7.1) Real Gases and Ideal Gases

<u>most important:</u> real gasses can't be compressed to a volume lower than the total molecular volume

<u>Idea Diagram:</u>

Gases

- Real
  - can't be compressed to a volume lower than total molec. volume
  - molecules interact
- Ideal
  - molecules do not interact

<u>Thermodynamic Law:</u> N/A

7.2) Equations of State for Real Gases and their range of applicability

<u>most important:</u> the equilibrium vapor pressure determined in this way for a given value of T is only in qualitative agreement with experiment

<u>Idea Diagram:</u>

$$P = RT\left[\frac{1}{V_m} + \frac{B(T)}{V_m^2}\right]$$

$$P = \frac{RT}{V_m - b} \longrightarrow P = \frac{RT}{V_m^2}\left(1 - \frac{C}{V_m T^3}\right)(V_m + B) - \frac{A}{V_m^2}$$

<u>Thermodynamic Law:</u> N/A

7.4) The Law of Corresponding States

most important: if two gases have the same values of T_r, P_r, and V_{mr}, they are in corresponding states

Idea Diagram:

$$P_r P_c = \frac{R T_r T_c}{V_{mr} V_{mc} - b} - \frac{a}{V_{mr}^2 V_{mc}^2}$$

$$\frac{a P_r}{27b^2} = \frac{8 a T_r}{27b(3bV_{mr} - b)} - \frac{a}{9b^2 V_{mr}^2}$$

or

$$P_r = \frac{8T_r}{3V_{mr} - 1} - \frac{3}{V_{mr}^2}$$

Thermodynamic Law:

7.5) Fugacity and the Equilibrium Constant for Real Gases

most important: (f) or fugacity can be viewed as the effective pressure that a real gas exerts

Idea Diagram:

$$\mu(T,P) = \mu^\circ(T) + RT \ln \frac{f}{f^\circ}$$

$$d\mu_{real} = V_m^{real} dP$$

$$\ln f = \ln P + \int_0^P \frac{z-1}{P'} dP \quad \text{or } f = \gamma(P,T)P$$

or

$$f = P\exp\left[\int_0^P \frac{(z-1)}{(P')} dP'\right]$$

Thermodynamic Law: N/A

8.1) What determines the Relative stability of solid, liquid, gas phases?

most important: an increase in P leads to boiling point elevation, freezing point elevation, and to freezing point depression

Idea Diagram:

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S_m \text{ and } \left(\frac{\partial \mu}{\partial P}\right) = V_m$$

$$\downarrow$$

$$S_m^{gas} > S_m^{liquid} > S_m^{solid}$$

Thermodynamic Law: N/A

8.2) The Pressure-Temperature Phase Diagram

most important: a pressure-temperature phase diagram represents the stability regions for a pure substance as a function of pressure and temperature

Idea Diagram:

P-T Diagram → standard boiling

→ coexistence curve

→ normal boiling temp.

→ vapor pressure

→ critical point

→ supercritical fluids

Thermodynamic Law: N/A

8.4) The Pressure-Volume and Pressure-Volume-Temperature Phase Diagrams

Most important: P-V-T Diagram is very useful for information on values of P, V, & T corresponding to one, two, three phase regions

Idea Diagram:

P-V-T Diagram

→ freeze drying

Thermodynamic Law: N/A

8.5) Providing a Theoretical Basis for the P-T phase Diagram

Most important: the slope for the solid-gas coexistance curve will be greater than that of the liquid-gas coexistance curve

Idea Diagram:

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$\hookrightarrow \left(\frac{dP}{dT}\right)_{fusion} = \frac{\Delta S_{fusion}}{\Delta V_{fusion}}$$

$$\hookrightarrow \left(\frac{dP}{dT}\right)_{vaporization} = \frac{\Delta S_{vaporization}}{\Delta V_{vaporization}}$$

Thermodynamic Law: N/A

8.7) The Vapor Pressure of a Pure substance Depends on the applied pressure

Most important: in the specific case of water an external pressure of 1 bar, the effect will be negligable

Idea Diagram:

$$RT\ln\left(\frac{P}{P^*}\right) = V_m^{liquid}(P - P^*)$$

Thermodynamic Law: N/A