Chapter 9

Professional Reference Shelf

R9.1. The Complete ARSST

The Advanced Reaction System Screening Tool (ARSST) is a calorimeter that is used routinely in industry to determine activation energies and to size vent relief valves for runaway exothermic reactions [*Chem. Eng. Progr.* **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 change in relative heating rates occurs is called the *onset* temperature. A schematic of the calorimeter is shown in Figure R9.1-1.

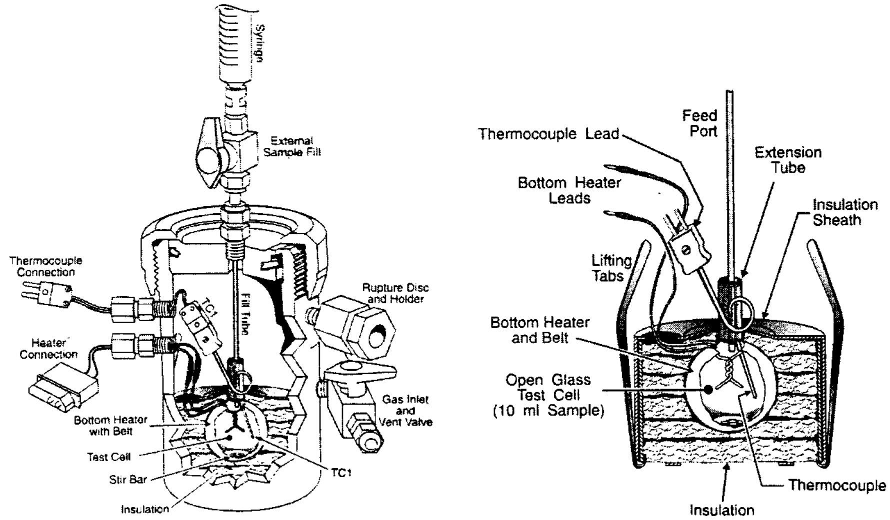

Figure R9.1-1 ARSST (a) Schematic of containment vessel and internals. (b) Test cell assembly. [Courtesy of Fauske & Associates, LLC.]

We shall take as our system the reactants, products, and inerts inside the spherical container as well as the spherical container itself; the mass of the container will adsorb some of the energy given off by the reaction. This system is well insulated and does not loose much heat to the surroundings. For this system, Equation (9-12) after neglecting ΔC_P becomes

$$\frac{dT}{dt} = \frac{\dot{Q} + (-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{P_i}} = \left[\frac{\dot{Q}}{\sum N_i C_{P_i}}\right] + \left[\frac{(-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{P_i}}\right] \qquad \text{(R9.1-1)}$$

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

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

Because the system is well insulated, we shall neglect the $\dot{Q}_C$ and further define

$$\dot{T}_E = \frac{\dot{Q}_E}{\sum N_i C_{P_i}} \tag{R9.1-2}$$

is called the *electrical heating rate*, $\dot{T}_E$. The second term, $\dot{T}_S$, in Equation (R9.1-1) is called the *self-heating rate*

$$\dot{T}_S = \frac{(-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{P_i}} \tag{R9.1-3}$$

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, of the reactor in order to prevent runaway reactions.

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 where the self-heating rate becomes greater than the electrical heating rate

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

This temperature is called the *onset* temperature. A typical thermal history is shown in Figure R9.1-2.

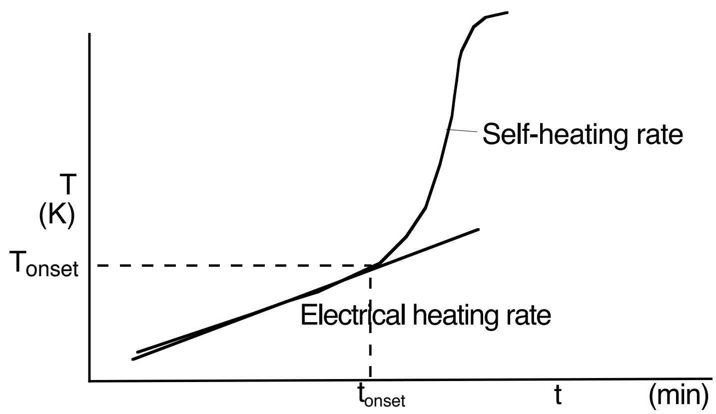

Figure R9.1-2 Typical temperature history for thermal scan with the ARSST.

The self-heating rate can be easily obtained by differentiating the temperature-time trajectory.

We can rewrite Equation (R9.1-1) in the form

$$\boxed{\frac{dT}{dt} = \dot{T}_E + \dot{T}_S} \tag{R9.1-4}$$

R9.1.1 The φ Factor – Accounting for the Heat Capacities of the Bomb Calorimeter

Because we are taking our system as the contents inside the bomb as well as the bomb itself, the term $\sum N_i C_{P_i}$ needs to be modified to account for the heat absorbed by the bomb calorimeter. Thus, we include terms for the mass of the calorimeter, m_b, and heat capacity of the calorimeter, $\tilde{C}_{P_b}$, that hold the reactants in the sum $\sum N_i C_{P_i}$.

Neglecting ΔC_P and assuming only A, B inerts are fed it can be shown that

$$\sum N_i C_{P_i} = N_{A0}C_{P_A} + N_{B0}C_{P_B} + N_i C_{P_i} + m_b \tilde{C}_{P_b} \tag{R9.1-5}$$

Further, we let mass inside the bomb (i.e., the mixture of reactants plus inerts) be m_S and let $\tilde{C}_{P_S}$ be the corresponding heat capacity of this mixture, then

$$m_S \tilde{C}_{P_S} = N_{A0}C_{P_A} + N_{B0}C_{P_B} + N_I C_{P_I}$$

where m_S is the total weight of sample inside the bomb and $\tilde{C}_{P_S}$ is the heat capacity of the sample. Using nomenclature in the ARSST instruction manual, we define parameter ϕ:

The ϕ factor

$$\phi = \frac{m_S \tilde{C}_{P_S} + m_b \tilde{C}_{P_b}}{m_S \tilde{C}_{P_S}} \tag{R9.1-6}$$

where ϕ accounts for the heat capacity of the bomb, that is,

$$\sum N_i C_{P_i} = m_S \tilde{C}_{P_S} \phi \tag{R9.1-7}$$

We want to keep ϕ as close to 1.0 as possible. Substituting for Equation (R9.1-7) into Equations (R9.1-2) and (R9.1-3)

$$\boxed{\dot{T}_E = \frac{\dot{Q}_E}{m_S \tilde{C}_{P_S} \phi}} \tag{R9.1-8}$$

$$\boxed{\dot{T}_S = \frac{(-\Delta H_{Rx})(-r_A V)}{m_S \tilde{C}_{P_S} \phi}} \tag{R9.1-9}$$

Application to a Hydrolysis of Acetic Anhydride. A 6.7 molar solution of acetic anhydride are placed in ARSST with a 20.2 M solution of water. The sample volume is 10 ml. We will analyze this system and compare theory and experiment to find the activation energy, E, and the heat of reaction, ΔH_{Rx}. We now apply our algorithm to analyzing the ARSST

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

$$A + B \longrightarrow 2C$$

These data are shown in Figure R9.1-3.

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		

Total volume 10 ml with
Water 3.638 g

Acetic anhydride 6.871 g
($M_s Cp_s$ = 28.012 J/°C and ϕ = 1.004 and $m_s\ Cp_s = \phi M_s Cp_s$)

$$\Sigma\Theta_{iC}C_{P_i} = (189.7 + 3(75.4)) = 415 \frac{J}{molK}$$

$$N_{A0} = C_{A0}V = (0.01 \ dm^3) 6.7 \frac{mol}{dm^3} = 0.067 \ mol$$

$$\dot{m}_S C_{P_S} = N_{A0} \Sigma\Theta_i C_{P_i} = (0.067)(415) = 28 \ J/C$$

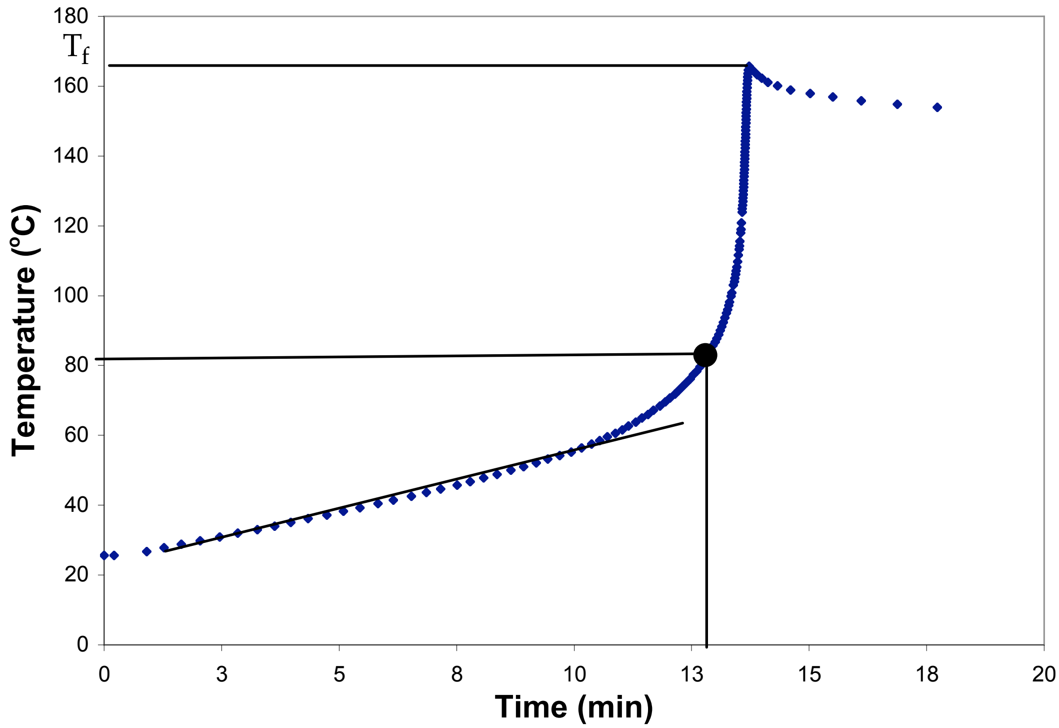

Figure R9.1-3 Temperature time trajectory for hydrolysis of acetic anhydride

We note from the figure that the time of onset is 13.3 minutes and the corresponding temperature is 85°C.

Parameters:

Starting temperature $T_o = 25.6°C$
From the temperature-time trajectory, the onset temperature (T_{onset}) is 85.7°C while the final temperature (T_f) is 165.7°C. The time to reach the onset temperature (t_{onset}) is 13.0 min.
Electrical heating rate $\dot{T}_E = 2°C/min$.

Solution

Determining Heat of Reaction

During the region where the $\dot{T}_S >> \dot{T}_E$ we can assume the system to operate adiabatically in which case Eqn. (8-49), for $\Delta C_P = 0$, i.e.,

$$N_{A0}X\left(-\Delta H_{Rx}\right)=\Sigma N_iC_{P_i}\left(T-T_{on}\right) \qquad \text{(R9.1-12)}$$

can be put in the form

$$N_{A0}\left(X-X_{on}\right)\left(-\Delta H_{Rx}\right)=\Sigma N_iC_{P_i}\left(T-T_{on}\right) \qquad \text{(R9.1-13)}$$

where X_{on} is the conversion at the onset temperature T_{on}. Assuming the reaction goes to completion, X=1 and $T = T_f$. Equation (R9.1-14) can be rearranged to obtain the heat of reaction

$$\left(-\Delta H_{Rx}\right)=\frac{\Sigma N_iC_{P_i}\left(T_f-T_{on}\right)}{N_{A0}\left(1-X_{on}\right)}=\frac{m_S\tilde{C}_{P_S}\phi\overbrace{\left(T_f-T_{on}\right)}^{\text{ATR}}}{N_{A0}\left(1-X_{on}\right)} \qquad \text{(R9.1-14)}$$

$$\text{Note: } \Sigma N_iC_{P_i}\equiv m_S\tilde{C}_{P_S}\phi$$

In terms of the mass of reactant A, $m_A = N_{A0}\left(MW_A\right)$,

$$\boxed{-\Delta H_{Rx}=\frac{C_{P_S}\phi\left(ATR\right)}{\left(m_A/m_S\right)\left(1-X_{on}\right)}\left(MW_A\right)} \qquad \text{(R9.1-15)}$$

where $ATR = (T_f - T_{on})$, is the adiabatic temperature rise and $\left(m_A/m_S\right)$ is the mass fraction of A in the calorimeter. This equation is the one in the ARSST instruction manual.

Conversion at the Onset Temperature (X_{onset})

Using Equations (9-1.3, 9-1.4) and the mole balance,

$$\frac{dC_A}{dt}=r_A \qquad \text{(R9.1-19)}$$

assuming the electrical heating rate is constant up to the onset temperature, one has:

$$\frac{dT}{dt}=\dot{T}_E+\frac{\left(-\Delta H_{Rx}\right)V}{m_S\tilde{C}_{P_S}\phi}\left(-\frac{dC_A}{dt}\right) \qquad \text{(R9.1-18)}$$

$$C_A=C_{A0}-C_{A0}X$$

or

$$\int_{T_0}^{T_{onset}}dT=\dot{T}_E\int_0^{t_{onset}}dt+\frac{\left(-\Delta H_{Rx}\right)VC_{A0}}{m_S\tilde{C}_{P_S}\phi}\int_0^{X_{onset}}dX \qquad \text{(R9.1-19)}$$

$$T_{onset}-T_0=\dot{T}_E\ t_{onset}+\frac{\left(-\Delta H_{Rx}\right)}{m_S\tilde{C}_{P_S}\phi}N_{A0}X_{onset} \qquad \text{(R9.1-20)}$$

From Equation (R9.1-12) for $X = 1$, $T = T_f$

$$-\Delta H_{Rx}N_{A0}=m_S\tilde{C}_{P_S}\phi\left(T_f-T_o\right) \qquad \text{(R9.1-21)}$$

Combining Equations (R9.1-21) and (R9.1-22)

$$\boxed{X_{onset} = \frac{T_{onset} - T_0 - \dot{T}_E \bullet t_{onset}}{T_f - T_0}} \qquad \text{(R9.1-22)}$$

The onset occurred after 13 minutes when the electrical heating rate was 2°C/min. The temperature at onset was 358.7K.

$$X_{onset} = \frac{85.7°C - 25.6°C - (2°C/\min * 13.3\min)}{165.7°C - 25.6°C} = 0.24$$

Heat of reaction (ΔH_{Rx})

From Equation (R9.1-14):

$$-\Delta H_{Rx} = \frac{m_S \tilde{C}_{P_S} \phi (T_f - T_{onset})}{N_{A0}(1 - X_{onset})} \qquad \text{(R9.1-14)}$$

$$-\Delta H_{Rx} = \frac{28\ \text{J/°C} * 1.004 * (165.7°C - 85.7°C)}{(6.7\,\text{mol/dm}^3) * 10 * 10^{-3}\,\text{dm}^3 * (1 - 0.24)} = 44{,}432\ \text{J/mol} = 44.4\ \text{kJ/mol}$$

Activation energy (E)

Determining the Activation Energy

The temperature-time trajectory for the hydrolysis of acetic anhydride is shown in Figure R9.1-3. The self-heating rate $\dot{T}_S$ can be calculated as a function of temperature from this curve or determined from the ARSST output directly.

To find the activation energy we begin by substituting for $-r_A$ in Equation (R9.1-9)

$$\dot{T}_S = \frac{(-\Delta H_{Rx})\left[(kC_A C_B)V\right]}{m_S C_{P_S} \phi}$$

for constant C_B,

$$\dot{T}_S = \frac{-\Delta H_{Rx}\left[Ae^{-E/RT} C_A C_{B0} V\right]}{m_S C_{P_S} \phi} \qquad \text{(R9.1-15)}$$

Shortly after onset, the electrical heating rate, $\dot{T}_E$, is either shut off, or becomes negligible wrt $\dot{T}_S$. We now take the log of the self-heating rate, $\dot{T}_S$ (c.f. Equation R9.1-15).

$$\ln \dot{T}_S = \ln \frac{(-\Delta H_{Rx})VC_{B0}}{m_S \tilde{C}_{P_S} \phi} + \ln A + \ln C_A - \frac{E}{RT} \qquad \text{(R9.1-16)}$$

and plot $\dot{T}_S$ vs, $\frac{1}{T}$ neglecting changes in $\ln C_A$ (i.e., use initial rates) to obtain the activation energy from the slope (–E/R) of the line as shown in Figure R9.1-4. $\dot{T}_S$ is generated directly from the computer linked to the ARSST.

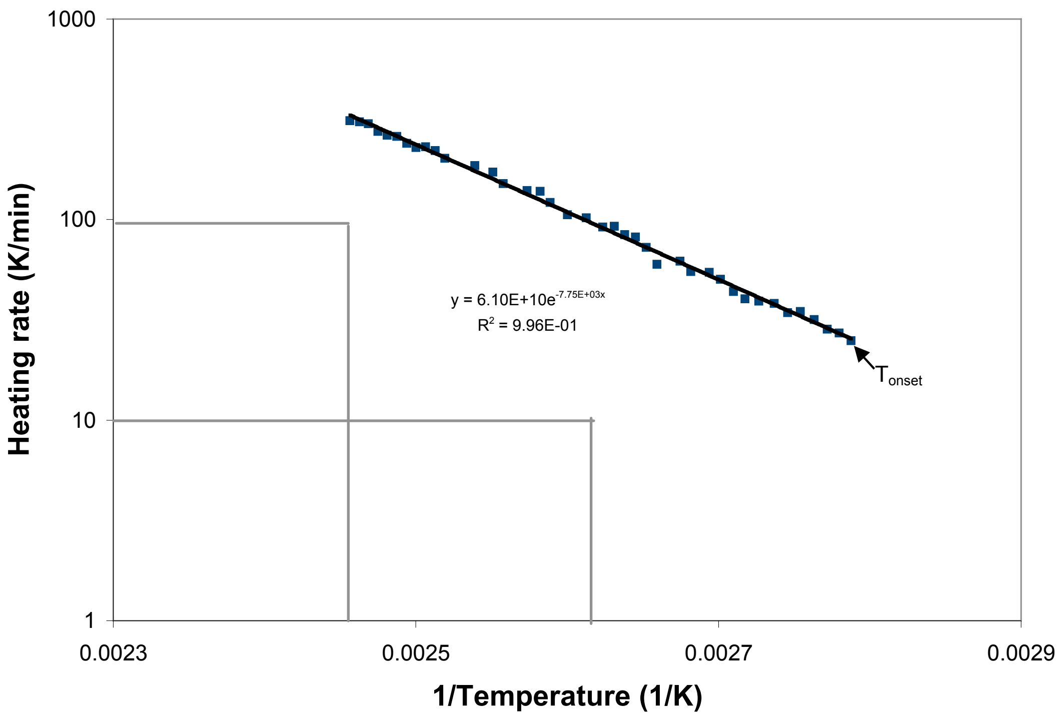

Figure R9.1-4 Arhenius plot of self-heating rate for of acetic anhydride.

From the slope of the plot we find the activation to be

$$E = -R \cdot \text{Slope} = -\left(1.987 \frac{\text{cal}}{\text{mol} \bullet \text{K}}\right)(-7,750\text{K})$$

$$E = 15.4 \frac{\text{kcal}}{\text{mol}}$$

<u>Calculating the Frequency Factor, A</u>

We now will calculate A using the onset temperature T_{on} and the heating rate at the onset, $\dot{T}_{Son}$. Recalling Equation (R9.1-11) and rearranging

$$A = \dot{T}_{Son}\left[\frac{\left(m_S \tilde{C}_{P_S}\right)}{\left(-\Delta H_{Rx}\right)C_A C_{B0} V}\right]\frac{1}{\left[\exp\left(-\frac{E}{RT_{on}}\right)\right]} \qquad \text{(R9.1-17)}$$

Now some conversion will have occurred during the electrical heating time, t_{elec}, up to the point of onset. In this case t_{elec} was 13 minutes to T_{onset}, which was 358.7K. Therefore the concentration of A at the onset is

$$C_A = C_{A0}\left(1 - X_{on}\right)$$

The equation for conversion at the onset was calculated using Equation (R9.1-22)

$$X_{onset} = 0.24$$

$$A = \frac{24.8\text{K}}{\text{min}}\left(\frac{1}{317\text{K}}\right)\frac{1}{\exp\left(\frac{-15400}{(1.987)(358.7)}\right)6.7(1-0.24)\left(\frac{\text{mol}}{\text{dm}^3}\right)}$$

$$= 3.7\times 10^{7}\left(\text{dm}^3/\text{mol}\right)/\text{min}$$

Table R9.1-1 Balance Equations

Mole Balance
$$\frac{dN_A}{dt} = r_A V$$

Rate Law
$$r_A = -k' C_A C_B$$

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

Stoichiometry
$$V = V_0$$

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{A0}(\Theta_B - X)$$

$$\Theta_B = 3$$

As a first approximation we take

$$C_B \cong C_{A0}\Theta_B = C_{B0}$$

(Note: In Problem P9-10$_C$ we do not assume C_{B0} is constant)

$$r_A = -k' C_{B0} C_A = Ae^{-E/RT} C_{B0} C_A \qquad \text{(R9.1-10)}$$

Combine
$$k = k' C_{B0}$$

$$\frac{dC_A}{dt} = -kC_A$$

Energy Balance
$$\frac{dT}{dt} = \dot{T}_E + \dot{T}_S \qquad \text{(R9.1-4)}$$

$$\dot{T}_E = \frac{\dot{Q}_E}{m_S \tilde{C}_{P_S}} \qquad \text{(R9.1-8)}$$

$$\dot{T}_S = \frac{(-\Delta H_{Rx})(-r_A V)}{m_S \tilde{C}_{P_S}} \qquad \text{(R9.1-9)}$$

$$\dot{T}_S = \frac{(-\Delta H_{Rx}) A \exp^{(-E/RT)} C_{B0} C_A V}{m_S \tilde{C}_{P_S}} \qquad \text{(R9.1-11)}$$

The equations shown in Table R9.1-1 are solved using the Polymath program shown in Table R9.1-2.

Table R9.1-2 Balance Equations

POLYMATH Results

POLYMATH Report 11-13-2003, Rev5.1.232

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	25	25
CA	6.7	5.158E-60	6.7	5.158E-60
T	298.6	298.6	427.51615	427.51615
CB0	20.1	20.1	20.1	20.1
V	0.01	0.01	0.01	0.01
mS_CpS	28.135	28.135	28.135	28.135
dHrx	-4.443E+04	-4.443E+04	-4.443E+04	-4.443E+04
A	3.7E+07	3.7E+07	3.7E+07	3.7E+07
E	1.54E+04	1.54E+04	1.54E+04	1.54E+04
R	1.987	1.987	1.987	1.987
Tedot	2	0	2	0
rA	-0.0266102	-4.5976307	-5.136E-59	-5.136E-59
Tsdot	0.420239	8.11E-58	72.607758	8.11E-58

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(CA)/d(t) = rA
[2] d(T)/d(t) = Tedot+Tsdot

Explicit equations as entered by the user

[1] CB0 = 20.1
[2] V = 0.01
[3] mS_CpS = 28.135
[4] dHrx = -44432
[5] A = 3.7e7
[6] E = 15400
[7] R = 1.987
[8] Tedot = if (T>85.7+273) then 0 else 2
[9] rA = -A*exp(-E/R/T)*CA*CB0
[10] Tsdot = (-dHrx)*(-rA*V)/mS_CpS

Comments

[1] d(CA)/d(t) = rA
Mole balance on Acetic Anhydride
[2] d(T)/d(t) = Tedot+Tsdot
Energy Balance
[3] rA = -A*exp(-E/R/T)*CA*CB0
Rate of the reaction-mol/l.min
[4] V = 0.01
Volume of the reactive solution-l
[5] mS_CpS = 28.135
J/C
[6] dHrx = -44432
Heat of reaction-J/mol
[7] A = 3.7e7
rate constant- 1/min
[8] E = 15400
cal/mol
[9] R = 1.987
cal/mol.K

```
[10]  Tedot = if (T>85.7+273) then 0 else 2
       (oK/min) After the onset point, electrical heating is only to compensate for heat loss
[11]  Tsdot =  (-dHrx)*(-rA*V)/mS_CpS
       Self-heating rate (oK/min)
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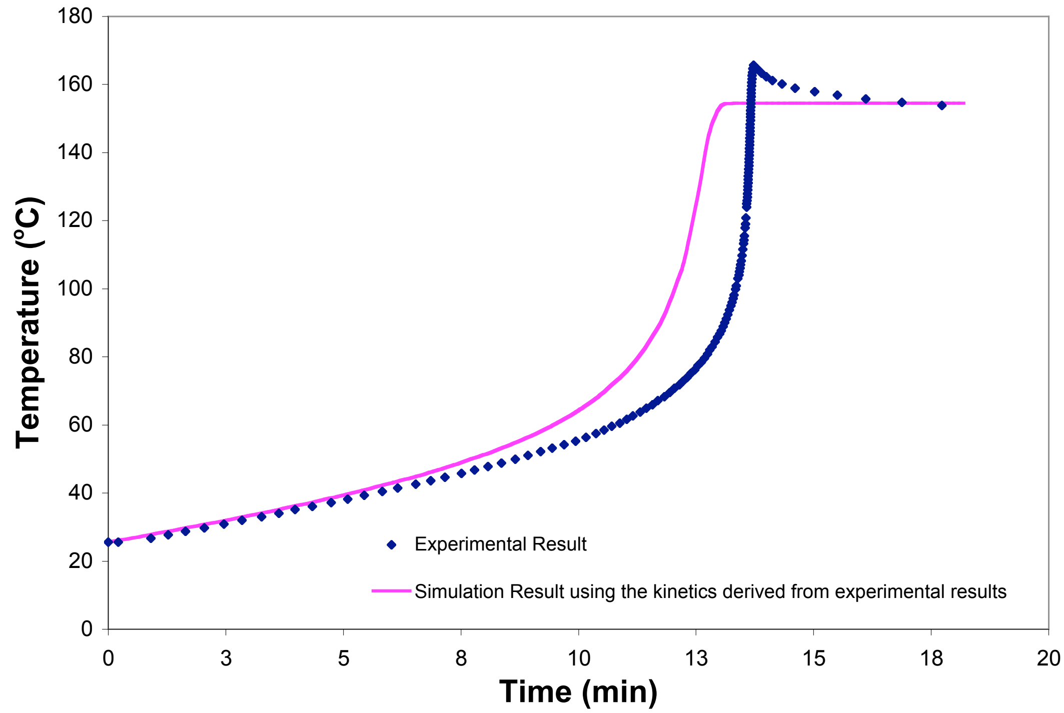
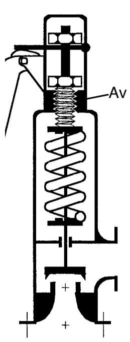


Figure R9.1-5 Comparison of model and experiment.

We now use the values of ΔH_{Rx}, E, and A to calculate the temperature-time trajectory. We note we get reasonable agreement between our model and experiment.

RELIEF VALVE SIZING CALCULATIONS



Typically two runs are made using the ARSST. One run is at the pressure of the relief valve or rupture desk stetting and one at the vessel rupture pressure.

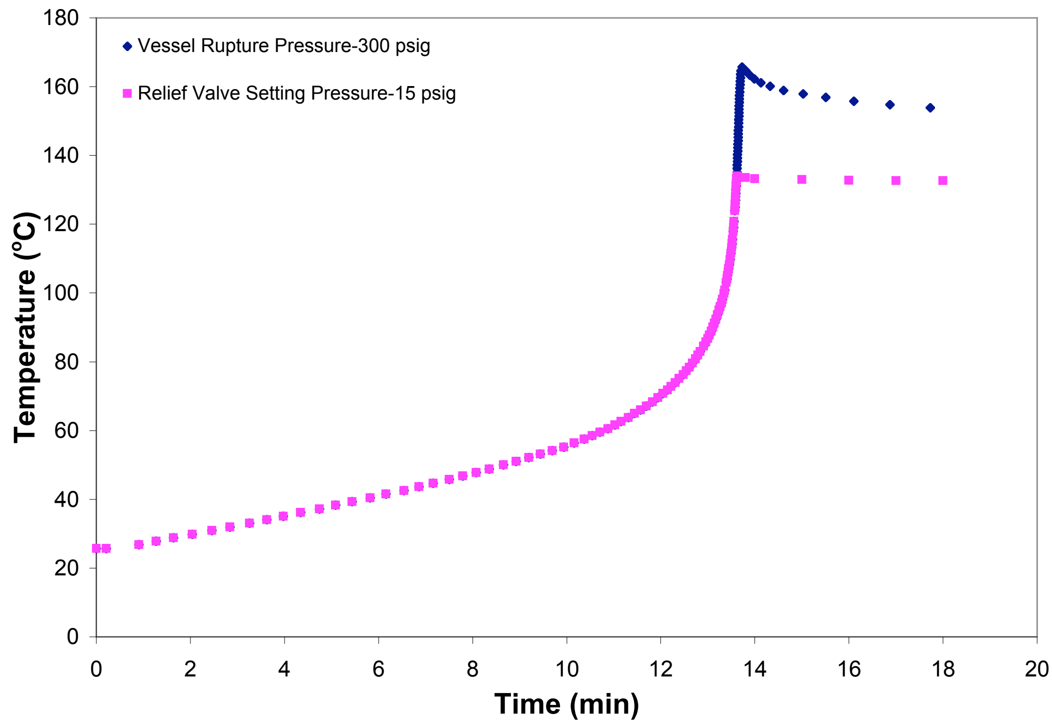


Figure R9.1-6 ARSST runs at 15 psig and 300 psig.

In sizing a relief valve we first need to find the tempering temperature, which is the temperature at which the self-heating rate drops to zero for a given pressure, either the rupture disk pressure or relief valve setting. The figure below shows the temperature as obtained from a plot of the self-heating rate, $\dot{T}_s$, as a function of temperature T

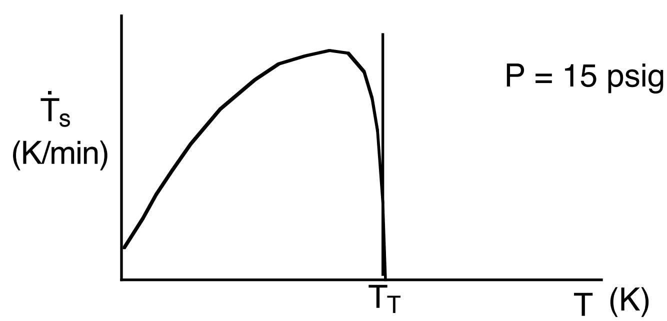


Figure R9.1-7 Finding the tempering temperature.

The tempering temperature, T_T, is the temperature at which $\dot{T}_s$ falls back to zero. The self-heating rate drops to zero shortly after the mixture reaches it's boiling point at the relief valve set pressure because the energy generated by the heat of reaction is taken up by the latest heat of vaporization from the boiling liquid. The second run is carried out at a higher pressure, the vessel rupture pressure setting, and the tempering temperature, T_T found in Run 1, is used to find the self-heating rate, $\dot{T}_{s1}$ at 300 psi which will be used to size the relief valve. Again, T_T is determined from the ram at 15 psig.

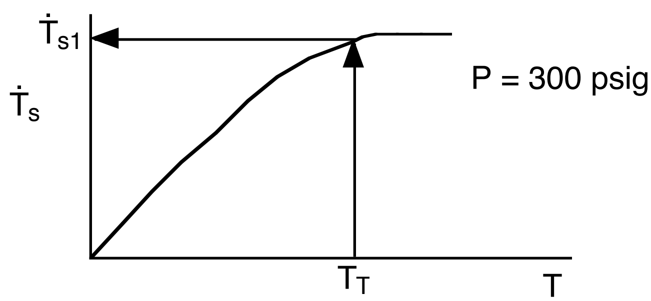


Figure R9.1-8 Finding the self-heating rate at the tempering temperature.

We now apply these concepts to the hydrolysis of acetic anhydride. From Figure R9.1-9, we see the temperature for the run at 15 psig is 134°C. This temperature corresponds to a heating rate T_{S1} of 311°C/min for the run at 300 psig.

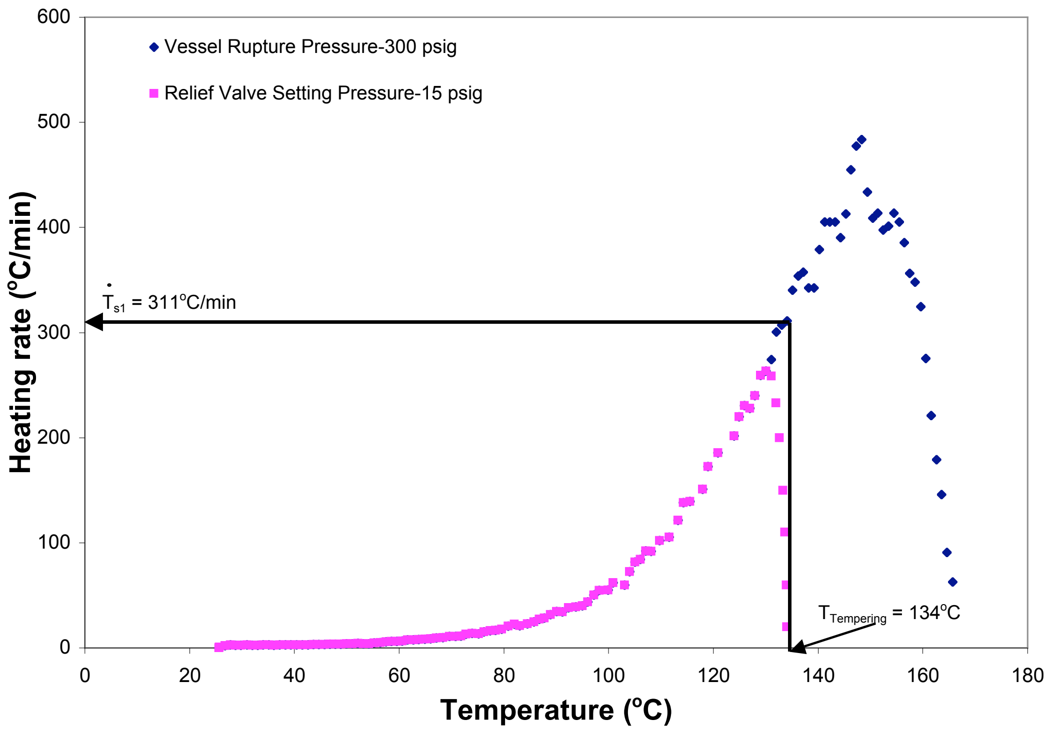
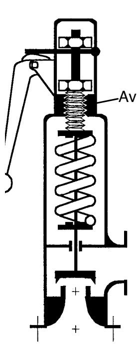


Figure R9.1-9 Self-heating curve for the hydrolysis of acetic anhydride



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 builds up to runaway and explosive conditions. There is a disk covering the vent in the relief valve that breaks once the reactor pressure exceeds the set pressure P_S, and allows the contents to flow out through the vent. The heat of vaporization from the liquid vaporizing at exit the vent once the pressure is released will also cool the reactor contents. The self-heating rate is used directly to calculate the vent size necessary to successfully release all the contents of the reactor. The necessary vent area is given by the equation.

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

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 kg.

Find the Vent Diameter Solution

The following is the procedure to calculate the diameter of the relief valve of a 2.3 m^3 industrial vessel.

Industrial Vessel volume = 2.3 m^3

Filling factor = 50% (i.e., the industrial reactor will be half full)

Solution density = 1000 kg/m^3

Vent Area (See ARSST Manual)

$$A = 1.5 * 10^{-5} \frac{m_S \dot{T}_S}{FP_S} \tag{R9.1-23}$$

m_S = mass of reactants = 2.3 m^3 * 50% * 1000 kg/m^3 = 1150 kg

T_T = Tempering Temperature = 134°C

$\dot{T}_S$= self-heating rate at tempering temperature = 311°C/min

F = flow reduction factor = 0.85 for L/D = 50 (From the ARSST manual, page 6-9, August 1999)

P_S = relief set pressure = 15 psig = 29.7 psia

So

$$A = 1.5 * 10^{-5} \frac{1150 * 311}{0.85 * 29.7} = 0.21 \text{ m}^2 \tag{R9.1-24}$$

Vent Diameter

$$D = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4 * 0.21 \text{ m}^2}{3.1416}} = 0.052 \text{ m} \tag{R9.1-25}$$

To insure safe operation we need a relief valve with a diameter of 5.2 cm or about 2 inches.