

CHEMICAL PROCESS CALCULATIONS

(Multiphase systems)

Lecture # 20: November 10, 2022

Multiphase systems

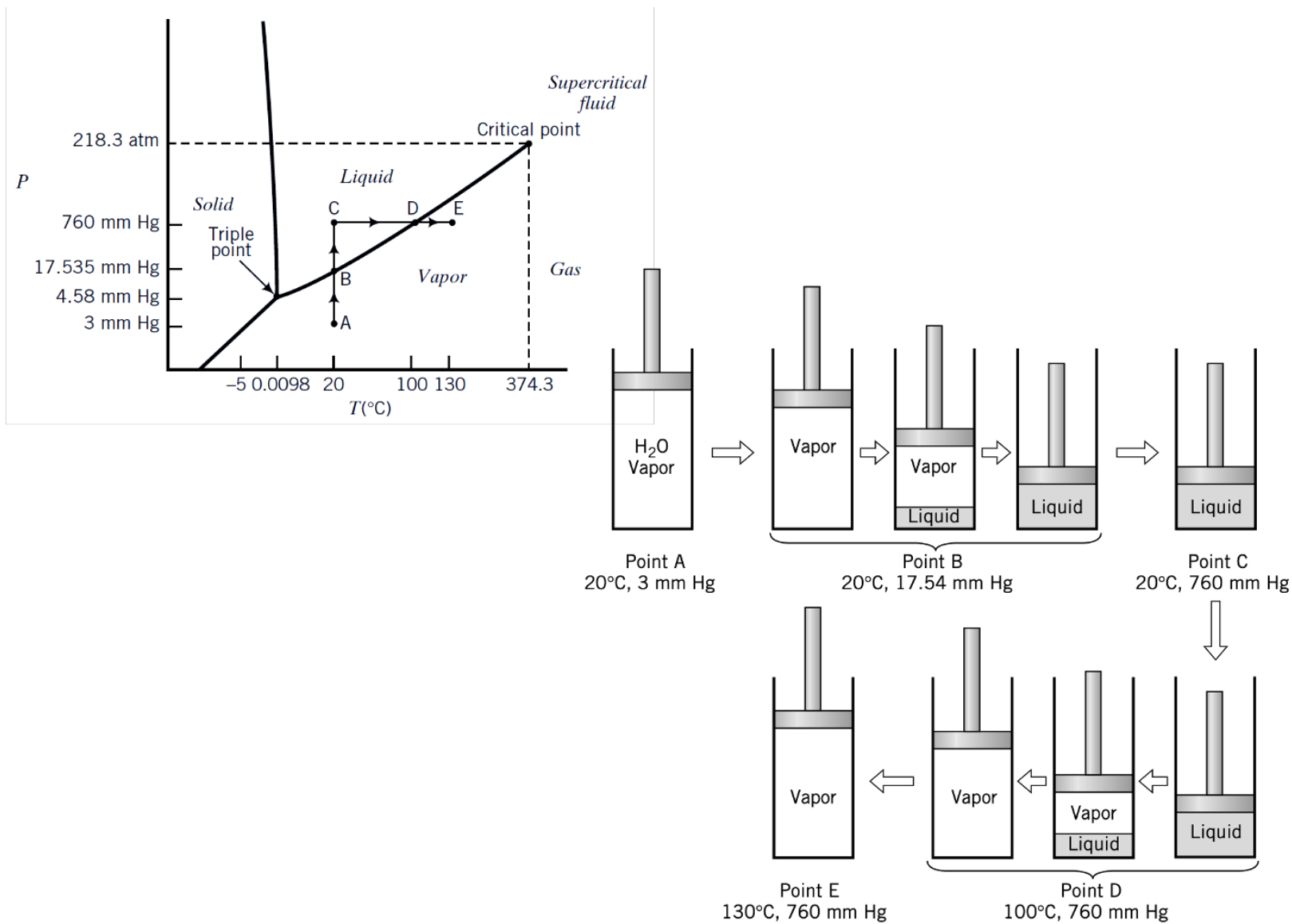
- Dissolving a component of a solid phase in a liquid solvent is referred to as **leaching**: Brewing a cup of coffee/Tea
- Product gas is contacted with a liquid solution in an **absorption** or **scrubbing** process: Removal of sulfur dioxide
- Separation process **distillation** exploits vapor pressure difference: Recovery of methanol from an aqueous solution
- **Liquid extraction**: Separation of paraffinic and aromatic hydrocarbons
- **Adsorption**: Separation of an isomeric mixture
- **Crystallization**: Separation of an isomeric mixture

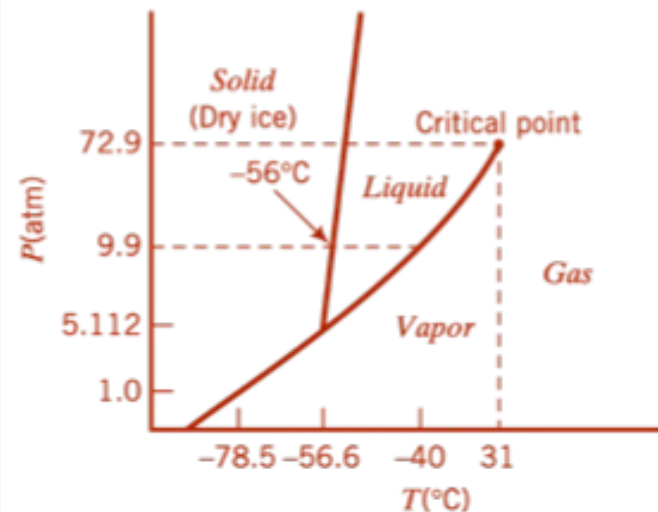
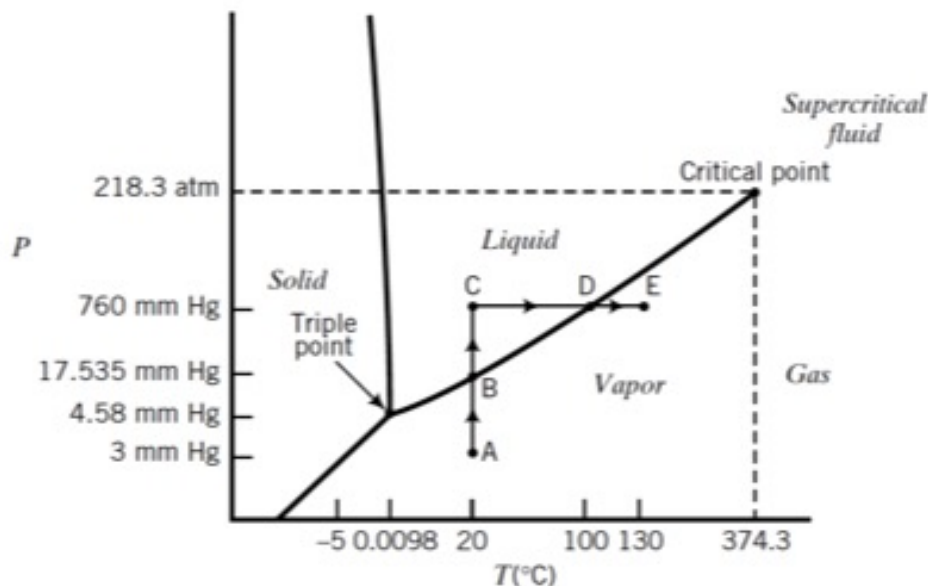
Multiphase systems

- Phase saturation
- Phase equilibrium
- Phase diagram
- Vapor pressure
- Boiling point
- Normal boiling point
- Melting point or freezing point
- Sublimation point
- Triple point
- Volatility

Multiphase systems

- Gibbs phase rule
 - Extensive variables: depend on the size of the system
 - Intensive variables: independent of system size
 - Mass and volume: extensive variables
 - Temperature, pressure, density and specific volume, and mass and mole fractions: intensive variables
- $DF = 2 + c - P$
 - P = number of phases in a system at equilibrium
 - c = number of chemical species





1. If T and P correspond to a point on the vapor–liquid equilibrium curve for a substance, P is the **vapor pressure** of the substance at temperature T , and T is the **boiling point** (more precisely, the **boiling point temperature**) of the substance at pressure P .
2. The boiling point of a substance at $P = 1$ atm is the **normal boiling point** of that substance.
3. If (T, P) falls on the solid–liquid equilibrium curve, then T is the **melting point** or **freezing point** at pressure P .
4. If (T, P) falls on the solid–vapor equilibrium curve, then P is the vapor pressure of the solid at temperature T , and T is the **sublimation point** at pressure P .
5. The point (T, P) at which solid, liquid, and vapor phases can all coexist is called the **triple point** of the substance.
6. The vapor–liquid equilibrium curve terminates at the **critical temperature** and **critical pressure** (T_c and P_c). Above and to the right of the critical point, two separate phases never coexist.

Estimation of Vapor Pressures

The **vapor pressure** of a species is a **measure of its volatility**: the higher the vapor pressure at a given temperature, the greater the volatility of the species at that temperature.

Clapeyron equation

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

Clausius–Clapeyron equation

heat of vaporization of a substance is independent of temperature

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

Antoine equation

$$\log_{10} p^* = A - \frac{B}{T + C}$$

The Gibbs Phase Rule

- The variables that describe the condition of a process system fall into two categories: **extensive variables, which depend on the size of the system**, and **intensive variables, which do not**.
- Mass and volume are examples of **extensive variables**;
- **Intensive variables** include temperature, pressure, density and specific volume, and mass and mole fractions of individual system components in each phase.

Π = number of phases in a system at equilibrium

c = number of chemical species

DF = degrees of freedom

The number of intensive variables that can be specified independently for a system at equilibrium is called the Degree of Freedom (DF).

$$DF = 2 + c - \Pi$$

1. *Pure liquid water*

One phase ($\Pi = 1$), one component ($c = 1$)



$$DF = 2 + 1 - 1 = 2$$

Two intensive variables must be specified to fix the state of the system, for example, T and P . Once these variables have been specified, other intensive variables such as density and viscosity may be determined.

2. *A mixture of liquid, solid, and vapor water*

Three phases ($\Pi = 3$), one component ($c = 1$)



$$DF = 2 + 1 - 3 = 0$$

No further information about the system may be specified and all intensive variables are fixed.

3. *A vapor–liquid mixture of acetone and methyl ethyl ketone*

Two phases ($\Pi = 2$), two components ($c = 2$)



$$DF = 2 + 2 - 2 = 2$$

1. A gas in equilibrium with a liquid must be saturated with the volatile components of that liquid.
2. The partial pressure of a vapor at equilibrium in a gas mixture containing a single condensable component cannot exceed the vapor pressure of the pure component at the system temperature. If $p_i = p_i^*$, the vapor is saturated; any attempt to increase p_i —either by adding more vapor to the gas phase or by increasing the total pressure at constant temperature—must instead lead to condensation.
3. A vapor present in a gas in less than its saturation amount is referred to as a **superheated vapor**. For such a vapor,

$$p_i = \boxed{y_i P < p_i^*(T)}$$

Raoult's Law, Single Condensable Species:

$$p_i = \boxed{y_i P = p_i^*(T)}$$

If a gas at temperature T and pressure P contains a saturated vapor whose mole fraction is y_i (mol vapor/mol total gas), and if this vapor is the only species that would condense if the temperature were slightly lowered, then the partial pressure of the vapour in the gas equals the pure-component vapor pressure $p_i^*(T)$ at the system temperature.

If a gas containing a single superheated vapor is cooled at constant pressure, the temperature at which the vapor becomes saturated is referred to as the **dew point** of the gas. From Raoult's law

$$p_i = y_i P = p_i^*(T_{\text{dp}})$$

The difference between the temperature and the dew point of a gas is called the **degrees of superheat** of the gas.

A stream of air at 100°C and 5260 mm Hg contains 10.0% water by volume.

1. Calculate the dew point and degrees of superheat of the air.
2. Calculate the percentage of the vapor that condenses and the final composition of the gas phase if the air is cooled to 80°C at constant pressure.
3. Calculate the percentage condensation and the final gas-phase composition if, instead of being cooled, the air is compressed isothermally to 8500 mm Hg.

$$p_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}}P = (0.100)(5260 \text{ mm Hg}) = 526 \text{ mm Hg}$$

$$p_{\text{H}_2\text{O}}^*(100^\circ\text{C}) = 760 \text{ mm Hg} > p_{\text{H}_2\text{O}} \implies \text{the vapor is superheated}$$

$$p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^*(T_{\text{dp}}) = 526 \text{ mm Hg}$$

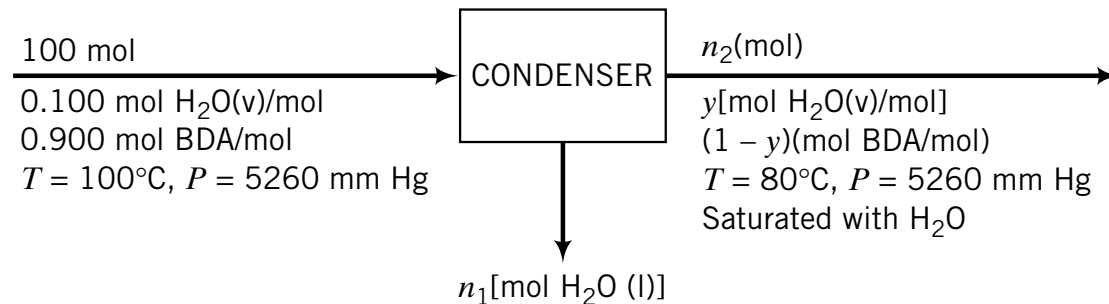
$T(^{\circ}\text{C})$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
90	525.76	527.76	529.77	531.78	533.80	535.82	537.86	539.90	541.95	544.00
91	546.05	548.11	550.18	552.26	554.35	556.44	558.53	560.64	562.75	564.87
92	566.99	569.12	571.26	573.40	575.55	577.71	579.87	582.04	584.22	586.41
93	588.60	590.80	593.00	595.21	597.43	599.66	601.89	604.13	606.38	608.64
94	610.90	613.17	615.44	617.72	620.01	622.31	624.61	626.92	629.24	631.57
95	633.90	636.24	638.59	640.94	643.30	645.67	648.05	650.43	652.82	655.22
96	657.62	660.03	662.45	664.88	667.31	669.75	672.20	674.66	677.12	679.69
97	682.07	684.55	687.04	689.54	692.05	694.57	697.10	699.63	702.17	704.71
98	707.27	709.83	712.40	714.98	717.56	720.15	722.75	725.36	727.98	730.61
99	733.24	735.88	738.53	741.18	743.85	746.52	749.20	751.89	754.58	757.29
100	760.00	762.72	765.45	768.19	770.93	773.68	776.44	779.22	782.00	784.78
101	787.57	790.37	793.18	796.00	798.82	801.66	804.50	807.35	810.21	813.08

$$T_{\text{dp}} = 90^{\circ}\text{C}$$

and the air has $100^{\circ}\text{C} - 90^{\circ}\text{C} = 10^{\circ}\text{C}$ of superheat

Since the air becomes saturated at 90°C , further cooling must lead to condensation. Since the products are liquid water in equilibrium with a gas phase, the water vapor in the gas must remain saturated.

Basis: 100 mol Feed Gas



Raoult's Law at Outlet

$$yP = p_{\text{H}_2\text{O}}^*(T)$$



$$y = \frac{p_{\text{H}_2\text{O}}^*(80^\circ\text{C})}{P} = \frac{355 \text{ mm Hg}}{5260 \text{ mm Hg}} = \boxed{0.0675 \frac{\text{mol H}_2\text{O}}{\text{mol}}}$$

$T(^{\circ}\text{C})$	0	1	2	3	4	5	6	7	8	9
50	92.51	97.20	102.09	107.20	112.51	118.04	123.80	129.82	136.08	142.60
60	149.38	156.43	163.77	171.38	179.31	187.54	196.09	204.96	214.17	223.73
70	233.7	243.9	254.6	265.7	277.2	289.1	301.4	314.1	327.3	341.0
80	355.1	369.7	384.9	400.6	416.8	433.6	450.9	468.7	487.1	506.1

Balance on Dry Air

$$\frac{100 \text{ mol}}{\quad} \Bigg| \frac{0.900 \text{ mol BDA}}{\text{mol}} = n_2(1 - y)$$

$$\Downarrow y = 0.0675$$

$$n_2 = 96.5 \text{ mol}$$

Total Mole Balance

$$100 \text{ mol} = n_1 + n_2$$

$$\Downarrow n_2 = 96.5 \text{ mol}$$

$$n_1 = 3.5 \text{ mol H}_2\text{O condensed}$$

Percentage Condensation

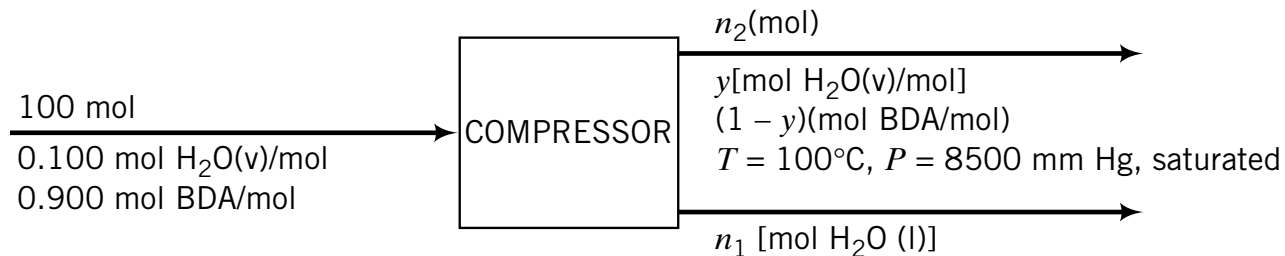
$$\frac{3.5 \text{ mol H}_2\text{O condensed}}{(0.100 \times 100) \text{ mol H}_2\text{O fed}} \times 100\% = \boxed{35\%}$$

Initially $y_{\text{H}_2\text{O}}P < p_{\text{H}_2\text{O}}^*(100^\circ\text{C})$. Saturation occurs when P is high enough for the inequality to become an equality, or

$$P_{\text{saturation}} = \frac{p_{\text{H}_2\text{O}}^*(100^\circ\text{C})}{y_{\text{H}_2\text{O}}} = \frac{760 \text{ mm}}{0.100} = 7600 \text{ mm Hg}$$

Any increase in P above 7600 mm Hg must cause condensation, so that the products from the compression to 8500 mm Hg must include a liquid stream.

Basis: 100 mol Feed Gas



Raoult's Law

$$y = \frac{p_{\text{H}_2\text{O}}^*(100^\circ\text{C})}{P} = \frac{760 \text{ mm Hg}}{8500 \text{ mm Hg}} = \boxed{0.0894 \frac{\text{mol H}_2\text{O}}{\text{mol}}}$$

Balance on Dry Air

$$(100 \text{ mol})(0.900) = n_2(1 - y)$$

$$\Downarrow y = 0.0894$$

$$n_2 = 98.8 \text{ mol}$$

Total Mole Balance

$$100 \text{ mol} = n_1 + n_2$$

$$\Downarrow n_2 = 98.8 \text{ mol}$$

$$n_1 = 1.2 \text{ mol H}_2\text{O condensed}$$

Percentage Condensation

$$\frac{1.2 \text{ mol H}_2\text{O condensed}}{(0.100 \times 100) \text{ mol H}_2\text{O fed}} \times 100\% = \boxed{12\%}$$