Reading HW 7

A. 7.1 Real Gases and Ideal Gases

I. P-V-T

a. P-V-T relationship of a real gas is the same as that for an ideal gas at low densities and high temperature

b. Ideal gas law provides an accurate description of P-V-T relationships for most gases

B. 7.2 Equations of State for Real Gases and Their range of applicability

I. Van der Waals equation of state

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

I. Real gas equation

II. Most widely known

II. Redlich-Kwong equation of state

a. $P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2 a}{\sqrt{T}} \frac{1}{V(V + nb)}$

I. Second useful equation of state

III. Beathe-Bridgeman equation of state

a. $P = \frac{RT}{V^2_m}\left(1 - \frac{c}{V_m T^3}\right)(V_m + B) - \frac{A}{V^2}$

b. $A = A_0\left(1 - \frac{a}{V_m}\right)$

I. $B = B_0\left(1 - \frac{b}{V_m}\right)$

IV. Viral Equation of State

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

C. 7.3 The Compression Factor

I. Compression Factor

a. $Z = \frac{V_m}{V_{ideal}} = \frac{PV}{RT}$

b. Variation of the compression factor with P at constant T

I. $\left(\frac{\partial Z}{\partial P}\right)_T = \left(\frac{\partial z}{\partial [RT/V]}\right) = \frac{1}{RT}\left(\frac{\partial z}{\partial [1/V]}\right)_T$

II. Boyle temperature

a. $T_B = \frac{a}{Rb}$

D. 7.4 The Law of Corresponding States

I. Law of corresponding states

a. If two gases have the same values for T, P, and V they're in corresponding states

b. $P_r P_c = \frac{RT_r T_c}{V_m V_m - b} - \frac{a}{V^2 V^2}$

A. 8.1 What determines the Relative stability of the Solid, liquid, and Gas Phases

I. Phase

a. The form of matter that is uniform with respect to chemical composition

b. The state of aggregation on both microscopic + macroscopic length scales

c. Substances can be found in solid, liquid, and gas

II. Equations

a. $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial [n G_m]}{\partial n}\right)_{T,P} = G_m$

I. Chemical Potential for a pure Substance

b. Differential $d\mu$

I. $d\mu = -S_m dT + V_m dP$

c. Entropy of the Phases

I. $S^{gas} >> S^{liquid} > S^{solid}$

III. Temperature Points

a. Boiling point elevation

I. An increase in P will lead to

II. $V^{gas} >> V^{liquid} >> 0$

b. Freezing point elevation

I. $V^{liquid} > V^{solid}$

c. Freezing point depression

I. $V_{liquid} < V^{solid}$

B. 8.2 The Pressure - Temperature Phase Diagram

I. Phase Diagram

a. Displays information graphically

b. Determined experimentally

I. Due to material-specific forces between atoms determing temperature and pressure at different phases

II. P-T Phase diagram

a. P, T points correspond to a single Solid, liquid, and gas phase

b. Triple Point

I. At a triple point all 3 phases coexist

II. Coexistence curve

1. Same two phases coexist at a equilibrium fall on a curve

III. Equations

a. Supercritical fluids

I. Substances where $T > T_c$ & $P > P_c$

b. $\Delta H = \Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{evaporization}$

I. ΔH for the process of solid → liquid → gas is identical to solid - gas

II. Strictly true at triple point

C 8.3 The Phase Rule

I. Phase Rule

a. links the number of degrees of freedom to the number of phases in a system at equilibrium

I. $F = 3 - P$

1. For a pure substance

b. Degrees of Freedom

I. Number of independent factors required to specify a system at equilibrium

II. Pure Substance System

1. Two degrees of freedom

D. 8.4 The Pressure-Volume and Pressure-Volume-Temperature Phase Diagram

I. P-V-T Phase diagram

a. Three dimmensional

b. Values of P, V, & T corresponding to Single-Phase, two phase regions and triple point

E. 8.5 Providing a theoretical basis for the P-T Phase diagram

I. Equations

a. Clapeyron Equation

I. $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$

II. Allows for a calculation of the slope of the Coexistence curves in P-T phase diagram

1. If ΔS and ΔV transitions are known

b. At the melting temperature

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

c. Trouton's Rule

I. $\Delta S_{vaporization} \approx 90 J\ mol^{-1} K^{-1}$ for liquids

1. Rule fails for liquids with strong interactions between -OH or -NH_2 groups forming hydrogen bonds

F. 8.6 Using the Clausius-Clapeyron Equation to calculate Vapor Pressure

I. Clausius - Clapeyron Equation

a. $\frac{dP}{P} = \frac{\Delta H_{vaporization}}{R} \frac{dT}{T^2}$

I. If the ideal gas law holds

a. Vapor Pressure of liquid

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

G. 8.7 The Vapor Pressure of a Pure Substance

I. Equations

a. $\mu_{liquid}(T,P) = \mu_{gas}(T,P)$

I. Calculate Partial Pressure

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

I. Integrated equation

II. Ideal gas value RT/P replaces V^{gas}

H. 8.8 Surface Tension

I. Surface tension

a. units are energy/area $J\ m^{-2}$ or $N\ m^{-1}$

b. $dA = \gamma\ d\sigma$

I. Predicts a liquid or bubble film suspended minimizing the surface area

II. Capillary

a. Capillary Rise

I. abillity for liquid to flow without assistance in narrow areas

b. Capillary depression

I. The liquid does not wet the walls of the container

1. example: Mercury

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

I. $2\gamma/r$ balanced by the weight of the column

II. $\rho g r$ is the gravitational field

III. Contact Angle

a. Wetting

I. corresponds to $\theta = 0°$

b. Nonwetting

I. corresponds to $\theta = 180°$

b. Intermediate cases

I. $P_{inner} = P_{outer} + \frac{2\gamma \cos\theta}{r}$

II. $h = \frac{2\gamma \cos\theta}{\rho g r}$

I. 8.9 Chemistry in Supercritical fluids

I. Supercritical fluids

a. Have a density that is a fraction of liquid-phase density near the critical point

b. Supercritical water acts like a non polar solvent

I. potential use at high temperature

J. 8.10 Liquid Crystal Displays

I. Liquid Crystals

a. Glasses

I. liquids with high velocity that can't achieve equilibrium on timescale of human life

b. Life crystals

I. Intermediate between liquids and solids