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7.1 Real Gases & Ideal Gases

- 1st assumption: gas molecules are point masses
 - Molecules occupy a finite volume \rightarrow a real gas can't be compressed to a volume that is less than the total molecular volume
- 2nd assumption: the molecules in the gas don't interact, but molecules in a real gas do interact with 1 another through a potential
- P-V-T relationship of a real gas is the same as that for an ideal gas at low densities & high T
- At high densities & low T, molecular interactions can't be neglected.

7.2 Equations of State for Real Gases & Their Range of Applicability

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

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

Beattie - Bridgeman equation of state:

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

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

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

- Vapor pressure: the temperature - dependent equilibrium pressure
- Critical constants: the corresponding values P_c & V_c which together
- Critical temperature: the temperature at which the range of V_m has shrunk to a single value.

7.3 The compression factor

- Compression Factor, z :

$$z = \frac{V_m}{V_m^{\text{ideal}}} = \frac{PV_m}{RT}$$

- $z = 1$ (ideal) for all value $P \neq V_m$

- $z > 1$, the real gas exerts a greater pressure than the ideal gas

- $z < 1$, the real gas exerts a smaller pressure than the ideal gas

- Compression factor with P at constant T

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

- Boyle temperature, T_B

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

- At Boyle temperature, $z \rightarrow 1$, $\left(\frac{\partial z}{\partial P}\right)_T \rightarrow 0$ as $P \rightarrow 0 \Rightarrow$ the behavior exhibited by an ideal gas

$$T = T_B, P \rightarrow 0 \text{ with respect to } \lim_{P \rightarrow 0} \left(\frac{\partial z}{\partial P}\right)_T$$

- Above Boyle temperature, $\left(\frac{\partial z}{\partial P}\right)_T > 0$ as $P \rightarrow 0$

- Below " ", $\left(\frac{\partial z}{\partial P}\right)_T < 0$ as $P \rightarrow 0$

- If $\lim_{P \rightarrow 0} \left(\frac{\partial z}{\partial P}\right)_T < 0$, $T < T_B$, the attractive part of the potential dominates

- If $\lim_{P \rightarrow 0} \left(\frac{\partial z}{\partial P}\right)_T > 0$, $T > T_B$, the repulsive part of the potential dominates

7.4 The Law of Corresponding States

$$T_n = \frac{T}{T_c} ; P_n = \frac{P}{P_c} ; V_{mn} = \frac{V_m}{V_c}$$

$$P_n P_c = \frac{RT_n T_c}{V_{mn} V_{mc} - b} - \frac{a}{V_{mn}^2 V_{mc}^2}$$

$$\Rightarrow \frac{a P_n}{27b^2} = \frac{8a T_n}{27b(3b V_{mn} - b)} - \frac{a}{9b^2 V_{mn}^2}$$

$$\Rightarrow P_n = \frac{8T_n}{3V_{mn} - 1} - \frac{3}{V_{mn}^2}$$

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

for $P_n < 5.5$, $z < 1$ as long as $T_n < 2 \Rightarrow$ the real gas exerts a smaller pressure than an ideal gas in this range of T_n and P_n

If $z > 1$ for $P_n > 7$ for all values of T_n = all values of P_n if $T_n > 4 \Rightarrow$ the real gas exerts a larger pressure than an ideal gas

7.5 Fugacity & the Equilibrium Constant for Real Gases

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

- Densities corresponding to the attractive range of the intermolecular potential, $G_m^{\text{real}} < G_m^{\text{ideal}} \Leftrightarrow f < P$
- " " " " " repulsive " " " " " , $G_m^{\text{real}} > G_m^{\text{ideal}} \Leftrightarrow f > P$

$$dG_m = V_m dP \quad (\text{constant } T)$$

$$\Rightarrow \begin{cases} d\mu_{\text{ideal}} = V_m^{\text{ideal}} dP \\ d\mu_{\text{real}} = V_m^{\text{real}} dP \end{cases}$$

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

$$\Rightarrow \int_{P_i}^{P_f} (d\mu_{\text{real}} - d\mu_{\text{ideal}}) = [\mu_{\text{real}}(P_f) - \mu_{\text{real}}(P_i)] - [\mu_{\text{ideal}}(P_f) - \mu_{\text{ideal}}(P_i)] \\ = \int_{P_i}^{P_f} (V_m^{\text{real}} - V_m^{\text{ideal}}) dP'$$

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

$$\text{Since } z = \frac{V_m^{\text{real}}}{V_m^{\text{ideal}}}$$

$$\ln f = \ln P + \int_0^P \frac{z-1}{P'} dP' \text{ or } f = P \exp \left[\int_0^P \left(\frac{z-1}{P'} \right) dP' \right] \text{ or } f = \gamma(P, T) P \quad (\text{depend on both } P \text{ & } T)$$

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

- Phase refers to a form of matter that is uniform with respect to chemical composition & the state of aggregation on both microscopic & macroscopic length scales.

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

$$\text{since } d\mu = dG_m$$

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

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

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

$$\left(\frac{\partial \mu}{\partial P} \right)_T = V_m \approx V_m^{\text{gas}} \gg V_m^{\text{liquid}} > 0 \Rightarrow \uparrow P \text{ leads to a boiling pt elevation}$$

$$\text{If } V_m^{\text{liquid}} > V_m^{\text{solid}} \Rightarrow \uparrow P \text{ leads to a freezing pt elevation}$$

$$\text{If } V_m^{\text{liquid}} < V_m^{\text{solid}} \Rightarrow \uparrow P \text{ leads to a freezing pt depression}$$

Sublimation temperature: the solid sublimes & the transition temperature T_s

Triple pt: all 3 phases coexist in equilibrium

8.2 The Pressure - Temperature Phase Diagram

- Phase diagram: consist of a single phase, 2 phases in equilibrium or 3 phases in equilibrium
 - P-T phase diagram: displays stability regions of a pure substance as a function of P & T
 - Coexistence curve: all P,T points for which the same 2 phases coexist at equilibrium fall on curve
 - Standard boiling temperature: the temperature at which the vapor pressure of the substance is 1 bar
 - Normal " " : " " " " " " " " " " " " " " " " " " 1 atm
 - Critical pt: whereas the liquid-solid coexistence curve extends indefinitely, the liquid-gas curve ends $\Rightarrow T_c = T \wedge P = P_c$
 - Supercritical fluids: $T > T_c \wedge P > P_c$

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

8.3 The Phase Rule

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

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

- A system of a pure substance has 2 degrees of freedom
 - The system has 1 degree of freedom in a 2 phase coexistence region
 - " " " 2 " " " " 3-phase " "
 - Phase rule links the # of degrees of freedom to the # of phases in a system at equilibrium

$$F = 3 - p \rightarrow \# \text{ of phase}$$

\swarrow

$\# \text{ of degrees of freedom}$

- Gibbs proved that no more than 3 phases of a pure substance

8.4 The Pressure - Volume and Pressure - Volume - Temperature Phase Diagrams

- P-V phase diagram : $V_m^{\text{liquid}} > V_m^{\text{solid}}$
 - + 2-phase coexistence curves of the P-T phase diagram become 2-phase regions because the volume of a system in which 2 phases coexist varies with the relative amount of the material in each phase

- For the pressure below the critical pt, the range in V over which the gas & liquid coexist because $V_m^{\text{solid}} < V_m^{\text{liquid}} \ll V_m^{\text{gas}}$
- process b shows an isobaric transition from solid to gas for P below the triple point pressure, for which the system has only 1 2-phase coexistence region (freeze drying)
- process c shows a constant volume transition from a system consisting of solid & vapor in equilibrium to a supercritical fluid.
- P-V-T phase diagram: the triple pt displayed in the P-T & P-V diagram is best displayed in 3D

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

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

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

$$d\mu_a = d\mu_b$$

$$\Leftrightarrow -S_{m\alpha} dT + V_{m\alpha} dP = -S_{m\beta} dT + V_{m\beta} dP$$

$$\Rightarrow (S_{m\beta} - S_{m\alpha}) dT = (V_{m\beta} - V_{m\alpha}) dP$$

$$\Rightarrow \Delta S_m dT = \Delta V dP$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta S_m}{\Delta V}$$

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

$\rightarrow \Delta S_m$ values for the fusion transition can be calculated from the enthalpy of fusion & the fusion temperature

- The entropy change for the processes solid (P, T) \rightarrow gas (P, T) and solid (P, T) \rightarrow liquid (P, T) \rightarrow gas (P, T) must be the same

$$\Rightarrow \Delta S_{\text{sublimation}} = \Delta S_{\text{fusion}} + \Delta S_{\text{vaporization}} > \Delta S_{\text{vaporization}}$$

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

$$\int_{P_i}^{P_f} \frac{dP}{T} = \int_{T_i}^{T_f} \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} dT = \int_{T_i}^{T_f} \frac{\Delta H_{\text{fusion}}}{\Delta V_{\text{fusion}}} \frac{dT}{T} \approx \frac{\Delta H_{\text{fusion}}}{\Delta V_{\text{fusion}}} \int_{T_i}^{T_f} \frac{dT}{T}$$

$$P_f - P_i = \frac{\Delta H_{\text{fusion}}}{\Delta V_{\text{fusion}}} \ln \frac{T_f}{T_i} = \frac{\Delta H_{\text{fusion}}}{\Delta V_{\text{fusion}}} \ln \frac{T_i + \Delta T}{T_i} \approx \frac{\Delta H_{\text{fusion}} \Delta T}{\Delta V_{\text{fusion}} T_i}$$

Clausius - Clapeyron equation

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

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

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

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

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

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

$$\left(\frac{\partial \mu_{\text{liquid}}(T, P)}{\partial P} \right)_T = \left(\frac{\partial \mu_{\text{gas}}(T, P)}{\partial P} \right)_T \left(\frac{\partial P}{\partial P} \right)_T$$

$$\text{Since } d\mu = -S_m dT + V_m dP, \quad \left(\frac{d\mu}{dP} \right)_T = V_m$$

$$\Rightarrow V_m^{\text{liquid}} = V_m^{\text{gas}} \left(\frac{\partial P}{\partial P} \right)_T \text{ or } \left(\frac{\partial P}{\partial P} \right)_T = \frac{V_m^{\text{liquid}}}{V_m^{\text{gas}}}$$

\uparrow vapor pressure P , \uparrow the total pressure P

$$\text{since } \frac{V_m^{\text{liquid}}}{V_m^{\text{gas}}} \ll 1 \Rightarrow V_m^{\text{gas}} = \frac{RT}{P}$$

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

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

8.8. Surface Tension

at constant $V \approx T$: $d\Delta = y d\sigma \rightarrow$ unit element of area
 surface tension (J/m^2)

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

$$F = 8\pi r y \pi$$

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

$P_{\text{inner}} - P_{\text{outer}} > 0$ as $r \rightarrow \infty \rightarrow$ the pressure differential exists only for a curved surface.

$$P_i - P_o = \frac{2y}{R_1} - \frac{2y}{R_2} = 2y \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$

- Alveoli: lung tissue is composed of small water-lined, air-filled chambers

- The pressure difference across the surface of a spherical air-filled cavity is proportional to the surface tension = inversely proportional to the radius of the cavity.

- Capillary rise and capillary are other consequences of the pressure differential across a curved surface

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

- The liquid-surface is characterized by the contact angle θ

- Complete wetting corresponds to $\theta = 0^\circ$, and complete nonwetting corresponds to $\theta = 180^\circ$

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