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Reading Assignment #7

03/30/2020

7.1 Real Gases and Ideal Gases

- the ideal gas equation of state has been assumed to be sufficiently accurate to describe the P-V-T relationship for a real gas
- assume: gas molecules are point masses and that the molecules in the gas do not interact
- the P-V-T relationship of a real gas is the same as that for an ideal gas at low density and high temps

7.2 Equations of State for Real Gases and their Range of Applicability

- van der Waals equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

- Redlich-Kwong equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m(V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2 a}{\sqrt{T} V(V + nb)}$$

- Beattie-Bridgeman equation of state:

$$P = \frac{RT}{V_m^2} \left(1 - \frac{c}{V_m T^3} \right) (V_m + B) - \frac{A}{V_m^2} \quad \text{with:}$$

$$A = A_0 \left(1 - \frac{a}{V_m} \right) \quad \text{and} \quad B = B_0 \left(1 - \frac{b}{V_m} \right)$$

- virial equation of state:

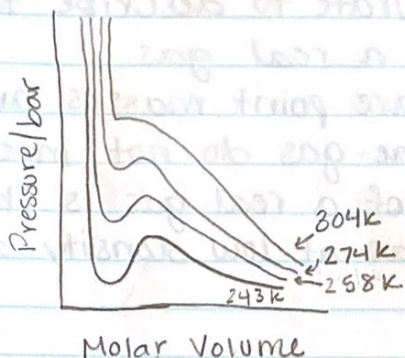
$$P = RT \left[\frac{1}{V_m} + \frac{B(T)}{V_m^2} + \dots \right]$$

- the temperature dependent equilibrium pressure is called the vapor pressure of the liquid
- the temp at which the range of V_m has shrunk to a single value is called the critical temp, T_c

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- T_c , P_c , V_c are called critical constants
- In the Maxwell construction, the oscillating region is replaced by the horizontal line for which the areas above and below the line are equal



7.3

The compression factor (z)

- $z = \frac{V_m}{V_m^{\text{ideal}}} = \frac{PV_m}{RT}$ For an ideal gas, $z = 1$ for all values of P and V_m
- If $z > 1$, the real gas exerts a greater pressure than the ideal gas
- If $z < 1$, the real gas exerts a smaller pressure than the ideal gas for the same values of T and V_m
- To understand why the low pressure value of z varies w/ T , we use the van de Waals equation

$$\left(\frac{\partial z}{\partial P}\right)_T = \left(\frac{\partial z}{\partial [RT/V_m]}\right)_T = \frac{1}{RT} \left(\frac{\partial z}{\partial [1/V_m]}\right)_T$$

- Boyle Temp (T_b) = $\frac{a}{Rb}$

7.4

The Law of Corresponding States

- different gases have the same equation of state equation if each gas is described by the

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- dimensionless reduced variables $T_r = T/T_c$, $P_r = P/P_c$ and $V_{mr} = V_m/V_{mc}$ rather than by T, P, V_m = law of corresponding states
- If 2 gases have the same values of T_r, P_r , and V_{mr} , they are in corresponding states
 - $P_r P_c = \frac{RT_r T_c}{V_{mr} V_{mc} - b} - \frac{a}{V_{mr}^2 V_{mc}^2}$ replace T_c, V_{mc} , and P_c with:
 - $P_c = \frac{a}{27b^2}$, $V_{mc} = 3b$, and $T_c = \frac{8a}{27Rb}$ ←
 - $a P_r = \frac{8a T_r}{27b^2 (3b V_{mr} - b)} - \frac{a}{9b^2 V_{mr}^2}$ or
 - $P_r = \frac{8 T_r}{3 V_{mr} - 1} - \frac{3}{V_{mr}^2}$
 - $Z_c = \frac{P_c V_c}{RT_c} = \left(\frac{1}{R}\right) \left(\frac{a}{27b^2}\right) (3b) \left(\frac{27Rb}{8a}\right) = \frac{3}{8}$

7.5 Fugacity and the Equilibrium Constant for real gases

- $\mu(T, P) = \mu^\circ(T) + RT \ln \frac{f}{f^\circ}$
- f = fugacity = the effective pressure that a real gas exerts
- $\ln(f) = \ln(P) + \int_0^P \frac{Z-1}{P'} dP'$ or $f = P \exp \left[\int_0^P \left(\frac{Z-1}{P'} \right) dP' \right]$
or $f = \gamma(P, T) P$
 - calculate f if Z is known
 - γ = fugacity coefficient, depends on P and T

8.1

What determines the relative stability of the solid, liquid, and gas phases?

- Phase refers to a form of matter that is uniform wrt chemical composition and the state of aggregation on a micro and macroscopic length scale.

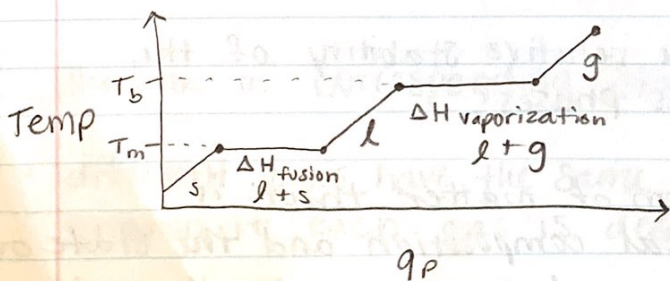
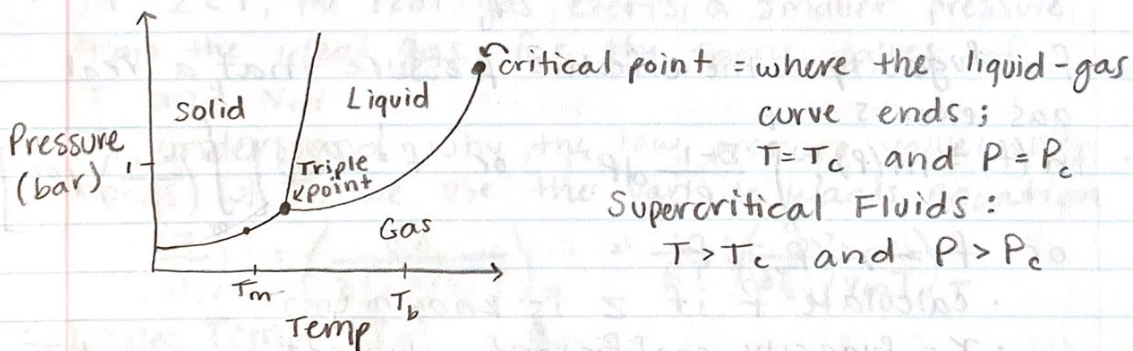
- how u changes with changes in P and T can be determined by:

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

- u decreases as the temp increases and it increases as the pressure increases
- $S_m^{\text{gas}} > S_m^{\text{liquid}} > S_m^{\text{solid}}$
- Because $V_m^{\text{gas}} \gg V_m^{\text{liquid}} > 0$ an increase in P always leads to a boiling point elevation.
- an increase in P leads to a freezing point elevation if $V_m^{\text{liquid}} > V_m^{\text{solid}}$ and to a freezing point depression if $V_m^{\text{liquid}} < V_m^{\text{solid}}$
- The P , V_m , and T values specify the triple point since all 3 phases coexist in equilibrium at this point

8.2 The Pressure-Temp Phase Diagram

- P - T phase diagram displays stability regions for a pure substance as a function of P and T



$$\Delta H = \Delta H_{\text{sublimation}}$$

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

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8.3 The Phase Rule

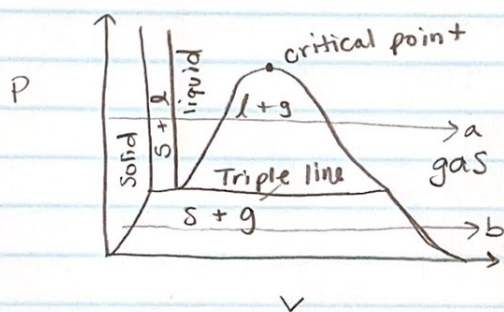
- $\mu_a(T, P) = \mu_b(T, P)$ Two phases a and b
- the phase rule links the # of degrees of freedom to the # of phases in a system at equilibrium

$$F = 3 - P$$

where F = # of degrees of freedom

P = # of phases

8.4 The Pressure-Volume and P-V-T Phase Diagrams



8.5 Providing a Theoretical Basis for the P-T Phase Diagram

- Clapeyron equation: $\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$

$$\Delta G_{\text{fusion}} = \Delta H_{\text{fusion}} - T \Delta S_{\text{fusion}} = 0$$

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

- Trouton's Rule: $\Delta S_{\text{vap}} \approx 90 \text{ J/mol}\cdot\text{K}$ for liquids

8.6 Using the Clausius-Clapeyron Equation to calculate Vapor Pressure as a Function of T

$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta H_{\text{vap}}}{R} \times \int_{T_i}^{T_f} \frac{dT}{T^2}$$

$$\ln\left(\frac{P_f}{P_i}\right) = -\frac{\Delta H_{\text{vap}}}{R} \times \left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

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- 8.7 The vapor pressure of a pure substance depends on the applied pressure

$$\frac{RT}{P} dP = V_m^{\text{liquid}} dP \quad \text{or} \quad RT \int_{P^*}^P \frac{dP'}{P'} = V_m^{\text{liquid}} \int_{P^*}^P dP'$$

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

- The vapor pressure, P , increases if the total pressure, P , increases

8.8 Surface Tension

$$dA = r d\sigma$$

- where A = Helmholtz energy, γ = surface tension, σ = area
- units of surface tension = J m^{-2} or energy/area = N m^{-1}
- inward & outward acting forces

$$4\pi r^2 P_{\text{outer}} + 8\pi r \gamma = 4\pi r^2 P_{\text{inner}}$$

$$\text{or } P_{\text{inner}} = P_{\text{outer}} + \frac{2\gamma}{r}$$

- $P_{\text{inner}} - P_{\text{outer}} \rightarrow 0$ as $r \rightarrow \infty$
- capillary rise and depression are other consequences of the pressure differential across a curved surface

$$h = \frac{2\gamma}{\rho g r}$$

- contact angle = θ
- complete wetting, $\theta = 0^\circ$
- complete nonwetting, $\theta = 180^\circ$

$$P_{\text{inner}} = P_{\text{outer}} + \frac{2\gamma \cos \theta}{r} \quad \text{and} \quad h = \frac{2\gamma \cos \theta}{\rho g r}$$

- the property of water that accounts for water supply to the top of a redwood is its high tensile strength