

## Unsteady state material balances

### Unsteady state material balances for a two-phase, multicomponent system

Name(s):\_

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#### Fill in all sections.

#### Student Learning Objectives

1. Write unsteady state material balances around semi-batch systems.
2. Use vapor pressure information to determine the composition of a vapor in equilibrium with a liquid.

#### Schematic and Dimensions

#### Before running the experiment:

1. Familiarize yourself with what is happening physically. In this experiment, a stream of  $N_2$  flows through a vessel we often call a “bubbler” (i.e., a vapor-liquid contactor) that initially contains an equimolar mixture of n-pentane and n-hexane in the liquid phase. The bottom of the vessel contains a diffuser so the bubbles are even distributed across the vessel diameter. As the  $N_2$  passes through the bubbler, some of the n-pentane and n-hexane evaporate, and flow out with the  $N_2$  that exits the bubbler. The bubbler can be set to one of three temperatures: 15, 20, or 25°C. All the tubing downstream of the bubbler (and the exhaust) are at a temperature of at least 25°C. The flow rate of  $N_2$  into the bubbler is fixed by a mass flow controller to be 35 standard  $cm^3/min$ . The entire system is assumed to operate at close to atmospheric pressure, although there would be some pressure drop between the inlet and outlet of the system. We measure the change in liquid level in the bubbler over time. As discussed below, this can be related to the molar flow rates of n-pentane and n-hexane out of the bubbler.

## Unsteady state material balances

2. Bubblers are often assumed to operate close to vapor-liquid equilibrium. Furthermore, pentane and n-hexane are chemically similar compounds that can be assumed to form an ideal solution, where Raoult's Law can determine the gas-phase pressure of each compound. Write the equations to determine the partial pressures of n-pentane and n-hexane exiting an equilibrated bubbler.
3. The bubbler can operate at one of three temperatures. How will operating at higher temperatures affect the flow rate coming out of the bubbler right after the experiment starts? How will it affect the vapor composition?
4. As the experiment proceeds, the composition of liquid remaining in the bubbler changes. How do you expect it to change? How will the change in composition affect the flow rate of the vapor exiting the bubbler over time?

### Running the experiment:

1. The tank initially contains a 50/50 molar mixture of n-pentane and n-hexane.
2. Turn on the temperature controller and set the reactor temperature to be 15°C.
3. Open the valve to the N<sub>2</sub> cylinder.
4. Open the valve at the bottom of the tank to start N<sub>2</sub> flow through the bubbler.
5. Record in Table 1 the liquid volume in the bubbler initially and at different time points, until the liquid level has declined to ~20% of its initial value. Below that level, the assumption of vapor-liquid equilibrium is not likely to hold due to the small volume of liquid in the container.
6. Convert the simulation time to physical time in the worksheet.
7. Reset the system to refill the bubbler.
8. Repeat this process, starting with step 2, for temperatures 20°C and 25°C and record measurements in Table 1.

## Unsteady state material balances

**Table 1**

15°C			20°C			25°C		
Simulation Time (s)	Physical Time (min)	Volume (cm <sup>3</sup> )	Simulation Time (s)	Physical Time (min)	Volume (cm <sup>3</sup> )	Simulation Time (s)	Physical Time (min)	Volume (cm <sup>3</sup> )

3. Plot volume versus physical time for the three experiments. What patterns do you see?

### After the experiment:

1. Use material balances and Raoult's law to compute the expected rate of volume decrease. This requires several steps. The equations for the composition of the vapor leaving the vessel, assuming vapor-liquid equilibrium, are:

$$y_i P = P_i = x_i P_i^{sat}$$

where  $P_i$  is the partial pressure of n-pentane or n-hexane,  $y_i$  is the mole fraction in the vapor,  $P$  is the total pressure (atmospheric),  $x_i$  is the liquid mole fraction, and  $P_i^{sat}$  is the saturation pressure at a given temperature. We can write one equation for n-pentane and one for n-hexane. Values for  $P_i^{sat}$  are calculated by the Antoine equation, and  $P_i^{sat}$  is fixed once the bubbler temperature is set.

2. Next, determine the molar flow rate of each component exiting the reactor. The  $N_2$  molar flow rate ( $F_{N_2}$ ) is set at 35 sccm; this can be converted to  $F_{N_2} = 0.0156$  mol/min of  $N_2$ . Because we do not expect  $N_2$  to accumulate in the vessel, this is also the molar flow rate of  $N_2$  exiting the reactor. The total pressure exiting the reactor is approximately 1.0 bar. The partial pressure of  $N_2$  is equal to this pressure minus the partial pressures of n-pentane and n-hexane:

$$P_{N_2} = 1.0 \text{ bar} - P_{n\text{-pent}} - P_{n\text{-hex}} = 1.0 \text{ bar} - x_{n\text{-pent}} P_{n\text{-pent}}^{sat} - x_{n\text{-hex}} P_{n\text{-hex}}^{sat}$$

Thus, the molar flow rate of n-pentane exiting the bubbler is equal to the flow rate of  $N_2$  through the bubbler, multiplied by the ratio of the n-pentane vapor phase mole fraction, i.e. ,

$$y_{pent} = \frac{F_{pent}}{F_{total}}$$

$$y_{N_2} = \frac{F_{N_2}}{F_{total}}$$

Dividing these two equations and rearranging:

$$F_{pent} = F_{N_2} \frac{y_{pent}}{y_{N_2}} = F_{N_2} \frac{P_{pent}}{P_{N_2}}$$

Then, the molar flow rate of each component would be:

$$F_{pent} = F_{N_2} \frac{x_{pent} P_{pent}^{sat}(T)}{1 - x_{pent} P_{pent}^{sat}(T) - x_{hex} P_{hex}^{sat}(T)}$$

$$F_{hex} = F_{N_2} \frac{x_{hex} P_{hex}^{sat}(T)}{1 - x_{pent} P_{pent}^{sat}(T) - x_{hex} P_{hex}^{sat}(T)}$$

## Unsteady state material balances

From these equations, we can determine the rate of mass flow out of each system from the molecular weight. And we can relate this to the drop in liquid level by dividing by the liquid density:

$$\dot{V}_{pent} = \frac{(MW)_{pent}}{\rho_{pent}} F_{N_2} \frac{x_{pent} P_{pent}^{sat}(T)}{1 - x_{pent} P_{pent}^{sat}(T) - x_{hex} P_{hex}^{sat}(T)}$$

$$\dot{V}_{hex} = \frac{(MW)_{hex}}{\rho_{hex}} F_{N_2} \frac{x_{hex} P_{hex}^{sat}(T)}{1 - x_{pent} P_{pent}^{sat}(T) - x_{hex} P_{hex}^{sat}(T)}$$

And the total rate of volume change is equal to the sum of these two volumetric flow rates, which can be compared to the experimental data.

3. By plugging in values of  $x_{pent} = x_{hex} = 0.50$ , we can determine the initial rate of volume decline. Try plugging in appropriate numbers for the other parameters. Does your answer agree with the slope at early times on your plot?

In the following section, the complete time-dependent solution is obtained by numerically solving the differential mass balances using Python or other software.

4. At long times, the composition of the remaining liquid changes, because n-pentane is removed from the system faster than n-hexane. (Why is that?) To account for this, we need to write an unsteady state mole balance:

$$\frac{dN_{pent}}{dt} = F_{N_2} \frac{x_{pent} P_{pent}^{sat}(T)}{1 - x_{pent} P_{pent}^{sat}(T) - x_{hex} P_{hex}^{sat}(T)}$$

where  $x_{pent} = N_{pent} / (N_{pent} + N_{hex})$ . We can write a similar equation for n-hexane:

$$\frac{dN_{hex}}{dt} = F_{N_2} \frac{x_{hex} P_{hex}^{sat}(T)}{1 - x_{pent} P_{pent}^{sat}(T) - x_{hex} P_{hex}^{sat}(T)}$$

These two differential equations must be solved simultaneously given a known initial value, i.e., this is an *initial value problem*. Solving these differential equations numerically gives the number of moles of each component as a function of time. Using the molecular weight and density of the two components, this can be converted into total liquid volume as a function of time for comparison to the experimental data.

Plot from Python below. Data from the digital experiment could be plotted to compare to the Python results. The blue curve is 15°C, the orange curve 20°C, and the green curve is 25°C.

## Unsteady state material balances

