot{m}_c C_{P_c} (T_{a1} - T) [1 - \exp(-UA/\dot{m}_c C_{P_c})] + \sum_{i=1}^q r_{ij} V \Delta H_{R_{xij}}(T) - \sum F_{i0} C_{P_i} (T - T_0)}{\sum N_i C_{P_i}} \quad (\text{S9-7})$$

CD-ROM MATERIAL



Summary Notes



Links



Solved Problems



Living Example Problem

• Learning Resources

1. *Summary Notes*
2. *Web links: SACHE Safety web site www.sache.org.* You will need to get the user name and password from your department chair. The kinetics (i.e., CRE) text, examples, and problems are marked K in the product sections: Safety, Health, and the Environment (S,H, & E).
3. *Solved Problems*
 - Example CD9-1 Startup of a CSTR
 - Example CD9-2 Falling Off the Steady State
 - Example CD9-3 Proportional-Integral (PI) Control

• Living Example Problems

1. *Example 9-1 Adiabatic Batch Reactor*
2. *Example 9-2 Safety in Chemical Plants with Exothermic Reactions*
3. *Example 9-3 Use of the ARSST*
4. *Example 9-4 Heat Effects in a Semibatch Reactor*
5. *Example 9-5 Startup of a CSTR*
6. *Example 9-6 Falling of the Upper Steady State*
7. *Example 9-7 Multiple Reactions in a Semibatch Reactor*
8. *Example RE9-1 Integral Control of a CSTR*
9. *Example RE9-2 Proportion-Integral Control of a CSTR*
10. *Example RE9-3 Linearized Stability*

• **Professional Reference Shelf**

R9.1 *The Complete ARSST*

In this section further details are given to size safety valves to prevent runaway reactions

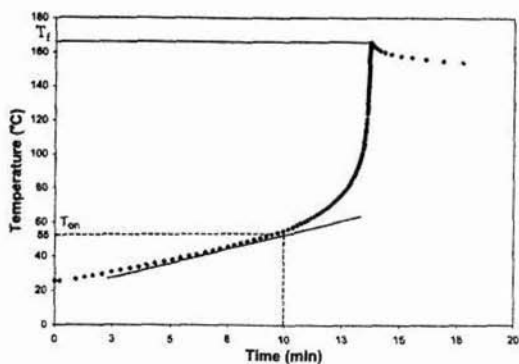
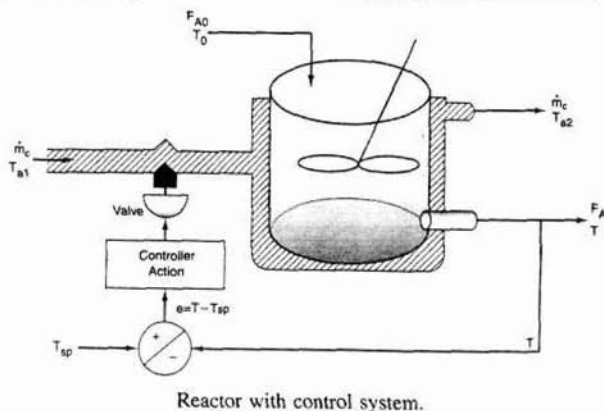


Figure E9-3.1 Temperature-time trajectory for hydrolysis of acetic anhydride.

R9.2. *Control of a CSTR*

In this section we discuss the use of proportional (P) and integral (I) control of a CSTR. Examples include I and PI control of an exothermic reaction.



Reactor with control system.

Proportional integral action

$$z = z_0 + k_c(T - T_{SP}) + \frac{k_c}{\tau} \int_0^t (T - T_{SP}) dt$$

R9.3. *Linearized Stability Theory*

In this section we learn if a perturbation will decay in an exponential manner ((a) below) in an oscillatory manner (b), grown exponentially (c), grown exponentially with oscillations (d), or just oscillate (e).

$$-r_A = -r_{AS} + (C_A - C_{AS}) \left. \frac{\partial(-r_A)}{\partial C_A} \right|_S + (T - T_S) \left. \frac{\partial(-r_A)}{\partial T} \right|_S \quad (\text{R9.3-11})$$

$$\tau \frac{dC_A}{dt} - (C_A - C_{AS}) - \tau k_S (C_A - C_{AS}) - \frac{E}{RT_S^2} (-r_{AS})(T - T_S) \quad (\text{R9.3-})$$

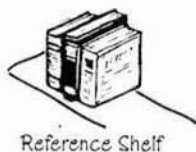



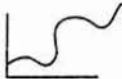
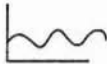


TABLE 9C-1 EIGENVALUES OF COUPLED ODES

A.	$\text{Tr} < 0$	$\text{Det} > 0$	<u>Stable</u>	
		$[\text{Tr}^2(\mathbf{M}) - 4\text{Det}(\mathbf{M})] > 0$		 (a)
		$(\text{Tr}^2(\mathbf{M}) - 4\text{Det}(\mathbf{M})) < 0$		 (b)
B.	$\text{Tr} > 0$	$\text{Det} > 0$	<u>Unstable</u>	
		$[\text{Tr}^2(\mathbf{M}) - 4\text{Det}(\mathbf{M})] > 0$		 (c)
		$[\text{Tr}^2(\mathbf{M}) - 4\text{Det}(\mathbf{M})) < 0$		 (d)
C.	$\text{Tr}(\mathbf{M}) = 0$	$\text{Det}(\mathbf{M}) > 0$	<u>Pure Oscillation</u>	
				 (e)

R9.4. Approach to the Steady-State Phase-Plane Plots and Trajectories of Concentration versus Temperature

Here we learn if the practical stability is exceeded during startup.

Example RE9-4.1 Start Up of a CSTR

Example RE9-4.2 Falling Off the Steady State

Example RE9-4.3 Revisit Example RE9-2.

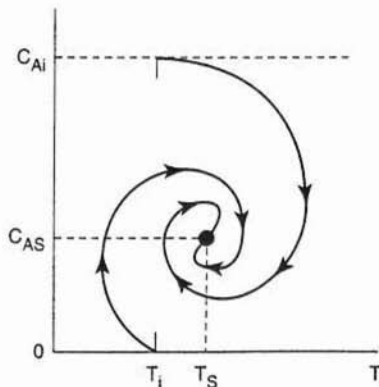


Figure CD9-5 Approach to the steady state.

R9.5. Adiabatic Operation of a Batch Reactor

R9.6. Unsteady Operation of Plug-Flow Reactors

QUESTIONS AND PROBLEMS



Creative Problems

P9-1_A Read over the problems at the end of this chapter. Refer to the guidelines given in Problem 4-1, and make up an original problem that uses the concepts presented in this chapter. To obtain a solution:

- Make up your data and reaction.
- Use a real reaction and real data.

Also,

- Prepare a list of safety considerations for designing and operating chemical reactors.

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).

P9-2_A Review the example problems in this chapter, choose one, and use a software package such as Polymath or MATLAB to carry out a parameter sensitivity analysis.

What if...

- Example 9-1.** How much time would it take to achieve 90% conversion if the reaction were started on a very cold day where the initial temperature was 20°F? (Methanol won't freeze at this temperature.)

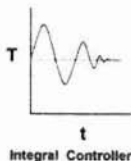
- Example 9-2.** Explore the ONCB explosion described in Example 9-2. Show that no explosion would have occurred if the cooling was not shut off for the 9.04-kmol charge of ONCB or if the cooling was shut off for 10 min after 45 min of operation for the 3.17-kmol ONCB charge. Show that if the cooling had been shut off for 10 min after 12 h of operation, no explosion would have occurred for the 9.04-kmol charge. Develop a set of guidelines as to when the reaction should be quenched should the cooling fail. Perhaps safe operation could be discussed using a plot of the time after the reaction began at which the cooling failed, t_0 , versus the length of the cooling failure period, t_f , for the different charges of ONCB. Parameter values used in this example predict that the reactor will explode at midnight. What parameter values would predict the time the reactor would explode at the actual time of 18 min after midnight? Find a set of parameter values that would cause the explosion to occur at exactly 12:18 A.M. For example, include heat capacities of metal reactor and/or make a new estimate of UA . Finally, what if a 1/2-in. rupture disk rated at 800 psi had been installed and did indeed rupture at 800 psi (270°C)? Would the explosion still have occurred? (Note: The mass flow rate \dot{m} varies with the cross-sectional area of the disk. Consequently, for the conditions of the reaction the maximum mass flow rate out of the 1/2-in. disk can be found by comparing it with the mass flow rate of 830 kg/min of the 2-in. disk.)

- Example 9-3.** What would be the conversion at the onset temperature if the heating rate were reduced by a factor of 10? Increased by a factor of 10?

- Example 9-4.** What would the X versus t and T versus t trajectories look like if the coolant rate is decreased by a factor of 10? Increased by a factor of 10?



Hall of Fame



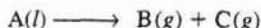
- (e) **Example 9-5.** Load the Living Example Problem for *Startup of a CSTR*, for an entering temperature of 70°F, an initial reactor temperature of 160°F, and an initial concentration of propylene oxide of 0.1 M. Try other combinations of T_0 , T_i , and C_{A_i} , and report your results in terms of temperature–time trajectories and temperature–concentration phase planes.
- (f) **Example 9-6.** Load the Living Example Problem for *Falling Off the Upper Steady State*. Try varying the entering temperature, T_0 , to between 80 and 68°F and plot the steady-state conversion as a function of T_0 . Vary the coolant rate between 10,000 and 400 mol/h. Plot conversion and reactor temperature as a function of coolant rate.
- (g) **Example 9-7.** What happens if you increase the heat transfer coefficient by a factor of 10 and decrease T_a to 280 K? Which trajectories change the most?
- (h) **Example RE9-1.** Load the Living Example Problem. Vary the gain, k_C , between 0.1 and 500 for the integral controller of the CSTR. Is there a lower value of k_C that will cause the reactor to fall to the lower steady state or an upper value to cause it to become unstable? What would happen if T_0 were to fall to 65°F or 60°F?
- (i) **Example RE9-2.** Load the Living Example Problem. Learn the effects of the parameters k_C and τ_I . Which combination of parameter values generates the least and greatest oscillations in temperature? Which values of k_C and τ_I return the reaction to steady state the quickest?
- (j) **Reactor Safety.** Enter the SACHE web site, www.sache.org. [Note you will need to obtain the user name and password for your school from your department chair or SACHE representative.] After entering hit the current year (e.g., 2004). Go to product: Safety, Health and the Environment (S,H, & E). The problems are for KINETICS (i.e., CRE). There are some example problems marked K and explanations in each of the above S,H, & E selections. Solutions to the problems are in a different section of the site. Specifically look at: *Loss of Cooling Water (K-1) Runaway Reactions (HT-1)*, *Design of Relief Values (D-2)*, *Temperature Control and Runaway (K-4)* and (K-5), and *Runaway and the Critical Temperature Region (K-7)*.

P9-3_B

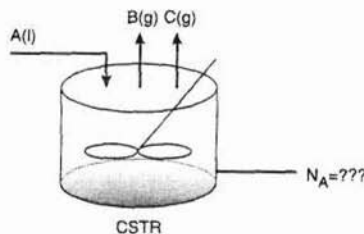
The following is an excerpt from *The Morning News*, Wilmington, Delaware (August 3, 1977): “Investigators sift through the debris from blast in quest for the cause [that destroyed the new nitrous oxide plant]. A company spokesman said it appears more likely that the [fatal] blast was caused by another gas—ammonium nitrate—used to produce nitrous oxide.” An 83% (wt) ammonium nitrate and 17% water solution is fed at 200°F to the CSTR operated at a temperature of about 520°F. Molten ammonium nitrate decomposes directly to produce gaseous nitrous oxide and steam. It is believed that pressure fluctuations were observed in the system and as a result the molten ammonium nitrate feed to the reactor may have been shut off approximately 4 min prior to the explosion. Can you explain the cause of the blast? If the feed rate to the reactor just before shutoff was 310 lb of solution per hour, what was the exact temperature in the reactor just prior to shutdown? Using the following data, calculate the time it took to explode after the feed was shut off for the reactor. How would you start up or shut down and control such a reaction?

Assume that at the time the feed to the CSTR stopped, there was 500 lb of ammonium nitrate in the reactor at a temperature of 520°F. The conversion in the reactor is virtually complete at about 99.99%. Additional data for this problem are given in Problem 8-3. How would your answer change if 100 lb of solution were in the reactor? 310 lb? 800 lb? What if $T_0 = 100^\circ\text{F}$? 500°F ?

P9-4_B The first-order irreversible reaction



is carried out adiabatically in a CSTR into which 100 mol/min of pure liquid A is fed at 400 K. The reaction goes virtually to completion (i.e., the feed rate into the reactor equals the product of reaction rate inside the reactor and the reactor volume).



How many moles of liquid A are in the CSTR under steady-state conditions? Plot the temperature and moles of A in the reactor as a function of time after the feed to the reactor has been shut off.

Additional information:

Temperature (K)	400	800	1200
k (min^{-1})	0.19	0.32	2.5
H_A (kJ/mol)	-38	-30	-22
H_B (kJ/mol)	-26	-22	-18
H_C (kJ/mol)	-20	-16	-12

P9-5_B The liquid-phase reaction in Problem P8-5 is to be carried out in a semibatch reactor. There is 500 mol of A initially in the reactor at 25°C. Species B is fed to the reactor at 50°C and a rate of 10 mol/min. The feed to the reactor is stopped after 500 mol of B has been fed.

- Plot the temperature and conversion as a function of time when the reaction is carried out adiabatically. Calculate to $t = 2$ h.
- Plot the conversion as a function of time when a heat exchanger ($UA = 100 \text{ cal/min} \cdot \text{K}$) is placed in the reactor and the ambient temperature is constant at 50°C. Calculate to $t = 3$ h.
- Repeat part (b) for the case where the reverse reaction cannot be neglected.

New parameter values:

$$k = 0.01 \text{ (dm}^3\text{/mol} \cdot \text{min)} \text{ at } 300 \text{ K with } E = 10 \text{ kcal/mol}$$

$$V_0 = 50 \text{ dm}^3, v_0 = 1 \text{ dm}^3\text{/min}, C_{A0} = C_{B0} = 10 \text{ mol/dm}^3$$

$$\text{For the reverse reaction: } k_r = 10 \text{ s}^{-1} \text{ at } 300 \text{ K with } E_r = 16 \text{ kcal/mol}$$

- P9-6_B** You are operating a batch reactor and the reaction is first-order, liquid-phase and exothermic. An inert coolant is added to the reaction mixture to control the temperature. The temperature is kept constant by varying the flow rate of the coolant (see Figure P9-6).

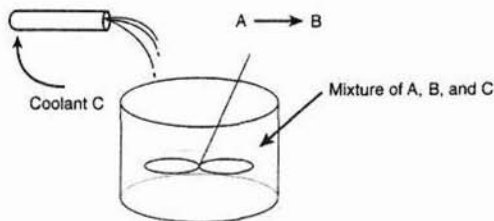


Figure P9-6

- (a) Calculate the flow rate of the coolant 2 h after the start of the reaction. (Ans.: $F_C = 3.157$ lb/s.)
- (b) It is proposed that rather than feeding a coolant to the reactor, a solvent be added that can be easily boiled off, even at moderate temperatures. The solvent has a heat of vaporization of 1000 Btu/lb and initially there are 25 lb mol of A placed in the tank. The initial volume of solvent and reactant is 300 ft³. Determine the solvent evaporation rate as a function of time. What is the rate at the end of 2 h?

Additional information:

Temperature of reaction: 100°F
 Value of k at 100°F: 1.2×10^{-4} s⁻¹
 Temperature of coolant: 80°F
 Heat capacity of all components: 0.5 Btu/lb·°F
 Density of all components: 50 lb/ft³
 $\Delta H_{R_x}^\circ$: -25,000 Btu/lb mol
 Initially:
 Vessel contains only A (no B or C present)
 C_{A0} : 0.5 lb mol/ft³
 Initial volume: 50 ft³

- P9-7_B** The reaction



is carried out adiabatically in a constant-volume batch reactor. The rate law

$$-r_A = k_1 C_A^{1/2} C_B^{1/2} - k_2 C_C$$

Plot the conversion, temperature, and concentrations of the reacting species as a function of time.

Additional information:

Entering Temperature = 100°C

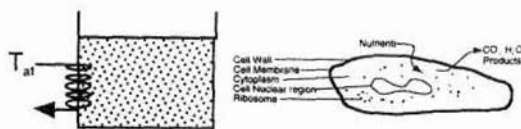
$$k_1 (373 \text{ K}) = 2 \times 10^{-3} \text{ s}^{-1} \quad E_1 = 100 \text{ kJ/mol}$$

$$k_2 (373 \text{ K}) = 3 \times 10^{-5} \text{ s}^{-1} \quad E_2 = 150 \text{ kJ/mol}$$

$$C_{A0} = 0.1 \text{ mol/dm}^3 \quad C_{pA} = 25 \text{ J/mol} \cdot \text{K}$$

$$C_{B0} = 0.125 \text{ mol/dm}^3 \quad C_{pB} = 25 \text{ J/mol} \cdot \text{K}$$

$$\Delta H_{Rx}^{\circ} (298 \text{ K}) = -40,000 \text{ J/mol A} \quad C_{pC} = 40 \text{ J/mol} \cdot \text{K}$$

P9-8_B The biomass reactionis carried out in a 25 dm³ batch chemostat with a heat exchanger.

The initial concentration of cells and substrate are 0.1 and 300 g/dm³, respectively. The temperature dependence of the growth rate follows that given by Aiba et al., Equation (7-61)⁵

$$\mu(T) = \mu(310 \text{ K}) f' = \mu_{1\max} \left[\frac{0.0038 \cdot T \exp[21.6 - 6700/T]}{1 + \exp[153 - 48,000/T]} \right] \frac{C_S}{K_m + C_S} \quad (7-61)$$

- For adiabatic operation and initial temperature of 278 K, plot T , f' , r_g , $-r_s$, C_C , and C_S as a function of time up to 300 hours. Discuss the trends.
- Repeat (a) and increase the initial temperature in 10°C increments up to 330 K and describe what you find. Plot the concentration of cells at 24 hours as a function of inlet temperature.
- What heat exchange area should be added to maximize the total number of cells at the end of 24 hours? For an initial temperature of 310 K and a constant coolant temperature of 290 K, what would be the cell concentration after 24 hours? (Ans. $C_C = \underline{\hspace{2cm}} \text{ g/dm}^3$.)

Additional Information:

$$Y_{CS} = 0.8 \text{ g cell/g substrate}$$

$$K_m = 5.0 \text{ g/dm}^3$$

$$\mu_{1\max} = 0.5 \text{ h}^{-1} \text{ (note } \mu = \mu_{\max} \text{ at } 310 \text{ K and } C_S \rightarrow \infty)$$

$$C_{p_s} = \text{Heat capacity of substrate solution including all cells}$$

$$C_{p_s} = 74 \text{ J/g/K}$$

$$m_c = 100 \text{ kg/h}$$

⁵ S. Abia, A. E. Humphrey, and N. F. Mills, *Biochemical Engineering* (New York: Academic Press, 1973).

$$\begin{aligned} \rho &= \text{density of solution including cells} = 1000 \\ \Delta H_{R_{xx}} &= -20,000 \text{ J/g cells} \\ C_{P_C} &= \text{Heat capacity of cooling water } 74 \text{ J/g/K} \\ U &= 50,000 \text{ J/h/K/m}^2 \end{aligned}$$

$$Q = \dot{m}_c C_{P_C} [T - T_a] \left[1 - \exp \left[-\frac{UA}{\dot{m}_c C_{P_C}} \right] \right]$$

P9-9_B The first order exothermic liquid-phase reaction



is carried out at 85°C in a jacketed 0.2-m³ CSTR. The coolant temperature in the reactor is 32°F. The heat-transfer coefficient is 120 W/m²·K. Determine the critical value of the heat-transfer area below which the reaction will run away and the reactor will explode [*Chem. Eng.*, 91(10), 54 (1984)].

Additional information:

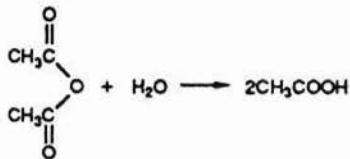
Specific reaction rate:

$$k = 1.1 \text{ min}^{-1} \text{ at } 40^\circ\text{C}$$

$$k = 3.4 \text{ min}^{-1} \text{ at } 50^\circ\text{C}$$

The heat capacity of the solution is 20 J/g·K. The solution density is 0.90 kg/dm³. The heat of reaction is -2500 J/g. The feed temperature is 40°C and the feed rate is 90 kg/min. MW of A = 90 g/mol. $C_{A0} = 2 \text{ M}$.

P9-10_C The ARSST adiabatic bomb calorimeter reactor can also be used to determine the reaction orders. The hydrolysis of acetic anhydride to form acetic acid was carried out adiabatically



The rate law is postulated to be of the form

$$-r_A = k C_A^\alpha C_B^\beta$$

The following temperature time data were obtained for two different critical concentrations of acetic anhydride under adiabatic operation. The heating rate was 2°C/min.

$$C_{A0} = 6.7 \text{ M}, C_{B0} = 0.2 \text{ M}$$

t (min)	0.0	2.0	4.3	6.2	8.1	10.2	12.0	13.0	13.5	13.6	13.7	13.8	14.0
T (K)	299	303	309	314	321	329	344	361	386	403	439	438	435

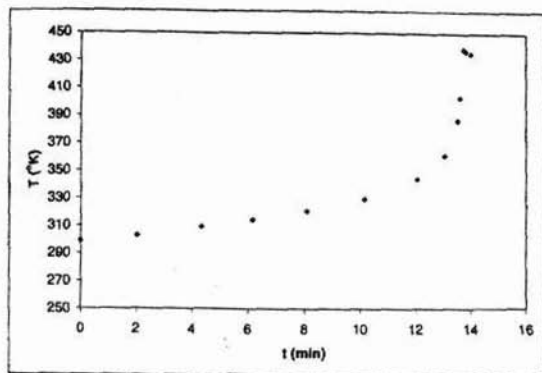


Figure P9-10.1 Data from Undergraduate Laboratory University of Michigan.

- (a) Assume $\Delta C_p = 0$ and show for complete conversion, $X = 1$, the difference between the final temperature, T_f , and the initial temperature, T_0 ,

$$T_f = T_0 + \frac{\Delta H_{Rx}^\circ}{\sum \Theta_i C_{p_i}} \quad (\text{P9-10.1})$$

- (b) Show that the concentration of A can be written as

$$C_A = C_{A0} - C_{A0} \frac{(T - T_0)}{(T_f - T_0)} = C_{A0} \left[\frac{T_f - T}{T_f - T_0} \right] \quad (\text{P9-10.2})$$

and C_B as

$$C_B = C_{B0} - C_{A0} \frac{(T - T_0)}{(T_f - T_0)} = C_{A0} \left[\frac{\Theta_B T_f - T + (T_0 - \Theta_B T_0)}{T_f - T_0} \right] \quad (\text{P9-10.3})$$

and $-r_A$ as

$$-r_A = \frac{k C_{A0}^{\alpha+\beta} [(T_f - T)^\alpha (\Theta_B T_f - T + (T_0 - \Theta_B T_0))^\beta]}{[T_f - T_0]^{\alpha+\beta}} \quad (\text{P9-10.4})$$

- (c) Show the unsteady energy balance can be written as

$$\frac{dT}{dt} = \left[\frac{-\Delta H_{Rx}^\circ}{\sum \Theta_i C_{p_i}} \right] \frac{k C_{A0}^{\alpha+\beta-1}}{[T_f - T_0]^{\alpha+\beta}} [(T_f - T)^\alpha (\Theta_B T_f - T + (T_0 - \Theta_B T_0))^\beta] \quad (\text{P9-10.5})$$

- (d) Assume first order in A and in B and that $\Theta_B = 3$ then show

$$\frac{dT}{dt} = \left[\frac{-\Delta H_{Rx}^\circ}{\sum \Theta_i C_{p_i}} \right] \frac{k C_{A0}}{(T_f - T_0)^2} [(T_f - T)(3T_f - T - 2T_0)] \quad (\text{P9-10.6})$$

(e) Rearrange Equation (P9-10.6) in the form

$$\ln \left(\frac{\frac{dT}{dt}}{[(T_f - T)(3T_f - T - 2T_0)]} \right) = \ln \left(\frac{k_1 C_{A0}}{(T_f - T_0)} \right) + \frac{E}{RT_1} - \frac{E}{RT} \quad (\text{P9-10.6})$$

(f) Plot the data to obtain the activation energy and the specific reaction rate k_1 .

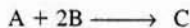
(g) Find the heat of reaction.

Additional information:

Chemical	Density (g/ml)	Heat capacity (J/g·°C)	MW	Heat capacity (J/mol·°C)
Acetic anhydride	1.0800	1.860	102	189.7
Water	1.0000	4.187	18	75.4
Glass cell (bomb)	0.1474	0.837		0.84 J/g·°C
Total volume	10 ml with			
Water	3.638 g			
Acetic anhydride	6.871 g			

$$(M_S C_{p_S} = 28.012 \text{ J/}^\circ\text{C and } \phi = 1.004 \text{ and } m_S C_{p_S} = \phi M_S C_{p_S})$$

P9-11_B The elementary irreversible liquid-phase reaction



is to be carried out in a semibatch reactor in which B is fed to A. The volume of A in the reactor is 10 dm³, the initial concentration of A in the reactor is 5 mol/dm³, and the initial temperature in the reactor is 27°C. Species B is fed at a temperature of 52°C and a concentration of 4 M. It is desired to obtain at least 80% conversion of A in as short a time as possible, but at the same time the temperature of the reactor must not rise above 130°C. You should try to make approximately 120 mol of C in a 24-hour day allowing for 30 min to empty and fill the reactor between each batch. The coolant flow through the reactor is 2000 mol/min. There is a heat exchanger in the reactor.

- (a) What volumetric feed rate (dm³/min) do you recommend?
 (b) How would your answer or strategy change if the maximum coolant flow rate dropped to 200 mol/min? To 20 mol/min?

Additional information:

$$\Delta H_{R_x}^\circ = -55,000 \text{ cal/mol A}$$

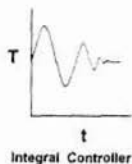
$$C_{p_A} = 35 \text{ cal/mol}\cdot\text{K}, \quad C_{p_B} = 20 \text{ cal/mol}\cdot\text{K}, \quad C_{p_C} = 75 \text{ cal/mol}\cdot\text{K}$$

$$k = 0.0005 \frac{\text{dm}^6}{\text{mol}^2 \cdot \text{min}} \text{ at } 27^\circ\text{C with } E = 8000 \text{ cal/mol}$$

$$UA = 2500 \frac{\text{cal}}{\text{min}\cdot\text{K}} \text{ with } T_a = 17^\circ\text{C}$$

$$C_p(\text{coolant}) = 18 \text{ cal/mol}\cdot\text{K}$$

[Old ex:



- P9-12_B** Read Section R9.2 on the CD-ROM and then rework Example RE9-1 using
- Only a proportional controller.
 - Only an integral controller.
 - A combined proportional and integral controller.
- P9-13_B** Apply the different types of controllers to the reactions in Problem P9-11.
- P9-14_B**
- Rework Example R9-1 for the case of a 5°F decrease in the outlet temperature when the controlled input variable is the reactant feed rate.
 - Consider a 5°F drop in the ambient temperature, T_a , when the controlled variable is the inlet temperature, T_0 .
 - Use each of the controllers (P with $k_C = 10$, I with $\tau_I = 1.0$ h, D with $\tau_D = 0.1$ h) to keep the reactor temperature at the unstable steady state (i.e., $T = 112.5^\circ\text{F}$ and $X = 0.3$).
- P9-15_B** Rework Problem P9-3 for the case when a heat exchanger with $UA = 10,000$ Btu/h-ft² and a control system are added and the mass flow rate is increased to 310 lb of solution per hour.
- Plot temperature and mass of ammonium nitrate in the tank as a function of time when there is no control system on the reactor. Assume that all the ammonium nitrate reacts, and show that the mass balance is

$$\frac{dM_A}{dt} = \dot{m}_{A0} - kM_A$$

There is 500 lb of A in the CSTR, and the reactor temperature, T , is 516°F at time $t = 0$.

- Plot T and M_A as a function of time when a proportional controller is added to control T_a in order to keep the reactor temperature at 516°F. The controller gain, k_C , is -5 with T_{a0} set at 975 R.
- Plot T and M_A versus time when a PI controller is added with $\tau_I = 1$.
- Plot T and M_A versus time when two PI controllers are added to the reactor: one to control T and a second to control M by manipulating the feed rate \dot{m}_{A0} .

$$\dot{m}_{A0} = \dot{m}_{A00} + \frac{k_{C2}}{\tau_{I2}} I_M + k_{C2}(M - M_{sp})$$

with $M_{sp} = 500$ lb, $k_{C2} = 25$ h⁻¹, $\tau_{I2} = 1$ h.

- P9-16_B** The elementary liquid phase reaction



is carried out in a CSTR. Pure A is fed at a rate of 200 lb mol/h at 530 R and a concentration of 0.5 lb mol/ft³. [M. Shacham, N. Brauner, and M. B. Cutlip, *Chem. Engr. Edu.* 28 (1), 30 (Winter 1994).] The mass density of the solution is constant at 50 lb/ft³.

- Plot $G(T)$ and $R(T)$ as a function of temperature.
- What are the steady-state concentrations and temperatures? [One answer $T = 628.645$ R, $C_A = 0.06843$ lb mol/ft³.] Which ones are stable? What is the extinction temperature?
- Apply the unsteady-state mole and energy balances to this system. Consider the upper steady state. Use the values you obtained in part (b) as your initial values to plot C_A and T versus time up to 6 hours and then to plot C_A versus T . What did you find? Do you want to change any of your answers to part (b)?



Hall of Fame

- (d) Expand your results for part (c) by varying T_o and T_a . [Hint: Try $T_o = 590^\circ\text{R}$]. Describe what you find.
- (e) What are the parameters in part (d) for the other steady states? Plot T and C_A as a function of time using the steady-state values as the initial conditions at the lower steady state by value of $T_o = 550\text{ R}$ and $T_o = 560\text{ R}$. Start at the lower steady state ($T = 547.1$, $C_A = 0.425$) and make a C_A/T phase-plane plot for the base case in part (a) $T_o = 530$. Now increase T_a to 550 and then to 560, and describe what you find. Vary T_o .
- (f) Explore this problem. Write a paragraph describing your results and what you learned from this problem.
- (g) Read Section 9.3 on the CD-ROM. Carry out a linearized stability analysis. What were your values of A, B, C, τ , J, L, and M? Find the roots for the upper, lower, and middle steady states you found in part (a).
- (h) Normalize x and y by the steady-state values, $x_1 = x/C_{A_s}$ and $y_1 = y/T_s$, and plot x_1 and y_1 as a function of time and also x_1 as a function of y_1 . Plot x_1 and y_1 as a function of time for each of the three steady states. [Hint: First try initial values of x and y of 0.02 and 2, respectively.]

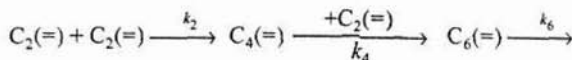
Additional information:

$$\begin{array}{ll}
 v = 400 \text{ ft}^3/\text{hr} & A = 250 \text{ ft}^2 \text{ (Heat Exchanger)} \\
 C_{A0} = 0.50 \text{ lb mol/ft}^3 & T_a = 530^\circ\text{R} \\
 V = 48 \text{ ft}^3 & T_o = 530^\circ\text{R} \\
 k \left\{ \begin{array}{l} A = 1.416 \times 10^{12} \text{ h}^{-1} \\ E = 30,000 \text{ BTU/lb mol} \\ R = 1.987 \text{ BTU/lb mol }^\circ\text{R} \\ U = 150 \text{ BTU/h-ft}^2\text{-}^\circ\text{R} \end{array} \right. & \begin{array}{l} \Delta H_{\text{Rx}} = -30,000 \text{ Btu/lb mol} \\ C_p = 0.75 \text{ Btu/lb }^\circ\text{R} \\ \rho = 50 \text{ lbm/ft}^3 \end{array}
 \end{array}$$

$$C_p = C_p \rho = \left(0.75 \frac{\text{BTU}}{\text{lb R}} \right) \left(50 \frac{\text{lb}}{\text{ft}^3} \right) = 37.5 \frac{\text{BTU}}{\text{ft}^3 \text{R}}$$

- P9-17_B** The reaction in Example 8-6 are to be carried out in a 10-dm³ batch reactor. Plot the temperature and the concentrations of A, B, and C as a function of time for the following cases:
- (a) Adiabatic operation.
- (b) Values of UA of 10,000, 40,000, and 100,000 J/min·K.
- (c) Use $UA = 40,000 \text{ J/min}\cdot\text{K}$ and different initial reactor temperatures.
- P9-18_B** The reaction in Problem P8-34_B is to be carried out in a semibatch reactor.
- (a) How would you carry out this reaction (i.e., T_o , v_o , T_i)? The molar concentrations of pure A and pure B are 5 and 4 mol/dm³ respectively. Plot concentrations, temperatures, and the overall selectivity as a function of time for the conditions you chose.
- (b) Vary the reaction orders for each reaction and describe what you find.
- (c) Vary the heats of reaction and describe what you find.
- P9-19_B** The following temperature–time data was taken on the ARSST. Determine the heat of reaction and the activation energy. Heat capacity of the solution $C_p = 18 \text{ cal/mol}\cdot\text{K}$.
- P9-20_D** The formation of high-molecular-weight olefins, for example,

Time (min)	0	2.1	3.75	6.0	8.2	11.4	15.4	20.4	25.7	28.4	31.0
$T (^{\circ}\text{C})$	18.0	21.5	25.5	30.7	36.0	39.5	42.5	46.8	52.53	57.1	62.3
Time (min)	33.2	34.45	35.2	35.8	36.8	37.2	37.8	38.0	38.2	38.0	40.6
$T (^{\circ}\text{C})$	68.8	74.2	78.3	82.8	94.0	103.8	125.3	142.3	157.0	166.8	164.6



is carried out in the CSTR shown in Figure P9-20(a) where (=) denotes the molecule is an olefin. The reaction is exothermic, and heat is removed from the reactor by heat exchange with a cooling water stream as shown in Figure P9-20(a).

Troubleshooting

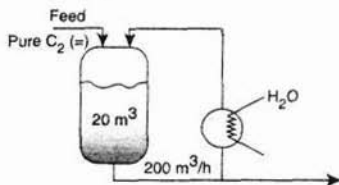


Figure P9-20(a)

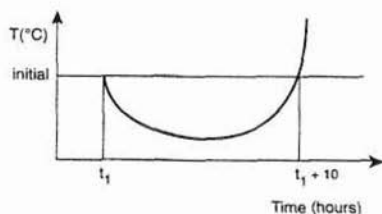
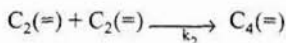


Figure P9-20(b)

Initially, there is a temperature controller that regulates the reactor temperature. At $t = t_1$, the controller is set into manual, and a step increase in the water flow rate through the heat exchanger was made. The temperature response is shown in Figure P9-20(b). What are the parameters to match this trend?

Explain the observed temperature–time trajectory. To make your analysis simpler, you may assume that the only reaction taking place is



with

$$-r_A = A e^{E/RT} C_2^2(=)$$

Also, you can assume that the exchanger is inside the reactor (to avoid recycle stream calculations). See P9-20 CD-ROM Complete Data Set.

• Additional Homework Problems

- CDP9-A_B The production of propylene glycol discussed in Examples 8-4, 9-4, 9-5, 9-6, and 9-7 is carried out in a semibatch reactor.
- CDP9-B_C Reconsider Problem P9-14 when a PI controller is added to the coolant stream.
- CDP9-C_B Calculate time to achieve 90% of equilibrium in a batch reactor. [3rd Ed. P9-8_B]
- CDP9-D_B Startup of a CSTR. [3rd Ed. P9-10_B]

SUPPLEMENTARY READING

1. A number of solved problems for batch and semibatch reactors can be found in
WALAS, S. M., *Chemical Reaction Engineering Handbook*. Amsterdam: Gordon and Breach, 1995, pp. 386–392, 402, 460–462, and 469.
2. Basic control textbooks
SEBORG, D. E., T. F. EDGAR, and D. A. MELLICHAMP, *Process Dynamic Control*, 2nd ed. New York: Wiley, 2004.
OGUNNAIKE, B. A., and W. H. RAY, *Process Dynamics, Modeling and Control*. Oxford: Oxford University Press, 1994.
3. A nice historical perspective of process control is given in
EDGAR, T. F., "From the Classical to the Postmodern Era," *Chem. Eng. E* 31, 12 (1997).

Links



1. The **SACHE web site** has a great discussion on reactor safety with examples (www.sache.org). You will need a user name and password; both can be obtained from your department chair. Hit 2003 Tab. Go to K Problems.
2. The **reactor lab** developed by Professor Herz and discussed in Chapters 4 and 5 could also be used here: www.reactorlab.net and also on the CD-ROM.