

Unsteady-State **9** *Nonisothermal* *Reactor Design*

Chemical Engineers are not gentle people, they like high temperatures and high pressures.

Steve LeBlanc

Overview. Up to now we have focused on the steady-state operation of nonisothermal reactors. In this section the unsteady-state energy balance will be developed and then applied to CSTRs, as well as well-mixed batch and semibatch reactors. In Section 9.1 we arrange the general energy balance (Equation 8-9) in a more simplified form that can be easily applied to batch and semibatch reactors. In Section 9.2 we discuss the application of the energy balance to the operation of batch reactors and discuss reactor safety and the reasons for the explosion of an industrial batch reactor. This section is followed by a description of the advanced reactor system screening tool (ARSST) and how it is used to determine heats of reaction, activation energies, rate constants, and the size of relief valves in order to make reactors safer. In Section 9.3 we apply the energy balance to a semibatch reactor with a variable ambient temperature. Section 9.4 discusses startup of a CSTR and how to avoid exceeding the practical stability limit. We close the chapter (Section 9.5) with multiple reactions in batch reactors.

9.1 The Unsteady-State Energy Balance

We begin by recalling the unsteady-state form of the energy balance developed in Chapter 8.

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_i H_i|_{\text{in}} - \sum_{i=1}^n F_i H_i|_{\text{out}} = \left(\frac{\partial \hat{E}_{\text{sys}}}{\partial t} \right) \quad (8-9)$$



We shall first concentrate on evaluating the change in the total energy of system wrt time, $d\hat{E}_{sys}/dt$. The total energy of the system is the sum of products of specific energies, E_i , of the various species in the system volume and the number of moles of that species:

$$\hat{E}_{sys} = \sum_{i=1}^n N_i E_i = N_A E_A + N_B E_B + N_C E_C + N_D E_D + N_I E_I \quad (8)$$

In evaluating \hat{E}_{sys} , we shall neglect changes in the potential and kinetic energies, and substitute for the internal energy U_i in terms of the enthalpy:

$$\hat{E}_{sys} = \sum_{i=1}^n N_i E_i = \sum_{i=1}^n N_i U_i = \left[\sum_{i=1}^n N_i (H_i - PV_i) \right]_{sys} = \sum_{i=1}^n N_i H_i - P \underbrace{\sum_{i=1}^n N_i \bar{V}_i}_V \quad (9)$$

We note the last term on the right-hand side of Equation (9-2) is just the total pressure times the total volume, i.e., PV . For brevity we shall write these sums

$$\Sigma = \sum_{i=1}^n$$

unless otherwise stated.

When no spatial variations are present in the system volume, and time variations in product of the total pressure and volume (PV) are neglected, the energy balance, substitution of Equation (9-2) into (8-9), gives

$$\dot{Q} - \dot{W}_s + \Sigma F_{i0} H_{i0}|_{in} - \Sigma F_i H_i|_{out} = \left[\Sigma N_i \frac{dH_i}{dt} + \Sigma H_i \frac{dN_i}{dt} \right]_{sys} \quad (9-3)$$

Recalling Equation (8-19),

$$H_i = H^\circ(T_R) + \int_{T_R}^T C_{pi} dT \quad (8-19)$$

and differentiating with respect to time, we obtain

$$\frac{dH_i}{dt} = C_{pi} \frac{dT}{dt} \quad (9-4)$$

Then substituting Equation (9-4) into (9-3) gives

$$\dot{Q} - \dot{W}_s + \Sigma F_{i0} H_{i0} - \Sigma F_i H_i = \Sigma N_i C_{pi} \frac{dT}{dt} + \Sigma H_i \frac{dN_i}{dt} \quad (9-5)$$

The mole balance on species i is

$$\frac{dN_i}{dt} = -v_i r_A V + F_{i0} - F_i \quad (9-6)$$

Using Equation (9-6) to substitute for dN_i/dt , Equation (9-5) becomes

$$\begin{aligned} \dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i \\ = \sum N_i C_{P_i} \frac{dT}{dt} + \sum v_i H_i (-r_A V) + \sum F_{i0} H_i - \sum F_i H_i \end{aligned} \quad (9-7)$$

Rearranging, and recalling $\sum v_i H_i = \Delta H_{R_x}$, we have

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum F_{i0} (H_i - H_{i0}) + (-\Delta H_{R_x})(-r_A V)}{\sum N_i C_{P_i}} \quad (9-8)$$

Substituting for H_i and H_{i0} for the case of no phase change gives us

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum F_{i0} C_{P_i} (T - T_{i0}) + [-\Delta H_{R_x}(T)](-r_A V)}{\sum N_i C_{P_i}} \quad (9-9)$$

Equation (9-9) applies to a semibatch reactor as well as unsteady-state operation of a CSTR.

For liquid-phase reactions where ΔC_p is small and can be neglected, the following approximation is often made:

$$\sum N_i C_{P_i} \cong \sum N_{i0} C_{P_i} = N_{A0} \overline{\sum \Theta_i C_{P_i}} = N_{A0} C_{P_s}$$

where C_{P_s} is the heat capacity of the solution. The units of $N_{A0} C_{P_s}$ are (cal/K) or (Btu/°R) and

$$\sum F_{i0} C_{P_i} = F_{A0} C_{P_s}$$

where the units of $F_{A0} C_{P_s}$ are (cal/s · K) or (Btu/h · °R).¹ With this approximation and assuming that every species enters the reactor at temperature T_0 , we have

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - F_{A0} C_{P_s} (T - T_0) + [-\Delta H_{R_x}(T)](-r_A V)}{N_{A0} C_{P_s}} \quad (9-10)$$

¹ We see that if heat capacity were given in terms of mass (i.e., $C_{P_{sm}} = \text{cal/g} \cdot \text{K}$) then both F_{A0} and N_{A0} would have to be converted to mass:

$$m_{A0} C_{P_{sm}} = N_{A0} C_{P_s}$$

and

$$\dot{m}_{A0} C_{P_{sm}} = F_{A0} C_{P_s}$$

but the units of the products would still be the same (cal/K) and (cal/s · K), respectively.

This form of the energy balance should be used when there is a phase change.

Energy balance on a transient CSTR or semibatch reactor.

9.2 Energy Balance on Batch Reactors

A batch reactor is usually well mixed, so that we may neglect spatial variations in the temperature and species concentration. The energy balance on batch reactors is found by setting F_{A0} equal to zero in Equation (9-10) yielding

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s + (-\Delta H_{R_x})(-r_A V)}{\sum N_i C_{P_i}}} \quad (9-11)$$

Equation (9-11) is the preferred form of the energy balance when the number of moles, N_i , is used in the mole balance rather than the conversion, X . The number of moles of species i at any X is

$$N_i = N_{A0}(\Theta_i + \nu_i X)$$

Consequently, in terms of conversion, the energy balance becomes

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s + (-\Delta H_{R_x})(-r_A V)}{N_{A0}(\sum \Theta_i C_{P_i} + \Delta C_p X)}} \quad (9-12)$$

Batch reactor energy
and mole balances

Equation (9-12) must be coupled with the mole balance

$$\boxed{N_{A0} \frac{dX}{dt} = -r_A V} \quad (2-6)$$

and the rate law and then solved numerically.

9.2.1 Adiabatic Operation of a Batch Reactor

Batch reactors operated adiabatically are often used to determine the reaction orders, activation energies, and specific reaction rates of exothermic reactions by monitoring the temperature–time trajectories for different initial conditions. In the steps that follow, we will derive the temperature–conversion relationship for adiabatic operation.

For adiabatic operation ($\dot{Q} = 0$) of a batch reactor ($F_{i0} \equiv 0$) and when the work done by the stirrer can be neglected ($\dot{W}_s \equiv 0$), Equation (9-11) can be written as

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



Reference Shelf

rearranging and expanding the summation term

$$-\Delta H_{R_x}(T)(-r_A V) = N_{A0}(C_{P_s} + \Delta C_p X) \frac{dT}{dt} \quad (9-13)$$

where as before

$$C_{P_s} = \sum \Theta_i C_{P_i} \quad (9-14)$$

From the mole balance on a batch reactor we have

$$N_{A0} \frac{dX}{dt} = -r_A V \quad (2-6)$$

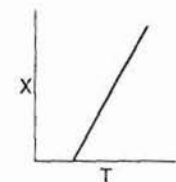
We combine Equations (9-13) and (2-6) to obtain

$$-[\Delta H_{R_x}^\circ + \Delta C_p(T - T_R)] \frac{dX}{dt} = [C_{P_s} + \Delta C_p X] \frac{dT}{dt} \quad (9-15)$$

Canceling dt , separating variables, integrating, and rearranging gives (see CD-ROM *Summary Notes* for intermediate steps)

$$X = \frac{C_{P_s}(T - T_0)}{-\Delta H_{R_x}(T)} = \frac{\sum \Theta_i C_{P_i}(T - T_0)}{-\Delta H_{R_x}(T)} \quad (9-16)$$

$$T = T_0 + \frac{[-\Delta H_{R_x}(T_0)]X}{C_{P_s} + X \Delta C_p} = T_0 + \frac{[-\Delta H_{R_x}(T_0)]X}{\sum_{i=1}^n \Theta_i C_{P_i} + X \Delta C_p} \quad (9-17)$$



Temperature conversion relationship for an adiabatic batch reactor (or any reactor operated adiabatically for that matter)

We note that for adiabatic conditions the relationship between temperature and conversion is the same for batch reactors, CSTRs, PBRs, and PFRs. Once we have T as a function of X for a batch reactor, we can construct a table similar to Table E8-3.1 and use techniques analogous to those discussed in Section 8.3.2 to evaluate the following design equation to determine the time necessary to achieve a specified conversion.

$$t = N_{A0} \int_0^x \frac{dX}{-r_A V} \quad (2-9)$$

Example 9-1 Adiabatic Batch Reactor

Although you were hoping for a transfer to the Bahamas, you are still the engineer of the CSTR of Example 8-8, in charge of the production of propylene glycol. You are considering the installation of a new glass-lined 175-gal CSTR, and you decide to make a quick check of the reaction kinetics. You have an insulated instrumented 10-gal stirred batch reactor available. You charge this reactor with 1 gal of methanol and 5 gal of water containing 0.1 wt % H_2SO_4 . For safety reasons, the reactor is



Living Example Problem

located in a storage shed on the banks of Lake Wobegon (you don't want the reactor plant to be destroyed if the reactor explodes). At this time of year, the initial temperature of all materials is 38°F.

How many minutes should it take the mixture inside the reactor to reach a conversion of 51.5% if the reaction rate law given in Example 8-8 is correct? What would be the temperature? Use the data presented in Example 8-8.

Solution

1. **Design Equation:**

$$N_{A0} \frac{dX}{dt} = -r_A V \quad (E9-1)$$

Because there is a negligible change in density during the course of this reaction, the volume V is assumed to be constant.

2. **Rate Law:**

$$-r_A = kC_A \quad (E9-2)$$

3. **Stoichiometry:**

$$C_A = \left(\frac{N_{A0}}{V} \right) (1 - X) \quad (E9-3)$$

4. **Combining Equations** (E9-1.1), (E9-1.2), and (2-6), we have

$$\frac{dX}{dt} = k(1 - X) \quad (E9-4)$$

From the data in Example 8-8,

$$k = (4.71 \times 10^9) \exp \left[\frac{-32,400}{(1.987)(T)} \right] \text{ s}^{-1}$$

or

$$k = (2.73 \times 10^{-4}) \exp \left[\frac{32,400}{1.987} \left(\frac{1}{535} - \frac{1}{T} \right) \right] \text{ s}^{-1} \quad (E9-5)$$

5. **Energy Balance.** Using Equation (9-17), the relationship between X and T for an adiabatic reaction is given by

$$T = T_0 + \frac{[-\Delta H_{Rx}(T_0)]X}{C_{p_s} + \Delta C_{p_s} X} \quad (E9-6)$$

6. **Evaluating the parameters** in the energy balance gives us the heat capacity of the solution:

$$\begin{aligned} C_{p_s} &= \sum \Theta_i C_{p_i} = \Theta_A C_{p_A} + \Theta_B C_{p_B} + \Theta_C C_{p_C} + \Theta_I C_{p_I} \\ &= (1)(35) + (18.65)(18) + 0 + (1.670)(19.5) \\ &= 403 \text{ Btu/lb mol A} \cdot ^\circ\text{F} \end{aligned}$$

From Example 8-8, $\Delta C_p = -7$ Btu/lb mol $\cdot^\circ\text{F}$ and consequently, the second term on the right-hand side of the expression for the heat of reaction,

$$\begin{aligned}\Delta H_{R_x}(T) &= \Delta H_{R_x}^\circ(T_R) + \Delta C_p(T - T_R) \\ &= -36,400 - 7(T - 528)\end{aligned}\quad (\text{E8-8.7})$$

is very small compared with the first term [less than 2% at 51.5% conversion (from Example 8-8)].

Taking the heat of reaction at the initial temperature of 515 $^\circ\text{R}$,

$$\begin{aligned}\Delta H_{R_x}(T_0) &= -36,400 - (7)(515 - 528) \\ &= -36,309 \text{ Btu/lb mol}\end{aligned}$$

Because terms containing ΔC_p are very small, it can be assumed that

$$\Delta C_p \approx 0$$

In calculating the initial temperature, we must include the temperature rise from the heat of mixing the two solutions:

$$\begin{aligned}T_0 &= (460 + 38) + 17 \\ &= 515^\circ\text{R}\end{aligned}$$

$$\begin{aligned}T &= T_0 - \frac{X[\Delta H_{R_x}(T_0)]}{C_{p_s}} = 515 - \frac{-36,309X}{403} \\ &= 515 + 90.1X\end{aligned}\quad (\text{E9-1.6})$$

A summary of the heat and mole balance equations is given in Table E9-1.1.

TABLE E9-1.1. SUMMARY

$\frac{dX}{dt} = k(1 - X)$
$k = 2.73 \times 10^{-4} \exp\left[\frac{32,400}{1.987}\left(\frac{1}{535} - \frac{1}{T}\right)\right]$
$T = 515 + 90.1X$
where T is in $^\circ\text{R}$ and t is in seconds.
A table similar to that used in Example 8-3 can now be constructed.

A software package (e.g., Polymath) was also used to combine Equations (E9-1.3), (E9-1.4), and (E9-1.6) to determine conversion and temperature as a function of time. Table E9-1.2 shows the program, and Figures E9-1.1 and E9-1.2 show the solution results.

TABLE E9-1.2. POLYMATH PROGRAM

POLYMATH Results

Example 9-1 Adiabatic Batch Reactor 04-14-2005, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	4000	4000
X	0	0	0.9999651	0.9999651
T	515	515	605.09685	605.09685
k	8.358E-05	8.358E-05	0.0093229	0.0093229

ODE Report (RKF45)

Differential equations as entered by the user

[1] $d(X)/d(t) = k*(1-X)$

Explicit equations as entered by the user

[1] $T = 515 + 90.1 * X$

[2] $k = 0.000273 * \exp(16306 * ((1/535) - (1/T)))$



Living Example Problem

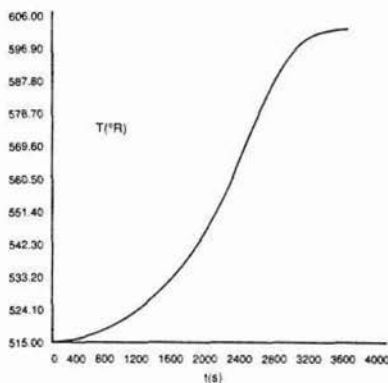


Figure E9-1.1 Temperature-time curve.

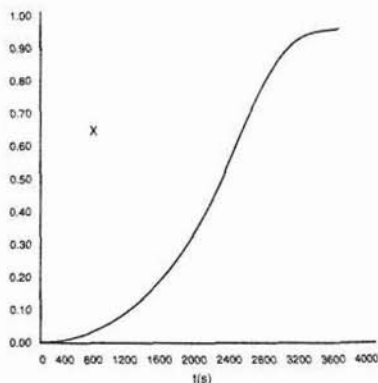


Figure E9-1.2 Conversion-time curve.

It is of interest to compare this residence time with the residence time in the 175-gal CSTR to attain the same conversion at the same final temperature of 582°R ($k = 0.0032 \text{ s}^{-1}$):

$$\tau = \frac{V}{v_0} = \frac{X}{k(1-X)} = \frac{0.515}{(0.0032)(0.485)} = 332 \text{ s} = 5.53 \text{ minutes}$$

This occasion is one when the increase in the reaction rate constant caused by the increase in temperature more than compensates for the decrease in rate caused by the decrease in concentration, so the residence time in the CSTR for this conversion is less than it would be in a batch or tubular plug-flow reactor.

9.2.2 Batch Reactor with Interrupted Isothermal Operation

In Chapter 4 we discussed the design of reactors operating isothermally. This operation can be achieved by efficient control of a heat exchanger. The following example shows what can happen when the heat exchanger suddenly fails.

Example 9-2 Safety in Chemical Plants with Exothermic Reactions²

A serious accident occurred at Monsanto plant in Sauget, Illinois, on August 8 at 12:18 A.M. (see Figure E9-2.1). The blast was heard as far as 10 miles away in Belleville, Illinois, where people were awakened from their sleep. The explosion occurred in a batch reactor that was used to produce nitroaniline from ammonia and *o*-nitrochlorobenzene (ONCB):

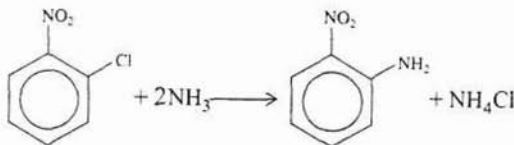


Figure E9-2.1 Aftermath of the explosion. (St. Louis Globe Democrat photo by Roy Cook. Courtesy of St. Louis Mercantile Library.)

This reaction is normally carried out isothermally at 175°C and about 500 psi. The ambient temperature of the cooling water in the heat exchanger is 25°C. By adjusting the coolant rate the reactor temperature could be maintained at 175°C. At the maximum coolant rate the ambient temperature is 25°C throughout the heat exchanger.

² Adapted from the problem by Ronald Willey, *Seminar on a Nitroaniline Reactor Rupture*. Prepared for SACHE, Center for Chemical Process Safety, American Institute of Chemical Engineers, New York (1994). Also see *Process Safety Progress*, vol. 20, no. 2 (2001), pp. 123–129. The values of $\Delta H_{R,x}$ and UA were estimated in the plant data of the temperature-time trajectory in the article by G. C. Vincent, *Loss Prevention*, 5, 46–52.



Living Example Problem

Was a *Potential Problem Analysis* carried out?

Let me tell you something about the operation of this reactor. Over the years the heat exchanger would fail from time to time, but the technicians would "Johnny on the Spot" and run out and get it up and running in 10 minutes or so, there was never any problem. One day it is hypothesized that someone looked at the reactor and said, "It looks as if your reactor is only a third full and you still have room to add more reactants and to make more product. How about filling it up to the top so we could triple production?" They did, and you can see what happened in Figure E9-2.1.

On the day of the accident, two changes in normal operation occurred.

1. The reactor was charged with 9.044 kmol of ONCB, 33.0 kmol of NH_3 , 103.7 kmol of H_2O . Normally, the reactor is charged with 3.17 kmol ONCB, 103.6 kmol of H_2O , and 43 kmol of NH_3 .
2. The reaction is normally carried out isothermally at 175°C over a 24-h period. Approximately 45 min after the reaction was started, cooling to the reactor failed, but only for 10 min. Cooling may have been halted for 10 min on previous occasions when the normal charge of 3.17 kmol of ONCB was used and no ill effects occurred.

A decision was made to triple production.

The reactor had a rupture disk designed to burst when the pressure exceeded approximately 700 psi. If the disk would have ruptured, the pressure in the reactor would have dropped, causing the water to vaporize, and the reaction would have been cooled (quenched) by the latent heat of vaporization.

Plot the temperature-time trajectory up to a period of 120 min after the reactants were mixed and brought up to 175°C . Show that the following three conditions had to have been present for the explosion to occur: (1) increased ONCB charge, (2) reactor stopped for 10 min, and (3) relief system failure.

Additional Information: The rate law is

$$-r_{\text{ONCB}} = k C_{\text{ONCB}} C_{\text{NH}_3} \quad \text{with} \quad k = 0.00017 \frac{\text{m}^3}{\text{kmol} \cdot \text{min}} \quad \text{at} \quad 188^\circ\text{C}$$

The reaction volume for the charge of 9.044 kmol of ONCB:

$$V = 3.265 \text{ m}^3 \text{ ONCB/NH}_3 + 1.854 \text{ m}^3 \text{ H}_2\text{O} = 5.119 \text{ m}^3$$

The reaction volume for the charge of 3.17 kmol of ONCB:

$$V = 3.26 \text{ m}^3$$

$$\Delta H_{\text{Rx}} = -5.9 \times 10^5 \text{ kcal/kmol}$$

$$E = 11,273 \text{ cal/mol}$$

$$C_{p_{\text{ONCB}}} = C_{p_A} = 40 \text{ cal/mol} \cdot \text{K}$$

$$C_{p_{\text{H}_2\text{O}}} = C_{p_W} = 18 \text{ cal/mol} \cdot \text{K} \quad C_{\text{NH}_3} = C_{p_B} = 8.38 \text{ cal/mol} \cdot \text{K}$$

Assume that $\Delta C_p \approx 0$:

$$UA = \frac{35.85 \text{ kcal}}{\text{min} \cdot ^\circ\text{C}} \quad \text{with} \quad T_a = 298 \text{ K}$$

Solution



Mole Balance:

$$\frac{dX}{dt} = -r_A \frac{V}{N_{A0}} \quad (\text{E9-2.1})$$

Rate Law:

$$-r_A = kC_A C_B \quad (\text{E9-2.2})$$

Stoichiometry (liquid phase):

$$C_A = C_{A0}(1 - X) \quad (\text{E9-2.3})$$

with

$$C_B = C_{A0}(\Theta_B - 2X) \quad (\text{E9-2.4})$$

$$\Theta_B = \frac{N_{B0}}{N_{A0}}$$

Combine:

$$-r_A = kC_{A0}^2(1 - X)(\Theta_B - 2X) \quad (\text{E9-2.5})$$

$$k = 0.00017 \exp \left[\frac{11273}{1.987} \left(\frac{1}{461} - \frac{1}{T} \right) \right] \frac{\text{m}^3}{\text{kmol} \cdot \text{min}}$$

Energy Balance:

$$\frac{dT}{dt} = \frac{UA(T_a - T) + (r_A V)(\Delta H_{Rx})}{\sum N_i C_{p_i}} \quad (\text{E9-2.6})$$

For $\Delta C_p = 0$,

$$NC_p = \sum N_i C_{p_i} = N_{A0}C_{p_A} + N_{B0}C_{p_B} + N_W C_{p_W}$$

Let Q_g be the heat generated [i.e., $Q_g = (r_A V)(\Delta H_{Rx})$] and let Q_r be the heat removed [i.e., $Q_r = UA(T - T_a)$]:

$$\frac{dT}{dt} = \frac{-Q_r}{N_{A0}C_{p_A} + N_{B0}C_{p_B} + N_W C_{p_W}} + \frac{Q_g}{N_{A0}C_{p_A} + N_{B0}C_{p_B} + N_W C_{p_W}} \quad (\text{E9-2.7})$$

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

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

Then

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{NC_p} \quad (\text{E9-2.8})$$

Parameter evaluation for day of explosion:

$$NC_p = (9.0448)(40) + (103.7)(18) + (33)(8.38)$$

$$NC_p = 2504 \text{ kcal/K}$$

A. Isothermal Operation Up to 45 Minutes

We will first carry out the reaction isothermally at 175°C up to the time the cooling was turned off at 45 min. Combining and canceling yields

$$\frac{dX}{dt} = kC_{A0}(1-X)(\Theta_B - 2X) \quad (\text{E9-2.9})$$

$$\Theta_B = \frac{33}{9.04} = 3.64$$

At 175°C = 448 K, $k = 0.0001167 \text{ m}^3/\text{kmol} \cdot \text{min}$. Integrating Equation (E9-2.9) gives us

$$t = \left[\frac{V}{kN_{A0}} \right] \left(\frac{1}{\Theta_B - 2} \right) \ln \frac{\Theta_B - 2X}{\Theta_B(1-X)} \quad (\text{E9-2.10})$$

Substituting the parameter values

$$45 \text{ min} = \left[\frac{5.119 \text{ m}^3}{0.0001167 \text{ m}^3/\text{kmol} \cdot \text{min} (9.044 \text{ kmol})} \right] \times \left(\frac{1}{1.64} \right) \ln \frac{3.64 - 2X}{3.64(1-X)}$$

Solving for X , we find that at $t = 45 \text{ min}$, then $X = 0.033$.

We will calculate the rate of generation Q_g at this temperature and conversion and compare it with the maximum rate of heat removal Q_r . The rate of generation Q_g is

$$Q_g = r_A V \Delta H_{R_x} = k \frac{N_{A0}(1-X)N_{A0}[(N_{B0}/N_{A0}) - 2X]V(-\Delta H_{R_x})}{V^2} \quad (\text{E9-2.11})$$

At this time (i.e., $t = 45 \text{ min}$, $X = 0.033$, $T = 175^\circ\text{C}$) we calculate k , then Q_r and Q_g . At 175°C, $k = 0.0001167 \text{ m}^3/\text{min} \cdot \text{kmol}$.

$$\begin{aligned} Q_g &= (0.0001167) \frac{(9.0448)^2(1-0.033)}{5.119} \left[\frac{33}{(9.0448)} - 2(0.033) \right] 5.9 \times 10^5 \\ &= 3830 \text{ kcal/min} \end{aligned}$$

The corresponding maximum cooling rate is

$$\begin{aligned} Q_r &= UA(T - 298) \\ &= 35.85(448 - 298) \\ &= 5378 \text{ kcal/min} \end{aligned} \quad (\text{E9-2.12})$$

Therefore

$$\boxed{Q_r > Q_g} \quad (\text{E9-2.13})$$

The reaction can be controlled. There would have been no explosion had the cooling not failed.

The calculation and results can also be obtained from the Polymath output on the CD-ROM



Living Example Problem

Everything is OK.

B. Adiabatic Operation for 10 Minutes

The cooling was off for 45 to 55 min. We will now use the conditions at the end of the period of isothermal operation as our initial conditions for adiabatic operation period between 45 and 55 min:

$$t = 45 \text{ min} \quad X = 0.033 \quad T = 448^\circ\text{C}$$

Between $t = 45$ and $t = 55$ min, $Q_r = 0$. The Polymath program was modified to account for the time of adiabatic operation by using an "if statement" for Q_r in the program, i.e., $Q_r = \text{if } (t > 45 \text{ and } t < 55) \text{ then } (0) \text{ else } (UA(T - 298))$. A similar "if statement" is used for isothermal operation, i.e., $(dT/dt) = 0$.

For the 45- to 55-min period without cooling, the temperature rose from 448 K to 468 K, and the conversion increased from 0.033 to 0.0424. Using this temperature and conversion in Equation (E9-2.11), we calculate the rate of generation Q_g at 55 min as

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

The maximum rate of cooling at this reactor temperature is found from Equation (E9-2.12) to be

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

Here we see that

$$Q_g > Q_r$$

(E9-2.14)

and the temperature will continue to increase. Therefore, the **point of no return** has been passed and the temperature will continue to increase, as will the rate of reaction until the explosion occurs.

C. Batch Operation with Heat Exchange

Return of the cooling occurs at 55 min. The values at the end of the period of adiabatic operation ($T = 468 \text{ K}$, $X = 0.0423$) become the initial conditions for the period of operation with heat exchange. The cooling is turned on at its maximum capacity, $Q = UA(298 - T)$, at 55 min. Table E9-2.1 gives the Polymath program to determine the temperature-time trajectory. Note that one can change N_{A0} and N_{B0} to 3.17 and 43 kmol in the program and show that if the cooling is shut off for 10 min, at the end of that 10 min Q_r will still be greater than Q_g and no explosion will occur.

The complete temperature-time trajectory is shown in Figure E9-2.2. One notes the long plateau after the cooling is turned back on. Using the values of Q_g and Q_r at 55 min and substituting into Equation (E9-2.8), we find that

$$\frac{dT}{dt} = \frac{(6591 \text{ kcal/min}) - (6093 \text{ kcal/min})}{2504 \text{ kcal}/^\circ\text{C}} = 0.2^\circ\text{C/min}$$

The point of no return

Interruptions in the cooling system have happened before with no ill effects.



Living Example Problem

The explosion occurred shortly after midnight.

TABLE E9-2.1. POLYMATH PROGRAM

ODE Report (RKF45)

Differential equations as entered by the user

- [1] $d(T)/d(t) = \text{if } (t < 45) \text{ then } (0) \text{ else } ((Q_g - Q_r)/NC_p)$
 [2] $d(X)/d(t) = -ra \cdot V / N_{ao}$

Explicit equations as entered by the user

- [1] $V = 3.265 + 1.854$
 [2] $N_{ao} = 9.045$
 [3] $UA = 35.83$
 [4] $k = 0.00017 \cdot \exp((11273/1.987) \cdot (1/461 - 1/T))$
 [5] $\Theta_{tB} = 33/9.045$
 [6] $T_1 = T - 273$
 [7] $ra = -k \cdot N_{ao}^2 \cdot (1-X) \cdot (\Theta_{tB} - 2 \cdot X) / V^2$
 [8] $Q_r = \text{if } (t > 45 \text{ and } t < 55) \text{ then } (0) \text{ else } (UA \cdot (T - 298))$
 [9] $\Delta H_{rx} = -590000$
 [10] $Q_g = ra \cdot V \cdot \Delta H_{rx}$
 [11] $NC_p = 2504$

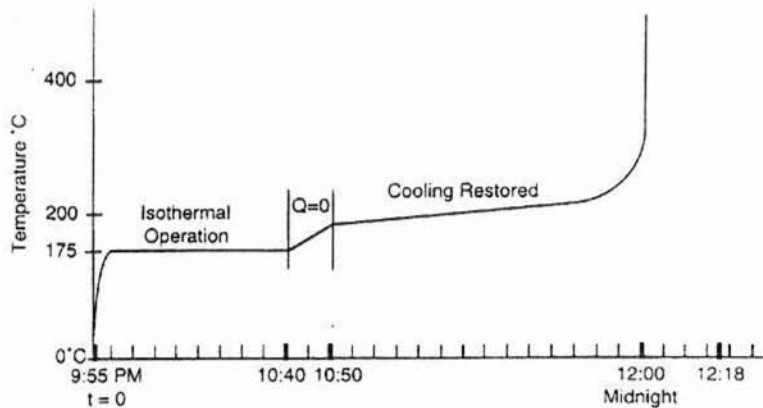
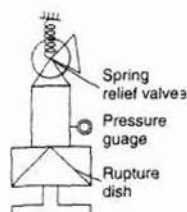


Figure E9-2.2 Temperature-time trajectory.

Consequently, even though dT/dt is positive, the temperature increases very slowly at first, $0.2^\circ\text{C}/\text{min}$. By 11:45, the temperature has reached 240°C and is beginning to increase more rapidly. One observes that 119 min after the batch was started, the temperature increases sharply and the reactor explodes at approximately midnight. If the mass and heat capacity of the stirrer and reaction vessel had been included in the NC_p term, the explosion would have occurred by 15 or so minutes, which would predict the actual time of explosion occurred, at 12:18 A.M.

When the temperature reached 300°C , a secondary reaction, the decomposition of nitroaniline to noncondensable gases such as CO , N_2 , and NO_2 , occurred, releasing even more energy. The total energy released was estimated to be $6.8 \times 10^6 \text{ kJ}$, which is enough energy to lift the entire 2500-ton building 300 m (the length of three football fields) straight up.



D. Disk Rupture

We note that the pressure relief disk should have ruptured when the temperature reached 265°C (ca. 700 psi) but did not and the temperature continued to rise. If it had ruptured and all the water had vaporized, 10⁶ kcal would have been drawn from the reacting solution, thereby lowering its temperature and quenching it.

If the disk had ruptured at 265°C (700 psi), the maximum mass flow rate, \dot{m}_{vap} , out of the 2-in. orifice to the atmosphere (1 atm) would have been 830 kg/min at the time of rupture.

$$\begin{aligned} Q_r &= \dot{m}_{\text{vap}} \Delta H_{\text{vap}} + UA(T - T_a) \\ &= 830 \frac{\text{kg}}{\text{min}} \times 540 \frac{\text{kcal}}{\text{kg}} + 35.83 \frac{\text{kcal}}{\text{K}} (538 - 298)\text{K} \\ &= 4.48 \times 10^5 \frac{\text{kcal}}{\text{min}} + 8604 \frac{\text{kcal}}{\text{min}} \\ &= 4.49 \times 10^5 \frac{\text{kcal}}{\text{min}} \end{aligned}$$

This value of Q_r is much greater than Q_g ($Q_g = 27,460$ kcal/min), so that the reaction could easily be quenched.

In summary, if any one of the following three things had *not* occurred the explosion would not have happened.

1. Tripled production
2. Heat exchanger failure for 10 minutes
3. Failure of the relieving device (rupture disk)

In other words, all the above had to happen to cause the explosion. If the relief had operated properly, it would not have prevented reaction runaway but it could have prevented the explosion. In addition to using rupture disks as relieving devices, one can also use pressure relief valves. In many cases sufficient care is not taken to obtain data for the reaction at hand and to use it to properly size the relief device. This data can be obtained using a batch reactor called the ARSST.

9.2.3 Reactor Safety: The Use of the ARSST to Find ΔH_{R_X} , E and to Size Pressure Relief Valves

The Advanced Reaction System Screening Tool (ARSST) is a calorimeter that is used routinely in industry experiments to determine activation energies, E ; frequency factors, A ; heats of reaction, ΔH_{R_X} ; and to size vent relief valves for runaway exothermic reactions [*Chemical Engineering Progress*, 96 (2), 17 (2000)]. The basic idea is that reactants are placed and sealed in the calorimeter which is then electrically heated as the temperature and pressure in the calorimeter are monitored. As the temperature continues to rise, the rate of reaction also increases to a point where the temperature increases more rapidly from the heat generated by the reaction (called the self-heating rate, \dot{T}_s) than the temperature increase by electrical heating. The temperature at which this

Use ARSST to find:
 E , activation energy
 A , frequency factor
 ΔH_{R_X} , heat of reaction

change in relative heating rates occurs is called the *onset* temperature. A schematic of the calorimeter is shown in Figure 9-1.

Experiments to
obtain data to design
safer reactors

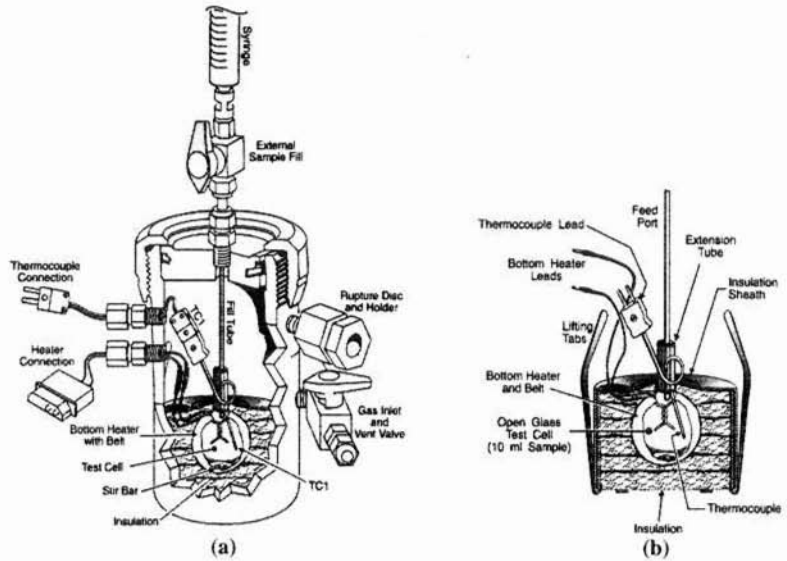


Figure 9-1 ARSST (a) Schematic of containment vessel and internals. (b) Test cell assembly. [Courtesy of Fauske & Associates.]

We shall take as our system the reactants, products and inerts inside the spherical container as well as the spherical container itself because the mass of the container may adsorb a little of the energy given off by the reaction. This system is well insulated and does not lose much heat to the surroundings. Neglecting ΔC_p , the energy balance on the ARSST, Equation (9-12), becomes

$$\frac{dT}{dt} = \frac{\dot{Q} + (-\Delta H_{R_x})(-r_A V)}{\sum N_i C_{p_i}} = \left(\frac{\dot{Q}}{\sum N_i C_{p_i}} \right) + \left(\frac{(\Delta H_{R_x})(-r_A V)}{\sum N_i C_{p_i}} \right) \quad (9-18)$$

The total heat added, \dot{Q} , is the sum of the electrical heat added, \dot{Q}_E , and the convective heat added term, $\dot{Q}_C = (UA[T_a - T])$

$$\dot{Q} = \dot{Q}_E + \underbrace{\dot{Q}_C}_{UA(T_a - T)}$$

Because the system is well insulated, we shall neglect the heat loss from the calorimeter to the surroundings, \dot{Q}_C , and further define

$$\dot{T}_E = \frac{\dot{Q}_E}{\sum N_i C_{P_i}} \quad (9-19)$$

\dot{T}_E is called the *electrical heating rate*. The second term in Equation (9-18) is called the *self-heating rate*, \dot{T}_S , that is,

$$\dot{T}_S = \frac{(-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{P_i}} \quad (9-20)$$

The self-heating rate, which is determined from the experiment, is what is used to calculate the vent size of the relief valve, A_{v_s} of the reactor in order to prevent runaway reactions from exploding (see PRS R9.4 on the CD-ROM).

The electrical heating rate is controlled such that the temperature rise, \dot{T}_E (typically 0.5–2°C/min), is maintained constant up to the temperature when the self-heating rate becomes greater than the electrical heating rate

$$\dot{T}_S > \dot{T}_E$$

Again, this temperature is called the *onset* temperature, T_{onset} . A typical thermal history of data collected by the ARSST is shown in Figure 9-2 in terms of the temperature-time trajectory.

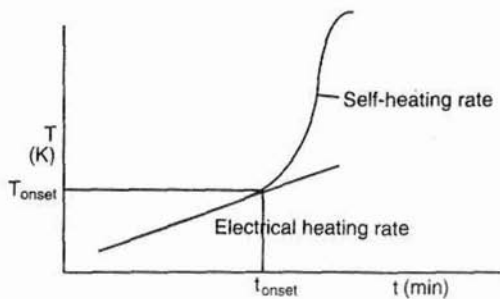


Figure 9-2 Typical temperature history for thermal scan with the ARSST.

The self-heating rate, \dot{T}_S , can be easily found by differentiating the temperature-time trajectory, or \dot{T}_S can be determined directly from the output instrumentation and software associated with the ARSST.

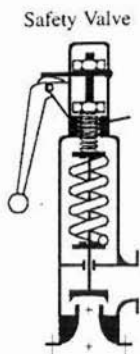
We can rewrite Equation (9-18) in the form

$$\frac{dT}{dt} = \dot{T}_E + \dot{T}_S \quad (9-18A)$$

The following example uses data obtained in the senior unit operations laboratory of the University of Michigan.



Relatively little conversion is achieved for $T < T_{\text{onset}}$



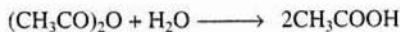
Side note: A relief valve is an instrument on the top of the reactor that releases the pressure and contents of the reactor before temperature and pressure build up to runaway and explosive conditions. The safety relief valve is similar to the rupture disk in that once the reactor pressure exceeds the set pressure P_S , the contents are allowed to flow out through the vent. When the pressure falls below the vapor pressure of the reactor contents, the latent heat of vaporization will cool the reactor. The self-heating rate may be used directly to calculate the vent size necessary to release all the contents of the reactor. The necessary vent area, A_V , is given by the equation for a vapor system and two-phase flashing flow.

$$A_V = 1.5 \cdot 10^{-5} \frac{m_S \dot{T}_S}{F P_S} (\text{in } m^2)$$

where F is a reduction factor for an ideal nozzle, P_S is the relief set pressure (psia), and m_S the mass of the sample in kg and \dot{T}_S is the self-heating rate discussed in the sample calculation in the *Professional Reference Shelf R9.1* on the CD-ROM.

Example 9-3 Use of the ARSST

We shall use the ARSST to study the reaction between acetic anhydride and water to form acetic acid



Acetic anhydride is placed in the ARSST to form a 6.7 molar solution of acetic anhydride and a 20.1 M solution of the water. The sample volume is 10 ml. The electrical heating is started, and the temperature and its derivative, \dot{T}_S , are recorded as a function of time by the ARSST system and computer. Analyze the data to find the heat of reaction $\Delta H_{R,x}$, the activation energy E , and the frequency factor A , and compare theoretical and experimental temperature-time trajectories.

The temperature-time trajectory is obtained directly from the computer link to the ARSST as is shown in Figure E9-3.1.

Physical Properties

Chemical	Density (g/ml)	Heat capacity (J/g°C)	MW	Heat capacity (J/mol°C)	Θ_p
Acetic anhydride	1.0800	1.860	102	189.7	1
Water	1.0000	4.187	18	75.4	3
Glass cell (bomb)	0.1474	0.837	—	0.84 J/g · K	—



Living Example Problem