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Reading Assignment 7.1: Properties of Real Gases

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A. van der Waals

B. Redlich-Kwong

7.1 - Real Gases and Ideal Gases

I. Two main deficiencies in ideal gas law model

A. Assumed gas molecules are point masses, but real gas have finite "V"

1. real gas can't be compressed to "V" less than total molecular "V"

B. Assumed gas molecules don't interact, but real gas molecules do

II. At low densities, P-V-T relationship for real gas same as for ideal gas

A. Also at high temperatures

$$\frac{mV}{T} = \frac{mV}{RT} = \frac{S}{V}$$

7.2 - Equations of State for Real Gases and their Range of Applicability

I. Van der Waals equation of state:

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

II. Redlich-Kwong equation of state:

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

1. more accurate results at 310 K than van der Waals

III. Beattie-Bridgeman equation of state: $w_1 w_2 T = H_F$

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

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

IV. Vapor Pressure

A. Temperature-dependent equilibrium pressure

V. Critical Temperature (T_c)

A. Temperature at which the range of V_m has shrunk to a single value

1. Above T_c , no liquid or gas phase can be distinguished

a. supercritical fluid

VI. Critical Constants (P_c and V_c)

A. Describe phase diagram of a pure substance

7.3 - The Compression Factor

I. Compression Factor (z)

$$A. z = \frac{V_m}{V_{\text{ideal}}} = \frac{PV_m}{RT}$$

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

2. $z > 1$, means real gas exerts greater pressure than ideal gas

3. $z < 1$, means real gas exerts smaller pressure than ideal gas

II. Boyle Temperature

$$A. T_B = \frac{a}{R_B}$$

1. Different for each gas

7.4 - The Law of Corresponding States

I. Law of Corresponding States

A. Different gases have the same equation of state if each gas is described by dimensionless reduced variables

$$1. T_r = \frac{T}{T_c}, P_r = \frac{P}{P_c}, V_{mr} = \frac{V_m}{V_{mc}}$$

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

1. obeyed by many gases when $T_r \geq 1$

2. Assumption that two parameters are sufficient to describe intermolecular potential

a. good assumption for spherical molecules

C. Error = $100\% \frac{z-1}{z}$ for pressure calculated by ideal gas law

7.5 - Fugacity and the Equilibrium Constant for Real Gases

I. Chemical Potential for Real Gas

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

1. f = fugacity

a. effective pressure that a real gas exerts

b. for densities in attractive range of intermolecular potential,

$$G_m^{\text{real}} < G_m^{\text{ideal}} \text{ and } f < P^\circ < V < mV$$

c. for densities in repulsive range of intermolecular potential,

$$G_m^{\text{real}} > G_m^{\text{ideal}} \text{ and } f > P^\circ < V < mV$$

$$d. f^\circ = P^\circ$$

$$2. f = P_e^{S_0^\circ} \left(\frac{z-1}{P^\circ} \right)^{kP^\circ} \quad \text{or } f = \gamma(P, T) P$$

a. can calculate "f" if "z" is known

b. γ = proportionality factor

1. also known as the fugacity coefficient

3. Relationship between γ and T_B (Boyle Temperature)

a. $T > T_B \rightarrow \gamma(P, T) > 1$ for all pressures, fugacity is greater than pressure and $\gamma > 1$

b. $T < T_B \rightarrow \gamma(P, T) < 1$ and fugacity is smaller than pressure

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

I. Phase

A. Refers to form of matter that is uniform with respect to chemical composition and state of aggregation

B. $\left(\frac{\partial U}{\partial T}\right)_P = -S_m$ and $\left(\frac{\partial U}{\partial P}\right)_T = V_m$

1. S_m and V_m are always positive, so

a. $U \downarrow, T \uparrow$

b. $U \uparrow, P \uparrow$

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

II. Boiling Point Elevation

A. $V_m^{\text{gas}} >> V_m^{\text{liquid}} > 0 \rightarrow$ increase in pressure

III. Freezing Point Elevation

A. $V_m^{\text{liquid}} > V_m^{\text{solid}} \rightarrow$ increase in pressure

IV. Freezing Point Depression

A. $V_m^{\text{liquid}} < V_m^{\text{solid}} \rightarrow$ increase in pressure

8.2 - The Pressure - Temperature Phase Diagram

I. P-T phase diagram

A. Displays stability regions for a pure substance as a function of pressure and temperature

1. At triple point, all three phases coexist

B. Coexistence Curve (3 of them)

1. Where two phases coexist at equilibrium

2. Slope of solid-gas and liquid-gas curves are always positive

3. Slope of solid-liquid curve is positive or negative

II. Boiling Point

A. Temperature where vapor pressure equals external pressure

1. Standard Boiling Temperature

a. Temp. where vapor pressure of substance is 1 bar

2. Normal Boiling Temperature

a. Temp. where vapor pressure of substance is 1 atm

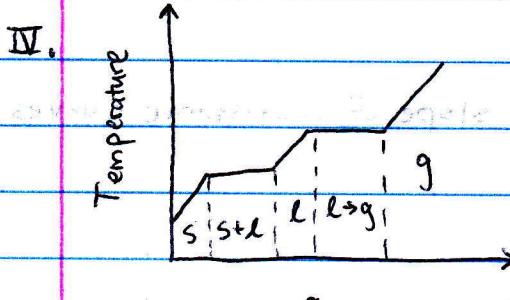
III. Critical Point

A. where liquid-gas curve ends

B. characterized by $T = T_c$ and $P = P_c$

C. Supercritical fluids

1. substances where $T > T_c$ and $P > P_c$



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

- B. For a pure substance, $F = 3 - p$
1. $F = \# \text{ of degrees of freedom}$
 2. $p = \# \text{ of phases}$
 3. Gibbs proves that no more than 3 phases can be in equilibrium

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

I. P-V-T Phase Diagram

A. Combine P-V phase diagram and P-T phase diagram

B. Can use to see temperature increases along segments for single-phase regions

C. Can also see constant temperature in two phase regions

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

I. Clapeyron Equation

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

1. Allows us to calculate the slope of coexistence curves in a P-T diagram

II. Trouton's Rule

A. $\Delta S_{\text{vap}} \approx 90 \text{ J/molK}$ for liquids

1. This rule fails for liquids that have strong interactions between molecules, like hydrogen bonds

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

I. Clausius - Clapeyron Equation

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

B. Vapor pressure of a liquid rises exponentially with temperature

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

I. If total pressure P increases, the vapor pressure increases but at a small rate because $V_m^{\text{liquid}} / V_m^{\text{gas}} \ll 1$.

A. $RT \ln \left(\frac{P}{P^*} \right) = V_m^{\text{liquid}} (P - P^*)$, where P^* = vapor pressure

8.8 - Surface Tension

I. Work and Surface Area

A. $dA = \gamma d\sigma$ ← unit element of area
↑
Helmholtz Energy
↑
surface tension

1. Surface tension has units J/m^2 or N/m

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

1. As $r \rightarrow \infty$, $(P_{\text{inner}} - P_{\text{outer}}) \rightarrow 0$

2. Pressure differential exists only for curved surface

a. vapor pressure depends on its radius

C. Pressure differential causes (1) capillary rise and (2) capillary depression

Surface tension of water = 72 dyne/cm

1. $\gamma_{\text{solid}} > \gamma_{\text{liquid}}$ → liquid wets surface

2. $\gamma_{\text{solid}} < \gamma_{\text{liquid}}$ → liquid avoids surface

$$3. h = \frac{2Y}{\rho g r} \quad \text{where } Y = \gamma_{\text{solid}} - \gamma_{\text{liquid}}$$

D. Contact angle (θ)

1. Characterizes liquid-surface

a. Wetting $\rightarrow \theta = 0^\circ$ { complete situation

b. Non-wetting $\rightarrow \theta = 180^\circ$

c. Intermediate angles

$$1. P_{\text{inner}} = P_{\text{outer}} + \frac{2Y \cos \theta}{r} \quad \text{and } h = \frac{2Y \cos \theta}{\rho g r}$$

$$\theta = \arctan \left(\frac{2Y \cos \theta}{\rho g r} \right)$$

$$\theta = \arctan \left(\frac{2Y}{\rho g r} \right)$$

Surface tension of water for curved surface

d. Adhesive forces due to liquid

C. Cohesive forces (1) covalent and (2) dispersion

forces