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Macro P. Chem.

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Reading HW #7

7.1) Real Gases and Ideal Gases

real gases cannot be compressed to a volume less than the total molecular volume

P-V-T always related regardless of ideal or real

7.2) Equations of State for Real Gases and Their Range of Applicability

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

Predict P-V behavior

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

7.3) The Compression Factor

$\lim_{P \to 0} (dz/dP)_T < 0$ then $T < T_B$

$Z = \frac{V_m}{V_m^{ideal}} = \frac{PV_m}{RT}$

Boyle temperature $T_B = \frac{a}{Rb}$ (different for each gas)

a & b → substance dependent

7.4) The Law of Corresponding States

Error $= 100\% \frac{z - 1}{z}$

$P_r = \frac{8T_r}{3V_{mr} - 1} - \frac{3}{V_{mr}^2}$ without reference to parameters a & b

7.5) Fugacity and the Equilibrium Constant for Real Gase

effective pressure that a real gas exerts

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

$\gamma(P,T)P = f$

γ fugacity coefficient

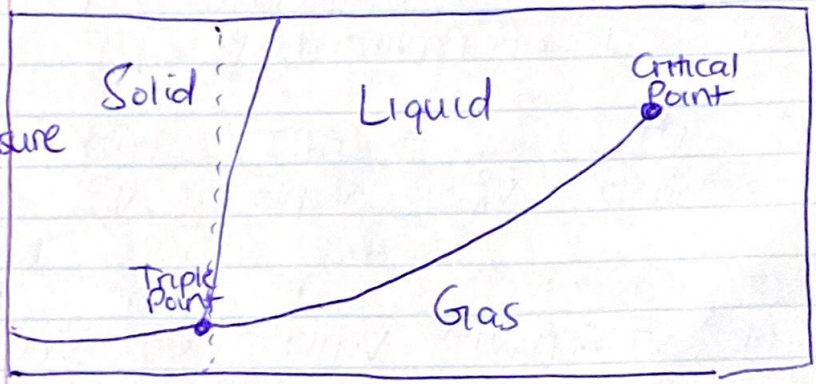
8.1.) What Determines the Relative Stability of the Solid, Liquid & Gas Phases?

μ decreases as temperature increases $\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$ (always positive) $\left(\frac{\partial \mu}{\partial P}\right)_T = V_m$

* $S_m^{gas} > S_m^{liq} > S_m^{sol}$

V_m same for

8.2 The Pressure-Temperature Phase Diagram



every substance is different

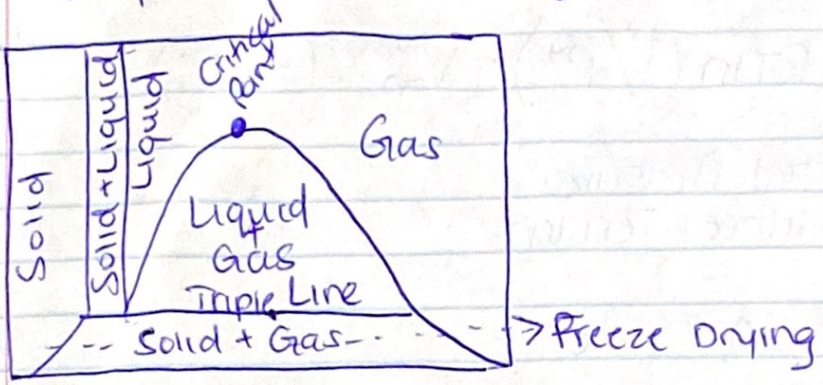
$\Delta H = \Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vaporization}$

8.3.) The Phase Rule

$$\mu_A(T,P) = \mu_B(T,P) = \mu_Y(T,P)$$

a system of pure substance has two degrees of freedom → $F = 3 - P$ ← # of phases

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



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

$$\left(\frac{dP}{dT}\right)_{\text{vaporization}} = \frac{\Delta S_{vap}}{\Delta V_{vap}} \approx 4.8 \times 10^{-2} \text{ bar K}^{-1}$$

Fusion $\longrightarrow \approx \pm 55 \text{ bar K}^{-1}$

Trouton's Rule $\longrightarrow \Delta S_{vap} \approx 90 \text{ J mol}^{-1} \text{K}^{-1}$

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

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

$\Delta H_{vaporization}$ can be substituted for $\Delta H_{sublimation}$

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

8.7) The Vapor Pressure of a Pure Substance Depends on the Applied Pressure

$$RT\ln(P/P^*) = V_m^{liquid}(P - P^*)$$

↑

8.8) Partial Pressure

↳ Surface Tension

$$dA = \gamma \, d\sigma$$

Capillary rising depression

$P_{inner} = P_{outer} + \frac{2\gamma}{r}$ → goes from $0 \to \infty$

↳ pressure differential across a curved surface