

***Chemical Biochemical and Engineering  
Thermodynamics 5th edition Sandler Solutions  
Manual***

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## 2

$$2.1 \quad \frac{d(C \cdot V)}{dt} = \frac{dM}{dt} = \dot{M}_{\text{IN}} - \dot{M}_{\text{OUT}}$$

a) at steady state

$$\dot{M}_{\text{IN}} = 1 \frac{\text{g}}{\text{min}} = \dot{M}_{\text{OUT}} = C \cdot \text{volumetric flow rate out}$$

$$1 \frac{\text{g}}{\text{min}} = C \times \frac{10 \text{ m}^3}{\text{min}} \quad C = \frac{1}{10} \frac{\text{g}}{\text{m}^3} = 0.1 \frac{\text{g}}{\text{m}^3}$$

$$\text{b) } V \frac{dC}{dt} = \dot{M} - C \times 10 \frac{\text{m}^3}{\text{min}} \quad V \frac{dC}{dt} = \dot{M} - C - 10 \frac{\text{m}^3}{\text{min}}$$

$$V = 6 \times 6 \times 3 = 108 \text{ m}^3 \quad V = 6 \times 6 \times 3 = 108 \text{ m}^3$$

$$108 \text{ m}^3 \frac{dC}{dt} = 1 \frac{\text{g}}{\text{min}} - C \times \frac{10 \text{ m}^3}{\text{min}}$$

$$\frac{dC}{dt} = \frac{1}{108} \frac{\text{g}}{\text{m}^3 \text{ min}} - C \frac{10}{108} \text{ m}^{-1}$$

or for C in  $\frac{\text{g}}{\text{m}^3}$

$$108 \frac{dC}{dt} = -(10C - 1) \quad 10.8 \frac{dC}{(C - 0.1)} = -dt$$

$$10.8 \ln \left( \frac{C - 0.1}{-0.1} \right) = -t$$

$$\text{For } C = 0.95 * 0.1 = 0.095 \quad 10.8 \ln \left( \frac{-0.005}{-0.1} \right) = -t$$

$$108 \ln 20 = t \quad t = 32.35 \text{ minutes}$$

$$2.2 \quad \frac{dC}{dt} = -kC \quad \ln \frac{C_f}{C_i} = -kt$$

$$\text{If } C_f = 0.5 C_i \quad \ln 0.5 = -kt \text{ or } k = \frac{\ln 2}{t}$$

for a half life of seven years  $k = 0.099 \text{ years}^{-1}$   
so that

$$\ln \frac{C_f}{22} = -k \cdot 25 = -0.099 \times 25 = -2.475$$

$$C_f = 22 \exp(-2.475) = 1.85 \text{ ppm}$$

$$2.3 \quad \text{Basis: 2-liter vessel} = 2000 \text{ cm}^3 = 2 \times 10^3 \times 10^{-6} \frac{\text{m}^3}{\text{cm}^3} = 2 \times 10^{-3} \text{ m}^3$$

$$\text{Initial moles of phosphine} = 5 \frac{\text{kmol}}{\text{m}^3} \times 10^3 \frac{\text{mol}}{\text{kmol}} \times 2 \times 10^{-5} \text{ m}^3 = 10 \text{ mol}$$

a) Mass balance from stoichiometry

| Species         | Initial | Final       |
|-----------------|---------|-------------|
| PH <sub>3</sub> | 10      | 10 - 4X = 7 |
| P <sub>4</sub>  | 0       | X           |
| H <sub>2</sub>  | 0       | 6X          |

$$\text{Since } 10 - 4X = 7 \quad 3 = 4X \quad X = \frac{3}{4}$$

$$\Rightarrow P_4 = 0.75 \text{ moles}$$

$$H_2 = 6 \text{ moles}$$

b)  $C_{PH_3}$  at any time =  $\frac{(10-4X) \text{ moles}}{2 \times 10^{-3} \text{ m}^3} = (5-2X) \times 10^{-3} \frac{\text{moles}}{\text{m}^3}$

Therefore

$$\frac{dC_{PH_3}}{dt} = 3.715 \times 10^{-6} C_{PH_3}$$

$$-2 \times 10^{-3} \frac{dX}{dt} = -3.715 \times 10^{-6} (5-2X) \times 10^{-3}$$

$$\frac{dX}{dt} = 3.715 \times 10^{-6} (2.5-X)$$

$$-\frac{dX}{2.5-X} = \frac{d(2.5-X)}{2.5-X} = -3.715 \times 10^{-6} dt$$

$$\ln(2.5-X)_t - \ln(2.5-X)_0 = -3.715 \times 10^{-6} t$$

$$\frac{2.5-X}{2.5} = e^{-2.715 \times 10^{-6} t}$$

$$2.5-X = 2.5 e^{-2.715 \times 10^{-6} t}$$

$$X = 2.5 \left( 1 - e^{-2.715 \times 10^{-6} t} \right)$$

Therefore

$$\text{Moles PH}_3 = 10 - 4X = 10 - 10 \left( 1 - e^{-2.715 \times 10^{-6} t} \right) = 10 e^{-2.715 \times 10^{-6} t}$$

$$\text{Moles PH}_4 = 2.5 \left( 1 - e^{-2.715 \times 10^{-6} t} \right)$$

$$\text{Moles H}_2 = 15 \left( 1 - e^{-2.715 \times 10^{-6} t} \right)$$

Time required for 3 moles to react = time for  $X = 0.75$

$$X = 2.5 \left( 1 - e^{-2.715 \times 10^{-6} t} \right) = 0.75$$

$$T = 1.314 \times 10^5 \text{ sec} = 36.49 \text{ hours}$$

2.4  $2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$

a) 0.5 moles NO produces 0.5 moles NO<sub>2</sub>

b)

| Species         | Initial Conc | Conc. at X |
|-----------------|--------------|------------|
| NO              | 1            | 1-2X       |
| O <sub>2</sub>  | 3            | 3-X        |
| NO <sub>2</sub> | 0            | 6X         |
|                 |              | <hr/> 4-X  |

$$\frac{dC_{NO}}{dt} = -1.4 \times 10^{-4} C_{NO}^2 C_{O_2}$$

$$\frac{d(1-2X)}{dt} = -1.4 \times 10^{-4} (1-2X)^2 (3-X) = -2 \frac{dX}{dt}$$

$$\Rightarrow \frac{dX}{dt} = 0.7 \times 10^{-4} (1-2X)^2 (3-X)$$

$$0.7 \times 10^{-4} t = \frac{1}{5(1-2X)} + \frac{1}{25} \ln \frac{(2X-1)}{(X-3)}$$

Now for 0.5 mole of NO to react  $\Rightarrow 1 - 2X = 0.5$   $X = 0.25$

$$0.7 \times 10^{-4} t = \frac{1}{5 \times 0.5} + \frac{1}{25} \ln (0.5/2.75) = 0.332$$

$$t = \frac{0.332}{0.7} \times 10^4 = 0.474 \times 10^4 \text{ sec} = 1.317 \text{ hrs}$$