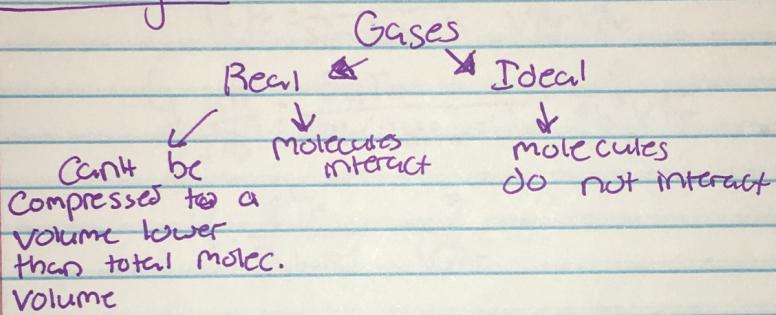


## 7.1) Real Gases and Ideal Gases

most important: real gases can't be compressed to a volume lower than the total molecular volume

Ideal Diagram:



Thermodynamic Law: N/A

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

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

Ideal Diagram:

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

Thermodynamic Law: 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

Ideal Diagram:

$$P_r P_c = \frac{\beta T_r T_c}{V_{mr} V_{mc} - b} - \frac{a_1}{V_{mr}^2 V_{mc}^2}$$
$$\downarrow \frac{a_1 P_r}{27b^2} = \frac{8a_1 T_r}{27b(3b V_{mr} - b)} - \frac{a_1}{9b^2 V_{mr}^2}$$

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

Ideal Diagram:

$$\mu(T, P) = \mu^\circ(T) + RT \ln \frac{f}{f^\circ}$$
$$\downarrow \Delta \mu_{\text{real}} = V_m^{\text{real}} \frac{df}{dp}$$
$$\downarrow \ln f = \ln P + \int_{P^\circ}^P \frac{z-1}{P'} dP$$
$$f = P \exp \left[ \int_0^P \frac{(z-1)}{(P')} dP \right] \quad \text{or } f = \chi(P, T) P$$

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:

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

$\downarrow$

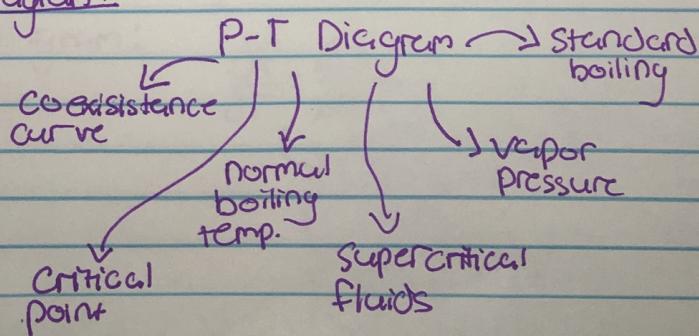
$$S_m^{\text{gas}} > S_m^{\text{liquid}} > S_m^{\text{solid}}$$

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:

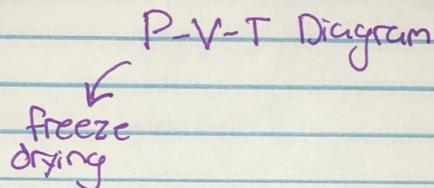


Thermodynamic Law: N/A

#### 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:



Thermodynamic Law: N/A

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

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

Idea Diagram:

$$\frac{\partial P}{\partial T} = \frac{\Delta S_m}{\Delta V_m}$$
$$\hookrightarrow \left(\frac{\partial P}{\partial T}\right)_{\text{Fusion}} = -\frac{\Delta S_{\text{Fusion}}}{\Delta V_{\text{Fusion}}} \text{ ex}$$
$$\hookrightarrow \left(\frac{\partial P}{\partial T}\right)_{\text{Vaporization}} = -\frac{\Delta S_{\text{Vaporization}}}{\Delta V_{\text{Vaporization}}}$$

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 negligible

Idea Diagram:

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

Thermodynamic Law: N/A