



جامعة الملك فهد للبترول والمعادن
King Fahd University of Petroleum & Minerals

Introduction to Chemical Engineering

CHE-201

INSTRUCTOR: Dr. Nabeel Salim Abo-Ghander

Chapter 6

Multiphase Systems

Introductory Statement:

A Phase is a state of matter.

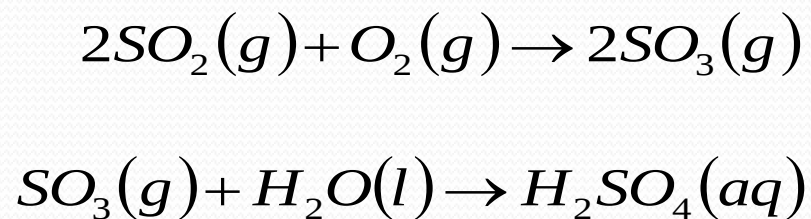
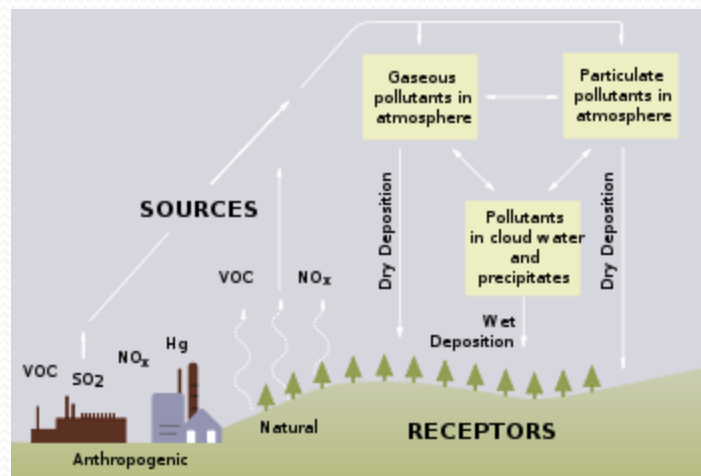
Do you believe that:

All chemical processes involve operations in which material is transferred from one phase (gas, solid, liquid) to another.

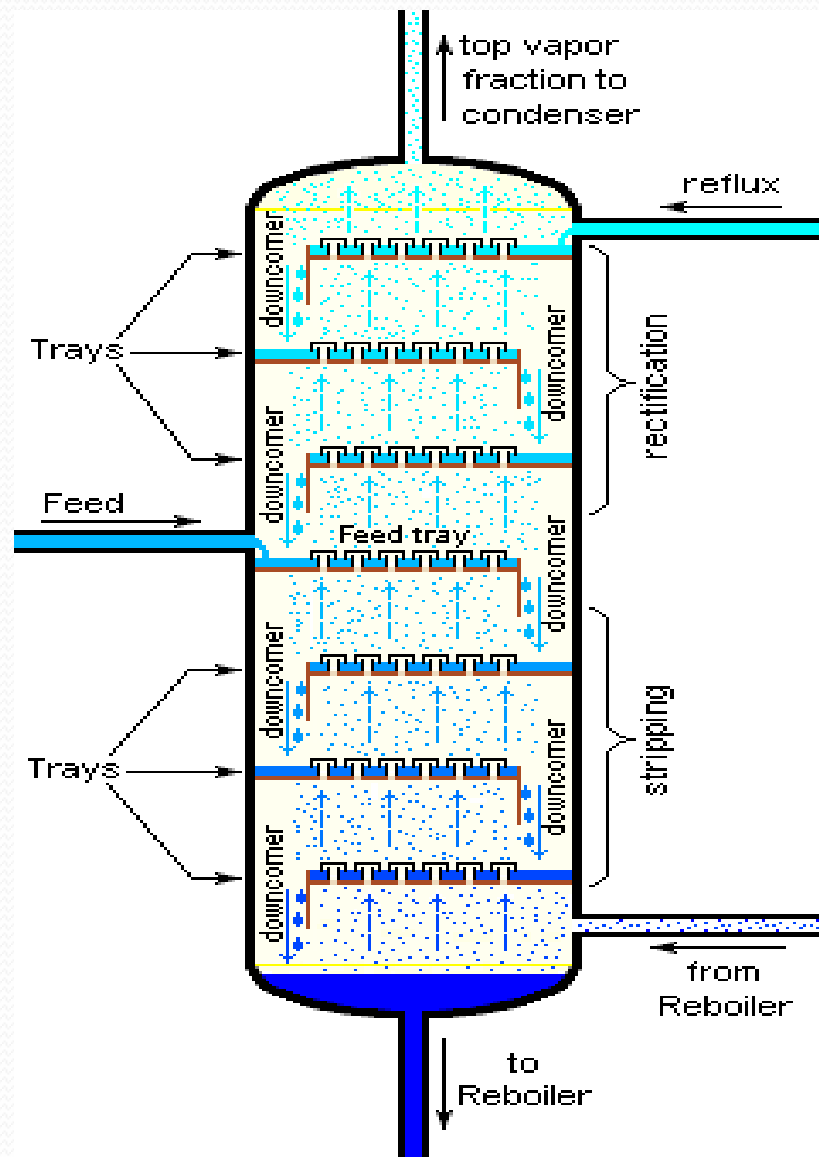
Brewing a cup of Coffee (leaching):



Removal of Sulfur dioxide from a gas stream (Scrubbing):



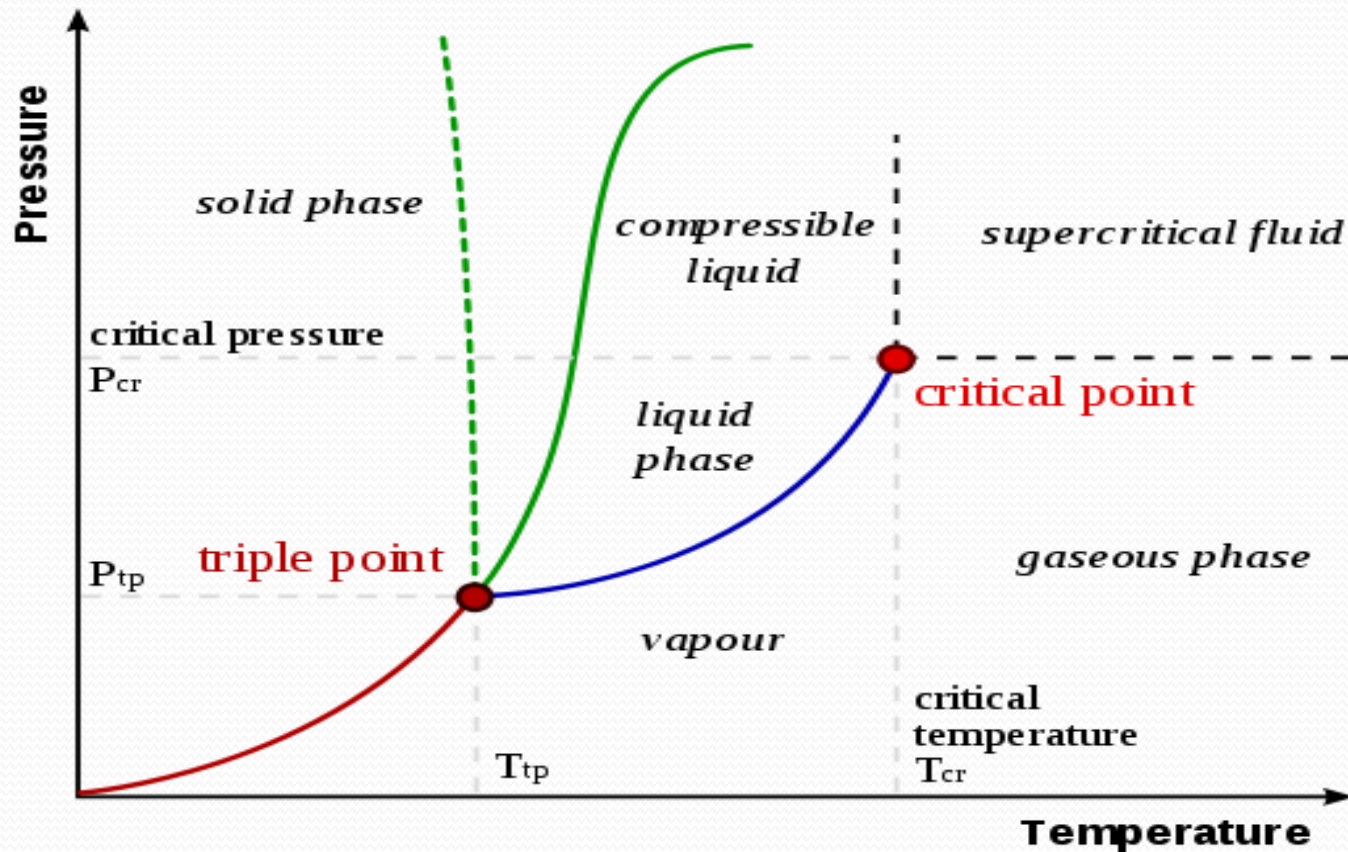
Separation:



Rate of transportation:

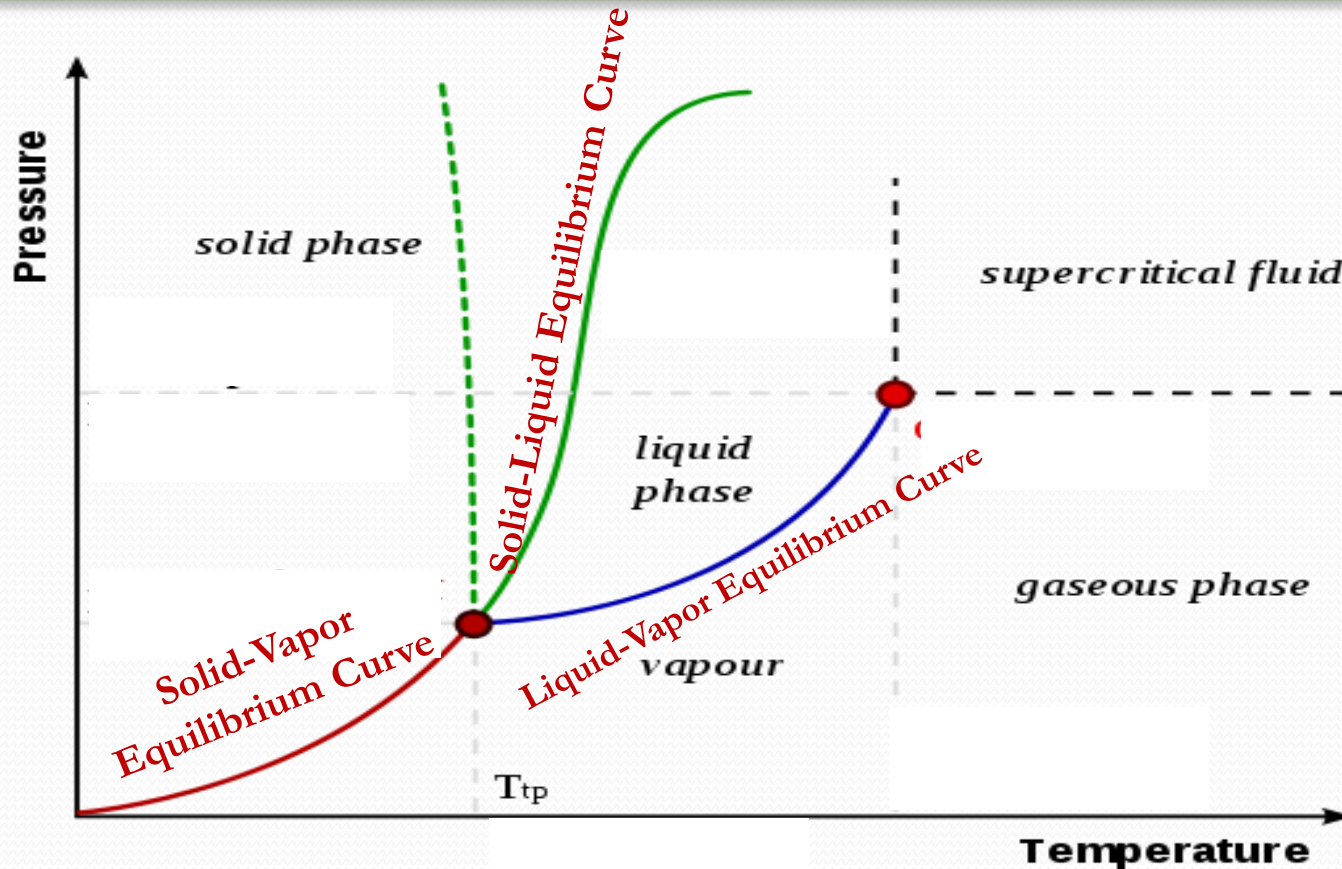
A species transfers from one phase to another until the second phase is saturated, i.e. holding as much as it can hold at the prevailing process condition. When the concentration of all species in each phase no longer change with time, the phase are said to be in phase equilibrium.

Phase Diagram:



Phase diagram of a pure species is defined as a plot of one system variable versus another showing the conditions at which the substances exist as a solid, a liquid and a gas.

Phase Diagram:



Crossing Phases doesn't occur instantaneously but gradually in which the substance passes through three main stages, i.e. phase 1, phase 1 & 2, then phase 2.

Main points on the phase diagram:

- Normal boiling point temperature is the point at which liquids start to boil at one atmospheric pressure.
- Triple point is the point at which the three phases, i.e. solid, liquid and vapor coexist in equilibrium.
- Critical temperature is the temperature at which a substance can't coexist in two phases whatever pressure is applied.
- Sublimation points are located on solid-vapor equilibrium curve.

6.1b Estimation of Vapor Pressures:

- Vapor pressure is the equilibrium pressure of the vapor above its liquid.
- It indicates the tendency of a species to transfer from one phase to another.
- Volatility of a species is the degree to which the species tends to transfer from liquid (or solid) to state to the vapor state.
- Four methods can be used to estimate the component vapor pressures:
 1. Vapor pressure tables in references
 2. Clapeyron equation.
 3. Cox chart.
 4. Antoine equation.

Clapeyron equation:

- It is an empirical equation given as:

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

Where:

p^* $\equiv$ vapor pressure of pure substance

T $\equiv$ absolute temperature

$\hat{V}_g, \hat{V}_l$ $\equiv$ specific molar volumes of vapor and liquid

$\Delta\hat{H}_v$ $\equiv$ latent heat of vaporization

Clapeyron equation:

At low pressure, $\hat{V}_l \approx 0.0 \Rightarrow (\hat{V}_g - \hat{V}_l) \approx \hat{V}_g$ and substituting for $\hat{V}_g$ from ideal gas law yields the Clausius-Clapeyron equation:

$$\frac{dp^*}{p^*} = \frac{\Delta \hat{H}_v}{R} \frac{dT}{T^2}$$

$$\ln(p^*) = -\frac{\Delta \hat{H}_v}{R} \left(\frac{1}{T} \right) + B$$

It is a straight line equations where a minimum of one point is needed to obtain the value of “B”.

Clapeyron equation:

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

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

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

$$p_1^* = 40\text{ mmHg}$$

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

$$p_2^* = 60\text{ mmHg}$$

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.

Cox Plot:

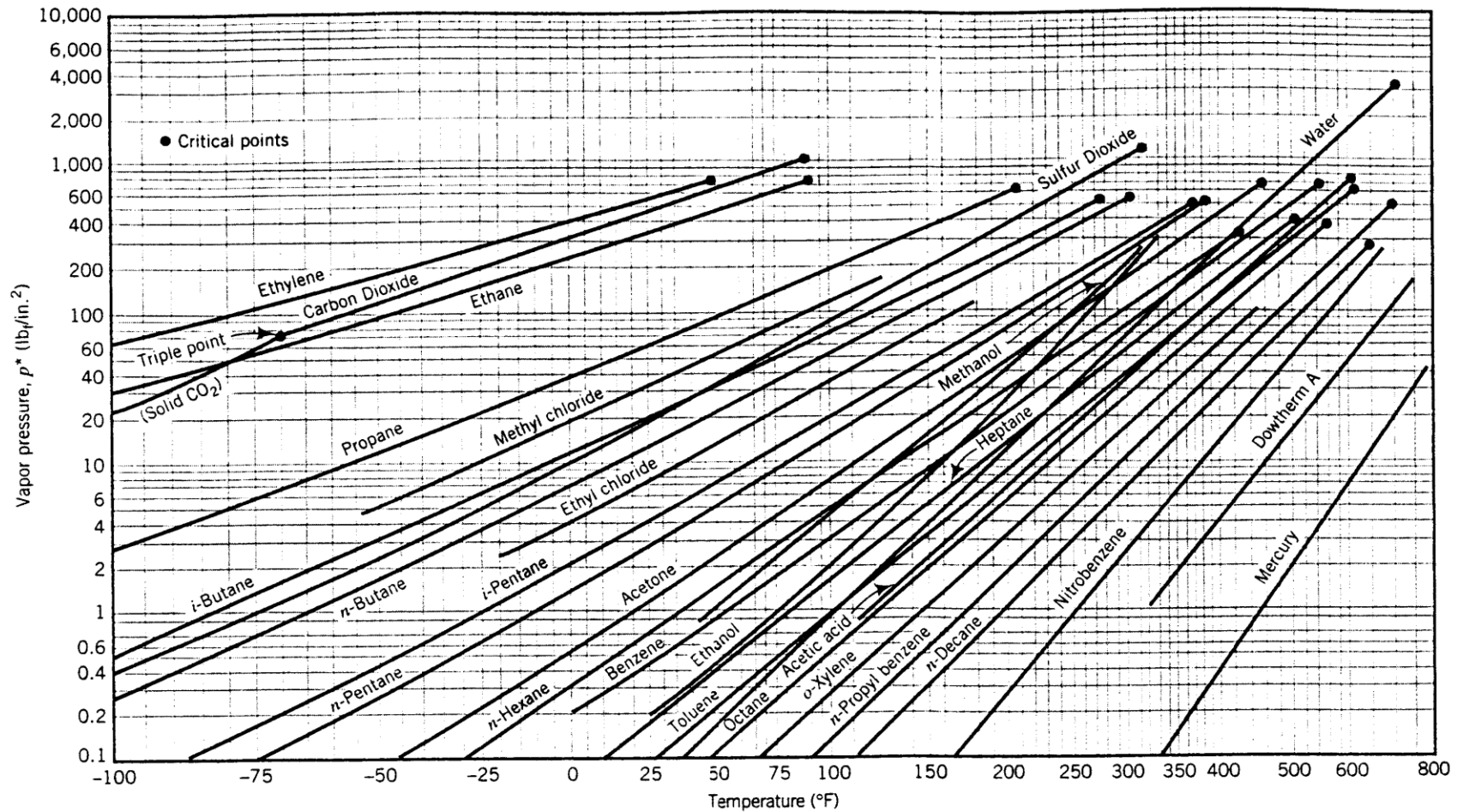


Figure 6.1-4 Cox chart vapor pressure plots. (From A. S. Foust et al., *Principles of Unit Operations*, Wiley, New York, 1960, p. 550.)

Antoine Equation:

It is an empirical equation expressed as:

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

where:

A, B, C are constant picked up from references

Table of Constant (Table B.4):

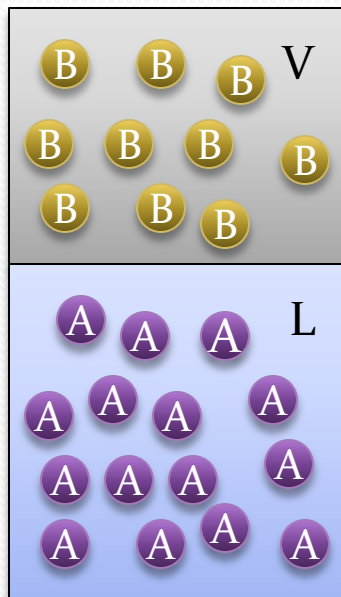
Table B.4 Antoine Equation Constants^a

$\log_{10} p^* = A - \frac{B}{T + C} \quad p^* \text{ in mm Hg, } T \text{ in } ^\circ\text{C}$					
<i>Example:</i> The vapor pressure of acetaldehyde at 25°C is determined as follows: $\log_{10} p_{\text{C}_2\text{H}_4\text{O}}^*(25^\circ\text{C}) = 8.00552 - \frac{1600.017}{25 + 291.809} = 2.9551$ $\Rightarrow p_{\text{C}_2\text{H}_4\text{O}}^*(25^\circ\text{C}) = 10^{2.9551} = 902 \text{ mm Hg}$					
Compound	Formula	Range (°C)	A	B	C
Acetaldehyde	C ₂ H ₄ O	−0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	C ₂ H ₄ O ₂	29.8 to 126.5	7.38782	1533.313	222.309
Acetic acid*	C ₂ H ₄ O ₂	0 to 36	7.18807	1416.7	225
Acetic anhydride	C ₄ H ₆ O ₃	62.8 to 139.4	7.14948	1444.718	199.817
Acetone	C ₃ H ₆ O	−12.9 to 55.3	7.11714	1210.595	229.664
Acrylic acid	C ₃ H ₄ O ₂	20.0 to 70.0	5.65204	648.629	154.683
Ammonia*	NH ₃	−83 to 60	7.55466	1002.711	247.885
Aniline	C ₆ H ₇ N	102.6 to 185.2	7.32010	1731.515	206.049
Benzene	C ₆ H ₆	14.5 to 80.9	6.89272	1203.531	219.888
<i>n</i> -Butane	<i>n</i> -C ₄ H ₁₀	−78.0 to −0.3	6.82485	943.453	239.711
<i>i</i> -Butane	<i>i</i> -C ₄ H ₁₀	−85.1 to −11.6	6.78866	899.617	241.942
1-Butanol	C ₄ H ₁₀ O	89.2 to 125.7	7.36366	1305.198	173.427
2-Butanol	C ₄ H ₁₀ O	72.4 to 107.1	7.20131	1157.000	168.279
1-Butene	C ₄ H ₈	−77.5 to −3.7	6.53101	810.261	228.066
Butyric acid	C ₄ H ₈ O ₂	20.0 to 150.0	8.71019	2433.014	255.189
Carbon disulfide	CS ₂	3.6 to 79.9	6.94279	1169.110	241.593
Carbon tetrachloride	CCl ₄	14.1 to 76.0	6.87926	1212.021	226.409
Chlorobenzene	C ₆ H ₅ Cl	62.0 to 131.7	6.97808	1431.053	217.550
Chlorobenzene*	C ₆ H ₅ Cl	0 to 42	7.10690	1500.0	224.0
Chlorobenzene*	C ₆ H ₅ Cl	42 to 230	6.94504	1413.12	216.0
Chloroform	CHCl ₃	−10.4 to 60.3	6.95465	1170.966	226.232
Chloroform*	CHCl ₃	−30 to 150	6.90328	1163.03	227.4
Cyclohexane	C ₆ H ₁₂	19.9 to 81.6	6.84941	1206.001	223.148
Cyclohexanol	C ₆ H ₁₂ O	93.7 to 160.7	6.25530	912.866	109.126
<i>n</i> -Decane	<i>n</i> -C ₁₀ H ₂₂	94.5 to 175.1	6.95707	1503.568	194.738
1-Decene	C ₁₀ H ₂₀	86.8 to 171.6	6.95433	1497.527	197.056
1,1-Dichloroethane	C ₂ H ₄ Cl ₂	−38.8 to 17.6	6.97702	1174.022	229.060
1,2-Dichloroethane	C ₂ H ₄ Cl ₂	−30.8 to 99.4	7.02530	1271.254	222.927
Dichloromethane	CH ₂ Cl ₂	−40.0 to 40	7.40916	1325.938	252.616
Diethyl ether	C ₄ H ₁₀ O	−60.8 to 19.9	6.92032	1064.066	228.799
Diethyl ketone	C ₅ H ₁₀ O	56.5 to 111.3	7.02529	1310.281	214.192
Diethylene glycol	C ₄ H ₁₀ O ₂	130.0 to 243.0	7.63666	1939.359	162.714
Dimethyl ether	C ₂ H ₆ O	−78.2 to −24.9	6.97603	889.264	241.957
Dimethylamine	C ₂ H ₇ N	−71.8 to 6.9	7.08212	960.242	221.667
<i>N,N</i> -Dimethylformamide	C ₃ H ₇ NO	30.0 to 90.0	6.92796	1400.869	196.434
1,4-Dioxane	C ₄ H ₈ O ₂	20.0 to 105.0	7.43155	1554.679	240.337
Ethanol	C ₂ H ₆ O	19.6 to 93.4	8.11220	1592.864	226.184
Ethanolamine	C ₂ H ₇ NO	65.4 to 170.9	7.45680	1577.670	173.368
Ethyl acetate	C ₄ H ₈ O ₂	15.6 to 75.8	7.10179	1244.951	217.881
Ethyl acetate*	C ₄ H ₈ O ₂	−20 to 150	7.09808	1238.710	217.0
Ethyl chloride	C ₂ H ₅ Cl	−55.9 to 12.5	6.98647	1030.007	238.612
Ethylbenzene	C ₈ H ₁₀	56.5 to 137.1	6.95650	1423.543	213.091

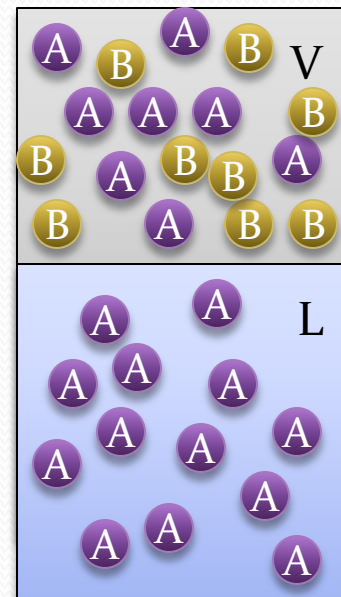
^aAdapted from T. Boublik, V. Fried, and E. Hala, *The Vapour Pressures of Pure Substances*, Elsevier, Amsterdam, 1973. If marked with an asterisk (*), constants are from *Lange's Handbook of Chemistry*, 9th Edition, Handbook Publishers, Inc., Sandusky, OH, 1956.

(continued)

6.2 The Gibbs Phase Rule:



At the beginning of contact, different T , P ,
and composition



At equilibrium, T , P ,
and no driving forces for mass or
molar between phases

6.2 The Gibbs Phase Rule:

➤ Variables can be divided into:

1. Extensive variables: depend on the system size. Examples, mass and volume.
2. Intensive variables: don't depend on the system size. Example, temperature, pressure, density, specific volume, and composition.

6.2 The Gibbs Phase Rule (Cont.):

- To correctly specify a system, only intensive variables are considered, mainly temperature, pressure and mole or mass fractions.
- The number of intensive variables which should be specified for a given system at equilibrium is calculated for nonreactive system by:

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

where:

DF : Degree of freedom

c : Number of chemical species

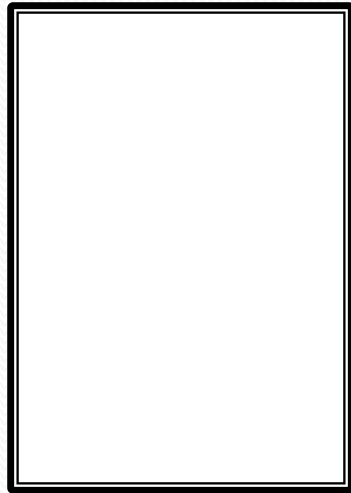
Π : Number of phases in a system at equilibrium

6.2 The Gibbs Phase Rule (Cont.):

Example 6.2-1: The Gibbs Phase Rule

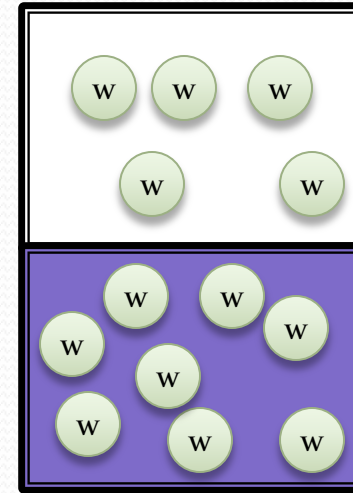
Determine the degree of freedom for each of the following systems at equilibrium. Specify a feasible set of independent variables for each system.

1. Pure liquid water.
2. A mixture of liquid, solid, and vapor water.
3. A vapor-liquid mixture of acetone and methyl ethyl ketone.



Dry Air at $T=75^{\circ}\text{C}$ and 760 mm Hg

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



Dry Air at $T=75^{\circ}\text{C}$ and 760 mm Hg

In contact with liquid water

Eventually equilibrium is established between the two phases.

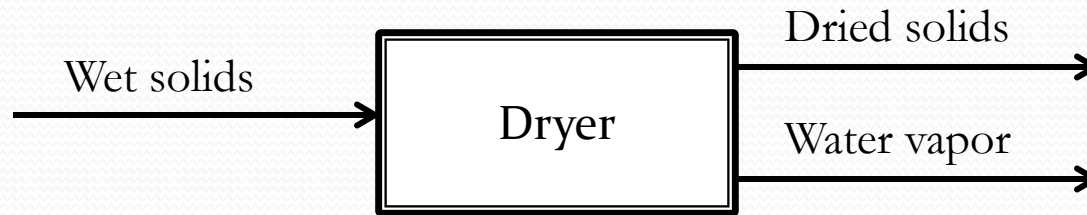
- Separation processes involving single condensable components are: evaporation, drying, humidification, condensation, and dehumidification.

Separation Processes:

•Evaporation:



•Drying:



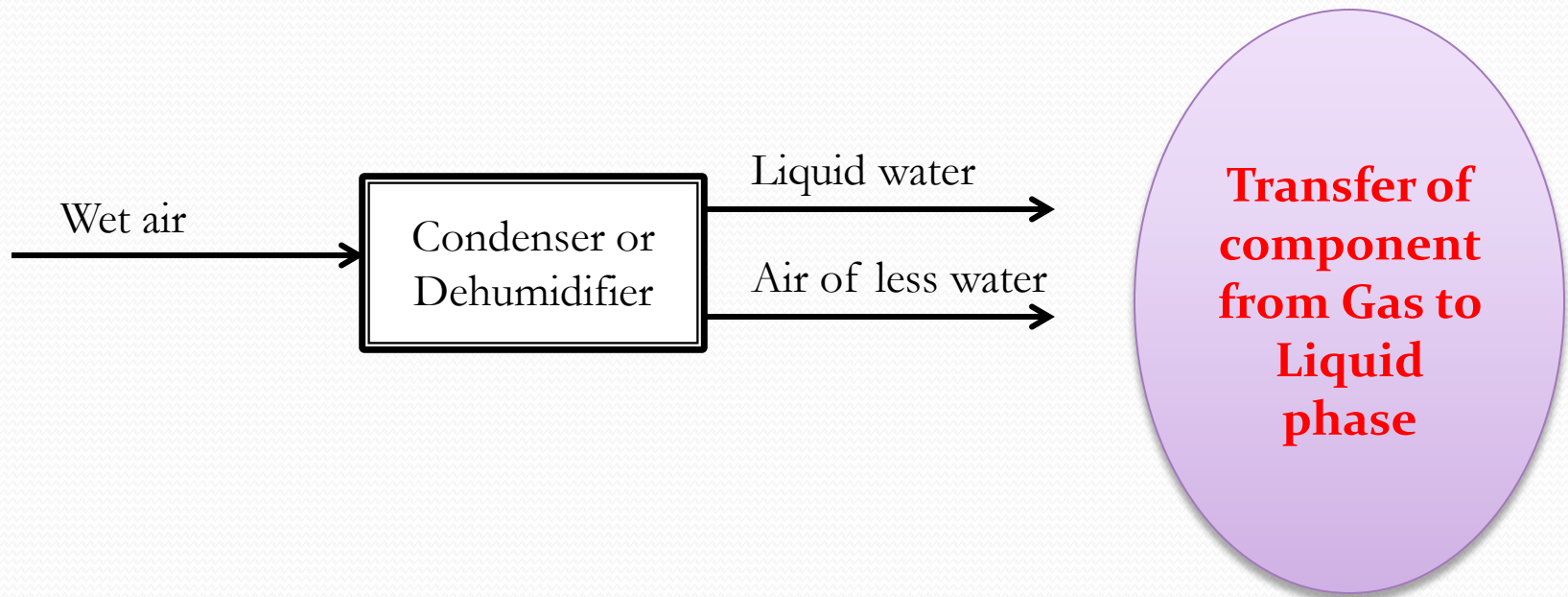
•Humidification:



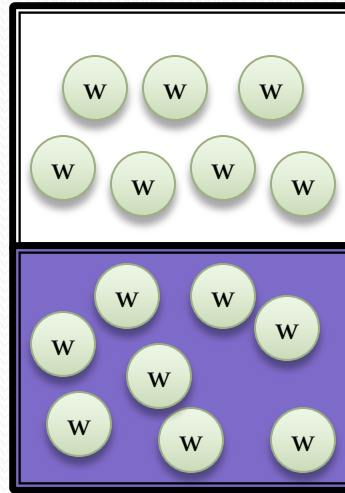
**Transfer
of
Liquid
into Gas
phase**

Separation Processes:

- Condensation and dehumidification:



Raoult's Law, Single Condensable Species



If a gas at temperature T and pressure P contains 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 vapor in the gas equals the pure-component vapor pressure at the system temperature:

Raoult's Law, Single Condensable Species:

$$p_i = y_i P = p_i^*(T)$$

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

Air and liquid water are contained at equilibrium in a closed chamber at 75°C and 760 mm Hg, calculate the molar composition of the gas phase.

Table B.3 in Appendix B: Vapor Pressure of Water

$T(^{\circ}\text{C})$	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
$T(^{\circ}\text{C})$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

Remarks on Equilibrium Concept:

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

$$p_i = y_i P < p_i^*(T)$$

- Achieving the condensation required changing the system conditions till equilibrium is maintained, then either the pressure is increased at constant temperature or the temperature is lowered at constant pressure.

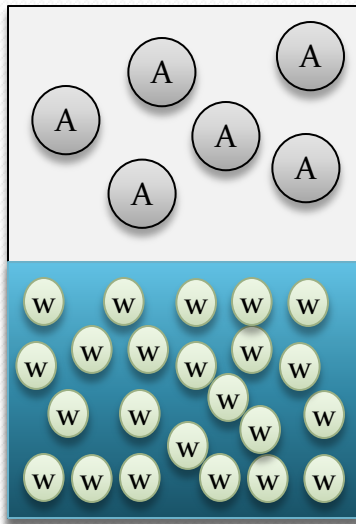
Remarks on Equilibrium Concept:

- 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:

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

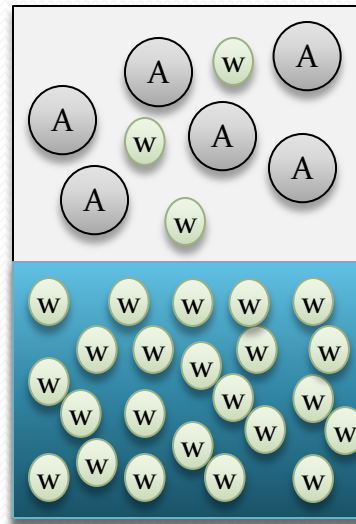
Degree of superheat of a gas is the difference between the temperature of the gas and the dew point.

Equilibrium Concept:



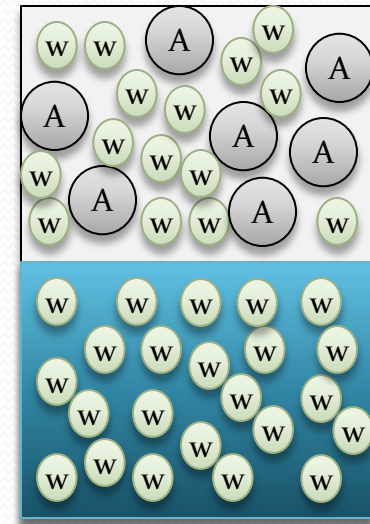
Beginning of contact
between the Phases

$$p_{H_2O} = 0.0 \text{ mmHg}$$



Air with
superheated vapor

$$p_{H_2O} = y_{H_2O}P < p_{H_2O}^*(T)$$



Air saturated with vapor

$$p_{H_2O} = y_{H_2O}P = p_{H_2O}^*(T)$$

Example 6.3-2 Material Balances Around a Condenser

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.
4. Suppose the process of part 2 is run, the product gas is analyzed, and the mole fraction of water differs considerably from the calculated value. What could be the responsible for the disparity between calculated and measured values? (List several possibilities).

Table B.3 in Appendix B: Vapor Pressure of Water

$T(^{\circ}\text{C})$	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

Table B.3 in Appendix B: Vapor Pressure of Water

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80	355.1	369.7	384.9	400.6	416.8	433.6	450.9	468.7	487.1	506.1
$T(^{\circ}\text{C})$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

- ✓ Relative Saturation (Relative Humidity)

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

- ✓ Molal Saturation (Molal Humidity):

$$s_m(h_m) = \frac{p_i}{P - p_i} = \frac{\text{moles of vapor}}{\text{moles of vapor} - \text{free(dry) gas}}$$

- ✓ Absolute Saturation (Absolute Humidity):

$$s_a(h_a) = \frac{p_i M_i}{(P - p_i) M_{dry}} = \frac{\text{mass of vapor}}{\text{mass of vapor} - \text{free(dry) gas}}$$

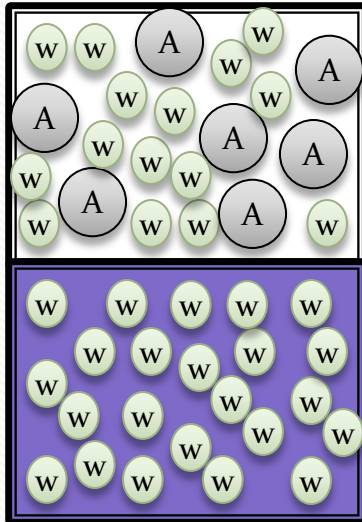
- ✓ Percentage Saturation (Percentage Humidity):

$$s_p(h_p) = \frac{s_m}{s_m^*} \times 100\% = \frac{p_i / (P - p_i)}{p_i^* / (P - p_i^*)} \times 100\%$$

Example 6.4-2:

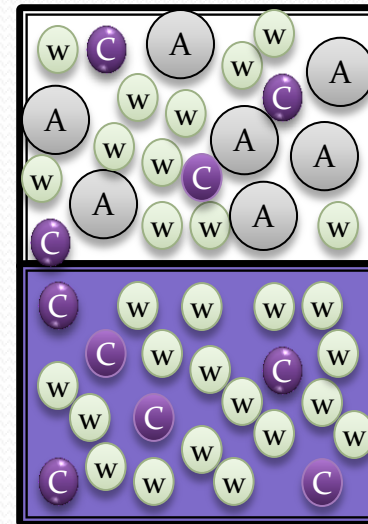
Humid air at 75°C, 1.1 bar, and 30% relative humidity is fed into a process until at a rate of 1000 m³/h. Determine:

1. The molar flowrate of water, dry air, and oxygen entering the process unit.
2. The molal humidity, absolute humidity, and percentage humidity of the air.
3. The dew point.



Already discussed in 6.3
(Pure Liquid)

$$p_i = y_i P = p_i^*(T)$$



Will be discussed in 6.4
(Liquid Mixtures)

$$p_i = y_i P = x_i p_i^*(T)$$

- ✓ General Raoult's law for multicomponent mixtures is:

$$p_i = y_i P = x_i p_i^*(T)$$

- ✓ If the liquid mixture is a diluted one, i.e. $x_i \approx 0.0$, Raoult's law can be reduced to:

$$p_i = y_i P = x_i H_i(T)$$

Henry's Law:

H_i : Henry's constant of i in a specific solvent

- ✓ If the liquid phase is a pure one, Raoult's law can be reduced into:

$$p_i = y_i P = p_i^*(T)$$

Problem 6.46:

A gas containing nitrogen, benzene, toluene is in equilibrium with a 40 mole% benzene-60 mole% toluene liquid mixture at 100°C and 10 atm. Estimate the gas-phase composition using a Raoult's law.

Use either Raoult's law or Henry's law to solve the following problems:

1. A gas containing 1.0 mol% ethane is in contact with water at 20°C and 20.0 atm. Estimate the mole fraction of the dissolved ethane.
2. An equimolar liquid mixture of benzene (B) and toluene (T) is in equilibrium with its vapor at 30°C. What is the system pressure and the composition of the vapor.

THANK YOU