or

$$k_{1,338} = 0.942 \text{ min}^{-1} \tag{ii}$$

Similarly, for the batch run at 25°C we find

$$k_{1,298} = 0.0909 \text{ min}^{-1} \tag{iii}$$

Assuming an Arrhenius temperature dependency, the ratio of forward rate constants at these two temperatures gives

$$\frac{k_{1,298}}{k_{1,338}} = \frac{0.0909}{0.942} = \frac{k_{10}e^{-E_1/R(298)}}{k_{10}e^{-E_1/R(338)}}$$

from which the activation energy of the forward reaction is evaluated, giving

$$E_1 = 11{,}600 \text{ cal/mol}$$

The complete rate constant of the forward reaction is then

$$k_1 = 3 \times 10^7 e^{-(11{,}600\text{cal/mol})/RT} = e^{17.2 - 11{,}600/RT}$$

Noting that $k_1/k_2 = K$ where K is given in Example 1, we then can find the value for k_2.

Summary. For the reversible first-order reaction of Examples 1 and 2 we have

---

$$A \underset{2}{\overset{1}{\rightleftarrows}} R; \qquad K = \frac{C_{Re}}{C_{Ae}}; \qquad -r_A = r_R = k_1 C_A - k_2 C_R$$

Equilibrium: $\quad K = e^{18{,}000/RT - 24.7}$

Rate constants: $\quad k_1 = e^{17.2 - 11{,}600/RT}, \text{ min}^{-1}$

$\qquad k_2 = e^{41.9 - 29{,}600/RT}, \text{ min}^{-1}$

From these values the X_A versus T chart for any specific C_{A0} can be prepared, and for this purpose the electronic computer is a great timesaver. Figure E2 is such a plot prepared for $C_{A0} = 1$ mol/liter and $C_{R0} = 0$. Also see the dust jacket of this book.

Since we are dealing with first-order reactions this plot can be used for any C_{A0} value by properly relabeling the rate curves. Thus for $C_{A0} = 10$ mol/liter simply multiply all the rate values on this graph by a factor of 10.

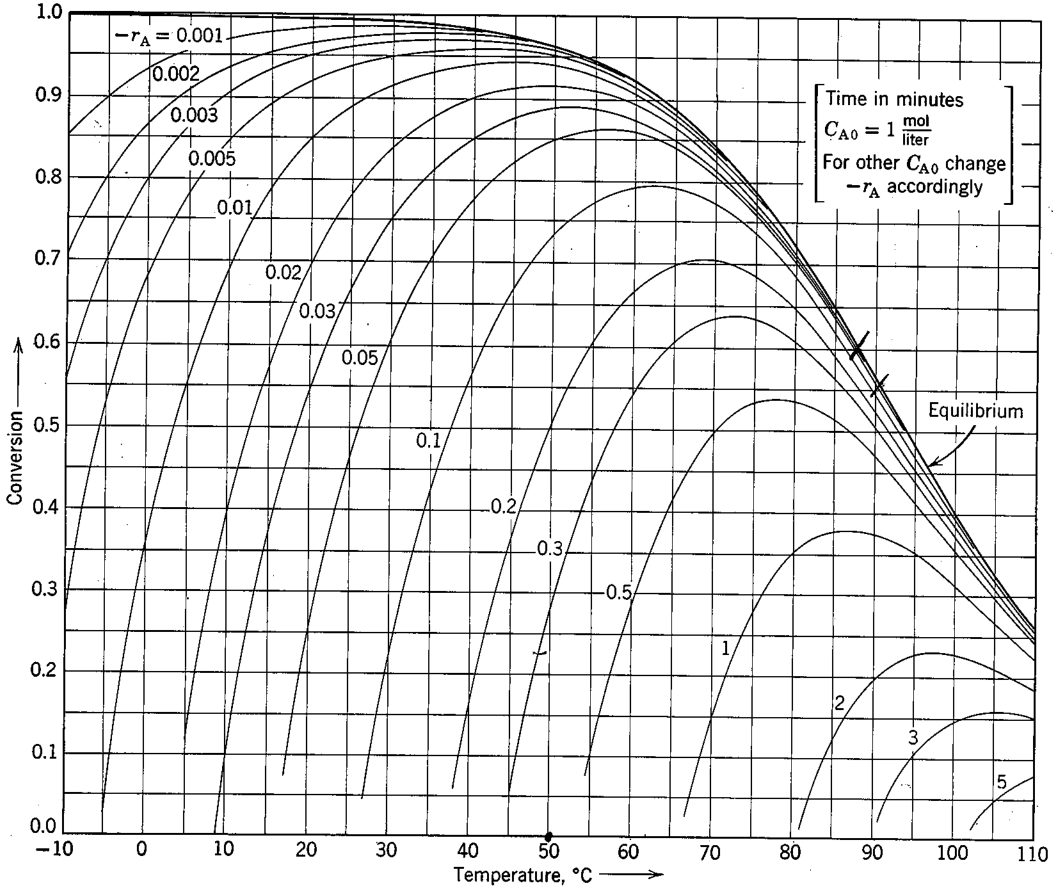
EXAMPLE 3. Performance for the optimal temperature progression

Using the optimal temperature progression in a plug flow reactor for the reaction of the previous examples

(*a*) Calculate the space time needed for 80% conversion of a feed where $C_{A0} = 1$ mol/liter.

(*b*) Plot the temperature and conversion profile along the length of the reactor.

Let the maximum allowable operating temperature be 95°C.



$-r_A = 0.001$
0.002
0.003
0.005
0.01
0.02
0.03
0.05
0.1
0.2
0.3
0.5
1
2
3
5
Time in minutes
$C_{A0} = 1 \frac{\text{mol}}{\text{liter}}$
For other C_{A0} change
$-r_A$ accordingly
Equilibrium
Conversion
Temperature, °C

FIGURE E2.

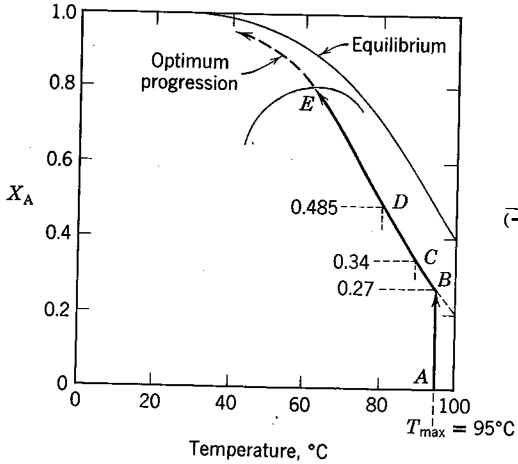


FIGURE E3a.

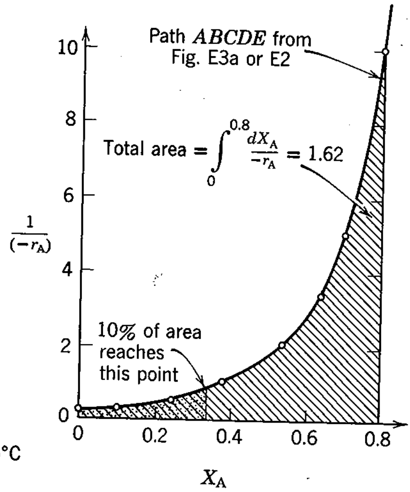


FIGURE E3b.

SOLUTION

(*a*) *Minimum space-time.* On the conversion-temperature graph (Fig. E2) draw the locus of maximum rates. Then remembering the temperature restriction draw the optimum path for this system (line *ABCDE* in Fig. E3*a*) and integrate graphically along this path to obtain

$$\tau_{opt} = C_{A0} \int_0^{0.8} \frac{dX_A}{(-r_A)_{\text{optimum path } ABCDE}}$$

From Fig. E3*b* the value of this integral is found to be

$$\tau = 1.62 \text{ min} = 97 \text{ sec}$$

(*b*) *T and X_A profiles through the reactor.* Let us take 10% increments through the reactor by taking 10% increments in area under the curve of Fig. E3*b*. This procedure gives $X_A = 0.34$ at the 10% point, $X_A = 0.485$ at the 20% point, etc. The corresponding temperatures are then 362°K at $X_A = 0.34$ (point *C*), 354°K at $X_A = 0.485$ (point *D*) etc.

In addition we note that the temperature starts at 95°C, and at $X_A = 0.27$ (point *B*) it drops. Measuring areas in Fig. E3*b* we see that this happens after the fluid has passed 7% of the distance through the reactor.

In this manner the temperature and conversion profiles are found. The result is shown in Fig. E3*c*.

EXAMPLE 4. Mixed reactor performance

A concentrated aqueous A-solution of the previous examples ($C_{A0} = 4$ mol/liter, $F_{A0} = 1000$ mol/min, $C_p = C_{p,H_2O}$) is to be 80% converted in a mixed reactor.

(*a*) What size of reactor is needed?

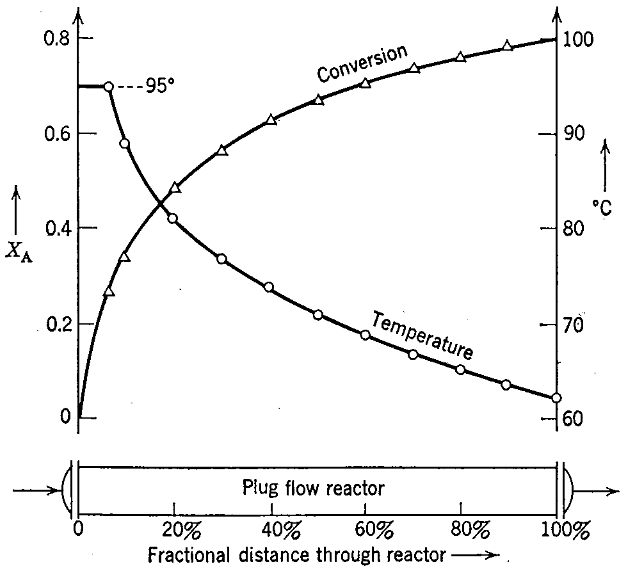


FIGURE E3c.

(*b*) What is the heat duty if feed enters at 25°C and product is to be withdrawn at this temperature?

(*c*) Compare this reactor size with the minimum size when the optimum temperature progression is used.

SOLUTION

(*a*) *Reactor volume.* For $C_{A0} = 4$ mol/liter we may use the X_A versus T chart of Fig. E2 as long as we multiply all rate values on this chart by 4.

Following Fig. 10 the mixed flow operating point should be located where the locus of optima intersects the 80% conversion line (point A on Fig. E4*a*). Here the reaction rate has the value

$$-r_A = 0.4 \text{ mol A converted/min}\cdot\text{liter}$$

From the performance equation for mixed reactors, Eq. 5.11, the volume required is given by

$$V = \frac{F_{A0}X_A}{(-r_A)} = \frac{(1000 \text{ mol/min})(0.80)}{0.4 \text{ mol/min}\cdot\text{liter}} = 2000 \text{ liters}$$

(*b*) *Heat duty.* The slope of the energy balance line is

$$\text{slope} = \frac{\mathbf{C_p}}{-\Delta\mathbf{H_r}} = \frac{(1000 \text{ cal/4 mol A}\cdot{}^\circ\text{K})}{(18{,}000 \text{ cal/mol A})} = \frac{1}{72}\ {}^\circ\text{K}^{-1}$$