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Macroscopic Physical Chem

Reading Assignment 7

7.1: Real Gases and Ideal Gases

- Gas molecules are point masses
- Molecules occupy a finite volume. \rightarrow a real gas cannot be compressed to a volume less than total molecular volume.
- Second assumption is that gas molecules do not interact but ^{real} gas molecules do interact through a potential
- The molecular volume is negligible compared w/ the volume the gas occupies
- The P-V-T relationship b/w a ideal gas is the same as that of a real gas.

7.2: Equations of state for real gases and their range of Applicability

- Real gas equations of state are best viewed as empirical equations whose functional form has been chosen to fit experimentally P-V-T data

- Van der Waals Equation

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

- Redlich - Kwong Equation of State

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

- Beattie - Bridgeman Equation

$$P = \frac{RT}{V_m^2} \left(\frac{1}{1} - \frac{C}{V_m T^3} \right) (V_m + B) - \frac{A}{V_m^2}$$
$$\hookrightarrow A = A_0 \left(1 - \frac{a}{V_m} \right), \quad B = B_0 \left(1 - \frac{b}{V_m} \right)$$

- Virial Equation of State

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

\hookrightarrow Always valid in convergence range

- Value of V when P becomes constant depends on T . $V \rightarrow$ decrease $P \rightarrow$ increases
- Vapor Pressure - temperature-dependent equilibrium
- As pressure further increases, system becomes single phase $O_2(l)$
- Critical Temperature: The temp at which the range of V_m shrinks to single phase.

$$\left(\frac{\partial p}{\partial V_m}\right)_{T=T_c} = 0 \text{ and } \left(\frac{\partial^2 p}{\partial V_m^2}\right)_{T=T_c} = 0$$

- T_c, p_c, V_c are the critical constants
- In the Maxwell Construction, the oscillating region is replaced by the horizontal lines to which the area above and below are equal.

$$T_B = a/R_b$$

7.3: The Compression Factor

- Compression factor, z , is determined by

$$z = V_m / V_{m, \text{ideal}} = pV_m / RT$$

→ a function of temperature

- We use the Van der Waals equation to understand the low pressure value.

$$z = V_m / V_{m, \text{ideal}} = pV_m / RT$$

- T_c and the corresponding values known as Boyle's T_B

$$T_B = a/R_b$$

- B/c the parameters a and b are ^{substance} temp dependent, T_B is different for each gas.

- At Boyle temp, $z \rightarrow 1$ and $\left(\frac{\partial z}{\partial p}\right)_T \rightarrow 0$

→ Only @ $T = T_B$ that a real gas exhibits ideal gas behavior

- The inequalities provides criterion to predict whether z increases or decreases w/ pressure.

- $\lim \left(\frac{\partial z}{\partial p}\right)_T$ is always positive @ high temp

- If $T < T_B$, $\lim \left(\frac{\partial z}{\partial p}\right)_T$ will always be negative

- If $\lim \left(\frac{\partial z}{\partial p}\right)_T < 0$, the attractive part of gas dominates

7.4: The Law of Corresponding States

- Different gases have the same equation of state if each gas is described by the dimensionless reduced variables → Law of Corresponding States

- P, V, T variables of two gases can be different for corresponding states

- Variables a and B are eliminated

$$P_R P_c = \frac{RT_c T_c}{V_{mr} V_{mc} b} - \frac{a}{V_{mr}^2 V_{mc}^2}$$

$$P_c = \frac{a}{27b^2} \quad V_{mc} = 3b \quad \text{and} \quad T_c = \frac{8a}{27Rb}$$

$$\frac{a P_c}{27b^2} = \frac{8 T_c}{27b(3b V_{mr} b)} - \frac{a}{ab^2 V_{mr}^2}$$

$$P_R = \frac{8 T_c}{3 V_{mr} b} - \frac{3}{V_{mr}^2}$$

- The law of corresponding states assumes two parameters are sufficient
- Assumes spheres b/c orientation would be negligible
- Errors can be calculated through

$$\% \text{ Error} = \frac{Z - 1}{Z} \cdot 100\%$$

- Compression factor @ critical point

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{1}{8} \cdot \frac{a}{27b} = \frac{1}{8} \cdot \frac{27Rb}{8a} = \frac{3}{8}$$

7.5: Fugacity and the equilibrium Constant for Real Gas

- For an ideal gas, the chemical potential as a function of the pressure has the form

$$\mu(T, P) = \mu^\circ(T) + RT \ln(P/P^\circ)$$

- To construct an analogous Equation

$$\mu(T, P) = \mu^\circ(T) + RT \ln(f/P^\circ)$$

→ f is fugacity

- For densities corresponding to attractive range $G_m^{\text{real}} < G_m^{\text{ideal}}$, $f < P$

$$dG_m = V_m dP$$

$$d\mu_{\text{ideal}} = V_m^{\text{ideal}} dp$$

$$d\mu_{\text{real}} = V_m^{\text{real}} dp$$

$$d\mu_{\text{real}} - d\mu_{\text{ideal}} = (V_m^{\text{real}} - V_m^{\text{ideal}}) dP$$

$$\int_{P_i}^P (d\mu_{\text{real}} - d\mu_{\text{ideal}}) = [\mu_{\text{real}}(P) - \mu_{\text{ideal}}(P)] - [\mu_{\text{ideal}}(P_i) - \mu_{\text{ideal}}(P_i)]$$

$$= \int_{P_i}^P (V_m^{\text{real}} - V_m^{\text{ideal}}) dP$$

$$\mu_{\text{real}}(P) - \mu_{\text{ideal}}(P) = - \int_0^P (V_m^{\text{real}} - V_m^{\text{ideal}}) dP'$$

$$\ln f - \ln P + \int_0^P (Z - 1) \frac{dP'}{P'} = \ln f - \ln P + \int_0^P \frac{Z - 1}{P'} dP' = \ln f - \ln P + \ln \left(\frac{f}{P} \right) = \ln \left(\frac{f}{P} \right) = \ln \gamma$$

- Fugacity Coefficient. γ is dependent on both P and T

$$K_f = \left(\frac{(f_{\text{NH}_3}/P^\circ)}{(f_{\text{N}_2}/P^\circ)(f_{\text{H}_2}/P^\circ)^{3/2}} \right) = \left(\frac{(\gamma_{\text{NH}_3} P/P^\circ)}{(\gamma_{\text{N}_2} P/P^\circ)(\gamma_{\text{H}_2} P/P^\circ)^{3/2}} \right) = K_P \left(\frac{\gamma_{\text{NH}_3}}{(\gamma_{\text{N}_2})^{1/2} (\gamma_{\text{H}_2})^{3/2}} \right)$$

8.1: What determines the relative stability of the solid, liquid, gas phase

• Phase: a form of matter relative w/ chemical composition

• For a pure substance, chemical composition is defined as

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,P} = \left(\frac{\partial (nG_m)}{\partial n} \right)_{T,P} = G_m$$

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

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

• S_m and V_m are always positive, μ decreases as temp increases.

$$\Delta S = \Delta H_{\text{transition}} / T$$

$$S_m^g > S_m^l > S_m^s$$

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

• $V_m^g > V_m^l > V_m^s > 0$, increase in $P \rightarrow$ increase in boiling point

• μ versus T curve for a gas shifts along the T axis

• $S \rightarrow l$ is energetically favorable.

8.2: The Pressure-Temperature Phase Diagram

• The usefulness of a phase diagram is that it displays this graphically

• P - T diagram displays stability region as a function of pressure and time

• Coexist Curve: All P, T points for which 2 phases coexistence

• Standard Boiling Temp: vapor pressure is one bar

• Normal Boiling Temp: vapor pressure = 1 atm

• Vapor Pressure: P

• Supercritical Fluids: $T > T_c$ $P > P_c$

$$\rightarrow q_p = \Delta H \quad \Delta H = C_p \Delta T$$

$$\Delta H = \Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporization}}$$

8.3: Phase Rule

$$\mu_a(T, P) = \mu_b(T, P)$$

$$\mu_a(T, P) = \mu_b(T, P) = \mu_g(T, P)$$

• A system of pure substances has two degrees of freedom

• Phase Rule: links the # of degrees of freedom w/ # of phases.

$$F = 3 - P$$

of degrees of freedom \rightarrow # of phases

8.4: The P-V and P-V-T phase diagrams

- Any diagram must contain all 3 to be complete
- $V_m^s < V_m^l < V_m^g$
- g-l coexistence region is broader than s-l phase
- In P-V phase diagram, the process involves large change in volume.
- P-V-T diagram displays the value of v, p, T
- P-T diagram is a projection of 3-D surface on the P-T plane

8.5: Providing a theoretical basis for the P-T phase diagram

$$\mu_a(P, T) = \mu_b(P, T)$$

- $P, T \rightarrow P + dP, T + dT$ such that pressure + temp still lie within coexistence curve

$$\mu_a(P, T) + d\mu_a = \mu_b(P, T) + d\mu_b$$

- In order for the two phases to remain in equilibrium

$$d\mu_a = d\mu_b$$

$$d\mu_a = -S_m^a dT + V_m^a dP \text{ and } d\mu_b = -S_m^b dT + V_m^b dP$$

$$-S_m^a dT + V_m^a dP = -S_m^b dT + V_m^b dP$$

$$(S_m^b - S_m^a) dT = (V_m^b - V_m^a) dP$$

$$\Delta S_m = S_m^b$$

$$\Delta V_m = V_m^b - V_m^a$$

$$\frac{dP}{dT} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} = \frac{\Delta H_{\text{vap}}}{TV_m^{\text{gas}}} = \frac{P \Delta H_{\text{vap}}}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H_{\text{vap}}}{R} \cdot \frac{dT}{T^2}$$

- Variation of vapor pressure is given by

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

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

8.7: The Vapor Pressure of pure substance depends on the applied Pressure

- Keeping T constant, enough argon gas is introduced into cylinder such that argon + $H_2O = 1$ bar.
- To calculate the partial pressure of water;

$$\mu_w(T, P) = \mu_w^g(T, P)$$

$$\left(\frac{\partial \mu_w(T, P)}{\partial P} \right)_T = \left(\frac{\partial \mu_w^g(T, P)}{\partial P} \right)_T \left(\frac{\partial P}{\partial P} \right)_T$$

$$V_m^{(l)} = V_m^{(g)} \left(\frac{\partial P}{\partial P} \right)_T \text{ or } \left(\frac{\partial P}{\partial P} \right)_T = \frac{V_m^{(l)}}{V_m^{(g)}}$$

- Vapor pressure increases if total pressure increase

$$RT/P dP = V_m^{(l)} dP \text{ or } RT \int_{P_0}^P \frac{dP'}{P'} = V_m^{(l)} \int_{P_0}^P dP'$$

$$RT \ln(p/p^\circ) = V_m(p - p^\circ)$$

For specific case of water

$$\ln(p/p^\circ) = \frac{V_m(p - p^\circ)}{RT} = \frac{(1.81 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})(1 - 0.316) \cdot 10^5 \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} = \boxed{7.04 \times 10^{-4}}$$

8.8: Surface Tension

- The work associated w/ the creation of additional surface area @ constant V and T is

$$dA = \gamma d\sigma$$

- Surface tension has units J m^{-2}

$$Q = 4\pi r^2 d\sigma = 8\pi r \gamma dr$$

$$F = 8\pi r \gamma$$

- Outward acting force is the sum of forces exerted by the external pressure and the force arising from the surface tension

$$4\pi r^2 d\sigma + 8\pi r \gamma = 4\pi r^2 p_{\text{inner}}$$

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

$$p_1 - p_2 = \frac{2\gamma}{r_1} - \frac{2\gamma}{r_2} = 2\gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right)$$

- Capillary rise and depression are other consequences of pressure

- The diff in pressure across the curved interface $\frac{2\gamma}{r}$ is balanced by the weight of the column in the gravitational field $\rho g h$

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

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