Chemical Engineering Principles 2 (0905212)

Multiphase Systems

Dr.-Ing. Zayed Al-Hamamre

1

Content

✓ **Introduction**
   o **Separation processes**
✓ **Single component phase equilibrium**
   o **Phase diagram**
   o **Vapor Pressures**
✓ **Gibbs phase rule**
✓ **Gas liquid system**

- Virtually all commercial chemical processes involve operations in which material is transferred from one phase (gas, liquid, or solid) into another

- Multiphase operations include all phase-change operations on a single species.

- Examples are freezing, melting, evaporation, and condensation, and most separation and purification processes, which are designed to separate components of mixtures from one another.

- Most separations are accomplished by feeding a mixture of species A and B into a two-phase system under conditions such that most of the A remains in its original phase and most of the B transfers into a second phase.

- The two phases then either

  o Separate themselves under the influence of gravity-as when gases and liquids or two immiscible liquids separate-or

 o Are separated with the aid of a device such as a filter or a skimmer.

Separation processes

Brewing a cup of coffee or the process in a coffee percolator

- Hot liquid water and solid ground coffee beans are contacted.

- Soluble constituents of the beans are transferred from the solid phase to a liquid solution (coffee), and then

- The residual solids (grounds) are filtered from the solution.
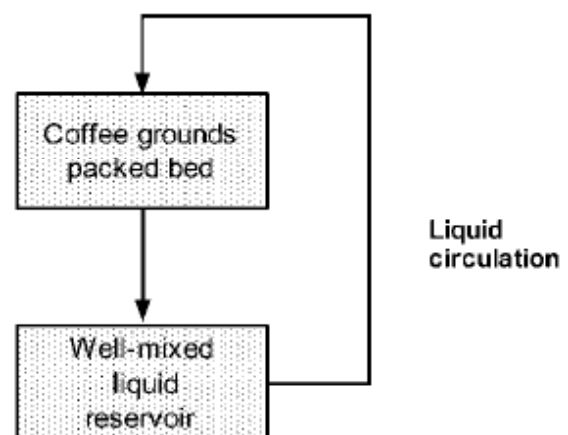
- The operation of dissolving a component of a solid phase in a liquid solvent is referred to as **leaching**.

Removal of sulfur dioxide from a gas stream

➢ For the removal of SO_2 from exhaust gas in combustion processes,

    o The combustion product gas is contacted with a liquid solution in an absorption or scrubbing process.

    o The SO_2 dissolves in the solvent and

    o The clean gas that remains is released to the atmosphere.

Recovery of methanol from an aqueous solution

➢ The separation process distillation exploits the difference in v*apor pressure .*

➢ Methanol has a higher *vapor pressure than water. meaning that it has a greater* tendency to vaporize when a mixture of the two species is heated.

➢ By partially vaporizing a liquid mixture, yielding a vapor relatively rich in methanol and a residual liquid relatively rich in water.

Separation of paraffinic and aromatic hydrocarbons or separation of biodiesel form unconverted oil

This process is known as liquid extraction

    o The paraffinic compounds are almost completely immiscible with liquid ethylene glycol, while

    o Aromatic compounds and ethylene glycol readily form homogeneous liquid mixtures

    o Paraffinics and aromatics may therefore be separated from each other by blending a mixture of the two

    o When allowed to settle, the aromatic compounds distribute between a paraffin-rich phase and a glycol phase.

Separation of an isomeric mixture.

para-xylene   ortho-xylene   meta-xylene
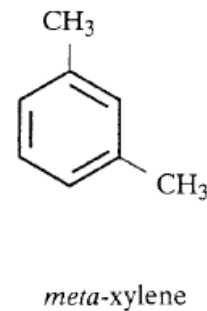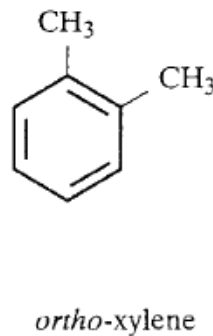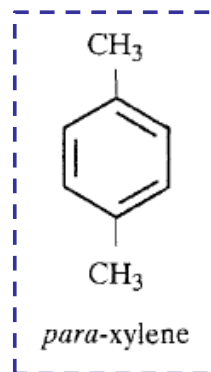
➤ In the synthesis of polyesters Para-xylene must be separated from the two isomers

➤ Two alternative commercial operations have been developed to perform the separation.

     o **Adsorption:** The isomers is contacted with a molecular sieve that has pores large enough to accommodate para-xylene but not the meta or ortho isomers

---

➤ **Crystallization:**

     o The Process is performed utilizing the difference in freezing points of the three isomers (para-xylene freezes at 13.3°C, ortho at -25.2°C, and meta at -47.9°C)

     o The mixture is cooled to a temperature at which para crystallizes and can then be separated physically from the remaining ortho and meta liquid.

➤ When a species transfers from one phase to another, the transfer rate generally decreases with time until the second phase is **saturated with the species.**

➤ When the concentrations of all species in each phase no longer change with time, the phases are said to be in **phase equilibrium.**

➤ The effectiveness of any of the separation processes described above depends both on

     o How species are distributed between the phases at equilibrium

     o The rate at which the system approaches equilibrium from its initial state.

Single component phase equilibrium

The critical temperature and the critical pressure

➢ A quantity of water is kept in a closed piston-fitted cylinder

➢ The cylinder temperature is first set to a specified value with the cylinder pressure low enough for all the water to be vapor;

➢ Then the water is compressed at constant temperature by lowering the piston until a drop of liquid water appears

➢ The pressure at which condensation begins (P_{cond}).

➢ The experiment is then repeated at several progressively higher temperatures.
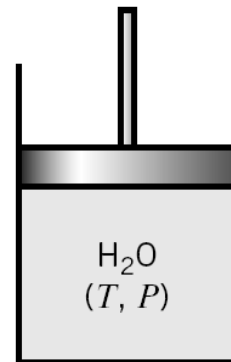
H_2O
(T, P)

Critical temperature and pressure

➢ At 25°C, water condenses at a very low pressure, and the density of the liquid is more than four orders of magnitude greater than that of the vapor.

➢ At higher temperatures, the condensation pressure increases and the densities of the vapor and liquid at condensation approach each other.

➢ At 374.15°C, the densities of the two phases are virtually equal, and above that temperature no phase separation is observed, no matter how high the pressure is raised

Run	$T(°C)$	$P_{cond}(atm)$	$\rho_v(kg/m^3)$	$\rho_l(kg/m^3)$
1	25.0	0.0329	0.0234	997.0
2	100.0	1.00	0.5977	957.9
3	201.4	15.8	8.084	862.8
4	349.8	163	113.3	575.0
5	373.7	217.1	268.1	374.5
6	374.15	218.3	315.5	315.5
7	>374.15	*No condensation occurs!*		

➢ The critical temperature of a species (T_c) is the highest temperature at which the species can coexist in two phases (liquid and vapor),

➢ The critical pressure (P_c) is the corresponding pressure at T_C

➢ A substance at T_c and P_c is said to be at its critical state

➢ A substance at $T > T_c$ and $P > P_c$ is said to be at its supercritical fluid
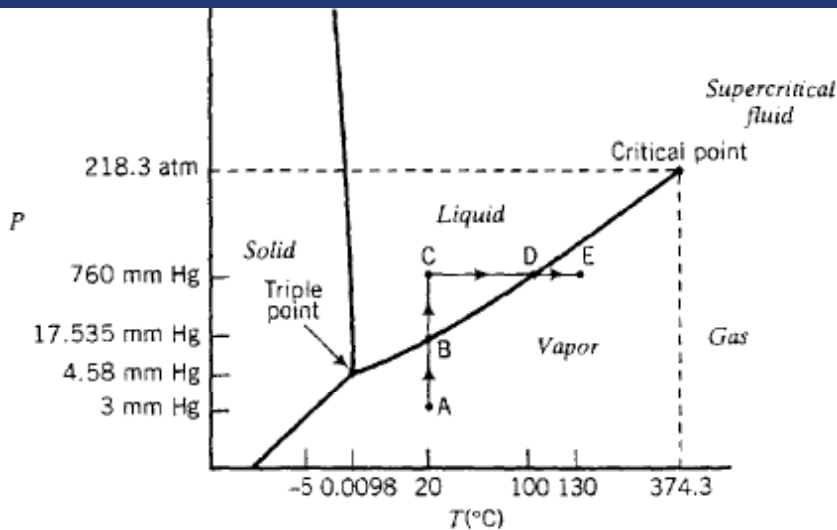
Phase Diagrams

➢ A **phase diagram of a pure substance is a plot of one system variable against another that** shows the conditions at which the substance exists as a solid. a liquid, and a gas.

➢ The most common of these diagrams plots pressure on the vertical axis versus temperature on the horizontal axis.

➢ The boundaries between the single-phase regions represent the pressures and temperatures at which two phases may coexist in equilibrium

➢ A gas that exists below its critical temperature is usually called a vapor because it can condense
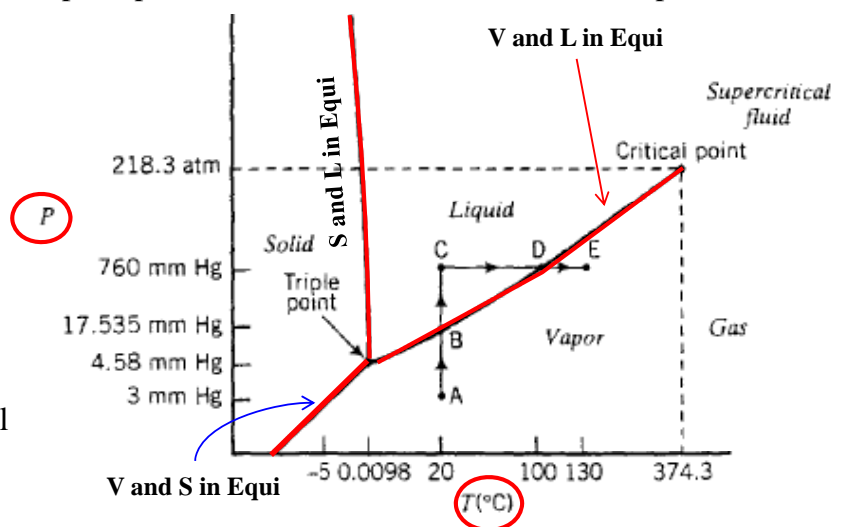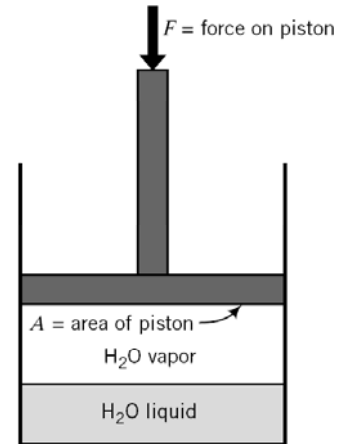
The phase diagram of water

$$P_{abs} = (F + W)/A$$

➤ A to C: pressure increase at constant temperature (compression , i.e. volume decrease, condensation).

➤ C to E: Heating at constant pressure (expansion with temperature rise)
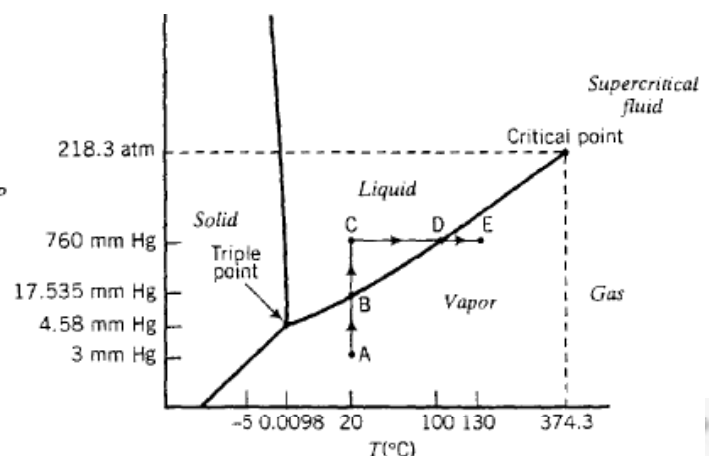
➤ **At point A:**

  o Water exists at 20ºC, and the force is set at a value such that the system pressure is 3 mm Hg.

  o At these conditions, water can only exist as a vapor .

  o Any liquid that may initially have been in the chamber evaporates, until finally the chamber contains only water vapor at 20ºC and 3 mm Hg.

➤ Suppose the force on the piston is slowly increased with the system temperature held constant at 20ºC until the pressure in the cylinder reaches 760 mm Hg, and thereafter

➤ Heat is added to the system with the pressure remaining constant until the temperature reaches 130°C.
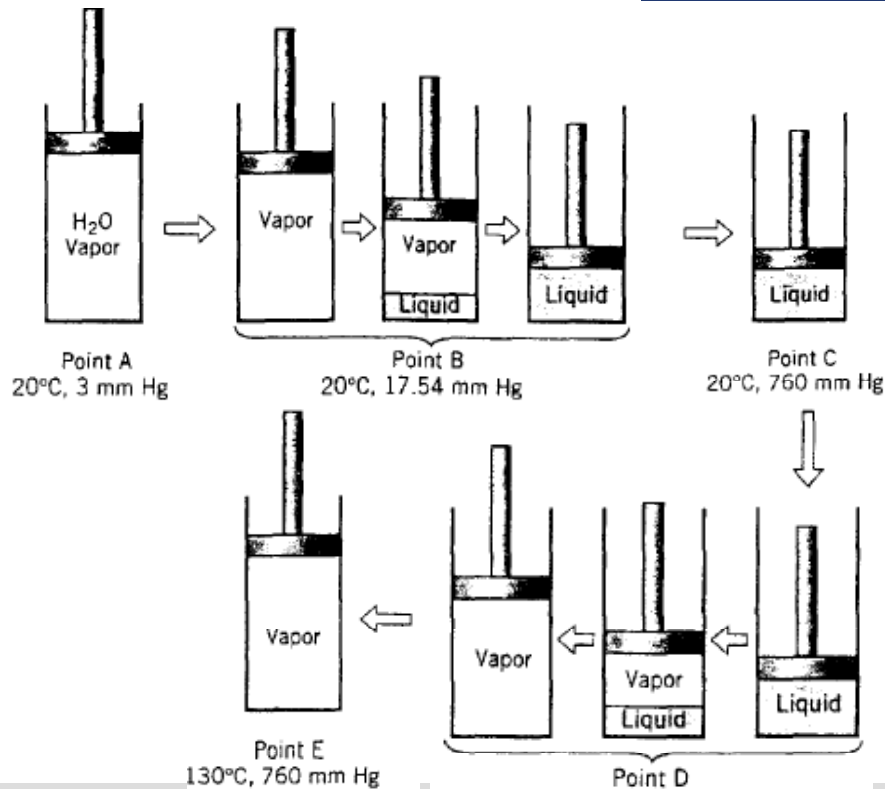
Point A
20°C, 3 mm Hg

Point B
20°C, 17.54 mm Hg

Point C
20°C, 760 mm Hg

Point E
130°C, 760 mm Hg

Point D
100°C, 760 mm Hg

---

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.

   ➢ At a given temperature there is only one pressure at which the liquid and vapor phases of a pure substance may exist in equilibrium

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.
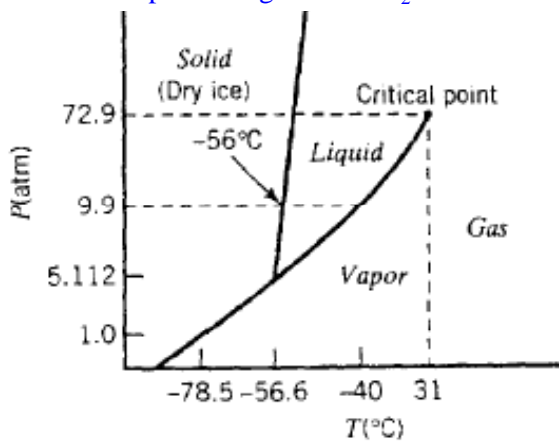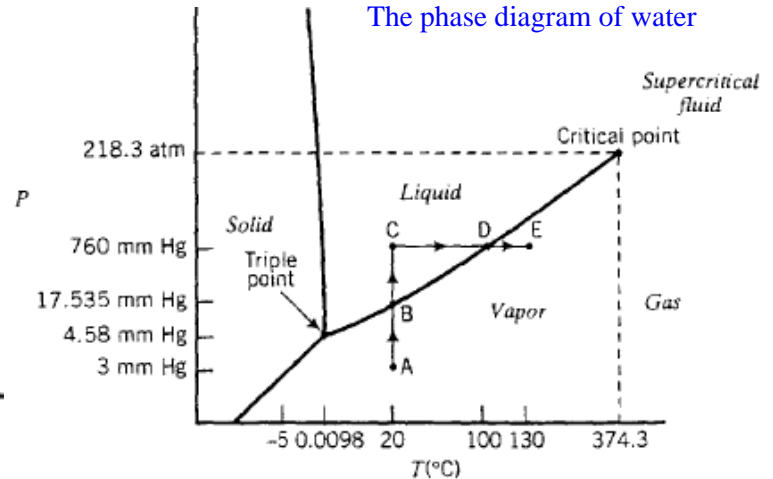
The phase diagram of CO_2

The phase diagram of water

- The freezing point of water decreases with increasing pressure.

- Most substances, including carbon dioxide, exhibit the opposite behavior

- Normal boiling and melting points for many substances are given in Table B.1 of Appendix B and for many more substances on pp. 2-7 through 2-47 of Perry's Chemical Engineers' Handbook, l and vapor pressures are tabulated on pp. 2-48 through 2-75 of the Handbook

Vaporization at constant T

condensation at constant T

sublime
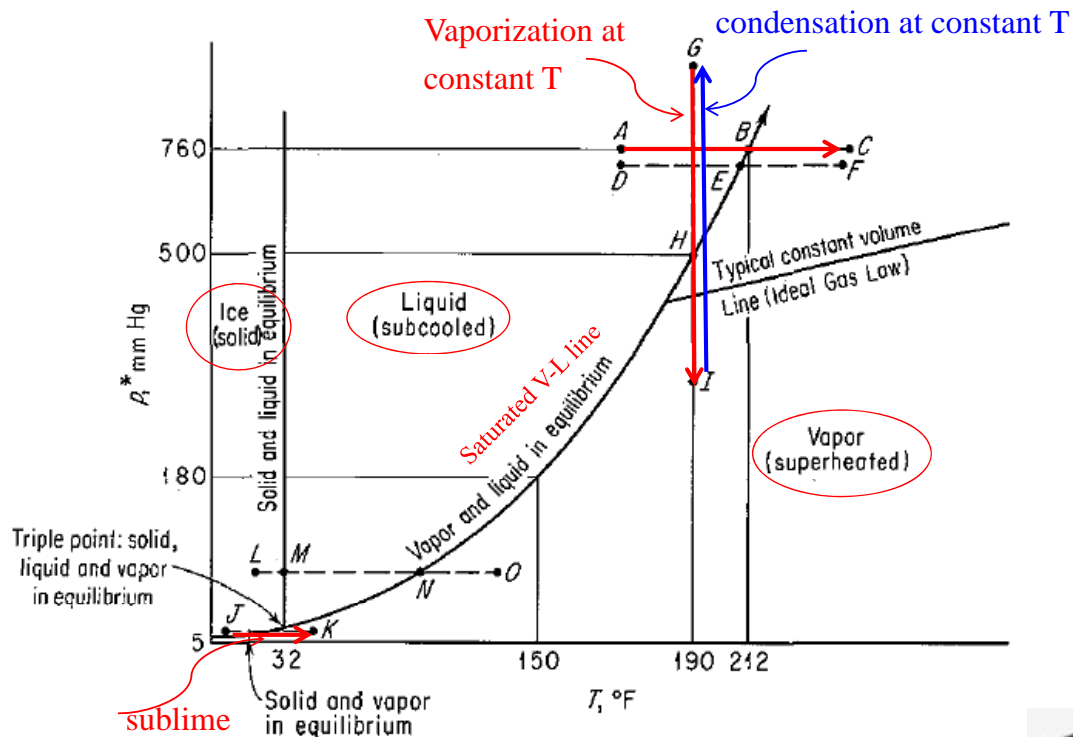
✓ The volatility of a species is the degree to which the species tends to transfer from the liquid (or solid) state to the vapor state.

✓ At a given temperature and pressure, a highly volatile substance is much more likely to be found as a vapor than is a substance with low volatility,

✓ which is more likely to be found in a condensed phase (liquid or solid).

➢ Separation processes such as distillation are used to separate more volatile species from less volatile species by partially vaporizing liquid mixtures.

➢ The vapor product is relatively rich in the more volatile feed components and the residual liquid is rich in the components with lower volatility.

➢ 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.

➢ Engineers who design and analyze separation processes therefore need to know the vapor pressures of process species as functions of temperature.

Estimation of Vapor Pressures

➢ The following methods can be used to determine a physical property of a process material:

  i. Look It Up

    o Perry's Chemical Engineers' Handbook, nth Edition, R. H. Perry and D. W. Green, Eds.McGraw-Hill, New York, 1997.

    o CRC Handbook of Chemistry and Physics, 79th Edition, D. Lide, Ed., Chemical Rubber Company, Boca Raton, FL, 1998

  ii. Estimate It

    o Interpolation or extrapolation

    o Using Correlations, available in

      ➢ Bruce E. Poling, John M. Prausnitz, John P. O'Connell, The Properties of Gases and Liquids, 5th Edition, McGraw-Hill, New York, 2004

  ii. Measure It

A relationship between p^*, the vapor pressure of a pure substance, and T, the absolute temperature, is the **Clapeyron equation**

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

where T is *absolute* temperature; $\hat{V}_g$ and $\hat{V}_l$ are the specific molar volumes (volume/mole) of gas (vapor) and liquid, respectively; and $\Delta \hat{H}_v$ is the **latent heat of vaporization,** or the energy required to vaporize one mole of the liquid

➢ Unless the pressure is extremely high, the specific volume of the liquid is negligible relative to that of the vapor $\quad$ (i.e., $\hat{V}_g - \hat{V}_l \approx \hat{V}_g$).

➢ Apply the ideal gas equation of state to the vapor and re-arranging the equation

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta \hat{H}_v}{R}$$

$$\frac{\Delta(lnP^*)}{\Delta(1/T)} = -\frac{\Delta \hat{H}_v}{R}$$

➢ Plot $\Delta(lnP^*)$ versus $\Delta(1/T)$ ➡ the slope at a given temperature equals $-\Delta \hat{H}_v/R$.

➢ If the heat of vaporization of a substance is independent of temperature

$$\ln p^* = -\frac{\Delta \hat{H}_v}{RT} + B \qquad \boxed{\text{Clausius–Clapeyron equation}}$$

where B is a constant that varies from one substance to another.

If you know $\Delta \hat{H}_v$ and p^* at a single temperature T_0, you can solve the Clausius–Clapeyron equation for B and thereafter use this equation to estimate p^* at any temperature close to T_0.

If you have p^* versus T data, you can plot $\ln p^*$ versus $1/T$ and determine $\Delta \hat{H}_v / R$ and B graphically

Example:

Vapor Pressure Estimation Using the Clausius–Clapeyron Equation

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

$$T_1 = 7.6°C, \qquad p_1^* = 40 \text{ mm Hg}$$
$$T_2 = 15.4°C, \qquad p_2^* = 60 \text{ mm Hg}$$

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.

Cox chart vapor pressure plots
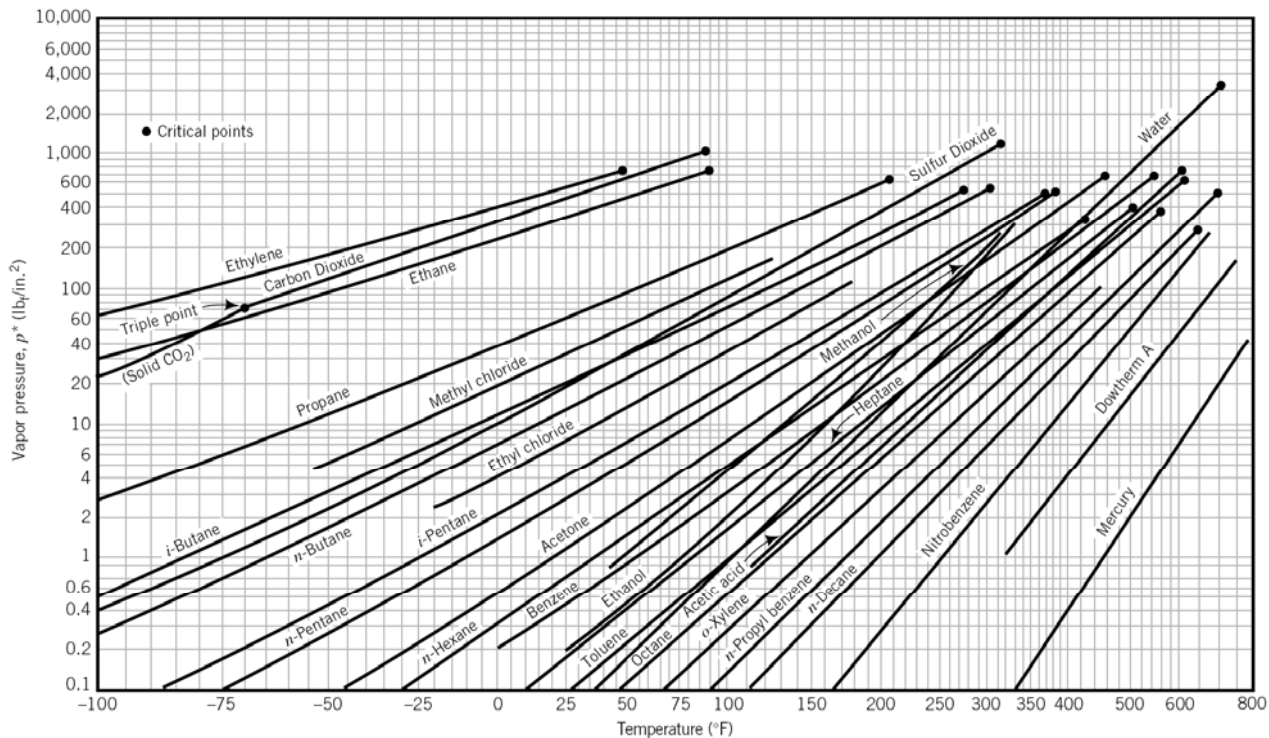
Estimation of Vapor Pressures

➤ A relatively simple empirical equation that correlates vapor pressure-temperature data
extremely well is the **Antoine equation.**

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

Values of A, B, and C for several compounds are listed in Table B.4. Observe the units of p^*
and T (mm Hg and °C for the constants in Table B.4) and the logarithm base (10 in the case
of Equation 6.1-4 and Table B.4).

Table B.4 Antoine Equation Constants[a]

$$\log_{10} p^* = A - \frac{B}{T + C} \qquad p^* \text{ in mm Hg,} \quad T \text{ in °C}$$

Example: The vapor pressure of acetaldehyde at 25°C is determined as follows:

$$\log_{10} p^*_{C_2H_4O}(25°C) = 8.00552 - \frac{1600.017}{25 + 291.809} = 2.9551$$

$$\implies p^*_{C_2H_4O}(25°C) = 10^{2.9551} = 902 \text{ mm Hg}$$

Table B.4 Antoine Equation Constants[a]

Compound	Formula	Range (°C)	A	B	C
Acetaldehyde	C_2H_4O	−0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	$C_2H_4O_2$	29.8 to 126.5	7.38782	1533.313	222.309
Acetic acid*	$C_2H_4O_2$	0 to 36	7.18807	1416.7	225
Acetic anhydride	$C_4H_6O_3$	62.8 to 139.4	7.14948	1444.718	199.817
Acetone	C_3H_6O	−12.9 to 55.3	7.11714	1210.595	229.664
Acrylic acid	$C_3H_4O_2$	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_6H_7N	102.6 to 185.2	7.32010	1731.515	206.049
Benzene	C_6H_6	14.5 to 80.9	6.89272	1203.531	219.888
n-Butane	n-C_4H_{10}	−78.0 to −0.3	6.82485	943.453	239.711
i-Butane	i-C_4H_{10}	−85.1 to −11.6	6.78866	899.617	241.942

Gibbs phase rule

Gibbs phase rule

➢ When two phases are brought into contact with each other,

   o A redistribution of the components of each phase normally takes place-species evaporate, condense, dissolve, or precipitate.

   o A state of equilibrium is reached when the temperatures and pressures of both phases are the same and the composition of each phase no longer changes with time.

➢ The variables that describe the condition of a process system fall into two categories:

   o Extensive variables, which depend on the size of the system, and

   o 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.

➤ The **degrees of freedom** of the system is the number of intensive variables that can be specified independently for a system at equilibrium.

➤ let

$$\Pi = \text{number of phases in a system at equilibrium}$$

$$c = \text{number of chemical species}$$

$$DF = \text{degrees of freedom}$$

The relationship among DF, Π, and c is given by the **Gibbs phase rule.**

If no reactions occur, the phase rule is

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

➤ If **r** independent reactions occur among the system components and the reactions proceed to equilibrium, then

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

29

Example:

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

1. *Pure liquid water*

30

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

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