# CHAPTER ELEVEN

**11.1**  **a.**  The peroxide mass fraction in the effluent liquid equals that in the tank contents, which is:

$$x_p = \frac{M_p}{M}$$

Therefore, the leakage rate of hydrogen peroxide is  $\underline{\underline{\dot{m}_1 M_p / M}}$

**b.**  <u>Balance on mass:</u>  Accumulation = input – output

$$\Downarrow$$

$$\underline{\frac{dM}{dt} = \dot{m}_0 - \dot{m}_1}$$

$$\underline{\underline{t = 0, \ M = M_0}} \text{ (mass in tank when leakage begins)}$$

<u>Balance on $H_2O_2$:</u>  Accumulation = input – output – consumption

$$\Downarrow$$

$$\underline{\underline{\frac{dM_p}{dt} = \dot{m}_0 x_{p0} - \dot{m}_1 \left( \frac{M_p}{M} \right) - kM_p}}$$

$$\underline{\underline{t = 0, \ M_p = M_{p0}}}$$

**11.2**  **a.**  <u>Balance on $H_3PO_4$:</u>  Accumulation = input
Density of $H_3PO_4$:  $\rho = 1.834 \text{ g / ml}$.
Molecular weight of $H_3PO_4$:  $M = 98.00 \text{ g / mol}$ .

$$\text{Accumulation} = \frac{dn_p}{dt} \text{ (kmol / min)}$$

$$\text{Input} = \frac{20.0 \text{ L}}{\text{min}} \left| \frac{1000 \text{ ml}}{\text{L}} \right| \frac{1.834 \text{ g}}{\text{ml}} \left| \frac{\text{mol}}{98.00 \text{ g}} \right| \frac{1 \text{ kmol}}{1000 \text{ mol}} = 0.3743 \text{ kmol / min}$$

$$\Downarrow$$

$$\underline{\frac{dn_p}{dt} = 0.3743}$$

$$\underline{\underline{t = 0, \ n_{p0} = 150 \times 0.05 = 7.5 \text{ kmol}}}$$

**b.**  $\displaystyle\int_{7.5}^{n_p} dn_p = \int_0^t 0.3743 \, dt \Rightarrow \underline{\underline{n_p = 7.5 + 0.3743t}}$  (kmol $H_3PO_4$ in tank)

$$\underline{\underline{x_p = \frac{n_p}{n} = \frac{n_p}{n_0 + n_p - n_{p0}} = \frac{7.5 + 0.3743t}{150 + 0.3743t}}} \quad \frac{\text{kmol } H_3PO_4}{\text{kmol}}$$

**c.**  $0.15 = \dfrac{7.5 + 0.3743t}{150 + 0.3743t} \Rightarrow t = \underline{\underline{47.1 \text{ min}}}$

**11.3** **a.** $\dot{m}_w = a + bt$ $(t = 0, \dot{m}_w = 750)$ & $(t = 5, \dot{m}_w = 1000) \Rightarrow \underline{\dot{m}_w (kg/h) = 750 + 50t(h)}$

Balance on methanol: Accumulation = Input – Output
$M$ = kg $CH_3OH$ in tank

$$\frac{dM}{dt} = \dot{m}_f - \dot{m}_w = 1200 \ kg/h - (750 + 50t) \ kg/h$$

$\Downarrow$

$$\frac{dM}{dt} = 450 - 50t \, (kg/h)$$

$\underline{\underline{t = 0, \ M = 750 \ kg}}$

**b.** $\int\limits_{750}^{M} dM = \int\limits_{0}^{t} (450 - 50t) dt$

$\Downarrow$

$M - 750 = 450t - 25t^2$

$\Downarrow$

$\underline{M = 750 + 450t - 25t^2}$

Check the solution in two ways:
(1) $t = 0$, $M = 750 \ kg \Rightarrow$ satisfies the initial condition;

(2) $\dfrac{dM}{dt} = 450 - 50t$ $\Rightarrow$ reproduces the mass balance.

**c.** $\dfrac{dM}{dt} = 0 \Rightarrow t = 450/50 = \underline{\underline{9 \ h}} \Rightarrow M = 750 + 450(9) - 25(9)^2 = \underline{\underline{2775 \ kg}}$ (maximum)

$M = 0 = 750 + 450t - 25t^2$

$$t = \frac{-450 \pm \sqrt{(450)^2 + 4(25)(750)}}{2(-25)} \Rightarrow t = \cancel{-1.54 \ h}, \ \underline{19.54 \ h}$$

**d.** $\dfrac{3.40 \ m^3 \ \Big| \ 10^3 \ liter \ \Big| \ 0.792 \ kg}{1 \ m^3 \ \Big| \ 1 \ liter} = 2693 \ kg$ (capacity of tank)

$M = 2693 = 750 + 450t - 25t^2$
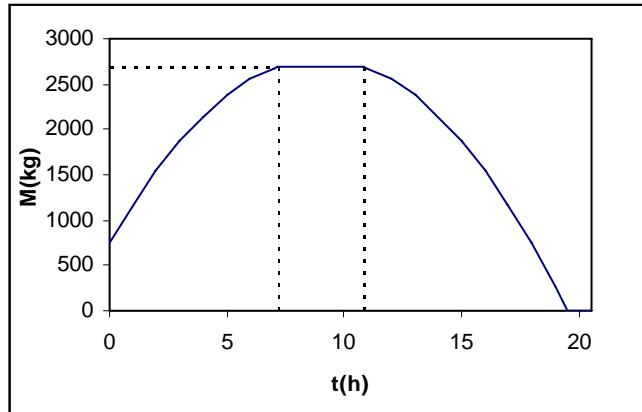
$$t = \frac{-450 \pm \sqrt{(450)^2 + 4(25)(750 - 2693)}}{2(-25)} \Rightarrow t = 7.19 \ h, 10.81 \ h$$

Expressions for M(t) are:

$$M(t) = \begin{cases} 750 + 450t - 25t^2 & (0 \le t \le 7.19 \text{ and } 10.81 \le t \le 19.54) \text{ (tank is filling or draining)} \\ 2693 & (7.19 \le t \le 10.81) \qquad \text{(tank is overflowing)} \\ 0 & (19.54 \le t \le 20.54) \qquad \text{(tank is empty, draining} \\ & \qquad\qquad\qquad\qquad\qquad\qquad \text{as fast as methanol is fed to it)} \end{cases}$$

**11.3 (cont'd)**



**11.4  a.**  <u>Air initially in tank:</u>  $N_0 = \dfrac{10.0 \text{ ft}^3 \mid 492°\text{R} \mid 1 \text{ lb - mole}}{\mid 532°\text{R} \mid 359 \text{ ft}^3(\text{STP})} = 0.0258$ lb - mole

<u>Air in tank after 15 s:</u>

$$\frac{P_f V}{P_0 V} = \frac{N_f RT}{N_0 RT} \Rightarrow N_f = N_0 \frac{P_f}{P_0} = \frac{0.0258 \text{ lb - mole} \mid 114.7 \text{ psia}}{\mid 14.7 \text{ psia}} = 0.2013 \text{ lb - mole}$$

<u>Rate of addition:</u>  $\dot{n} = \dfrac{(0.2013 - 0.0258) \text{ lb - mole air}}{15 \text{ s}} = \underline{\underline{0.0117 \text{ lb - mole air/s}}}$

**b.**  <u>Balance on air in tank:</u>  Accumulation = input

$$\underline{\frac{dN}{dt} = 0.0117(\text{lb - moles/s})}; \ \ t = 0, \underline{\underline{N = 0.0258 \text{ lb - mole}}}$$

**c.**  <u>Integrate balance:</u>  $\displaystyle\int_{0.0258}^{N} dN = \int_{0}^{t} \dot{n}\, dt \Rightarrow \underline{\underline{N = 0.0258 + 0.0117t}} \ (\text{lb - mole air})$

<u>Check the solution in two ways:</u>

(1) $t = 0, N = 0.0258$ lb - mole $\Rightarrow$ satisfies the initial condition

(2) $\dfrac{dN}{dt} = 0.0117$ lb - mole air / s $\Rightarrow$ reproduces the mass balance

**d.**  $t = 120 \text{ s} \Rightarrow N = 0.0258 + (0.0117)(120) = 1.43$ lb - moles air

$\underline{O_2 \text{ in tank}} = 0.21(1.43) = \underline{\underline{0.30 \text{ lb - mole } O_2}}$

**11.5** **a.** Since the temperature and pressure of the gas are constant, a volume balance on the gas is equivalent to a mole balance (conversion factors cancel).

Accumulation = Input – Output

$$\frac{dV}{dt} = \frac{540 \text{ m}^3}{\text{h}} \left| \frac{1 \text{ h}}{60 \text{ min}} - \dot{v}_w \left(\text{m}^3/\text{min}\right) \right.$$

$t = 0, V = 3.00 \times 10^3 \text{ m}^3 (t = 0 \text{ corresponds to 8:00 AM})$

$$\int_{3.00\times10^3}^{V} dV = \int_0^t (9.00 - \dot{v}_w) dt \Rightarrow \underline{\underline{V(\text{m}^3) = 3.00 \times 10^3 + 9.00t - \int_0^t \dot{v}_w dt}} \quad t \text{ in minutes}$$

**b.** Let $\dot{v}_{wi}$ = tabulated value of $\dot{v}_w$ at $t = 10(i-1)$ $\qquad i = 1, 2, ..., 25$

$$\int_0^{240} \dot{v}_w dt \cong \frac{10}{3} \left[ \dot{v}_{w1} + \dot{v}_{w25} + 4 \sum_{i=2,4,...}^{24} \dot{v}_{wi} + 2 \sum_{i=3,5,...}^{24} \dot{v}_{wi} \right] = \frac{10}{3} \left[ 11.4 + 9.8 + 4(124.6) + 2(113.4) \right]$$

$$= 2488 \text{ m}^3$$

$$V = 3.00 \times 10^3 + 9.00(240) - 2488 = \underline{\underline{2672 \text{ m}^3}}$$

**c.** Measure the height of the float roof (proportional to volume).
The feed rate decreased, or the withdrawal rate increased between data points, or the storage tank has a leak, or Simpson's rule introduced an error.

**d.**
```
          REAL VW(25), T, V, V0, H
          INTEGER I
          DATA V0, H/3.0E3, 10./
          READ (5, *) (VW(I), I = 1, 25)
          V= V0
          T=0.
          WRITE (6, 1)
          WRITE (6, 2) T, V
          DO 10 I = 2, 25
                T = H * (I – 1)
                V = V + 9.00 * H – 0.5 * H * (VW(I – 1) + VW(I))
                WRITE (6, 2) T, V
     10   CONTINUE
      1   FORMAT ('TIME (MIN)  VOLUME (CUBIC METERS)')
      2   FORMAT (F8.2, 7X, F6.0)
          END
   $DATA
   11.4   11.9    12.1    11.8    11.5    11.3
   ⋮
```

Results:

| TIME (MIN) | VOLUME (CUBIC METERS) |
|---|---|
| 0.00 | 3000. |
| 10.00 | 2974. |
| 20.00 | 2944. |
| ⋮ | ⋮ |
| 230.00 | 2683. |
| 240.00 | 2674. |

$$V_{\text{trapezoid}} = 2674 \text{ m}^3; \ V_{\text{Simpson}} = 2672 \text{ m}^3; \ \frac{2674 - 2672}{2672} \times 100\% = \underline{\underline{0.07\%}}$$

Simpson's rule is more accurate.

**11.6**  **a.**  $\dot{v}_{out}\left(\text{L/min}\right)=kV\left(\text{L}\right)\underset{\underset{\dot{v}_{out}=60}{V=300}}{\Rightarrow}\underline{\underline{\dot{v}_{out}=0.200V}}\quad\dot{v}_{out}=20.0\ \text{L/min}\Rightarrow\underline{\underline{V_s=100\ \text{L}}}$

**b.**  <u>Balance on water:</u> Accumulation = input – output (L/min).
(Balance volume directly since density is constant)

$$\dfrac{dV}{dt}=20.0-0.200V$$
$$\underline{\underline{t=0,V=300}}$$

**c.**  $\dfrac{dV}{dt}=0=200-0.200V_s\Rightarrow\underline{\underline{V_s=100\ \text{L}}}$

The plot of V vs. t begins at (t=0, V=300). When t=0, the slope (dV/dt) is
$20.0-0.200(300)=-40.0$. As t increases, V decreases. $\Rightarrow dV/dt=20.0-0.200V$
becomes less negative, approaches zero as $t\rightarrow\infty$. The curve is therefore <u>concave up.</u>
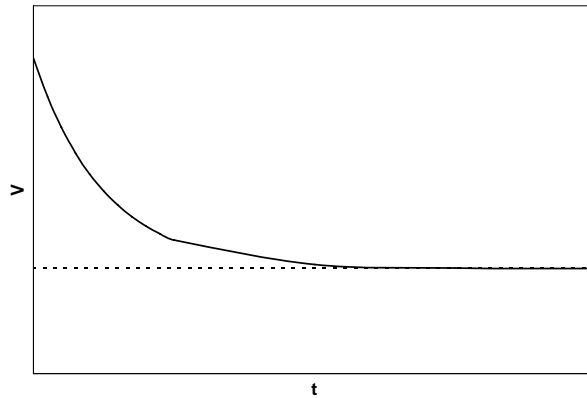


**d.**  $\displaystyle\int_{300}^{V}\dfrac{dV}{20.0-0.200V}=\int_{0}^{t}dt$

$\Rightarrow-\dfrac{1}{0.200}\ln\left(\dfrac{20.0-0.200V}{-40.0}\right)=t$

$\Rightarrow-0.5+0.005V=\exp(-0.200t)\Rightarrow\underline{\underline{V=100.0+200.0\exp(-0.200t)}}$

$V=1.01(100)=101\ \text{L}\ \left(1\%\ \text{from steady state}\right)\Rightarrow$

$101=100+200\exp(-0.200t)\Rightarrow t=\dfrac{\ln(1/200)}{-0.200}=\underline{\underline{26.5\ \text{min}}}$

**11.7**  **a.**  A plot of $D$ (log scale) vs. $t$ (rectangular scale) yields a straight line through the points ($t = 1$ week, $D = 2385$ kg/week ) and ($t = 6$ weeks, $D = 755$ kg/week ).

$$\ln D = bt + \ln a \Leftrightarrow D = ae^{bt}$$

$$b = \frac{\ln D_2/D_1}{t_2 - t_1} = \frac{\ln(755/2385)}{6-1} = -0.230$$

$$\ln a = \ln D_1 - bt_1 = \ln(2385) + (0.230)(1) = 8.007 \Rightarrow a = e^{8.007} = 3000$$

$$\Downarrow$$

$$\underline{\underline{D = 3000e^{-0.230t}}}$$

**b.**  Inventory balance:  Accumulation = –output

$$\frac{dI}{dt} = -3000e^{-0.230t} \text{ (kg/week)}$$

$$\underline{\underline{t = 0, I = 18{,}000 \text{ kg}}}$$

$$\int_{18{,}000}^{I} dI = \int_0^t -3000e^{-0.230t}\,dt \Rightarrow I - 18{,}000 = \frac{3000}{0.230}e^{-0.230t}\Big]_0^t \Rightarrow \underline{\underline{I = 4957 + 13{,}043e^{-0.230t}}}$$

**c.**  $t = \infty \Rightarrow \underline{\underline{I = 4957 \text{ kg}}}$

**11.8**  **a.**  Total moles in room:  $N = \dfrac{1100 \text{ m}^3}{} \left| \dfrac{273 \text{ K}}{295 \text{ K}} \right| \dfrac{10^3 \text{ mol}}{22.4 \text{ m}^3(\text{STP})} = 45{,}440$ mol

Molar throughput rate:  $\dot{n} = \dfrac{700 \text{ m}^3}{\text{min}} \left| \dfrac{273 \text{ K}}{295 \text{ K}} \right| \dfrac{10^3 \text{ mol}}{22.4 \text{ m}^3(\text{STP})} = 28{,}920$ mol/min

$\underline{SO_2 \text{ balance}}$  ($t = 0$ is the instant after the $SO_2$ is released into the room):

$$N(\text{mol})x(\text{mol } SO_2/\text{mol}) = \text{mol } SO_2 \text{ in room}$$
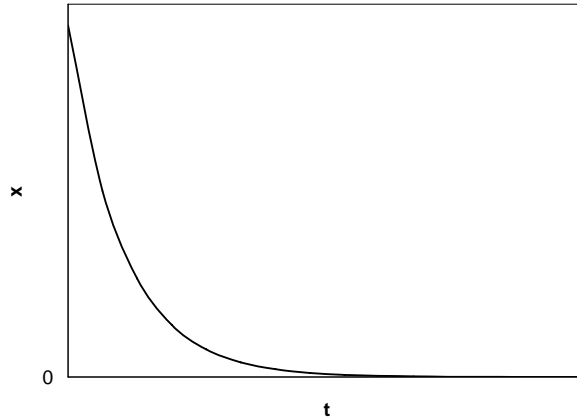
Accumulation = –output.

$$\frac{d}{dt}(Nx) = -\dot{n}x \underset{\substack{N=45{,}440 \\ \dot{n}=28{,}920}}{\Rightarrow} \frac{dx}{dt} = -0.6364x$$

$$t = 0, x = \frac{1.5 \text{ mol } SO_2}{45{,}440 \text{ mol}} = 3.30 \times 10^{-5} \text{ mol } SO_2/\text{mol}$$

**b.**  The plot of x vs. t begins at (t=0, x=3.30×10⁻⁵).  When t=0, the slope (dx/dt) is $-0.6364 \times 3.30 \times 10^{-5} = -2.10 \times 10^{-5}$.  As t increases, x decreases.$\Rightarrow$ $dx/dt = -0.6364x$ becomes less negative, approaches zero as $t \to \infty$.  The curve is therefore concave up.

**11.8 (cont'd)**



c.  Separate variables and integrate the balance equation:

$$\int_{3.30\times10^{-5}}^{x} \frac{dx}{x} = \int_{0}^{t} -0.6364dt \Rightarrow \ln\frac{x}{3.30\times10^{-5}} = -0.6364t \Rightarrow \underline{\underline{x = 3.30\times10^{-5}e^{-0.6364t}}}$$

Check the solution in two ways:

(1) $t = 0$, $x = 3.30\times10^{-5}$ mol $SO_2$ / mol $\Rightarrow$ satisfies the initial condition;

(2) $\dfrac{dx}{dt} = -0.6364\times3.30\times10^{-5}e^{-0.6364t} = -0.6364x \Rightarrow$ reproduces the mass balance.

d.  $C_{SO_2} = \dfrac{45,440 \text{ moles}}{1100 \text{ m}^3}\bigg|\dfrac{x \text{ mol } SO_2}{\text{mol}}\bigg|\dfrac{1 \text{ m}^3}{10^3 \text{ L}} = 4.131\times10^{-2}x = \underline{\underline{1.3632\times10^{-6}e^{-0.6364t}}} \text{ mol } SO_2 \text{ / L}$

i)  $t = 2 \text{ min} \Rightarrow C_{SO_2} = \underline{\underline{3.82\times10^{-7}\dfrac{\text{mol } SO_2}{\text{liter}}}}$

ii)  $x = 10^{-6} \Rightarrow t = \dfrac{\ln\left(10^{-6}/3.30\times10^{-5}\right)}{-0.6364} = \underline{\underline{5.5 \text{ min}}}$

e.  The room air composition may not be uniform, so the actual concentration of the $SO_2$ in parts of the room may still be higher than the safe level.  Also, "safe" is on the average; someone would be particularly sensitive to $SO_2$.

**11.9 a.** <u>Balance on CO</u>: Accumulation=-output

$N$ (mol) $x$ (mol CO / mol) $=$ total moles of CO in the laboratory

Molar flow rate of entering and leaving gas: $\dot{n}$ $(\dfrac{\text{kmol}}{\text{h}}) = \dfrac{P\dot{V}_p}{RT}$

Rate at which CO leaves: $\dot{n}$ $(\dfrac{\text{kmol}}{\text{h}})$ $x\left(\dfrac{\text{kmol CO}}{\text{kmol}}\right) = \dfrac{P\dot{V}_p}{RT} x$

CO balance: Accumulation = -output

$$\dfrac{d(Nx)}{dt} = -\dfrac{P\dot{V}_p}{RT} x \Rightarrow \dfrac{dx}{dt} = -\left(\dfrac{P}{NRT}\right)\dot{V}_p x$$

$$\Downarrow PV = NRT$$

$$\dfrac{dx}{dt} = -\dfrac{\dot{V}_p}{V} x$$

$$t = 0,\ x = 0.01\ \dfrac{\text{kmol CO}}{\text{kmol}}$$

**b.** $\displaystyle\int_{0.01}^{x} \dfrac{dx}{x} = -\dfrac{\dot{V}_p}{V}\int_0^{t_r} dt \Rightarrow t_r = -\dfrac{V}{\dot{V}_p}\ln(100x)$

**c.** $V = 350\ \text{m}^3$

$t_r = -\dfrac{350}{700}\ln\left(100 \times 35 \times 10^{-6}\right) = \underline{\underline{2.83\ \text{hrs}}}$

**d.** The room air composition may not be uniform, so the actual concentration of CO in parts of the room may still be higher than the safe level. Also, "safe" is on the average; someone could be particularly sensitive to CO.

<u>Precautionary steps</u>:
Purge the laboratory longer than the calculated purge time. Use a CO detector

to measure the real concentration of CO in the laboratory and make sure it is

lower than the safe level everywhere in the laboratory.

**11.10 a.** Total mass balance: Accumulation = input – output

$$\dfrac{dM}{dt} = \dot{m} - \dot{m}(\text{kg/min}) = 0 \Rightarrow \therefore\ \underline{\underline{M\ \text{is a constant} = 200\ \text{kg}}}$$

**b.** Sodium nitrate balance: Accumulation = - output
$x = $ mass fraction of $NaNO_3$

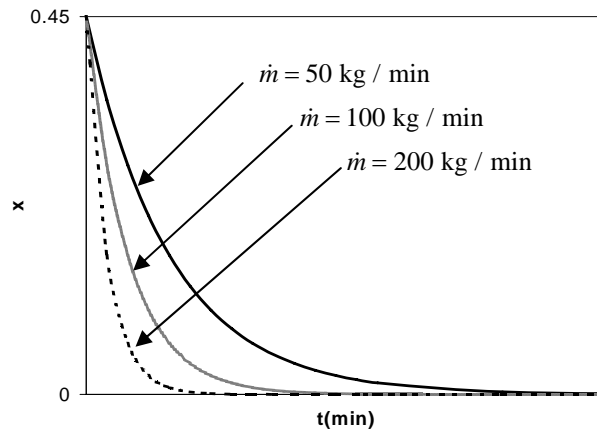$$\dfrac{d(xM)}{dt} = -x\dot{m}(\text{kg/min})$$

$$\Downarrow$$

$$\dfrac{dx}{dt} = -\dfrac{\dot{m}}{M} x = -\dfrac{\dot{m}}{200} x$$

$$\underline{\underline{t = 0,\ x = 90/200 = 0.45}}$$

**11.10 (cont'd)**

c.



$$\frac{dx}{dt} = -\frac{\dot{m}}{200}x < 0 \text{ , x decreases when t increases}$$

$\dfrac{dx}{dt}$ becomes less negative until x reaches 0;

Each curve is concave up and approaches x = 0 as t → ∞;

$\dot{m}$ increases ⟹ $\dfrac{dx}{dt}$ becomes more negative ⟹ x decreases faster.

d. $\displaystyle\int_{0.45}^{x}\frac{dx}{x} = -\int_{0}^{t}\frac{\dot{m}}{M}dt \quad \Rightarrow \quad \ln\frac{x}{0.45} = -\frac{\dot{m}}{200}t \Rightarrow \underline{\underline{x = 0.45\exp\left(-\frac{\dot{m}t}{200}\right)}}$

Check the solution:

(1) t = 0, x = 0.45 ⟹ satisfies the initial condition;

(2) $\dfrac{dx}{dt} = -0.45 \times \dfrac{\dot{m}}{200}\exp(-\dfrac{\dot{m}t}{200}) = -\dfrac{\dot{m}}{200}x \Rightarrow$ satisfies the mass balance.
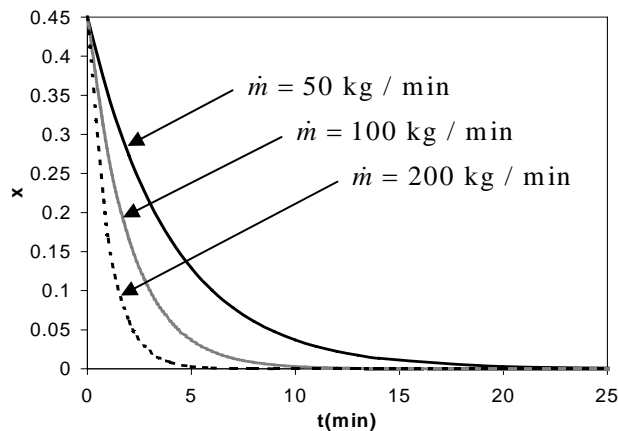


e. $\dot{m} = 100 \text{ kg/min} \Rightarrow t = -2\ln\left(x_f/0.45\right)$

90% ⟹ $x_f = 0.045 \Rightarrow \underline{\underline{t = 4.6 \text{ min}}}$

99% ⟹ $x_f = 0.0045 \Rightarrow \underline{\underline{t = 9.2 \text{ min}}}$

99.9% ⟹ $x_f = 0.00045 \Rightarrow \underline{\underline{t = 13.8 \text{ min}}}$

**11.11 a.** <u>Mass of tracer in tank:</u> $V\left(m^3\right)C\left(kg/m^3\right)$

<u>Tracer balance:</u> Accumulation = –output. If perfectly mixed, $C_{out} = C_{tank} = C$

$$\frac{d(VC)}{dt} = -\dot{v}C \;(kg/min) \xrightarrow{\text{V is constant}} \begin{array}{l} \dfrac{dC}{dt} = -\dfrac{\dot{v}}{V}C \\[2mm] t = 0, C = \dfrac{m_0}{V} \end{array}$$

**b.** $\displaystyle\int_{m_0/V}^{C}\frac{dC}{C} = -\int_0^t \frac{\dot{v}}{V}dt \Rightarrow \ln\left(\frac{C}{m_0/V}\right) = -\frac{\dot{v}t}{V} \Rightarrow C = \frac{m_0}{V}\exp\left(-\frac{\dot{v}t}{V}\right)$

**c.** Plot $C$ (log scale) vs $t$ (rect. scale) on semilog paper: Data lie on straight line (verifying assumption of perfect mixing) through $\left(t = 1, C = 0.223\times 10^{-3}\right)$ & $\left(t = 2, C = 0.050\times 10^{-3}\right)$.

$$-\frac{\dot{v}}{V} = \frac{\ln(0.050/0.223)}{2-1} = -1.495 \text{ min}^{-1}$$

$$\Downarrow$$

$$V = \left(30 \text{ m}^3/\text{min}\right)/\left(1.495 \text{ min}^{-1}\right) = \underline{\underline{20.1 \text{ m}^3}}$$

**11.12 a.** In tent at any time, P=14.7 psia, V=40.0 ft³, T=68°F=528°R

$$\Rightarrow N = \frac{PV}{RT} = m(\text{liquid}) = \frac{14.7 \text{ psia} \quad \Big| \quad 40.0 \text{ ft}^3}{10.73 \dfrac{\text{ft}^3\cdot\text{psia}}{\text{lb-mole}\cdot^o\text{R}} \quad \Big| \quad 528 \;^o\text{R}} = \underline{\underline{0.1038 \text{ lb-mole}}}$$

**b.** <u>Molar throughout rate:</u>

$$\dot{n}_{in} = \dot{n}_{out} = \dot{n} = \frac{60 \text{ ft}^3}{\text{min}} \left| \frac{492^\circ\text{R}}{528^\circ\text{R}} \right| \frac{16.0 \text{ psia}}{14.7 \text{ psia}} \left| \frac{1 \text{ lb-mole}}{359 \text{ ft}^3(\text{STP})} = 0.1695 \text{ lb-mole/min} \right.$$

<u>Moles of O$_2$ in tank</u>$= N(\text{lb-mole}) \times \left(\dfrac{\text{lb-mole O}_2}{\text{lb-mole}}\right)$

<u>Balance on O$_2$:</u> Accumulation = input – output

$$\frac{d(Nx)}{dt} = 0.35\dot{n} - x\dot{n} \Rightarrow 0.1038\frac{dx}{dt} = 0.1695(0.35 - x) \Rightarrow \begin{array}{l} \dfrac{dx}{dt} = 1.63(0.35 - x) \\[2mm] t = 0, x = 0.21 \end{array}$$

**c.** $\displaystyle\int_{0.21}^{x}\frac{dx}{0.35 - x} = \int_0^t 1.63dt \Rightarrow -\ln\frac{(0.35 - x)}{(0.35 - 0.21)} = 1.63t$

$$\Rightarrow \frac{0.35 - x}{0.14} = e^{-1.63t} \Rightarrow \underline{\underline{x = 0.35 - 0.14e^{-1.63t}}}$$

$$x = 0.27 \Rightarrow t = \frac{1}{1.63}\left[-\ln\left(\frac{0.35 - 0.27}{0.35 - 0.21}\right)\right] = \underline{\underline{0.343 \text{ min}}} \text{ (or } \underline{\underline{20.6 \text{ s}}})$$

**11.13 a.** <u>Mass of isotope at any time</u> $= V(\text{liters})C(\text{mg isotope}/\text{liter})$

<u>Balance on isotope:</u> Accumulation = –consumption

$$\frac{d}{dt}(VC) = -kC\left(\frac{\text{mg}}{\text{L}\cdot\text{s}}\right)V(\text{L}) \xrightarrow{\text{Cancel V}} \quad \frac{dC}{dt} = -kC$$

$$t = 0, C = C_0$$

<u>Separate variables and integrate</u>

$$\int_{C_0}^{C}\frac{dC}{C} = \int_0^t -k\,dt \Rightarrow \ln\left(\frac{C}{C_0}\right) = -kt \Rightarrow t = \frac{-\ln(C/C_0)}{k}$$

$$C = 0.5C_0 \Rightarrow t_{1/2} = \frac{-\ln(0.5)}{k} \Rightarrow t_{1/2} = \frac{\ln 2}{k}$$

**b.** $t_{1/2} = 2.6\text{ hr} \Rightarrow k = \dfrac{\ln 2}{2.6\text{ hr}} = 0.267\text{ hr}^{-1}$

$$C = 0.01C_0 \xrightarrow[t=-\ln(C/C_0)/k]{} t = \frac{-\ln(0.01)}{0.267} = \underline{\underline{17.2\text{ hr}}}$$

**11.14** $A \rightarrow$ products

**a.** <u>Mole balance on $A$:</u> Accumulation = –consumption

$$\frac{d(C_A V)}{dt} = -kC_A V \qquad (V \text{ constant; cancels})$$

$$t = 0, C_A = C_{A0}$$

$$\Rightarrow \int_{C_{A0}}^{C_A}\frac{dC_A}{C_A} = \int_0^t -k\,dt \Rightarrow \ln\left(\frac{C_A}{C_{A0}}\right) = -kt \Rightarrow \underline{\underline{C_A = C_{A0}\exp(-kt)}}$$

**b.** Plot $C_A$ (log scale) vs. $t$ (rect. scale) on semilog paper. The data fall on a straight line (verifies assumption of first-order) through $(t = 21.3,\ C_A = 0.0262)$ & $(t = 120.0,\ C_A = 0.0185)$.

$$\ln C_A = -kt + \ln C_{A0}$$

$$-k = \frac{\ln(0.0185/0.0262)}{120.0 - 21.3} = -3.53 \times 10^{-3}\text{ min}^{-1} \Rightarrow \underline{\underline{k = 3.5 \times 10^{-3}\text{ min}^{-1}}}$$

**11.15** $2A \rightarrow 2B + C$

**a.** <u>Mole balance on $A$:</u> Accumulation = –consumption

$$\frac{d(C_A V)}{dt} = -kC_A^2 V \qquad (V \text{ constant; cancels})$$

$$t = 0, C_A = C_{A0}$$

$$\Rightarrow \int_{C_{A0}}^{C_A}\frac{dC_A}{C_A^2} = \int_0^t -k\,dt \Rightarrow -\frac{1}{C_A} + \frac{1}{C_{A0}} = -kt \Rightarrow \underline{\underline{C_A = \left[\frac{1}{C_{A0}} + kt\right]^{-1}}}$$

**11.15 (cont'd)**

**b.** $C_A = 0.5C_{A0} \Rightarrow -\dfrac{1}{0.5C_{A0}} + \dfrac{1}{C_{A0}} = -kt_{1/2} \Rightarrow t_{1/2} = \dfrac{1}{kC_{A0}}$ ; but $C_{A0} = \dfrac{n_{A0}}{V} = \dfrac{P_0}{RT} \Rightarrow \underline{\underline{t_{1/2} = \dfrac{RT}{kP_0}}}$

$n_A = 0.5n_{A0}$

$n_B = (0.5n_{A0} \text{ mol } A \text{ react.})(2 \text{ mol } B/2 \text{ mol } A \text{ react.}) = 0.5n_{A0}$

$n_C = (0.5n_{A0} \text{ mol } A \text{ react.})(1 \text{ mol } C/2 \text{ mol } A \text{ react.}) = 0.25n_{A0}$

total moles $= 1.25n_{A0} \Rightarrow P_{1/2} = 1.25\dfrac{n_{A0}RT}{V} = \underline{\underline{1.25P_0}}$

**c.** Plot $t_{1/2}$ vs. $1/P_0$ on rectangular paper. Data fall on straight line (verifying 2nd order

decomposition) through $(t_{1/2} = 1060, 1/P_0 = 1/0.135)$ & $(t_{1/2} = 209, 1/P_0 = 1/0.683)$

Slope: $\dfrac{RT}{k} = \dfrac{1060 - 209}{1/0.135 - 1/0.683} = 143.2 \text{ s} \cdot \text{atm}$

$\Rightarrow k = \dfrac{(1015 \text{ K})(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})}{143.2 \text{ s} \cdot \text{atm}} = \underline{\underline{0.582 \text{ L/mol} \cdot \text{s}}}$

**d.** $t_{1/2} = \dfrac{RT}{k_0 P_0}\exp\left(\dfrac{E}{RT}\right) \Rightarrow \ln\left(\dfrac{t_{1/2}P_0}{RT}\right) = \ln\dfrac{1}{k_0} + \dfrac{E}{R}\dfrac{1}{T}$

Plot $t_{1/2}P_0/RT$ (log scale) vs. $1/T$ (rect. scale) on semilog paper.

$\left[t_{1/2}(\text{s}), P_0 = 1 \text{ atm}, R = 0.08206 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K}), \text{T(K)}\right]$

Data fall on straight line through $(t_{1/2}P_0/RT = 74.0, 1/T = 1/900)$ &

$(t_{1/2}P_0/RT = 0.6383, 1/T = 1/1050)$

$\dfrac{E}{R} = \dfrac{\ln(0.6383/74.0)}{1/1050 - 1/900} = 29{,}940 \text{ K} \xrightarrow{R=8.314 \text{ J/ (mol} \cdot \text{K)}} \underline{\underline{E = 2.49 \times 10^5 \text{ J/mol}}}$

$\ln\dfrac{1}{k_0} = \ln(0.6383) - \dfrac{29{,}940}{1050} = -28.96 \Rightarrow \underline{\underline{k_0 = 3.79 \times 10^{12} \text{ L/(mol} \cdot \text{s})}}$

**e.** $T = 980 \text{ K} \Rightarrow k = k_0\exp\left(-\dfrac{E}{RT}\right) = 0.204 \text{ L/(mol} \cdot \text{s})$

$C_{A0} = \dfrac{0.70(1.20 \text{ atm})}{(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(980 \text{ K})} = 1.045 \times 10^{-2} \text{ mol/L}$

$\downarrow 90\% \text{ conversion}$

$C_A = 0.10C_{A0} \Rightarrow t = \dfrac{1}{k}\left[\dfrac{1}{C_A} - \dfrac{1}{C_{A0}}\right] = \dfrac{1}{0.204}\left[\dfrac{1}{1.045 \times 10^{-3}} - \dfrac{1}{1.045 \times 10^{-2}}\right]$

$= 4222 \text{ s} = \underline{\underline{70.4 \text{ min}}}$

**11.16** $A \to B$

**a.** Mole balance on $A$: Accumulation = –consumption($V$ constant)

$$\frac{dC_A}{dt} = -\frac{k_1 C_A}{1 + k_2 C_A}$$

$$t = 0, C_A = C_{A0}$$

$$\int_{C_{A0}}^{C_A} \frac{1 + k_2 C_A}{k_1 C_A} dC_A = \int_0^t -dt \Rightarrow \frac{1}{k_1} \ln \frac{C_A}{C_{A0}} + \frac{k_2}{k_1}(C_A - C_{A0}) = -t \Rightarrow \underline{\underline{t = \frac{k_2}{k_1}(C_{A0} - C_A) - \frac{1}{k_1} \ln \frac{C_A}{C_{A0}}}}$$

**b.** Plot $t/(C_A - C_{A0})$ vs. $\ln(C_A / C_{A0})/(C_{A0} - C_A)$ on rectangular paper:

$$\underbrace{\frac{t}{(C_{A0} - C_A)}}_{y} = \underbrace{-\frac{1}{k_1}}_{\text{slope}} \overbrace{\frac{\ln(C_A/C_{A0})}{C_{A0} - C_A}}^{x} + \underbrace{\frac{k_2}{k_1}}_{\text{intercept}}$$

Data fall on straight line through $\left( \overbrace{116.28}^{y_1}, \overbrace{-0.2111}^{x_1} \right)$ & $\left( \overbrace{130.01}^{y_2}, \overbrace{-0.2496}^{x_2} \right)$

$$-\frac{1}{k_1} = \frac{130.01 - 116.28}{-0.2496 - (-0.2111)} = -356.62 \Rightarrow \underline{\underline{k_1 = 2.80 \times 10^{-3} \text{ L/(mol·s)}}}$$

$$\frac{k_2}{k_1} = 130.01 + 356.62(-0.2496) = 41.00 \Rightarrow \underline{\underline{k_2 = 0.115 \text{ L/mol}}}$$

**11.17** $CO + Cl_2 \Rightarrow COCl_2$

**a.**
$$\frac{3.00 \text{ L}}{} \left| \frac{273 \text{ K}}{303.8 \text{ K}} \right| \frac{1 \text{ mol}}{22.4 \text{ L(STP)}} = 0.12035 \text{ mol gas}$$

$$\left. \begin{aligned} (C_{CO})_i &= 0.60(0.12035 \text{ mol})/3.00 \text{ L} = \underline{\underline{0.02407 \text{ mol/L CO}}} \\ (C_{Cl_2})_i &= 0.40(0.12035 \text{ mol})/3.00 \text{ L} = \underline{\underline{0.01605 \text{ mol/L Cl}_2}} \end{aligned} \right\} \text{initial concentrations}$$

$$\left. \begin{aligned} C_{CO}(t) &= 0.02407 - C_p(t) \\ \overline{\overline{C_{Cl_2}(t) = 0.01605 - C_p(t)}} \end{aligned} \right\} \text{Since 1 mol } COCl_2 \text{ formed requires 1 mol of each reactant}$$

**b.** Mole balance on Phosgene: Accumulation = generation

$$\frac{d(VC_p)}{dt} = \frac{8.75 C_{CO} C_{Cl_2}}{\left(1 + 58.6 C_{Cl_2} + 34.3 C_p\right)^2} \xrightarrow{V = 3.00 \text{ L}} \underline{\underline{\begin{aligned} \frac{dC_p}{dt} &= \frac{2.92(0.02407 - C_p)(0.01605 - C_p)}{\left(1.941 - 24.3 C_p\right)^2} \\ t &= 0, C_p = 0 \end{aligned}}}$$

**c.** $Cl_2$ limiting; 75% conversion $\Rightarrow C_p = 0.75(0.01605) = 0.01204 \text{ mol/L}$

$$\underline{\underline{t = \frac{1}{2.92} \int_0^{0.01204} \frac{\left(1.941 - 24.3 C_p\right)^2}{(0.02407 - C_p)(0.01605 - C_p)} dC_p}}$$

d.
```
        REAL F(51), SUM1, SUM2, SIMP
        INTEGER I, J, NPD(3), N, NM1, NM2
        DATA NPD/5, 21, 51/
        FN(C) = (1.441 – 24.3 * C) ** 2/(0.02407 – C)/(0.01605 – C)
        DO 10 I = 1, 3
            N = NPD(I)
            NM1 = N – 1
            NM2 = N – 2
            DO 20 J = 1, N
                C = 0.01204 * FLOAT(J – 1)/FLOAT(NM1)
                F(J) = FN(C)
  20        CONTINUE
            SUM1 = 0.
            DO 30 J = 2, NM1, 2
                SUM = SUM1 + F(S)
  30        CONTINUE
            SUM2 = 0.
            DO 40 J = 3, NM2, 2
                SUM2 = SUM2 + F(J)
  40        CONTINUE
            SIMP = 0.01204/FLOAT(NM1)/3.0 * (F(1) + F(N) + 4.0 * SUM1 + 2.0 * SUM2)
            T = SIMP/2.92
            WRITE (6, 1) N, T
  10    CONTINUE
   1    FORMAT (I4, 'POINTS —', 2X, F7.1, 'MINUTES')
        END
```
RESULTS
5 POINTS —   91.0 MINUTES
21 POINTS — 90.4 MINUTES
51 POINTS — 90.4 MINUTES
$t$ = 90.4 minutes

**11.18 a.**  Moles of $CO_2$ in liquid phase at any time $= V\left(cm^3\right)C_A\left(mols/cm^3\right)$

Balance on $CO_2$ in liquid phase:  Accumulation = input

$$\frac{d}{dt}\left(VC_A\right) = kS\left(C_A^* - C_A\right)\left(\frac{mols}{s}\right) \underset{\div V}{\Rightarrow} \frac{dC_A}{dt} = \frac{kS}{V}\left(C_A^* - C_A\right)$$
$$t = 0, C_A = 0$$

Separate variables and integrate.  Since $p_A = y_A P$ is constant, $C_A^* = p_A/H$ is also a constant.

$$\int_0^{C_A} \frac{dC_A}{C_A^* - C_A} = \int_0^t \frac{kS}{V}\, dt \Rightarrow -\ln\left(C_A^* - C_A\right)\Big]_{C_A=0}^{C_A} = \frac{kS}{V}t$$

$$\Rightarrow \ln\left[\underbrace{\frac{C_A^* - C_A}{C_A^*}}_{1-C_A/C_A^*}\right] = -\frac{kS}{V}t \overset{exp(\ )}{\Rightarrow} 1 - \frac{C_A}{C_A^*} = e^{-kSt/V} \Rightarrow C_A = C_A^*\left(1 - e^{-kSt/V}\right)$$

**11.18 (cont'd)**

**b.** $\quad t = -\dfrac{V}{kS}\ln\left[1 - \dfrac{C_A}{C_A^*}\right]$

$\qquad V = 5\,\text{L} = 5000\,\text{cm}^3,\ k = 0.020\ \text{cm/s},\ S = 78.5\,\text{cm}^2,\ C_A = 0.62 \times 10^{-3}\ \text{mol}/\text{cm}^3$

$\qquad C_A^* = y_A P/H = (0.30)(20\ \text{atm})\big/\!\left(9230\ \text{atm}\cdot\text{cm}^3/\text{mol}\right) = 0.65 \times 10^{-3}\ \text{mol}/\text{cm}^3$

$\qquad t = -\dfrac{\left(5000\ \text{cm}^3\right)}{(0.02\ \text{cm/s})\left(78.5\ \text{cm}^2\right)}\ln\left(1 - \dfrac{0.62 \times 10^{-3}}{0.65 \times 10^{-3}}\right) = 9800\ \text{s} \Rightarrow \underline{\underline{2.7\ \text{hr}}}$

(We assume, in the absence of more information, that the gas-liquid interfacial surface area equals the cross sectional area of the tank. If the liquid is well agitated, $S$ may in fact be much greater than this value, leading to a significantly lower $t$ than that to be calculated)

**11.19** $\quad A \rightarrow B$

**a.** $\quad$ <u>Total Mass Balance:</u> Accumulation = input

$$\frac{dM}{dt} = \frac{d(\rho V)}{dt} = \rho \dot{v}$$

$$\Downarrow$$

$$\underline{\underline{\frac{dV}{dt} = \dot{v}}}$$

$$\underline{\underline{t = 0,\ V = 0}}$$

$\qquad$ <u>A Balance:</u> Accumulation = input – consumption

$$\frac{dN_A}{dt} = C_{A0}\dot{v} - (kC_A)V \xrightarrow[\;C_A = N_A/V\;]{} \qquad \underline{\underline{\frac{dN_A}{dt} = C_{Ao}\dot{v} - kN_A}}$$

$$\underline{\underline{t = 0,\ N_A = 0}}$$

**b.** $\quad$ Steady State: $\dfrac{dN_A}{dt} = 0 \Rightarrow \underline{\underline{N_A = \dfrac{C_{A0}\dot{v}}{k}}}$

**c.** $\quad \displaystyle\int_0^V dV = \int_0^t \dot{v}\,dt \Rightarrow \underline{\underline{V = \dot{v}t}}$

$$\int_0^{N_A} \frac{dN_A}{C_{A0}\dot{v} - kN_A} = \int_0^t dt$$

$$\Rightarrow -\frac{1}{k}\ln\left(\frac{C_{A0}\dot{v} - kN_A}{C_{A0}\dot{v}}\right) = t \Rightarrow \frac{C_{A0}\dot{v} - kN_A}{C_{A0}\dot{v}} = e^{-kt}$$

$$\Rightarrow \underline{\underline{N_A = \frac{C_{A0}\dot{v}}{k}\left[1 - \exp(-kt)\right]}} \quad t \rightarrow \infty \Rightarrow \underline{\underline{N_A = \frac{C_{A0}\dot{v}}{k}}}$$

$$\underline{\underline{C_A = \frac{N_A}{V} = \frac{C_{A0}[1 - \exp(-kt)]}{kt}}}$$

**11.19 (cont'd)**

When the feed rate of A equals the rate at which A reacts, $N_A$ reaches a steady value.
$N_A$ would never reach the steady value in a real reactor. The reasons are:
(1) In our calculation, $V = \dot{v}t \Rightarrow t \to \infty,\ V \to \infty$.

   But in a real reactor, the volume is limited by the reactor volume;

(2) The steady value can only be reached at $t \to \infty$. In a real reactor, the reaction time is finite.

**d.** $\displaystyle \lim_{t\to\infty} C_A = \lim_{t\to\infty} \frac{C_{A0}[1-\exp(-kt)]}{kt} = \lim_{t\to\infty} \frac{C_{A0}}{kt} = \underline{\underline{0}}$

From part c, $t \to \infty$, $N_A \to$ a finite number, $V \to \infty \Rightarrow C_A = \dfrac{N_A}{V} \to 0$

**11.20 a.** $\displaystyle MC_v \frac{dT}{dt} = \dot{Q} - \dot{W}$

$\left\| \begin{array}{l} M = (3.00\ \text{L})(1.00\ \text{kg}/\text{L}) = 3.00\ \text{kg} \\[4pt] C_v = C_p = (0.0754\ \text{kJ}/\text{mol}\cdot^{\circ}\text{C})(1\ \text{mol}/0.018\ \text{kg}) = 4.184\ \text{kJ}/\text{kg}\cdot^{\circ}\text{C} \\[4pt] \dot{W} = 0 \end{array} \right.$

$\dfrac{dT}{dt} = 0.0797\dot{Q}\ (\text{kJ}/\text{s})$

$\underline{\underline{t = 0,\ T = 18^{\circ}\text{C}}}$

**b.** $\displaystyle \int_{18^{\circ}\text{C}}^{100^{\circ}\text{C}} dT = \int_0^{240\ \text{s}} 0.0797\dot{Q}\ dt \Rightarrow \dot{Q} = \frac{100-18}{240 \times 0.0797} = 4.287\ \frac{\text{kJ}}{\text{s}} = \underline{\underline{4.29\ \text{kW}}}$

**c.** Stove output is much greater.
Only a small fraction of energy goes to heat the water.
Some energy heats the kettle.
Some energy is lost to the surroundings (air).

**11.21 a.** <u>Energy balance:</u> $\displaystyle MC_v \frac{dT}{dt} = \dot{Q} - \dot{W}$

$\left\| \begin{array}{l} M = 20.0\ \text{kg} \\[4pt] C_v \approx C_p = (0.0754\ \text{kJ}/\text{mol}\cdot^{\circ}\text{C})(1\ \text{mol}/0.0180\ \text{kg}) = 4.184\ \text{kJ}/(\text{kg}\cdot^{\circ}\text{C}) \\[4pt] \dot{Q} = (0.97)(2.50) = 2.425\ \text{kJ/s} \\[4pt] \dot{W} = 0 \end{array} \right.$

$\underline{\underline{\dfrac{dT}{dt} = 0.0290\ (^{\circ}\text{C/s})}}$ , $\underline{\underline{t = 0,\ T = 25^{\circ}\text{C}}}$

The other 3% of the energy is used to heat the vessel or is lost to the surroundings.

**b.** $\displaystyle \int_{25^{\circ}\text{C}}^{T} dT = \int_0^{t} 0.0290\,dt \Rightarrow \underline{\underline{T = 25^{\circ}\text{C} + 0.0290t\,(s)}}$

**c.** $T = 100^{\circ}\text{C} \Rightarrow t = (100-25)/0.0290 = 2585\ \text{s} \Rightarrow \underline{\underline{43.1\ \text{min}}}$

No, since the vessel is closed, the pressure will be greater than 1 atm (the pressure at the normal boiling point).
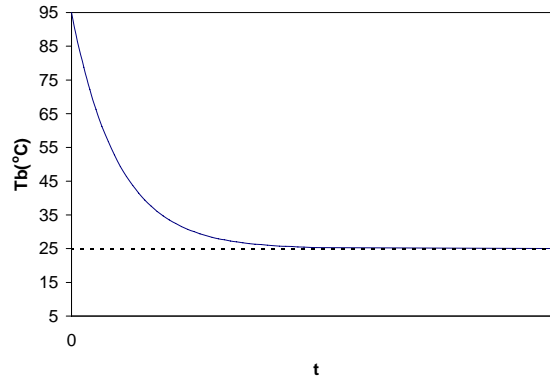
**11.22 a.** Energy balance on the bar

$$MC_v \frac{dT_b}{dt} = \dot{Q} - \dot{W} = -UA(T_b - T_w)$$

Table B.1
↓

$M = (60 \text{ cm}^3)(7.7 \text{ g/cm}^3) = 462 \text{ g}$
$C_v = 0.46 \text{ kJ/(kg·°C)}, \; T_w = 25°C$
$U = 0.050 \text{ J/(min · cm}^2\text{·°C)}$
$A = 2[(2)(3) + (2)(10) + (3)(10)]\text{cm}^2 = 112 \text{ cm}^2$

$$\frac{dT_b}{dt} = -0.02635(T_b - 25) \; (°C/min)$$

$$t = 0, \; T_b = 95°C$$

**b.** $\quad \dfrac{dT_b}{dt} = 0 = -0.02635(T_{bf} - 25) \Rightarrow T_{bf} = 25°C$



**c.** $\quad \displaystyle\int_{95}^{T_b} \frac{dT_b}{T_b - 25} = \int_0^t -0.02635 dt$

$$\Rightarrow \ln\left(\frac{T_b - 25}{95 - 25}\right) = -0.02635t$$

$$\Rightarrow T_b(t) = 25 + 70\exp(-0.02635t)$$

Check the solution in three ways:

(1) t = 0, $T_b = 25 + 70 = 95°C \Rightarrow$ satisfies the initial condition;

(2) $\dfrac{dT_b}{dt} = -70 \times 0.02635 e^{-0.02635t} = -0.02635(T_b - 25) \Rightarrow$ reproduces the mass balance;

(3) t → ∞, $T_b = 25°C \Rightarrow$ confirms the steady state condition.

$T_b = 30°C \Rightarrow \underline{t = 100 \text{ min}}$

**11.23**



12.0 kg/min  25°C → [box] → 12.0 kg/min  T (°C)
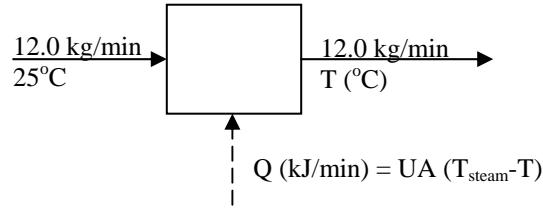
$Q$ (kJ/min) = UA ($T_{steam}$-T)

**a.** Energy Balance: $MC_v \dfrac{dT}{dt} = \dot{m}C_p(25 - T) + UA(T_{steam} - T)$
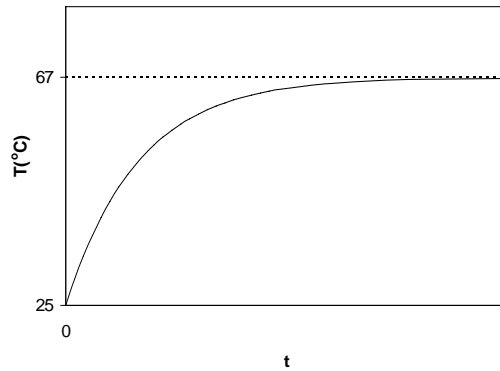
$M = 760$ kg

$\dot{m} = 12.0$ kg/min

⟹ $dT/dt = 1.50 - 0.0224T$ (°C/min), $t = 0$, $T = 25°C$

$C_v \approx C_p = 2.30$ kJ/(min·°C)

$UA = 11.5$ kJ/(min·°C)

$T_{steam}$(sat'd; 7.5bars) $= 167.8°C$

**b.** Steady State: $\dfrac{dT}{dt} = 0 = 1.50 - 0.0224T_s \Rightarrow T_s = 67°C$



**c.** $\displaystyle\int_{25}^{T_f} \dfrac{dT}{1.50 - 0.0224T} = \int_0^t dt \Rightarrow t = -\dfrac{1}{0.0224}\ln\left(\dfrac{1.50 - 0.0224T}{0.94}\right) \Rightarrow T = \dfrac{1.50 - 0.94\exp(-0.0224t)}{0.0224}$

$t = 40$ min. $\Rightarrow T = 49.8°C$

**d.** $U$ changed. Let $x = (UA)_{new}$. The differential equation becomes:

$\dfrac{dT}{dt} = 0.3947 + 0.096x - (0.01579 + 5.721x)T$

$\displaystyle\int_{25}^{55} \dfrac{dT}{0.3947 + 0.096x - (0.01579 + 5.721 \times 10^{-4} x)T} = \int_0^{40} dt$

$\Rightarrow -\dfrac{1}{0.01579 + 5.721 \times 10^{-4} x}\ln\left[\dfrac{0.3947 + 0.096x - \left(0.01579 + 5.721 \times 10^{-4} x\right) \times 55}{0.3947 + 0.096x - \left(0.01579 + 5.721 \times 10^{-4} x\right) \times 25}\right] = 40$

$\Rightarrow x = 14.27$ kJ / (min·°C)

$\dfrac{\Delta U}{U_{initial}} = \dfrac{\Delta(UA)}{(UA)_{initial}} = \dfrac{14.27 - 11.5}{11.5} \times 100\% = 24.1\%$

**11.24 a.** Energy balance: $MC_v \dfrac{dT}{dt} = \dot{Q} - \dot{W}$

$$\Bigg\Downarrow \begin{array}{l} \dot{W} = 0, \ C_v = 1.77 \ \text{J/g·°C} \\ M = 350 \ \text{g}, \ \dot{Q} = 40.2W = 40.2 \ \text{J/s} \end{array}$$

$$\left. \begin{array}{l} \dfrac{dT}{dt} = 0.0649 \ (\text{°C/s}) \\ t = 0, \ T = 20\text{°C} \end{array} \right\} \Rightarrow \begin{array}{l} T = 20 + 0.0649t(\text{s}) \\ T = 40\text{°C} \Rightarrow t = 308 \ \text{s} \Rightarrow \underline{5.1 \ \text{min}} \end{array}$$

**b.** The benzene temperature will continue to rise until it reaches $T_b = 80.1\text{°C}$ ; thereafter the heat input will serve to vaporize benzene isothermally.

Time to reach $T_b$ (neglect evaporation): $t = \dfrac{80.1 - 20}{0.0649} = 926 \ \text{s}$

Time remaining: $40 \ \text{minutes} \ (60 \ \text{s/min}) - 926 \ \text{s} = 1474 \ \text{s}$

Evaporation: $\Delta \hat{H}_v = (30.765 \ \text{kJ/mol})(1 \ \text{mol}/78.11 \ \text{g})(1000 \ \text{J/kJ}) = 393 \ \text{J/g}$

Evaporation rate $= (40.2 \ \text{J/s})/(393 \ \text{J/g}) = 0.102 \ \text{g/s}$

Benzene remaining $= 350 \ \text{g} - (0.102 \ \text{g/s})(1474 \ \text{s}) = \underline{\underline{200 \ \text{g}}}$

**c.** 1. Used a dirty flask. Chemicals remaining in the flask could react with benzene. Use a clean flask.
2. Put an open flask on the burner. Benzene vaporizes $\Rightarrow$ toxicity, fire hazard.
  Use a covered container or work under a hood.
3. Left the burner unattended.
4. Looked down into the flask with the boiling chemicals. Damage eyes. Wear goggles.
5. Rubbed his eyes with his hand. Wash with water.
6. Picked up flask with bare hands. Use lab gloves.
7. Put hot flask on partner's homework. Fire hazard.

**11.25 a.** Moles of air in room: $n = \dfrac{60 \ \text{m}^3}{} \left| \dfrac{273 \ \text{K}}{283 \ \text{K}} \right| \dfrac{1 \ \text{kg - mole}}{22.4 \ \text{m}^3 (\text{STP})} = 2.58 \ \text{kg - moles}$

Energy balance on room air: $nC_v \dfrac{dT}{dt} = \dot{Q} - \dot{W}$

$$\Bigg\Downarrow \begin{array}{l} \dot{Q} = \dot{m}_s \Delta \hat{H}_v (\text{H}_2\text{O, 3bars, sat'd}) - 30.0(T - T_0) \\ \dot{W} = 0 \end{array}$$

$$nC_v \dfrac{dT}{dt} = \dot{m}_s \Delta \hat{H}_v - 30.0(T - T_0)$$

$$\Bigg\Downarrow \begin{array}{l} N = 2.58 \ \text{kg - moles} \\ C_v = 20.8 \ \text{kJ/(kg - mole·°C)} \\ \Delta \hat{H}_v = 2163 \ \text{kJ/kg} \ (\text{from Table B.6}) \\ T_0 = 0\text{°C} \end{array}$$

$$\underline{\underline{\dfrac{dT}{dt} = 40.3\dot{m}_s - 0.559T \ (\text{°C/hr})}}$$

$$\underline{\underline{t = 0, \ T = 10\text{°C}}}$$

(Note: a real process of this type would involve air escaping from the room and a constant pressure being maintained. We simplify the analysis by assuming $n$ is constant.)

**11.25 (cont'd)**

   **b.**  At steady-state, $dT/dt = 0 \Rightarrow 40.3\dot{m}_s - 0.559T = 0 \Rightarrow \dot{m}_s = \dfrac{0.559T}{40.3}$

       $T = 24°C \Rightarrow \underline{\underline{\dot{m}_s = 0.333 \ \text{kg/hr}}}$

   **c.**  Separate variables and integrate the balance equation:

$$\int_{10}^{T_f} \frac{dT}{40.3\dot{m}_s - 0.559T} = \int_0^t dt \quad \xrightarrow[\substack{T_f = 23°C}]{\dot{m}_s = 0.333} \quad \int_{10}^{23} \frac{dT}{13.4 - 0.559T} = t$$

$$\Downarrow$$

$$t = -\frac{1}{0.559}\ln\left[\frac{13.4 - 0.559(23)}{13.4 - 0.559(10)}\right] = \underline{\underline{4.8 \ \text{hr}}}$$

**11.26 a.**  Integral energy balance $(t = 0 \ \text{to} \ t = 20 \ \text{min})$

$$Q = \Delta U = MC_v\Delta T = \frac{250 \ \text{kg}}{} \left| \frac{4.00 \ \text{kJ}}{\text{kg·°C}} \right| \frac{(60-20)°\text{C}}{} = 4.00 \times 10^4 \ \text{kJ}$$

Required power input:  $\dot{Q} = \dfrac{4.00 \times 10^4 \ \text{kJ}}{20 \ \text{min}} \left| \dfrac{1 \ \text{min}}{60 \ \text{s}} \right| \dfrac{1 \ \text{kW}}{1 \ \text{kJ/s}} = \underline{\underline{33.3 \ \text{kW}}}$

   **b.**  Differential energy balance:  $MC_v\dfrac{dT}{dt} = \dot{Q} \quad \xrightarrow[\substack{C_v = 4.00 \ \text{kJ/kg·°C}}]{M = 250 \ \text{kg}} \quad \begin{array}{l} \dfrac{dT}{dt} = 0.001\dot{Q}(t) \\[2mm] \underline{\underline{t = 0, \ T = 20°C}} \end{array}$

Integrate:  $\displaystyle\int_{20°C}^{T} dT = \int_0^t 0.001 \ \dot{Q} \ dT \Rightarrow T = 20°C + \int_0^t \dot{Q}dt$

Evaluate the integral by Simpson's Rule (Appendix A.3)

$$\int_0^{600 \ \text{s}} \dot{Q}dt = \frac{30}{3}[33 + 4(33 + 35 + 39 + 44 + 50 + 58 + 66 + 75 + 85 + 95)$$

$$+2(34 + 37 + 41 + 47 + 54 + 62 + 70 + 80 + 90) + 100] = 34830 \ \text{kJ}$$

$$\Rightarrow T(600 \ \text{s}) = 20°C + (0.001 \ °C/\text{kJ})(34830 \ \text{kJ}) = \underline{\underline{54.8°C}}$$

   **c.**  Past 600 s, $\dot{Q} = 100 + \dfrac{10 \ \text{kW}}{60 \ \text{s}}(t - 600 \ \text{s}) = t/6$

$$T = 20 + 0.001\int_0^t \dot{Q}dt = 20 + 0.001\left[\underbrace{\int_0^{600}\dot{Q}dt}_{34830} + \int_{600}^t \frac{t}{6}dt\right]$$

$$\Rightarrow T = 54.8 + \frac{0.001}{6}\left(\frac{t^2}{6} - \frac{600^2}{2}\right) \Rightarrow t(\text{s}) = \sqrt{12000(T - 24.8)}$$

$$T = 85°C \Rightarrow t = 850 \ \text{s} = 14 \ \text{min}, \ 10 \ \text{s} \Rightarrow \underline{\underline{\text{explosion at } 10:14 + 10 \ \text{s}}}$$

**11.27  a.** <u>Total Mass Balance:</u>

Accumulation=Input– Output

$$\Downarrow$$

$$\frac{dM_{tot}}{dt} = \dot{m}_i - \dot{m}_o \Rightarrow \frac{d(\rho V)}{dt} = 8.00\rho - 4.00\rho \xrightarrow{\rho=constant} \begin{array}{l} \dfrac{dV}{dt} = 4.00 \text{ L / s} \\[4pt] \underline{\underline{t = 0, \ V_0 = 400 \text{ L}}} \end{array}$$

<u>KCl Balance:</u>

Accumulation=Input-Output$\Rightarrow \dfrac{dM_{KCl}}{dt} = \dot{m}_{i,KCl} - \dot{m}_{o,KCl} \Rightarrow \dfrac{d(CV)}{dt} = 1.00 \times 8.00 - 4.00C$

$$\Rightarrow V\frac{dC}{dt} + C\frac{dV}{dt} = 8 - 4C \xrightarrow{dV/dt = 4} \begin{array}{l} \dfrac{dC}{dt} = \dfrac{8 - 8C}{V} \\[4pt] \underline{\underline{t = 0, \ C_0 = 0 \text{ g / L}}} \end{array}$$

**b.** (i)The plot of V vs. t begins at (t=0, V=400).  The slope (=dV/dt) is 4 (a positive constant). V increases linearly with increasing t until V reaches 2000.  Then the tank begins to overflow and V stays constant at 2000.
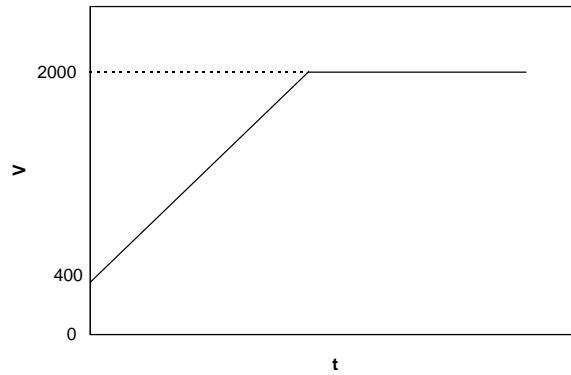


(ii) The plot of C vs. t begins at (t=0, C=0). When t=0, the slope (=dC/dt) is (8-0)/400=0.02. As t increases, C increases and V increases (or stays constant)$\Rightarrow$ dC/dt=(8-8C)/V becomes less positive, approaches zero as t→ ∞.  The curve is therefore <u>concave down.</u>
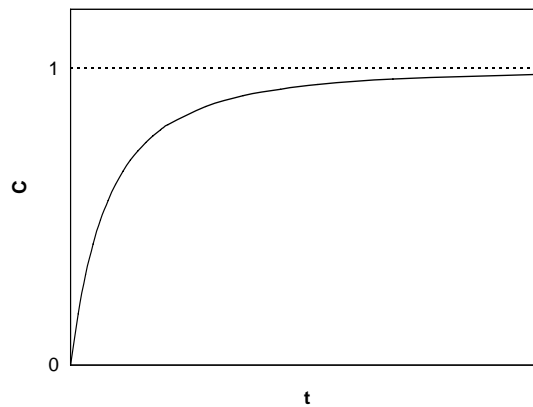


**c.** $\dfrac{dV}{dt} = 4 \Rightarrow \displaystyle\int_{400}^{V} dV = 4\int_0^t dt \Rightarrow \underline{\underline{V = 400 + 4t}}$

**11.27 (cont'd)**

$$\frac{dC}{dt} = \frac{8 - 8C}{V} \xrightarrow{V = 400 + 4t} \frac{dC}{dt} = \frac{1 - C}{50 + 0.5t}$$

$$\int_0^C \frac{dC}{1 - C} = \int_0^t \frac{dt}{50 + 0.5t} \Rightarrow -\ln(1 - C)\Big]_0^C = 2\ln(50 + 0.5t)\Big]_0^t$$

$$\Rightarrow \ln(1 - C)^{-1} = 2\ln\frac{50 + 0.5t}{50} = \ln(1 + 0.01t)^2$$

$$\Rightarrow \frac{1}{1 - C} = (1 + 0.01t)^2 \Rightarrow \underline{\underline{C = 1 - \frac{1}{(1 + 0.01t)^2}}}$$

When the tank overflows, $V = 400 + 4t = 2000 \Rightarrow t = 400$ s

$$C = 1 - \frac{1}{(1 + 0.01 \times 400)^2} = \underline{\underline{0.96 \text{ g / L}}}$$

**11.28  a.** Salt Balance on the 1st tank:

Accumulation=-Output
⇓

$$\frac{d(C_{S1}V_1)}{dt} = -C_{S1}\dot{v} \Rightarrow \frac{dC_{S1}}{dt} = -C_{S1}\frac{\dot{v}}{V_1} = -0.08C_{S1}$$

$$\underline{\underline{C_{S1}(0) = 1500/500 = 3 \text{ g / L}}}$$

Salt Balance on the 2nd tank:
Accumulation=Input-Output
⇓

$$\frac{d(C_{S2}V_2)}{dt} = C_{S1}\dot{v} - C_{S2}\dot{v} \Rightarrow \frac{dC_{S2}}{dt} = (C_{S1} - C_{S2})\frac{\dot{v}}{V_2} = 0.08(C_{S1} - C_{S2})$$

$$\underline{\underline{C_{S2}(0) = 0 \text{ g / L}}}$$
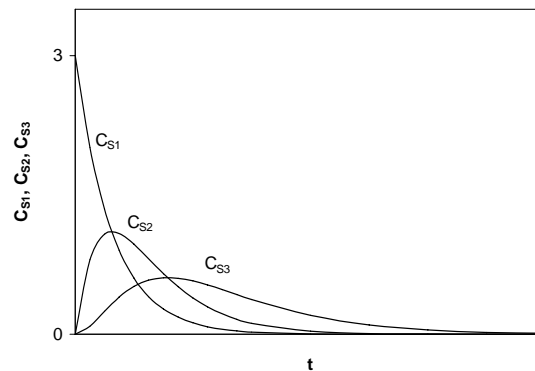
Salt Balance on the 3rd tank:
Accumulation=Input-Output
⇓

$$\frac{d(C_{S3}V_3)}{dt} = C_{S2}\dot{v} - C_{S3}\dot{v} \Rightarrow \frac{dC_{S3}}{dt} = (C_{S2} - C_{S3})\frac{\dot{v}}{V_3} = 0.04(C_{S2} - C_{S3})$$

$$\underline{\underline{C_{S3}(0) = 0 \text{ g / L}}}$$

**b**.



11-22

**11.28 (cont'd)**

The plot of $C_{S1}$ vs. t begins at (t=0, $C_{S1}$=3). When t=0, the slope (=$dC_{S1}/dt$) is $-0.08 \times 3 = -0.24$. As t increases, $C_{S1}$ decreases $\Rightarrow dC_{S1}/dt$=-0.08$C_{S1}$ becomes less negative, approaches zero as t→∞. The curve is therefore concave up.

The plot of $C_{S2}$ vs. t begins at (t=0, $C_{S2}$=0). When t=0, the slope (=$dC_{S2}/dt$) is $0.08(3-0) = 0.24$. As t increases, $C_{S2}$ increases, $C_{S1}$ decreases ($C_{S2} < C_{S1}$)$\Rightarrow dC_{S2}/dt$ =0.08($C_{S1}$-$C_{S2}$) becomes less positive until $dC_{S2}/dt$ changes to negative ($C_{S2} > C_{S1}$). Then $C_{S2}$ decreases with increasing t as well as $C_{S1}$. Finally $dC_{S2}/dt$ approaches zero as t→∞. Therefore, $C_{S2}$ increases until it reaches a maximum value, then it decreases.

The plot of $C_{S3}$ vs. t begins at (t=0, $C_{S3}$=0). When t=0, the slope (=$dC_{S3}/dt$) is $0.04(0-0) = 0$. As t increases, $C_{S2}$ increases ($C_{S3} < C_{S2}$)$\Rightarrow dC_{S3}/dt$ =0.04($C_{S2}$-$C_{S3}$) becomes positive $\Rightarrow C_{S2}$ increases with increasing t until $dC_{S3}/dt$ changes to negative ($C_{S3} > C_{S1}$). Finally $dC_{S3}/dt$ approaches zero as t→∞. Therefore, $C_{S3}$ increases until it reaches a maximum value then it decreases.

**c.**
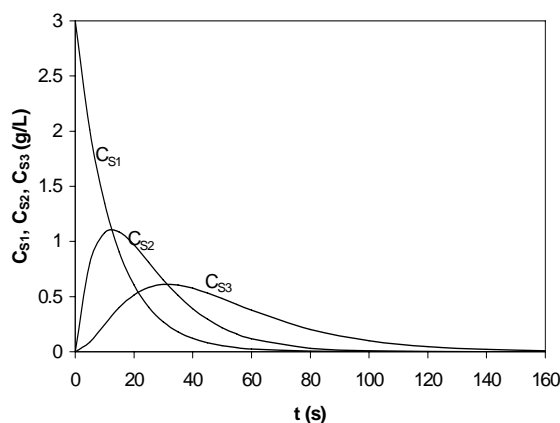


**11.29 a.** (i) Rate of generation of B in the 1$^{st}$ reaction:  $r_{B1} = 2r_1 = 0.2C_A$

(ii) Rate of consumption of B in the 2$^{nd}$ reaction:  $-r_{B2} = r_2 = 0.2C_B^2$

**b.** Mole Balance on A:
Accumulation=-Consumption
$\Downarrow$

$$\frac{d(C_A V)}{dt} = -0.1C_A V \Rightarrow \frac{dC_A}{dt} = -0.1C_A$$

$$t = 0, \; C_{A0} = 1.00 \text{ mol / L}$$
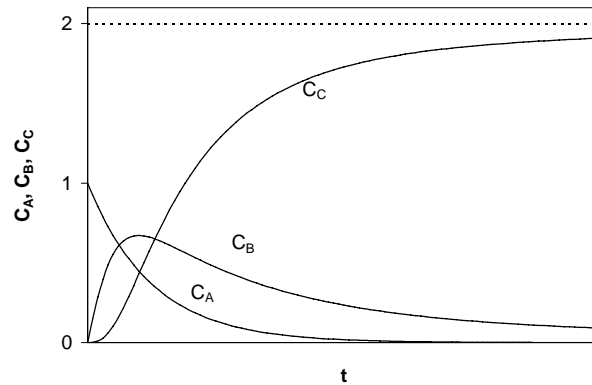
Mole Balance on B:
Accumulation= Generation-Consumption
$\Downarrow$

$$\frac{d(C_B V)}{dt} = 0.2C_A V - 0.2C_B^2 V \Rightarrow \frac{dC_B}{dt} = 0.2C_A - 0.2C_B^2$$

$$t = 0, \; C_{B0} = 0 \text{ mol / L}$$

11-23

**11.29 (cont'd)**

    **c.**



The plot of $C_A$ vs. t begins at (t=0, $C_A$=1). When t=0, the slope (=$dC_A/dt$) is $-0.1 \times 1 = -0.1$. As t increases, $C_A$ decreases $\Rightarrow dC_A/dt = -0.1C_A$ becomes less negative, approaches zero as t→∞. $C_A$→0 as t→∞. The curve is therefore <u>concave up.</u>

The plot of $C_B$ vs. t begins at (t=0, $C_B$=0). When t=0, the slope (=$dC_B/dt$) is $0.2(1-0) = 0.2$. As t increases, $C_B$ increases, $C_A$ decreases ($C_B^2 < C_A$)$\Rightarrow dC_B/dt = 0.2(C_A - C_B^2)$ becomes less positive until $dC_B/dt$ changes to negative ($C_B^2 > C_A$). Then $C_B$ decreases with increasing t as well as $C_A$. Finally $dC_B/dt$ approaches zero as t→∞. Therefore, $C_B$ increases first until it reaches a maximum value, then it decreases. $C_B$→0 as t→∞.

The plot of $C_C$ vs. t begins at (t=0, $C_C$=0). When t=0, the slope (=$dC_C/dt$) is $0.2(0) = 0$. As t increases, $C_B$ increases $\Rightarrow dC_C/dt = 0.2 C_B^2$ becomes positive also increases with increasing t $\Rightarrow C_C$ increases faster until $C_B$ decreases with increasing t $\Rightarrow dC_C/dt = 0.2 C_B^2$ becomes less positive, approaches zero as t→∞ so $C_C$ increases more slowly. Finally $C_C$→2 as t→∞. The curve is therefore S-<u>shaped.</u>

    **d.**
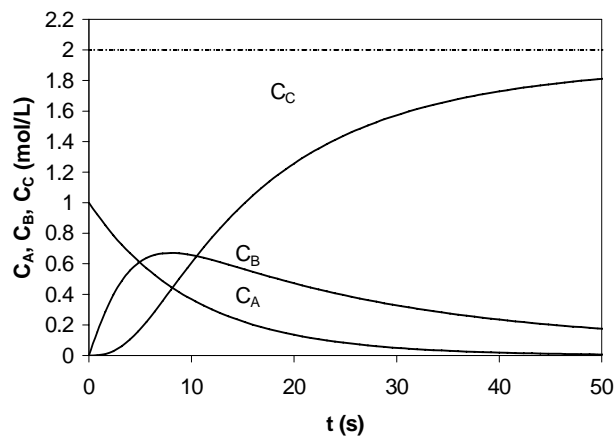
**11.30 a.** When $x = 1$, $\underline{\underline{y = 1}}$.

$$y = \frac{ax}{x+b} \overset{x=1, y=1}{\Rightarrow} 1 = \frac{a}{1+b} \Rightarrow \underline{\underline{a = 1+b}}$$

**b.** Raoult's Law: $\quad p_{C_5H_{12}} = yP = xp*_{C_5H_{12}}(46^\circ C) \Rightarrow y = \dfrac{xp*_{C_5H_{12}}(46^\circ C)}{P}$

Antoine Equation: $\quad p*_{C_5H_{12}}(46^\circ C) = 10^{\left(6.84471 - \frac{1060.793}{46+231.541}\right)} = 1053$ mm Hg

$$\Rightarrow y = \frac{xp*_{C_5H_{12}}(46^\circ C)}{P} = \frac{0.7 \times 1053}{760} = \underline{\underline{0.970}}$$

$$\begin{cases} y = \dfrac{ax}{x+b} \overset{x=0.70,\ y=0.970}{\Longrightarrow} 0.970 = \dfrac{0.70a}{0.70+b} \cdots\cdots(1) \\ \text{From part (a), } a = 1+b \cdots\cdots\cdots\cdots\cdots\cdots\cdots(2) \end{cases} \Rightarrow \begin{cases} \underline{\underline{a = 1.078}} \\ \underline{\underline{b = 0.078}} \end{cases}$$

**c.** Mole Balance on Residual Liquid:
Accumulation=-Output
$$\Downarrow$$

$$\frac{dN_L}{dt} = -\dot{n}_V$$

$$\underline{\underline{t = 0,\ N_L = 100 \text{ mol}}}$$

Balance on Pentane:
Accumulation=-Output
$$\Downarrow$$

$$\frac{d(N_L x)}{dt} = -\dot{n}_V\, y \Rightarrow x\frac{dN_L}{dt} + N_L\frac{dx}{dt} = -\dot{n}_V\frac{ax}{x+b}$$

$$\Downarrow dN_L / dt = -\dot{n}_V$$

$$\frac{dx}{dt} = -\frac{\dot{n}_V}{N_L}\left(\frac{ax}{x+b} - x\right)$$

$$\underline{\underline{t = 0,\ x = 0.70}}$$

**d.** Energy Balance: Consumption=Input
$$\Downarrow$$

$$\dot{n}_V \Delta\widehat{H}_{vap} = \dot{Q} \overset{\Delta\widehat{H}_{vap} = 27.0 \text{ kJ/mol}}{\Longrightarrow} \dot{n}_V = \frac{\dot{Q}}{(27.0 \text{ kJ/mol})}$$

From part (c), $\dfrac{dN_L}{dt} = -\dot{n}_V \overset{t=0,\ N_L = 100 \text{ mol}}{\Longrightarrow} N_L = 100 - \dot{n}_V t = 100 - \dfrac{\dot{Q}t}{27.0}$

$$\frac{\dot{n}_V}{N_L} = \frac{\dot{Q}/27.0}{100 - \dfrac{\dot{Q}t}{27.0}}$$

Substitute this expression into the equation for dx/dt from part (c):

**11.30 (cont'd)**

$$\frac{dx}{dt} = -\frac{\dot{n}_V}{N_L}\left(\frac{ax}{x+b} - x\right) = -\frac{\dot{Q}/27.0}{100 - \dfrac{\dot{Q}t}{27.0}}\left(\frac{ax}{x+b} - x\right)$$
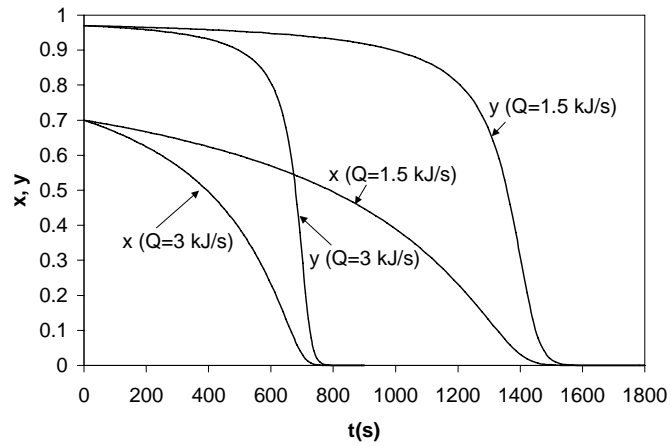
$$x(0) = 0.70$$

**e.**



**f.** The mole fractions of pentane in the vapor product and residual liquid continuously decrease over a run. The initial and final mole fraction of pentane in the vapor are 0.970 and 0, respectively. The higher the heating rate, the faster $x$ and $y$ decrease.