We have seen in the text that exothermic reactions in a CSTR can lead to unstable operating conditions. There are two approaches to testing for stability, the first is graphical and is conceptually easier to grasp and the second is mathematically rigorous. You should become familiar with both and be able to apply the rigorous test, since it will work in all situations. **Both** approaches require the simulataneous solution of the material and energy balances to establish the temperature and composition exiting the reactor. The first method, which employs the Van Heerden diagram, examines the rate of energy removal and generation about this operating temperature. The second method evaluates the unsteady-state material and energy balances at the steady-state solution to determine if small excursions in temperature or composition always restore the system to the steady-state values.

To illustrate the concepts and to get an intuitive feel for CSTR stability, we will use an example based on propylene oxide (PO) hydrolysis to propylene glycol (PG) [adapted from Fogler]. The reaction

$$\mathrm{CH_2(O)CHCH_3} \; + \mathrm{H_2O} \;\overset{\mathrm{H_2SO_4}}{\longrightarrow}\; \mathrm{CH_2(OH)CH_2(OH)CH_3} \tag{1}$$

is conducted in a large excess of water (W) and with a methanol (ME) co-solvent. Under the conditions we will examine

$$r = \left(16.96 \times 10^{12} \times \exp\left(\frac{-32,400\text{Btu/lbmole}}{RT}\right) \text{hr}^{-1}\right) \times c_{\text{propylene oxide}}$$

The CSTR parameters and inlet conditions are

Base Case

variable	value	units
V_R	40.1	ft^3
Q_f	326.34	ft^3/hr
N_{POf}	43.03	lbmole/hr
N_{Wf}	802.8	lbmole/hr
N_{MEf}	71.78	lbmole/hr
N_{PGf}	0	lbmole/hr
T_f	75	°F
A_h	40	ft^2
T_a	85	°F
U	100	Btu/hr-ft^2-°F

Thermodynamic data are tabulated. You will need to assume the heat capacity does not change with temperature.

Thermodynamic Properties

Compound	$\overline{C}_p$ (Btu/lbmole-°F)	$\overline{H}_f^{518}$ (Btu/lbmole)
propylene oxide	35	-66,600
water	18	-123,000
propylene glycol	46	-226,000
methanol	19.5	-

The material and energy balances for this single reaction system reduce to

$$0 = c_{PO} + c_{PO}k\theta - c_{POf} \tag{2}$$

$$0 = UA(T_a - T) - \Delta H_R k c_{PO} V_R + \sum N_{jf}\overline{C}_{pj}(T_f - T) \tag{3}$$

The solution to these two algebraic equations for the Base Case conditions is

$$c_{PO} = 0.0892 \qquad \text{lbmole/ft}^3$$

$$T = 560.31 \qquad \text{R}$$

The graphical test for stability (a Van Heerden Diagram) entails substituting c_{PO} from Equation 2 into Equation 3

$$0 = UA(T_a - T) - \frac{\Delta H_R k c_{POf} V_R}{1 + k\theta} + \sum N_{jf}\overline{C}_{pj}(T_f - T) \tag{4}$$

and resorting Equation 4 to give

$$UA(T - T_a) + \sum N_{jf}\overline{C}_{pj}(T - T_f) = -\frac{\Delta H_R k c_{POf} V_R}{1 + k\theta} \tag{5}$$

Recognizing that we need only consider stability for exothermic reactions, we choose to rewrite the last term in Equation 5

$$UA(T - T_a) + \sum N_{jf}\overline{C}_{pj}(T - T_f) = \frac{|\Delta H_R| k c_{POf} V_R}{1 + k\theta} \tag{6}$$

The two sides of Equation 6 are renamed

$$Q_{\text{removal}} = UA(T - T_a) + \sum N_{jf}\overline{C}_{pj}(T - T_f)$$

$$Q_{\text{generation}} = \frac{|\Delta H_R| k c_{POf} V_R}{1 + k\theta}$$

Note the simultaneous solution to Equations 2 and 3 is also the solution to Equation 6, *i.e.*

$$Q_{\text{removal}} = Q_{\text{generation}}$$

As you run the simulation (`cstr_vanheerden_jacobian.m`) for the Base Case, curves for Q_{removal} and $Q_{\text{generation}}$ are generated. Notice they intersect at $T = 560.31R$. This CSTR condition is stable because the slope of the removal curve is greater than the slope of the generation curve. Using the plots can you describe why it is stable?

Now let's consider the rigorous test of stability. Following the the development in the text we must evaluate the partial derivatives of the unsteady-state material and energy balances for a STR at the steady-state solution. These values are the elements of the Jacobian of the linearized equations. We will let propylene oxide be component A

The material balance is

$$\frac{dc_A}{dt} = \frac{c_{Af} - c_A}{\theta} - kc_A = f_1(c_A, T)$$

and the partial derivatives are

$$\frac{\partial f_1}{\partial c_A} = \frac{-1}{\theta} - k = a_{11}$$

$$\frac{\partial f_1}{\partial T} = -kc_{As}\frac{E}{RT_s^2} = a_{12}$$

The energy balance is

$$\frac{dT}{dt} = \frac{UA(T_a - T)}{V_R \sum_j c_j \overline{C}_{pj}} - \frac{\Delta H_R k c_A}{\sum_j c_j \overline{C}_{pj}} + \frac{Q_f \sum_j c_{jf} \overline{C}_{pj}(T_f - T)}{V_R \sum_j c_j \overline{C}_{pj}} = f_2(c_A, T)$$

and the partial derivatives are

$$\frac{\partial f_2}{\partial c_A} = \frac{-\Delta H_R k}{\sum_j c_j \overline{C}_{pj}} = a_{21}$$

$$\frac{\partial f_2}{\partial T} = \frac{-UA}{V_R \sum_j c_j \overline{C}_{pj}} - \frac{\Delta H_R k c_{As} E}{\sum_j c_j \overline{C}_{pj} R T_s^2} - \frac{\sum_j N_{jf} \overline{C}_{pj}}{V_R \sum_j c_j \overline{C}_{pj}} = a_{22}$$

The solution ($T = 560.31$ and $c_A = 0.0892$) is stable if the eigenvalues of the Jacobian have negative real values, which can be found numerically within Matlab using the command lines

```
A = [a11, a12; a21, a22]
eigenvalues_of_the_Jacobian = eig(A)
```

You could also solve the determinant of the following

$$\begin{vmatrix} a_{11}-\lambda & a_{12} \\ a_{21} & a_{22}-\lambda \end{vmatrix} = 0$$

which is a quadratic equation in λ, viz.

$$\lambda^2 - (a_{11}+a_{22})\lambda + (a_{11}a_{22} - a_{21}a_{12}) = 0$$

For the Base Case, which is illustrated in the simulation output,

$$A = \begin{bmatrix} -12.035 & -0.018047 \\ 2682.2 & 2.3508 \end{bmatrix}$$

and the eigenvalues are -6.6681 and -3.0163, so the solution is stable.

Now explore the effects of changing some operating parameters that could be affected by plant conditions. Consider what would happen if the cooling fluid medium temperature changed. For this example we have set it to a constant, such as would be found for boiling a fluid. If the pressure on the boiling side changed, the temperature T_a would change. Change this by 20 degrees and see how the temperature and composition in the reactor change. Could you have predicted these trends? Next consider that the cooling line gets fouled so the overall heat transfer coefficient decreases by 30%. Test the effect of changing U by up to 30%. (Note if you change these variables by too much the algebraic equation solver in Matlab will not converge for the initial guess in the program.)