Chapter 6 Multiphase Systems

Name: _____ Date: _____

Chapter 6 will introduce student to operations in chemical processes which involve the change of a material from one phase into another. These phase changes are used in separation and purification processes. The following problems build upon the fundamentals covered in your text as applied to hydrogen processing, hydrogen as an energy carrier, and the use of hydrogen in fuel cells.

- 6.1-1 Vapor Pressure Estimation Using the Clausius-Clapeyron Equation
- 6.3-1 Composition of a Saturated Gas-Vapor System
- 6.3-2 Material Balances Around a Condenser
- 6.3-3 Relative Humidity
- 6.4-1 Humidification of Air for Proton-Exchange Membrane Fuel Cells
- 6.4-5 Boiling Point of a Mixture

Example 6.1-1 Vapor Pressure Estimation Using the Clausius-Clapeyron Equation

Methanol is the fuel used in Direct-Methanol Fuel Cells, which have application in portable devices such as cell phones and laptop computers. The vapor pressure of methanol p* at different temperatures was obtained from Flick, E.W., *Industrial Solvents Handbook*, 5th Edition, and these values are summarized in the following table:

T (°C)	p*(Pa)
20	1.32×10^4
100	3.47 x 10 ⁵

Determine the vapor pressure of methanol at the operation temperature of a Direct-Methanol Fuel Cell of 60 $^{\circ}$ C.

Strategy

The Clausius-Clapeyron equation allows the calculation of the vapor pressure as a function of temperature. However, there are some additional parameters such as the heat of vaporization and the parameter B that must be calculated in order to use this equation.

Solution

The Clausius-Clapeyron equation is shown below:

$$\ln p^* = -\frac{\Delta \hat{H}_v}{RT} + B$$

Recalling the equation of a straight line:

$$y = mx + b$$

The Clausius-Clapeyron equation can be compared to the equation of a straight line, with:

y = ln p*
$$x = \frac{1}{T}$$

m = $-\frac{\Delta \hat{H}_v}{R}$ b = B

When a set of data is given, the slope can be calculated with the following equation:

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$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

Using the variables from Clausius-Clapeyron equation yields:

$$-\frac{\Delta \hat{H}_{v}}{R} = \frac{\ln p_{2}^{*} - \underline{\qquad}}{\frac{1}{T_{2}} - \frac{1}{T_{1}}}$$

This equation can be rearranged by applying the properties of logarithms to get:

$$-\frac{\Delta \hat{H}_{v}}{R} = \frac{\left(\ln \frac{p_{2}^{*}}{p_{1}^{*}}\right)(T_{1}T_{2})}{T_{1}-T_{2}}$$

Substituting the data from the table gives:

$$\frac{\Delta \hat{H}_{v}}{R} = -\frac{\left(\ln \frac{Pa}{Pa}\right)(293.15K)(-K)}{293.15K - K}$$
$$m = \frac{\Delta \hat{H}_{v}}{R} = 4470 \text{ K}$$

The Clausius-Clapeyron equation can be solved for the parameter B to yield:

$$B = \ln p^* + \frac{\Delta \hat{H}_v}{RT}$$

Substituting any of the data points into this equations, allows us to calculate B:

B = ln (_____) + (4470 K)
$$\left(\frac{1}{293.15 K}\right)$$

B = _____

If the values calculated for B and the slope, m are substituted into the original Clausius-Clapeyron equation we get:

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$$\ln p^* = -4470 \left(\frac{1}{T}\right) +$$

where:

T = Temperature (K) p* = Vapor pressure of methanol (Pa)

Now the operation temperature of a direct-methanol fuel cell can be entered into this equation to calculate the vapor pressure of methanol at this temperature:

$$\ln p^* = -4470 \left(\frac{1}{333.15} \right) + ____$$

$$\ln p^* = ____$$

Solving for p* gives:

$$p^* = e^{-----}$$
 $p^* = ____ Pa$

Example 6.3-1 Composition of a Saturated Gas-Vapor System

The air entering a proton-exchange membrane fuel cell on the cathode side is in equilibrium with liquid water at the operation temperature of 80 $^{\circ}$ C and a total pressure of 2.5 bar. Calculate the composition of the exhaust gases if the air composition is 15 mol % of oxygen and 85 mol % of nitrogen on a dry basis.

Strategy

Since the gas and liquid are in equilibrium, Raoult's Law is applicable for this problem, and can be used to determine the mol fraction of water in the exhaust gases.

Solution

Raoult's Law is applicable for processes where the gas in the liquid are in equilibrium, and it is given by the following equation:

$$y_{_{H_2O}} = \frac{p_{_{H_2O}}^*}{P}$$

The value of the vapor pressure of water at the temperature of 80 $^{\circ}$ C can be found in Table B.3 of Felder & Rousseau:

$$p_{H_{2}0}^{*}(@ 80 \ ^{\circ}C) = ___ mm Hg$$

Substituting the vapor pressure and the absolute pressure values into Raoult's Law gives:

$$y_{H_{2^{O}}} = \frac{\operatorname{mm} Hg\left(\frac{bar}{760 \operatorname{mm} Hg}\right)}{2.5 \operatorname{bar}}$$
$$y_{H_{2^{O}}} = \underbrace{\operatorname{mol} H_{2^{O}}}{\operatorname{mol} \operatorname{humid} \operatorname{air}}$$

Since only air and water are present in the exhaust gases, the sum of the molar fractions of water and dry air must be equal to 1:

$$y_{dry air} + y_{H_2O} = 1$$

Solving for the molar fraction of dry air and substituting the known value yields:

$$y_{dry air} = 1 - y_{H_2O} = 1 - \underline{\qquad}$$
$$y_{dry air} = \underline{\qquad} \frac{mol dry air}{mol humid air}$$

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From the molar fraction of dry air, we can calculate the molar fractions of oxygen and nitrogen, using the information about the composition of dry air:

$$\begin{split} y_{O_2, \text{wet basis}} &= y_{O_2, \text{dry basis}} y_{\text{dry air}} \\ y_{N_2, \text{wet basis}} &= y_{N_2, \text{dry basis}} y_{\text{dry air}} \end{split}$$

The known molar fractions can be substituted into these two equations to get:

$$y_{O_{2},\text{wet basis}} = \left(\underbrace{----\frac{\text{mol }O_{2}}{\text{mol }\text{dry air}}}_{\text{mol }\text{dry air}} \right) \left(\underbrace{----\frac{\text{mol }\text{dry air}}{\text{mol }\text{humid }\text{air}}}_{\text{mol }\text{humid }\text{air}} \right)$$
$$y_{O_{2},\text{wet }\text{basis}} = 0.122 \frac{\text{mol }O_{2}}{\text{mol }\text{wet }\text{air}}$$
$$y_{N_{2},\text{wet }\text{basis}} = \left(\underbrace{----\frac{\text{mol }N_{2}}{\text{mol }\text{dry }\text{air}}}_{\text{mol }\text{dry }\text{air}} \right) \left(\underbrace{----\frac{\text{mol }\text{dry }\text{air}}{\text{mol }\text{wet }\text{air}}}_{\text{mol }\text{wet }\text{air}} \right)$$

Example 6.3-2 Material Balances Around a Condenser

The process occurring in a Proton-Exchange Membrane Fuel Cell uses Hydrogen electrons to power an electric load. The products of the reaction taking place in a fuel cell are water vapor and heat.

The electrolyte membrane must be wet in order to facilitate the transfer of hydrogen protons through it. The steam being produced in a fuel cell enters a condenser, which will return the liquid water into the fuel cell, to maintain the membrane at an adequate humidity.

A stream of air is exiting a fuel cell at a temperature of 87 $^{\circ}$ C and a pressure of 21.8 psi and it contains 25 mol % of water.

(a) Determine the dew point and the degrees of superheat of the air.

Strategy

For this problem, we will assume that the air and the water are in equilibrium. Thus, we can use Raoult's Law to compare the partial pressure of water to the vapor pressure at the dew point temperature.

Solution

First, the partial pressure of water in the air entering the condenser must be determined. This can be done using the definition of partial pressure:

$$\mathbf{p}_{\mathrm{H}_{2}\mathrm{O}} = \mathbf{y}_{\mathrm{H}_{2}\mathrm{O}}\mathbf{P}$$

Substituting the values on the right hand side of the equation, we have:

$$p_{H_2O} = \left(0.25 \frac{\text{mol } H_2O}{\text{mol}}\right) (\underline{\qquad} \text{psi}) \left(\frac{760 \text{ mm } Hg}{\underline{\qquad} \text{psi}}\right)$$
$$p_{H_2O} = \underline{\qquad} \text{mm } Hg$$

If we are assuming equilibrium between the two phases, the partial pressure of water must be equal to the vapor pressure at the dew point. This can be written as follows:

$$p_{H_{2^{O}}} = p_{H_{2^{O}}}^{*} (@T_{dp})$$

Table B.3 of Felder & Rousseau is giving the vapor pressure of liquid water at different temperatures. We need to find a temperature at which the vapor pressure will be equal to the partial pressure.

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Since there is no value identical to the partial pressure, a linear interpolation can be done, using the following data from Table B.3 of Felder & Rousseau:

T (°C)	p*
74	277.2 mm Hg
T _{dp}	mm Hg
75	289.1 mm Hg

The interpolation will be done with the following equation:

$$\frac{T_{dp} - T_{Low}}{T_{High} - T_{Low}} = \frac{p_{T_{dp}}^* - p_{T_{Low}}^*}{p_{T_{High}}^* - p_{T_{Low}}^*}$$

Substituting the values from the table and solving for T_{dp} , we have:

$$T_{dp}(^{\circ}C) = \left(\frac{\text{mm Hg} - 277.2 \text{ mm Hg}}{289.1 \text{ mm Hg} - 277.2 \text{ mm Hg}}\right) (75^{\circ}C - 74^{\circ}C) + 74^{\circ}C$$
$$\boxed{T_{dp}} = \underline{\qquad }^{\circ}C}$$

The degrees of superheat of the air entering the condenser can be obtained by substracting the dew point from the temperature of the air:

Degrees of superheat = $__^{\circ}C - 74.4^{\circ}C$ Degrees of superheat = $__^{\circ}C$

(b) Determine the composition of the gas exiting the condenser at 60 $^{\circ}$ C and the same pressure as part (a). What is the percentage of condensed water?

Strategy

To solve this problem, material balances have to be done on the condenser. To determine the composition of the gas in the outlet stream, we will use Raoult's Law. A basis of 100 moles of humid air entering the condenser will be selected.

Solution

We can start by making a diagram of the process around the condenser:



The molar fraction of water in the air exiting the condenser can be obtained from Raoult's Law, as shown below:

$$y_{H_{2^{O}}} = \frac{p_{H_{2^{O}}}^{*}(@ 60^{\circ}C)}{P}$$

The value of the vapor pressure of water at 60 °C can be found in Table B.3 to be:

$$p_{H_{2}O}^{*}(@ 60^{\circ}C) = ___ mm Hg$$

Substituting into Raoult's Law, we get:

$$y_{H_{2}O} = \frac{\text{mm Hg}}{21.8 \text{ psi}\left(\frac{\text{mm Hg}}{14.7 \text{ psi}}\right)}$$
$$y_{H_{2}O} = \frac{\text{moles } H_{2}O}{\text{mol}}$$

Since only water and air are exiting in the gas stream, the composition of air will be given by:

$$y_{dry air} = 1 - y_{H_2O} = 1 - \underline{\qquad}$$
$$y_{dry air} = \underline{\qquad} \frac{moles dry air}{mol}$$

To determine the amount of water that condenses in the process, overall and component material balances can be performed on the condenser:

Balance on Dry Air

Input = Output

$$100 \text{ moles}\left(\underline{\qquad} \frac{\text{moles dry air}}{\text{mol}}\right) = n_2 \text{ moles}\left(y_{\text{dry air}} \frac{\text{moles dry air}}{\text{mol}}\right)$$

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Substituting the molar fraction of dry air and solving for n_2 gives:



Overall Balance

Input = Output 100 moles = $n_1 + n_2$

Substituting the amount of humid air exiting the condenser, n_2 and solving for n_1 :

 $n_1 = 100 \text{ moles} - ___ \text{ moles}$ $n_1 = ___ \text{ moles } H_2O$

Now we can calculate the percentage of water condensation:

Percentage condensation = $\frac{\text{H}_2\text{O condensed}}{\text{H}_2\text{O fed}} \times 100$

Substituting the obtained values yields:

Percentage condensation =
$$\frac{\text{moles H}_2\text{O}}{100 \text{ moles}\left(0.25 \frac{\text{moles H}_2\text{O}}{\text{mol}}\right)} \times 100$$

Example 6.3-3 Relative Humidity

Air is being fed to the cathode side of a proton-exchange membrane fuel cell at a temperature of 25 °C and a pressure of 3 bar. In order to allow the hydrogen protons to flow from the anode side to the cathode side through the polymer-electrolyte membrane, the air has a relative humidity of 80%.

(a) If the volumetric flow rate of humid air is $0.83 \text{ m}^3/\text{h}$, determine the molar flow rates of water, dry air and oxygen entering the fuel cell.

Strategy

Based on the relative humidity information, we can determine the molar fraction of water in the air and using the ideal gas equation of state, we can obtain the molar flow rates of each component in the air feed stream. The molar composition of dry air will be considered to be 21 % oxygen and 79 % nitrogen.

Solution

First, we can calculate the partial pressure of water by using the definition of relative humidity:

$$h_{r} = \frac{p_{H_{2}O}}{p_{H_{2}O}^{*}}$$

Since the water is entering at 25 °C, the value of the vapor pressure at this temperature can be found in Table B.3 of Felder & Rousseau to be:

$$p_{H_{2^0}}^*(25 \text{ °C}) = ___ mm Hg$$

Substituting into the definition of relative humidity and solving for the partial pressure of water $p_{\rm H2O}$ will give:

$$p_{H_{2}O} = h_r p_{H_{2}O}^* = 0.8 (___ mm Hg)$$

 $p_{H_{2}O} = ___ mm Hg$

It is known that the partial pressure can be calculated using the following equation:

$$\mathbf{p}_{\mathrm{H}_{2}\mathrm{O}} = \mathbf{y}_{\mathrm{H}_{2}\mathrm{O}}\mathbf{P}$$

The total pressure of the air is given in the problem statement. Hence we can substitute the pressure values and solve for the molar fraction of water in the feed stream to yield:

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The molar flow rate of air can be obtained using ideal gas equation of state using the volumetric flow rate given in the problem statement. After entering the known information into this equation, we have:



Now we can use the molar fraction of water to determine the flow rate of water into the fuel cell.

$$\dot{n}_{_{H_2O}} = y_{_{H_2O}}\dot{n}$$

Entering the molar flow rate of humid air \dot{n} and the molar fraction of water $\,y_{_{\rm H_2O}}^{},\,gives:$



Since only water and air are present in the feed stream, the air flow rate can be calculated as follows:

$$\dot{n}_{dry air} = (1 - y_{H_2O})\dot{n}$$

Substituting the known quantities into this equation yields:

$$\dot{n}_{dry air} = \left(0.9916 \frac{\text{moles dry air}}{\text{mol}}\right) \left(\underline{\qquad} \frac{\text{moles humid air}}{\text{hr}}\right)$$
$$\frac{\dot{n}_{dry air} = 99.61 \frac{\text{moles dry air}}{\text{hr}}}{\text{hr}}$$

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If we multiply this result by the molar fraction of oxygen in dry air, we can obtain the molar flow rate of oxygen. After substituting the numeric values we have:



(b) Determine the absolute humidity, molal humidity and percentage humidity of the air.

Strategy

We can use the definitions of absolute, molal and percentage humidities to solve this problem. These definitions are given in equations 6.3-5, 6.3-6 and 6.3-7 of Felder & Rousseau.

Solution

The following equations will be used to solve this problem:

Molal humidity,
$$h_m = \frac{\text{moles } H_2O}{\text{moles dry air}}$$

Absolute humidity,
$$h_a = \frac{\text{mass } H_2O}{\text{mass dry air}}$$

Percentage humidity,
$$h_p = \frac{p_{H_2O} / (P - p_{H_2O})}{p_{H_2O}^* / (P - p_{H_2O}^*)} \times 100$$

Substituting the known quantities into each of these three equations gives:

$$h_{m} = \frac{\frac{\text{moles } H_{2}O}{hr}}{\frac{99.61 \frac{\text{moles } \text{dry air}}{hr}}{hr}}$$

$$h_{m} = \underline{\qquad} \frac{\frac{\text{moles } H_{2}O}{\text{moles } \text{dry air}}}{\frac{\text{moles } H_{2}O}{\text{moles } \text{dry air}}}$$

Daniel López Gaxiola Jason M. Keith The equation for the absolute humidity can be written as:

$$h_{a} = \frac{\text{moles } H_{2}O}{\text{moles dry air}} \frac{M_{H_{2}O}}{M_{dry air}}$$

where M_{H2O} and $M_{dry air}$ are the molecular weights of water and dry air, respectively.

$$h_{a} = \frac{\frac{\text{moles } H_{2}O}{\text{hr}} \left(\frac{g H_{2}O}{\text{mol } H_{2}O} \right)}{99.61 \frac{\text{moles } \text{dry air}}{\text{hr}} \left(\frac{g \text{ dry air}}{\text{mol } \text{dry air}} \right)}{\left(\frac{g \text{ dry air}}{\text{mol } \text{dry air}} \right)}$$

To calculate the percentage humidity, we substitute the pressure values into the equation defining the percentage humidity, to yield:



(c) What is the dew point temperature of the humid air entering the fuel cell?

Strategy

To solve this problem, we can use Raoult's Law. In order to do this, it will be assumed that the dry air and the water are in equilibrium.

Solution

Raoult's Law is described by the following equation:

$$p_{H_2O} = p_{H_2O}^* (@T_{dp})$$

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We need to look in Table B.3 of Felder & Rousseau for a value of the vapor pressure equal to the partial pressure of water. The temperature at which these two pressures are equal will be the dew point of the humid air.

The most approximate values of the vapor pressure to the partial pressure of water were obtained from Table B.3 and are shown below:

T (°C)	p* (mm Hg)
21.2	18.880
21.3	18.996
21.4	19.113

If we calculate the ratio of the partial pressure to the vapor pressure at 21.3 °C, we have:

 $r = \frac{19.01 \text{ mm Hg}}{18.996 \text{ mm Hg}} = _$

Thus, we can tell that the approximate value of the dew point temperature is:



Example 6.4-1 Humidification of Air for Proton-Exchange Membrane Fuel Cells

The air entering the cathode side of a fuel cell must contain a specific amount of water. Since the reaction occurring inside a fuel cell is producing water, the exhaust air can transfer some of this water by mixing with the fresh air stream entering the fuel cell. The fuel cell is operating at 80 $^{\circ}$ C and at a total pressure of 1.5 atm. A diagram of the humidifier is shown below.



Determine the flow rate and relative humidity of the air exiting to the atmosphere and the composition of the air entering the fuel cell.

Strategy

To solve this problem, we need to perform overall and component balances in the humidifier. To determine the unknown flow rates and compositions we need to use the definition of relative humidity, as well as the ideal gas equation of state. A basis of 100 moles/hr of fresh air will be selected.

Solution

Since the relative humidity of the air entering the fuel cell stack is given, the composition of this stream can be determined by applying the definition of relative humidity:

$$h_{\rm r} = \frac{p_{\rm H_2O}}{p_{\rm H_2O}^*}$$

The value of the vapor pressure at the operation temperature of 80 $^{\circ}$ C can be found in Table B.3 of Felder & Rousseau to be:

 $p_{H_{2}O}^{*} = ___m mm Hg$

Daniel López Gaxiola Jason M. Keith The partial pressure is given by:

$$p_{H_2O} = y_{H_2O}P$$

Substituting this equation into the definition of relative humidity and solving for the molar fraction of water $y_{2,H2O}$ yields:

$$y_{2,H_2O} =$$
 P

Entering the quantities into this equation, we can determine the composition of the humid air fed into the fuel cell:



Since the volumetric flow rate \dot{V}_2 is given, we can use this value and the ideal gas equation of state to obtain the molar flow rate \dot{n}_2 :

$$\dot{n}_2 = \frac{P\dot{V}}{RT}$$

Substituting the values on the right-hand side of this equation gives:



To determine the flow rate of air exiting to the atmosphere, we can perform an overall material balance on the humidifier:

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$$\dot{n}_1 + \dot{n}_3 = \dot{n}_2 + \dot{n}_4$$

If we substitute the known flow rates n_1 , n_2 and n_3 and solve for n_4 , we have:



The composition of the air $y_{4,H2O}$ can be obtained by doing a water balance around the humidifier:

Input = Output
$$y_{3,H_2O}\dot{n}_3 = y_{2,H_2O}\dot{n}_2 + y_{4,H_2O}\dot{n}_4$$

Substituting the numeric values into this equation and solving for the molar fraction of water $y_{4,H2O}$ gives:



Example 6.4-5 Boiling Point of a Mixture

The following is a Temperature-Composition diagram for a methanol/water mixture, obtained from *Separation Process Engineering* by P.C. Wankat, 2nd Edition. A mixture of methanol and water is used as fuel for direct-methanol fuel cells. It is known that this mixture will boil at a temperature of 82 °C. What is the composition of this liquid mixture? What is the composition of the first bubble formed at this temperature?



Strategy

We can obtain the composition of both the liquid and the vapor by reading the T-x,y diagram.

Solution

First we need to locate the boiling temperature of the mixture. From this point, we move down vertically to read the composition of the liquid (dashed line).

To determine the composition of the first bubble formed at this temperature, from the boiling temperature, we move horizontally to the right until reaching the vapor line and move down vertically to read the composition (dotted line).



From the diagram, the composition of the mixture and the bubble were found to be:

