

Lecture 7.

Vapor-Liquid Equilibria



Vapor and Gas

Vapor

A substance that is below its critical temperature.

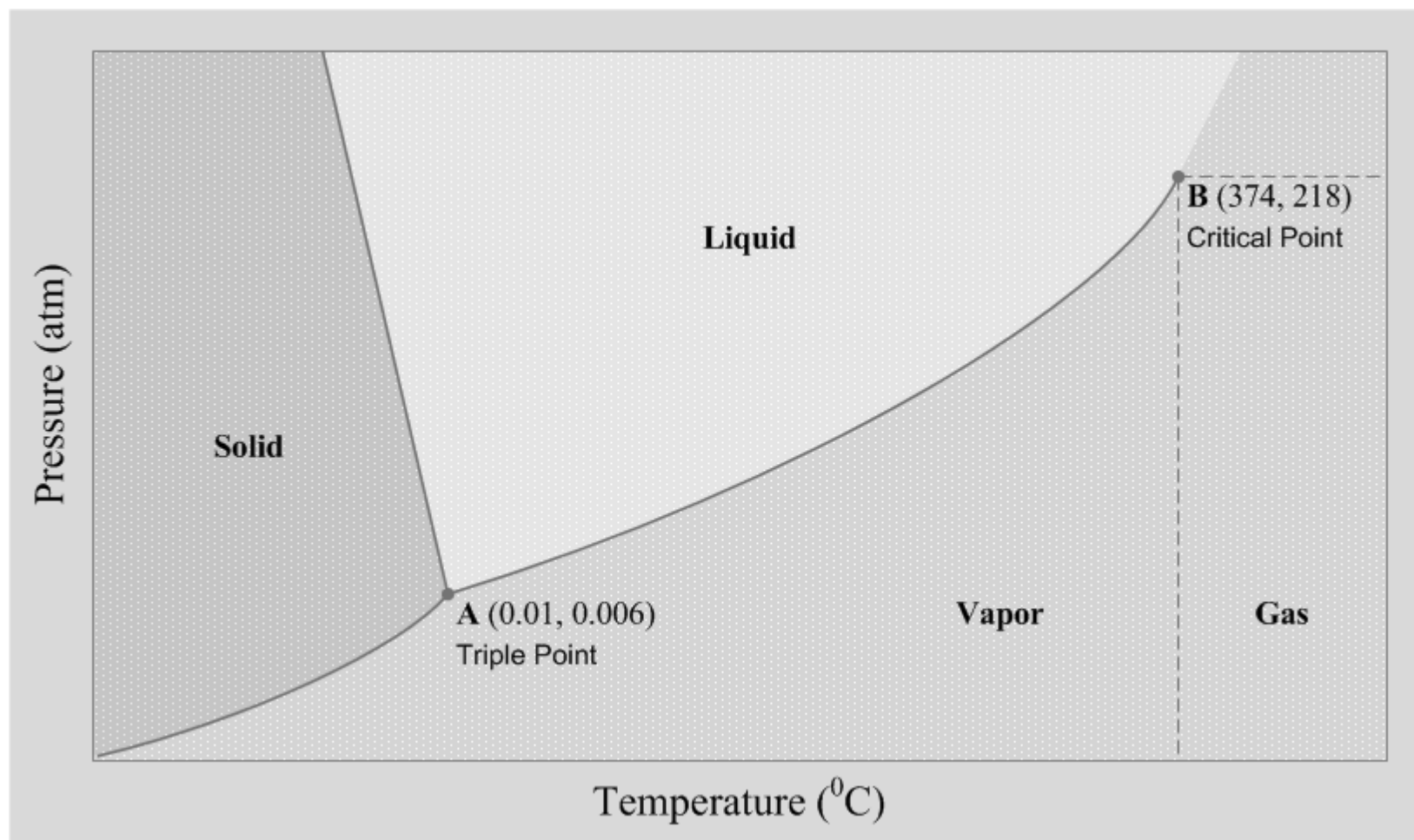
Gas

A substance that is above its critical temperature (but below the critical pressure).

For the same pressure, a vapor is more easily condensed while a gas is normally non-condensable.



The PT Diagram



Definition of Terms

Vapor Pressure

Pressure of the vapor when the vapor and liquid of a pure component are in equilibrium. Also referred to as saturated pressure.

Saturated Temperature

Temperature at which the vapor and liquid will co-exist at a given pressure. Commonly referred to as the boiling or condensation point.

Dew Point

The temperature when the vapor starts to condense.

Bubble Point

The temperature when the liquid starts to vaporize.



Definition of Terms

Saturated Vapor and Saturated Liquid

Vapor and liquid at the saturated P and saturated T .

Subcooled Liquid

A liquid that is below its saturated T at a given pressure.

Compressed Liquid

A liquid that is above its saturated P at a given temperature.

Superheated Vapor

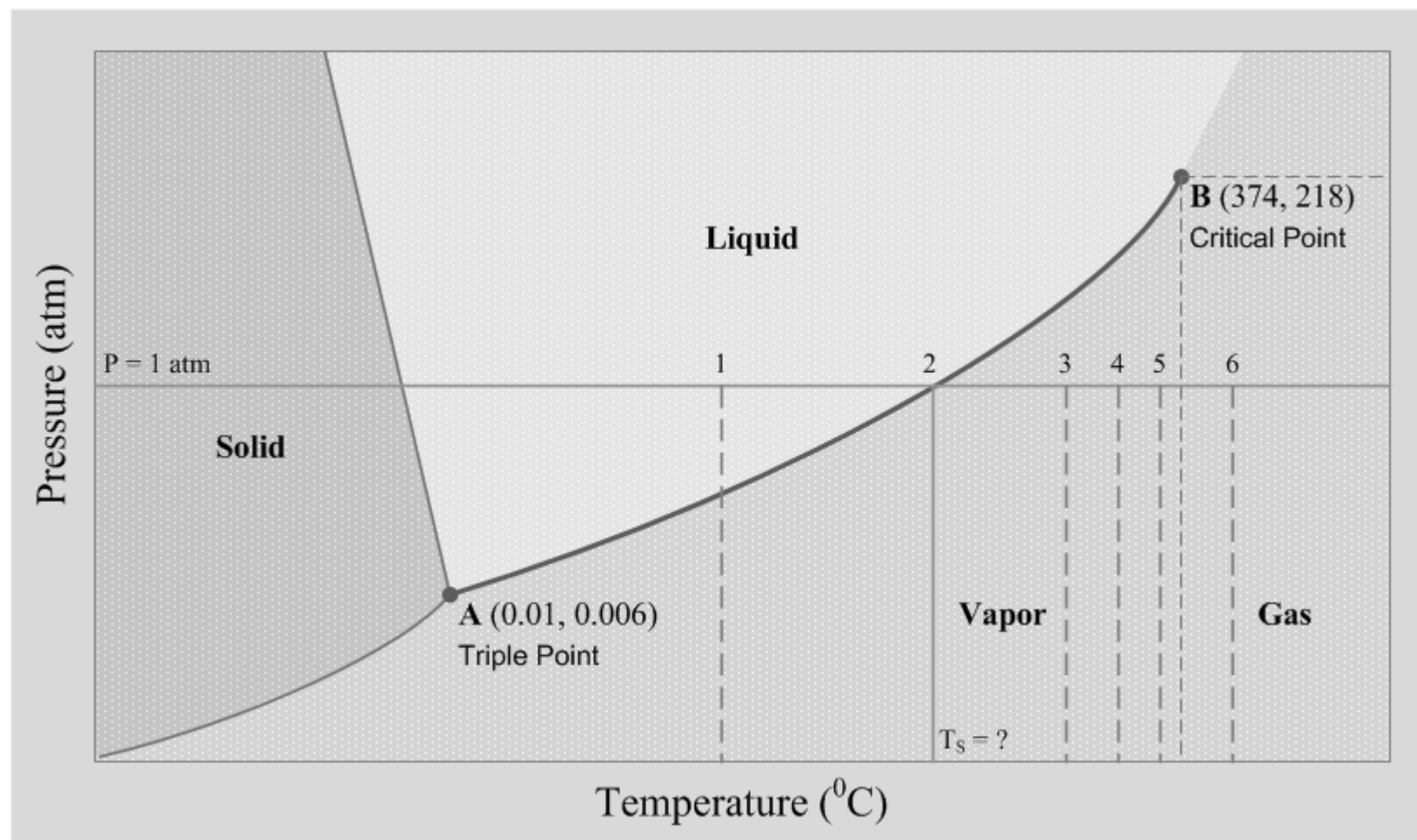
A vapor that is above its saturated T at a given pressure.

Quality

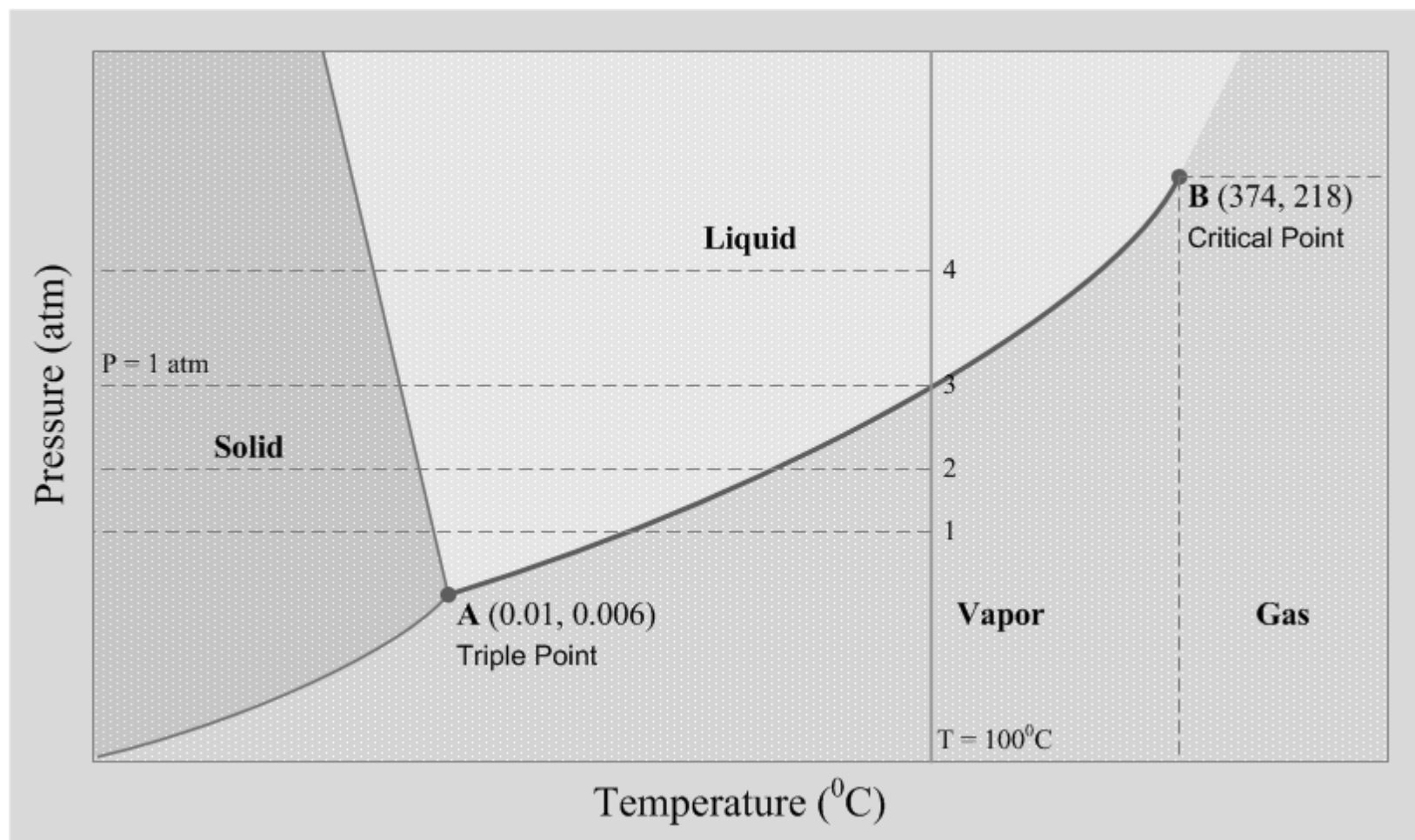
For a saturated mixture, quality refers to the mass fraction of the vapor in the mixture.



The PT Diagram



The PT Diagram



Saturated and Superheated Steam Tables

Saturated water—Temperature table

Temp., T °C	Sat. press., P_{sat} kPa	Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, $\text{kJ/kg} \cdot \text{K}$		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.2281	0.001000	106.32	42.020	2346.6	2388.7	42.022	2477.2	2519.2	0.1511	8.7488	8.8999
15	1.7057	0.001001	77.885	62.980	2332.5	2395.5	62.982	2465.4	2528.3	0.2245	8.5559	8.7803
20	2.3392	0.001002	57.762	83.913	2318.4	2402.3	83.915	2453.5	2537.4	0.2965	8.3696	8.6661

Superheated water

T °C	v m^3/kg	u kJ/kg	h kJ/kg	s $\text{kJ/kg} \cdot \text{K}$	v m^3/kg	u kJ/kg	h kJ/kg	s $\text{kJ/kg} \cdot \text{K}$	v m^3/kg	u kJ/kg	h kJ/kg
$P = 0.01 \text{ MPa (45.81}^\circ\text{C)}^*$					$P = 0.05 \text{ MPa (81.32}^\circ\text{C)}$				$P = 0.10 \text{ MPa (99}^\circ\text{C)}$		
Sat. [†]	14.670	2437.2	2583.9	8.1488	3.2403	2483.2	2645.2	7.5931	1.6941	2505.6	267
50	14.867	2443.3	2592.0	8.1741							
100	17.196	2515.5	2687.5	8.4489	3.4187	2511.5	2682.4	7.6953	1.6959	2506.2	267
150	19.513	2587.9	2783.0	8.6893	3.8897	2585.7	2780.2	7.9413	1.9367	2582.9	277
200	21.826	2661.4	2879.6	8.9049	4.3562	2660.0	2877.8	8.1592	2.1724	2658.2	287
250	24.136	2736.1	2977.5	9.1015	4.8206	2735.1	2976.2	8.3568	2.4062	2733.9	297



Properties of Saturated Mixture

For a saturated mixture,

$$\hat{V}_l(1 - x) + \hat{V}_g(x) = \hat{V}_{\text{mixture}}$$

$$\hat{H}_l(1 - x) + \hat{H}_g(x) = \hat{H}_{\text{mixture}}$$

$$\hat{U}_l(1 - x) + \hat{U}_g(x) = \hat{U}_{\text{mixture}}$$

where x = mass fraction of vapor in the mixture.



Example 7/8-1. Vapor-Liquid Properties of Water

For each of the conditions of temperature and pressure listed below for water, state whether the water is a solid, liquid, saturated mixture, or superheated vapor. If it is a saturated mixture, calculate the quality.

State	P (kPa)	T (K)	V (m ³ /kg)
1	2000	475	---
2	1000	500	0.2206
3	101.3	400	---
4	245.6	400	0.505



Example 7-1. Vapor-Liquid Properties of Water

Using the saturated steam table,

State	P (kPa)	T (K)	Phase
1	2000	475	Liquid
2	1000	500	Vapor
3	101.3	400	Vapor
4	245.6	400	Saturated



Example 7-1. Vapor-Liquid Properties of Water

From the saturated steam pressure table,

175	116.04	0.001057	1.0037
200	120.21	0.001061	0.88578
225	123.97	0.001064	0.79329
250	127.41	0.001067	0.71873
275	130.58	0.001070	0.65732

By 2-point linear interpolation, properties at $P = 245.6$ can be estimated:

$$\hat{V}_l = \underline{\hspace{2cm}} \text{ m}^3 / \text{ kg} \quad \text{and} \quad \hat{V}_g = \underline{\hspace{2cm}} \text{ m}^3 / \text{ kg}$$



Example 7-1. Vapor-Liquid Properties of Water

If x is the quality of the saturated mixture, then

$$\left(\frac{\quad}{\quad} \frac{\text{m}^3}{\text{kg}} \right) (1 - x) + \left(\frac{\quad}{\quad} \frac{\text{m}^3}{\text{kg}} \right) (x) = 0.505 \frac{\text{m}^3}{\text{kg}}$$

Solving for x ,

$$\mathbf{x = 0.69}$$



Change of Vapor Pressure with Temperature

Many functional forms have been proposed to predict vapor pressure (p^*) from temperature. One of these functions is the Antoine equation:

$$\ln(p^*) = A - \frac{B}{C + T}$$

Where p^* = vapor pressure of the substance, mmHg

T = temperature, K

A, B, C = constants for each substance



Change of Vapor Pressure with Temperature

The Clapeyron equation is another function relating vapor pressure p^* and temperature T :

$$\frac{dp^*}{dT} = \frac{\Delta \hat{H}_V}{T(\hat{V}_g - \hat{V}_l)}$$

Where p^* = vapor pressure of the substance
 T = temperature
 $\Delta \hat{H}_V$ = latent heat of vaporization
 \hat{V}_g, \hat{V}_l = specific molar volumes of vapor and liquid, respectively



Change of Vapor Pressure with Temperature

Simplifications of the Clapeyron equation:

1. Specific molar volume of liquid is very small compared to specific molar volume of the vapor, such that

$$(\hat{V}_g - \hat{V}_l) \approx \hat{V}_g$$

2. The vapor is assumed to behave ideally.

$$\hat{V}_g = \frac{RT}{P^*}$$



Change of Vapor Pressure with Temperature

The Clapeyron equation then becomes,

$$\frac{dP^*}{dT} = \frac{P^* \Delta \hat{H}_V}{RT^2}$$

Separating the variables and integrating to yield the Clausius-Clapeyron equation,

$$\frac{dP^*}{P^*} = \frac{\Delta \hat{H}_V}{R} \left(\frac{dT}{T^2} \right)$$
$$\ln(P^*) = -\frac{\Delta \hat{H}_V}{RT} + B$$



Example 7-2. Estimation of Normal BP Using the Antoine Equation

Determine the % error if the Antoine equation is used to estimate the normal boiling point of benzene. From literature value, the normal boiling point of benzene is 353.26 K.

Solution:

For benzene, values of the constants for the Antoine equation are:

$$A = 15.9008$$

$$B = 2788.51$$

$$C = -52.36$$



Example 7-2. Estimation of Normal BP Using the Antoine Equation

Using the Antoine equation,

$$\ln(760 \text{ mmHg}) = 15.9008 - \frac{2788.51}{-52.36 + T}$$

Solving for temperature, **T = 353.3 K**

The percent error is,

$$\% \text{ error} = \frac{|353.26 \text{ K} - 353.3 \text{ K}|}{353.26 \text{ K}} \times 100 \approx 0.01\%$$



Example 7-3. Clausius-Clapeyron Equation

The vapor pressure of benzene is measured at two temperatures, with the following results:

$$T_1 = 7.6\text{ }^{\circ}\text{C}$$

$$P^*_1 = 40\text{ mm Hg}$$

$$T_2 = 15.4\text{ }^{\circ}\text{C}$$

$$P^*_2 = 60\text{ mm Hg}$$

Calculate the latent heat of vaporization and the parameter B in the Clausius-Clapeyron equation and then estimate P^* at 42.2°C using this equation.



Example 7-3. Clausius-Clapeyron Equation

The Clausius-Clapeyron is a linear equation with:

$$x = \frac{1}{T} \qquad y = \ln(P^*)$$

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

Solving for slope, m:

$$m = -\frac{\Delta\hat{H}_V}{R} = \frac{\Delta y}{\Delta x} = \frac{\ln(P^*_2) - \ln(P^*_1)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \frac{T_1 T_2 \ln(P^*_2 / P^*_1)}{(T_1 - T_2)}$$



Example 7-3. Clausius-Clapeyron Equation

Using absolute values for temperature:

$$T_1 = 280.8 \text{ K and } T_2 = 288.6 \text{ K}$$

The slope is computed as:

$$m = -\frac{\Delta \hat{H}_v}{R} = \frac{(280.8 \text{ K})(288.6 \text{ K}) \ln \left(\frac{60 \text{ mmHg}}{40 \text{ mmHg}} \right)}{(280.8 \text{ K} - 288.6 \text{ K})}$$

$$m = -\frac{\Delta \hat{H}_v}{R} = -4213 \text{ K}$$



Example 7-3. Clausius-Clapeyron Equation

And the latent heat of vaporization is:

$$\Delta\hat{H}_V = 4213 \text{ K} (R) = 4213 \text{ K} \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) = 35,030 \frac{\text{J}}{\text{mol}}$$

The intercept b ($b = B$) can be determined as follows:

$$B = \ln(P^*_1) + \frac{\Delta\hat{H}_V}{RT_1} = \ln(P^*_2) + \frac{\Delta\hat{H}_V}{RT_2}$$

$$B = \ln(40) + \left(\frac{4213}{280.8} \right) = 18.69$$



Example 7-3. Clausius-Clapeyron Equation

The Clausius-Clapeyron equation for benzene can now be written as:

$$\ln(P^*) = -\frac{4213}{T} + 18.69$$

At $T = 42.2^\circ\text{C} = 315.4 \text{ K}$, the vapor pressure of benzene is

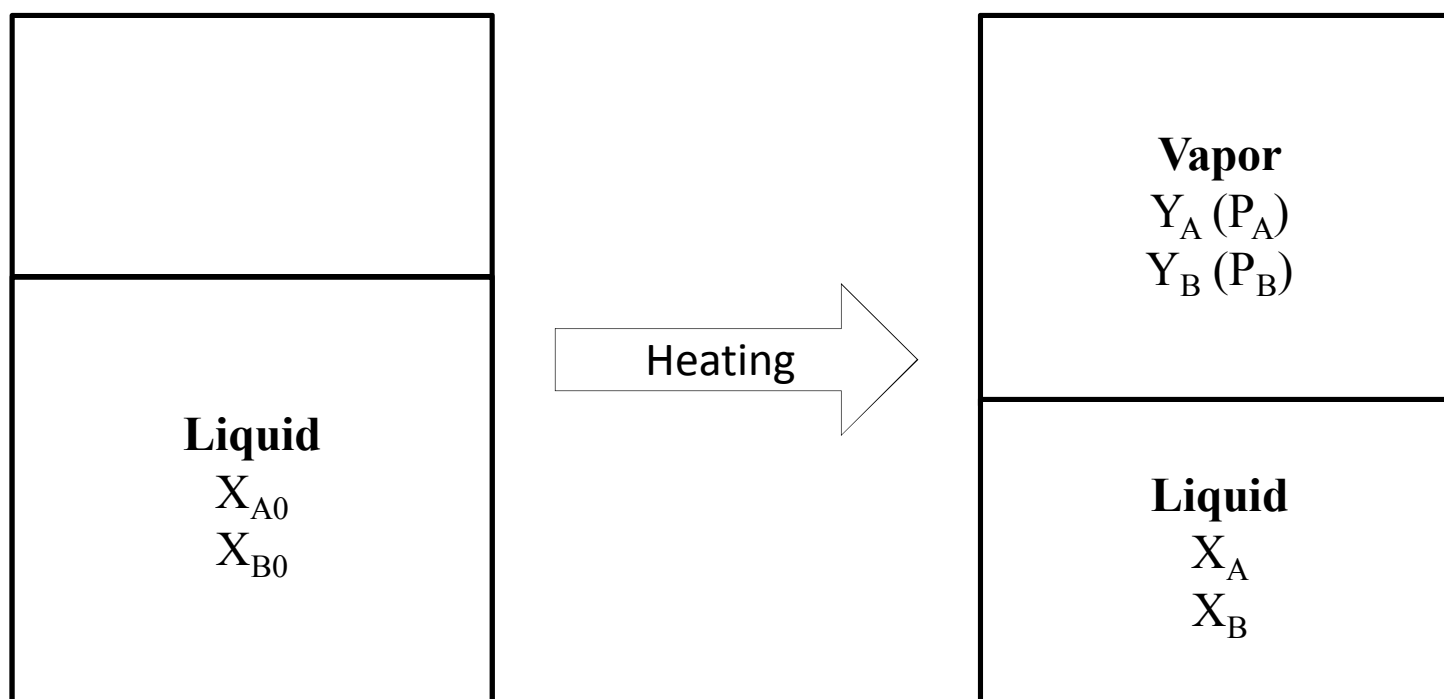
$$\ln(P^*) = -\frac{4213}{315.4} + 18.69 = 5.334$$

$$P^* = \exp(5.334) = 207 \text{ mmHg}$$



Vapor-Liquid Equilibrium for Multi-component Systems

Consider a binary mixture with components A and B.



Note: X, Y = mole fractions of the component in the vapor and liquid phases, respectively.



Vapor-Liquid Equilibrium for Multi-component Systems

For multi-component systems,

$$P_i = f(x_i)$$

This functional relationship is given by

1. Raoult's Law – generally used when x_i is close to 1.
2. Henry's Law – generally used when x_i is close to 0.



Vapor-Liquid Equilibrium for Multi-component Systems

Henry's Law:

$$P_i = x_i H_i$$

where P_i = partial pressure of component i in the vapor phase.

= $y_i P_T$ (if the vapor behaves ideally)

x_i = mole fraction of component i in the liquid phase.

H_i = Henry's law constant



Vapor-Liquid Equilibrium for Multi-component Systems

Raoult's Law:

$$P_i = x_i P_i^*$$

where P_i = partial pressure of component i in the vapor phase.

= $y_i P_T$ (if the vapor behaves ideally)

x_i = mole fraction of component i in the liquid phase.

P_T = total pressure



Vapor-Liquid Equilibrium for Multi-component Systems

If the vapor behaves ideally, the Raoult's law becomes

$$y_i P_T = x_i P_i^*$$

Rearranging the equation,

$$\frac{y_i}{x_i} = \frac{P_i^*}{P_T} = K_i$$

where K_i is the V-L equilibrium constant.



Example 7-4. Vapor-Liquid Equilibrium Calculation

Suppose that a liquid mixture of 4.0% n-hexane (**A**) in n-octane (**B**) is vaporized. What is the composition of the first vapor formed if the total pressure is 1.00 atm?

Values of the Antoine constants for n-octane are:

$$A = 15.9798$$

$$B = 3127.60$$

$$C = -63.63$$



Example 7-4. Vapor-Liquid Equilibrium Calculation

Solution:

Assuming the vapor behaves ideally, the composition of the vapor is determined using the Raoult's law:

$$y_A = \frac{P_A^*}{P_T} x_A$$

$$y_B = \frac{P_B^*}{P_T} x_B$$



Example 7-4. Vapor-Liquid Equilibrium Calculation

Upon formation of the first vapor, the composition of the liquid is essentially the same as the initial composition.

Hence,

$$x_A = 0.040 \text{ and } x_B = 1 - x_A = 0.960$$

The vapor pressures of A and B are calculated using the Antoine equation:

$$\ln(P^*) = A - \frac{B}{C + T}$$



Example 7-4. Vapor-Liquid Equilibrium Calculation

For n-hexane:

$$P^*_A = \exp\left(15.8366 - \frac{2697.55}{-48.78 + T}\right)$$

For n-octane:

$$P^*_B = \exp\left(15.9798 - \frac{3127.60}{-63.63 + T}\right)$$

Since vaporization temperature is not given, the next step in the calculation is to determine its value.



Example 7-4. Vapor-Liquid Equilibrium Calculation

For the vapor mixture,

$$P_T = P_A + P_B$$

Using Raoult's Law,

$$P_T = P_A^* x_A + P_B^* x_B = 1.00 \text{ atm} = 760 \text{ mmHg}$$

Using the expressions for the vapor pressures as defined by the Antoine equation

$$e^{\left(15.8366 - \frac{2697.55}{-48.78 + T}\right)} (0.040) + e^{\left(15.9798 - \frac{3127.60}{-63.63 + T}\right)} (0.960) = 760$$



Example 7-4. Vapor-Liquid Equilibrium Calculation

The last equation is a non-linear equation. To find the value of T , Newton's method is used by defining $f(T)$ as:

$$f(T) = 0.040e^{\left(15.8366 - \frac{2697.55}{-48.78 + T}\right)} + 0.960e^{\left(15.9798 - \frac{3127.60}{-63.63 + T}\right)} - 760 = 0$$

Similar to example 6-4, the temperature value that will satisfy this equation is determined using the following iteration formula:

$$T_{k+1} = T_k - \frac{f(T_k)}{f'(T_k)}$$



Example 7-4. Vapor-Liquid Equilibrium Calculation

Differentiating $f(T)$:

$$f'(T) = \frac{107.902e^{\left(15.8366 - \frac{2697.55}{-48.78+T}\right)}}{(T - 48.78)^2} + \frac{3002.496e^{\left(15.9798 - \frac{3127.60}{-63.63+T}\right)}}{(T - 63.63)^2}$$

Any value for the temperature may be used as initial guess.
For this example, the following initial guess is used:

$$T_0 = 1000 \text{ K}$$



Example 7-4. Vapor-Liquid Equilibrium Calculation

Step	$T_K(K)$	$f(T)$	$f'(T)$	$T_{K+1}(K)$	E
0	1000.0	313163.50	1109.32	717.70	282.301
1	717.70	74657.88	544.43	580.57	137.13
2	580.57	20838.65	248.65	496.76	83.81
3	496.76	6084.77	111.72	442.30	54.46
4	442.30	1721.87	52.72	409.64	32.66
5	409.64	403.40	29.46	395.95	13.69
6	395.95	51.14	22.21	393.65	2.30
7	393.65	1.24	21.12	393.59	0.06



Example 7-4. Vapor-Liquid Equilibrium Calculation

For $T = 393.59 \text{ K}$, the vapor pressures of n-hexane and n-octane are:

$$P_A^* = 3019.92 \text{ mm Hg}$$

$$P_B^* = 665.86 \text{ mm Hg}$$

And the composition of the first vapor formed is:

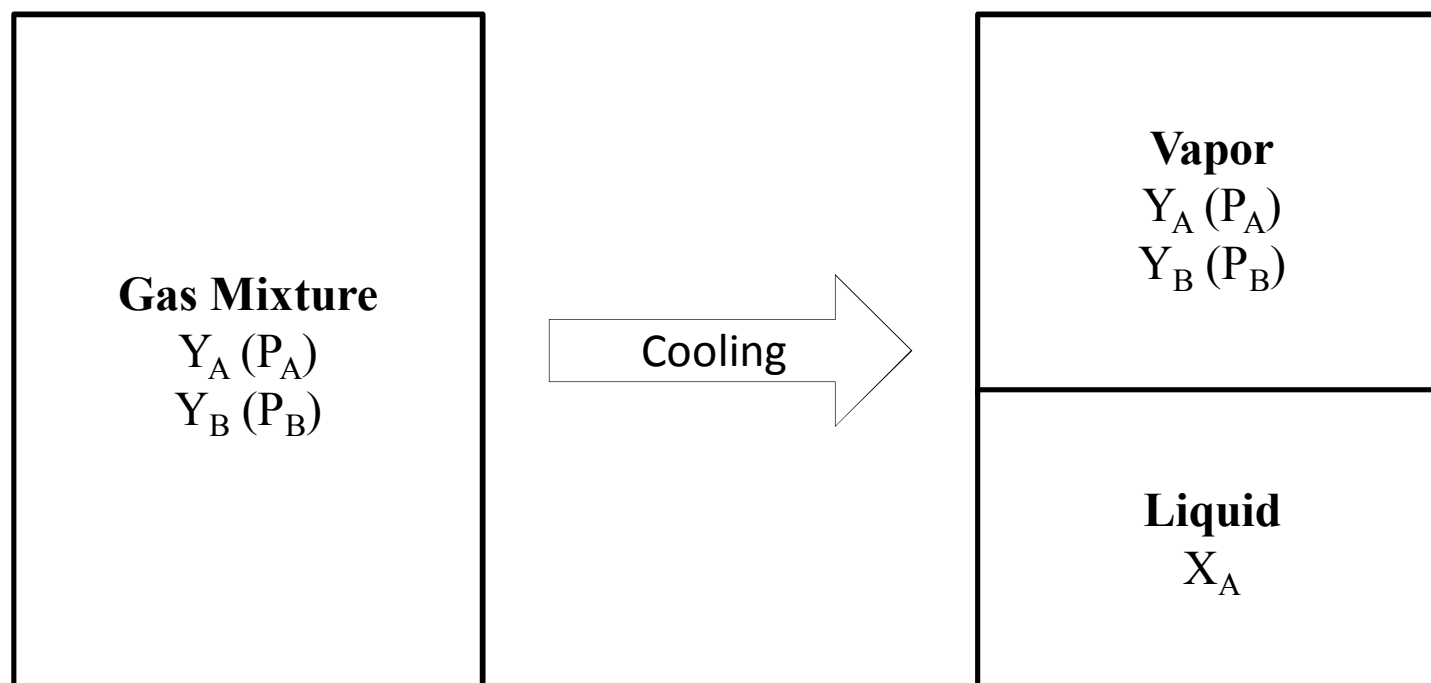
$$y_A = \frac{3019.92}{760} (0.040) = 0.159$$

$$y_B = \frac{665.68}{760} (0.960) = 0.841$$



Vapor-Liquid Equilibrium for Multi-component Systems

Consider a mixture of a vapor (A) and a non-condensable gas (B).



Vapor-Liquid Equilibrium for Multi-component Systems

(Terms and symbols in parenthesis refer specifically to air-water system.)

Relative Saturation (Relative Humidity)

$$s_r(h_r) = \frac{P_v}{P_v^*} \times 100$$

Absolute Saturation (Absolute Humidity)

$$s_a(h_a) = \frac{\text{mass of vapor}}{\text{mass of vapor-free gas}} = \frac{P_v MW_v}{(P_T - P_v) MW_G}$$

Molal Saturation (Molal Humidity)

$$s_m(h_m) = \frac{\text{moles of vapor}}{\text{moles of vapor-free gas}} = \frac{P_v}{(P_T - P_v)}$$



Example 7-5. Humidity of Air

Humid air at 75°C, 1.1 bar, and 30% relative humidity is fed into a process unit at a rate of 1000 m³/h. Determine:

- a. the molar flow rates of water, dry air, and oxygen entering the process unit.
- b. the molal humidity and absolute humidity.
- c. the dew point.

Assume ideal gas behavior.



Example 7-5. Humidity of Air

Solution for (a):

Determine the mole fraction of water:

$$y_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{T}}}$$

The partial pressure of water is calculated from relative humidity:

$$P_{\text{H}_2\text{O}} = P^*_{\text{H}_2\text{O}} \left(\frac{h_r}{100} \right)$$



Example 7-5. Humidity of Air

At $T = 75^{\circ}\text{C}$,

$$P^*_{\text{H}_2\text{O}} = 289 \text{ mm Hg}$$

And the partial pressure of water is,

$$P_{\text{H}_2\text{O}} = (289 \text{ mm Hg})(0.3) = 86.7 \text{ mm Hg}$$

For a total pressure of $1.1 \text{ bar} = 825 \text{ mm Hg}$, the mole fraction of water is,

$$y_{\text{H}_2\text{O}} = \frac{86.7 \text{ mm Hg}}{825 \text{ mm Hg}} = 0.105 \frac{\text{mol H}_2\text{O}}{\text{mol HA}}$$



Example 7-5. Humidity of Air

Determine the molar flow rate of humid air:

$$\vec{n}_A = \frac{P \vec{V}}{RT} = \frac{(1.1 \text{ bar})(1000 \text{ m}^3 / \text{h})}{\left(0.0831 \frac{\text{m}^3 \cdot \text{bar}}{\text{kmol} \cdot \text{K}}\right)(75 + 273 \text{ K})} = 38.0 \frac{\text{kmol}}{\text{h}}$$

The molar flow rate of water can now be obtained:

$$\vec{n}_{\text{H}_2\text{O}} = \left(38.0 \frac{\text{kmol HA}}{\text{h}}\right) \left(\frac{0.105 \text{ kmol H}_2\text{O}}{\text{kmol HA}}\right) = 3.99 \frac{\text{kmol H}_2\text{O}}{\text{h}}$$



Example 7-5. Humidity of Air

The molar flow rate of dry air:

$$\dot{n}_{\text{DA}} = \left(38.0 \frac{\text{kmol}}{\text{h}} \right) \left(\frac{(1 - 0.105) \text{ kmol DA}}{\text{kmol HA}} \right) = 34.0 \frac{\text{kmol DA}}{\text{h}}$$

The molar flow rate of O_2 :

$$\dot{n}_{\text{O}_2} = \left(34.0 \frac{\text{kmol DA}}{\text{h}} \right) \left(\frac{0.21 \text{ kmol O}_2}{\text{kmol DA}} \right) = 7.14 \frac{\text{kmol O}_2}{\text{h}}$$



Example 7-5. Humidity of Air

Solution for (b):

The absolute humidity (h_a):

$$h_a = \frac{P_{H_2O} MW_{H_2O}}{(P_T - P_{H_2O}) MW_{DA}} = \frac{(86.7)(18)}{(825 - 86.7)(29)} = 0.0726 \frac{\text{kg H}_2\text{O}}{\text{kg DA}}$$

The molal humidity (h_m):

$$h_m = \frac{P_{H_2O}}{(P_T - P_{H_2O})} = \frac{86.7}{(825 - 86.7)} = 0.117 \frac{\text{mol H}_2\text{O}}{\text{mol DA}}$$



Example 7-5. Humidity of Air

Solution for (c):

At the dew point,

$$P_{\text{H}_2\text{O}} = P^*_{\text{H}_2\text{O}} = 86.7 \text{ mmHg}$$

From vapor pressure data for water, this vapor pressure of water occurs at:

$$T = 48.7^\circ\text{C}$$

This is the dew point since at this temperature, water will start to condense.

