

Reading Assignment 7

7.1 Real Gases and Ideal Gases

- ideal gas law provides accurate description of the P-V-T relationship for many gases; however, it describes the P-V relationship for water for a wide range of P and V values
 - 1st assumpt. gas molecules are point masses, occupying a finite volume; therefore, a real gas cannot be compressed to a volume that is less than the actual molecular volume.
 - 2nd assumpt. molecules in the gas do not interact, but molecules in a real gas do because the potential has a short range; its effect is negligible at low densities, which correspond to large distances between molecules.

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

- van der Waals equation of state

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

- Redlich-Kwong equation of state

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

a and b have different values for each gas.

- Beattie-Bridgeman equation of state (not as important right now)

$$P = \frac{RT}{Vm^2} \left(1 - \frac{c}{VmT^3} \right) (Vm + B) - \frac{A}{Vm}$$

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

- virial equation of state

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

doesn't converge at high pressure

- the principal limitation of the ideal gas law is that it does not predict that a gas can be liquified under appropriate conditions.

- vapor pressure of the liquid is the temperature-dependent equilibrium pressure

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

T_c = critical temperature

7.3 The Compression Factor

- compression factor, z

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

for ideal gas, $z=1$ for all values of P and V_m

- boyle temperature T_B

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

7.4 The law of corresponding states

↳ if two gases have the same values of T_r , P_r and V_{mr} ,

they are in corresponding states.

$$\frac{aP_r}{27b^2} = \frac{8aT_r}{27b(3bV_{mr}-b)} - \frac{9b^2V_{mr}^2}{3}$$

$$P_r = \frac{8T_r}{3V_{mr}-1} - \frac{3}{V_{mr}^2}$$

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

7.5 Fugacity and the Equilibrium Constant for Real Gases

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

$f \Rightarrow$ fugacity, the effective pressure that

a real gas exerts.

- $\ln f = \ln P + \int_0^P \frac{Z-1}{P'} dP' \text{ or } f = P \exp \left[\int_0^P \left(\frac{Z-1}{P'} \right) dP' \right]$

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

↳ fugacity coefficient

8.1 What Determines the Relative Stability of the Solid, Liquid, and Gas Phase?

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

- $\mu \Rightarrow$ chemical potential for pure substance
- S_m and V_m are always positive
- μ decreases as the temperature increases and it increases as the pressure increases.
- entropy of three phases follows:
 $S_m^{\text{gas}} > S_m^{\text{liquid}} > S_m^{\text{solid}}$

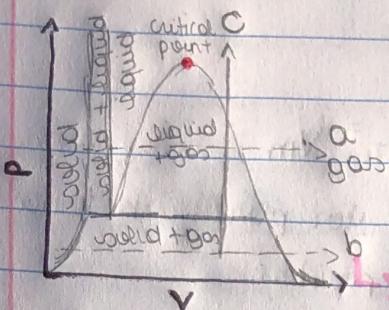
8.2 The Pressure-Temperature Phase Diagram

- P-T phase diagram displays stability regions for a pure substance as a function of pressure and temperature.
 - coexistence curve: all P, T points for which the same two phases coexist at equilibrium
 - standard boiling temp. is the T at which the vapor pressure of the substance is 1 atm.
 - normal boiling temp. is the T at which the vapor pressure of the substance is atm.
- $\Delta H = \Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporization}}$

8.3 The Phase Rule

- because T and P can be varied independently in a single-phase region, a system of a pure substance has two degrees of freedom.
- phase rule, links the number of degrees of freedom to the number of phases in a system at equilibrium : $F = 3 - p$

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



P-T phase-diagram combined with a

P-V phase diagram, and then combine

these two representations into a P-V-T

phase diagram

freeze drying

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

- Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$\Delta S_m = S_{m_B} - S_{m_A} \quad \text{and} \quad \Delta V_m = V_{m_B} - V_{m_A}$$

- Trouton's rule: states that $\Delta S_{\text{vap}} \approx 90 \text{ J/mole K}$ for liquids

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

Clausius-Clapeyron equation

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

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

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

- Vapor pressure is used to denote the partial pressure of water in the gas phase, and P is used to denote the sum of the oxygen and water partial pressures.

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

$L > 1 \text{ bar}$

8.8 Surface Tension

- work associated with the creation of additional surface area at constant V and T is

$$dA = \gamma d\sigma$$

\hookrightarrow surface tension

- the inward acting force is the sum of the force exerted by the external pressure and the force arising from the surface tension, whereas the outward acting force arises solely from the pressure in the liquid

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

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

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

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

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