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CHE 3220

Reading Assignment 7 : 7.1-7.5, 8.1-8.8

7.1 Real Gases and Ideal Gases

I. Ideal Gas

- A. Provides accurate description of P-V-T relationship
- B. Microscopic Model Definitions
 - 1. Gas molecules are point masses
 - 2. Molecules don't react in the gas

II. Real Gas

- A. Same P-V-T relationship with an ideal gas at low densities and high temperature
- B. Molecular interactions can't be neglected at higher densities and low temperatures

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

I. Real Gas Equations of State

A. Van der Waals: $P = \frac{RT}{Vm - b} - \frac{a}{Vm^2} = \frac{nRT}{Vm - nb} - \frac{n^2a}{Vm^2}$

B. Redlich-Kwong: $P = \frac{RT}{Vm - b} - \frac{a}{\sqrt{T}} \frac{1}{Vm(Vm+b)} = \frac{nRT}{Vm - nb} - \frac{n^2a}{\sqrt{T}} \frac{1}{Vc(Vmb)}$

C. Beattie-Bridgeman: $P = \frac{RT}{Vm} \left(1 - \frac{C}{VmT^3}\right) (Vm + b) - \frac{A}{Vm}$ with

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

D. Virial: $P = RT \left[\frac{1}{Vm} + \frac{B(T)}{Vm} + \dots \right]$

7.3 The Compression Factor

I. $Z = \frac{Vm}{Vm_{ideal}} = \frac{PV_m}{RT}$

A. For an ideal gas, $Z=1$ for all values of P and V_m

1. $Z > 1$: real gas exerts greater pressure than ideal gas

2. $Z < 1$: real gas exerts less pressure than ideal gas

B. Boyle temperature

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

a. Parameters a and b are substance dependent

b. At $T=T_b$, a real gas exhibits ideal behavior as $P \rightarrow 0$ with respect to $\lim_{P \rightarrow 0} (\partial z / \partial P)_T$

c. If $\lim_{P \rightarrow 0} (\partial z / \partial P)_T < 0$ for a particular gas, $T < T_b$, and the attractive part of the potential dominates, and vice versa.

7.4 The Law of Corresponding States

I. $T_r = T/T_c$, $P_r = P/P_c \Rightarrow V_{mr} = V_m/V_{mc}$

A. If two gases have the same T_r , P_r , and V_{mr} values, they are in corresponding states.

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

1. Relates T_r , P_r , and V_{mr} without reference to parameter a and b .

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

D. For Van der Waals equation of state $z_c = 3/8$

1. Critical compressibility is independent of a and b

7.5 Fugacity and the Equilibrium Constant for Real Gases

I. For ideal gas: $N(T, P) = N^\circ(T) + RT \ln \frac{P}{P^\circ}$

For real gas: $N(T, P) = N^\circ(T) + RT \ln \frac{f}{P^\circ}$

A. Fugacity, f , is the effective pressure a real gas exerts

1. For densities corresponding to attractive range of intermolecular potential, $G_m^{\text{real}} < G_m^{\text{ideal}}$ and $f < P$.

2. For densities corresponding to repulsive range of intermolecular potential, $G_m^{\text{real}} > G_m^{\text{ideal}}$ and $f > P$.

3. Fugacity has the limiting behaviour that $f \rightarrow P$ as $P \rightarrow 0$.

4. Standard state of fugacity f° , is defined as the value that the fugacity will have if gas behaved ideally at 1 bar pressure.

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

6. $\ln f = \ln P + \int_P^{P^\circ} \frac{z-1}{P'} dP' \text{ or } f = P \text{ext} \left[\int_0^{P^\circ} \left(\frac{z-1}{P'} \right) dP' \right] \text{ or } f = \gamma(P, T)P$

a. It is seen that f and P are related by the proportionality factor γ , which is called the fugacity coefficient.

b. γ is not a constant since it depends on both P and T .

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

I. Phases are a form of matter that is uniform with respect to chemical composition and state of aggregation on both the microscopic and macroscopic length scales

A. The criterion for stability at constant temperature and pressure is that Gibbs energy, $G(T, P, n)$, be minimized.

1. The chemical potential $\mu = \left(\frac{\partial G}{\partial n}\right)_{T, P} = \left(\frac{\partial \ln \sigma_m}{\partial n}\right)_{T, P} = \sigma_m$.

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

a. S_m and V_m are always positive

b. μ decreases as the temperature increases

c. μ increases as the pressure increases

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

C. Because $V_m^{\text{gas}} >> V_m^{\text{liquid}} > 0$, an increase in P always leads to a boiling point elevation

D. An increase in P leads to a freezing point elevation if $V_m^{\text{liquid}} > V_m^{\text{solid}}$ and to a freezing point depression if $V_m^{\text{liquid}} < V_m^{\text{solid}}$

1. Triple point: Point where all three phases coexist at equilibrium

8.2 The Pressure-Temperature Phase Diagram

I. Phase diagrams graphically represent the phases of a substance.

A. A P-T phase diagram displays stability regions for a pure substance as a function of pressure and temperature

1. All three phases exist at the triple point.

2. All P,T points for which the same two phases coexist at equilibrium fall on a coexistence curve.

B. The standard boiling temperature is the temperature at which the vapor pressure of the substance is 1 bar.

C. The normal boiling temperature is the temperature at which the vapor pressure of the substance is 1 atm.

D. The liquid-gas curve ends at the critical point characterized by

$T = T_c$ and $P = P_c$

For $T > T_c$ and $P > P_c$, the liquid and gas phases have the same density.

2. Substances where $T > T_c$ and $P > P_c$ are supercritical fluids.

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

8.3 The Phase Rule

I. The coexistence of two phases, α and β , of a substance requires that chemical potentials are equal

$$N_\alpha(T, P) = N_\beta(T, P)$$

B. If three phases, α , β , and γ coexist at equil. b/w them

$$N_\alpha(T, P) = N_\beta(T, P) = N_\gamma(T, P)$$

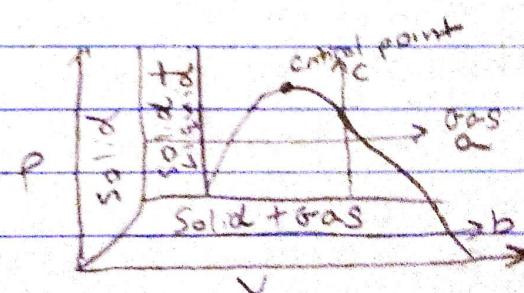
C. A system of a pure substance has two degrees of freedom and T and P can be varied independently in a single-phase region.

D. The phase rule links the number of degrees of freedom to the number of phases in a system at equilibrium:

$$\text{I. for a pure substance, } F = 3 - p.$$

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

I. A P-V phase diagram displays single- and two-phase coexistence regions, a critical point, and a triple point.



A. The diagram above shows a P-V phase diagram where $V_{\text{liquid}} > V_{\text{solid}}$.

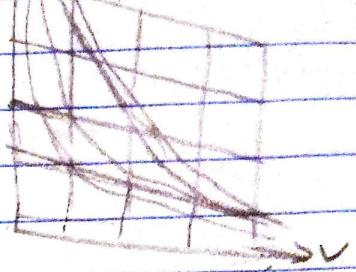
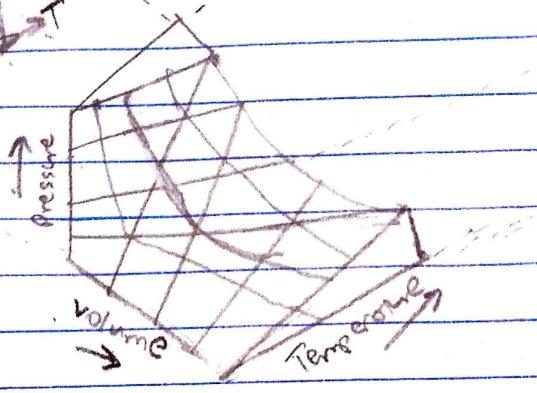
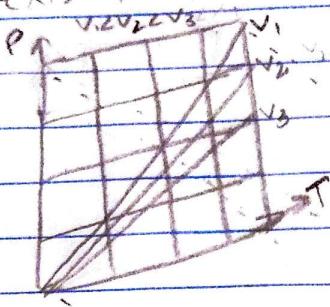
1. Process a shows a solid converted to a gas by increasing the temperature in an isobaric pressure for which P is greater than triple-point pressure.

2. Process b is known as freeze drying, and portrays an isobaric transition from solid to gas for P below the triple point pressure, for which the system has only one two-phase

coexistence region.

3. Process C shows a constant volume transition from a system consisting of solid and vapor in equilibrium to a supercritical fluid.

II. A P-V-T diagram is used for ideal gases and does not exist in the form of condensed phases.



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

I. The Clapeyron equation calculates the slope of the coexistence curves in a P-T phase diagram if ΔS_m and ΔV_m are known:

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

B. At melting temperature, $\Delta G_{\text{fusion}} = \Delta H_{\text{fusion}} - T\Delta S_{\text{fusion}} = 0$

$$C. \left(\frac{dP}{dT}\right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx \frac{22 \text{ J mol}^{-1} \text{ K}^{-1}}{2.0 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}} = \pm 5.5 \times 10^6 \text{ Pa K}^{-1} = \pm 55 \text{ bar K}^{-1}$$

$$D. \left(\frac{dP}{dT}\right)_{\text{vaporization}} = \frac{\Delta S_{\text{vaporization}}}{\Delta V_{\text{vaporization}}} \approx \frac{95 \text{ J mol}^{-1} \text{ K}^{-1}}{2.0 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}} \approx 4.8 \times 10^3 \text{ Pa K}^{-1} = 4.8 \times 10^2 \text{ bar K}^{-1}$$

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

I. Vapor pressure of a liquid increases with increasing temperature

$$A. \text{Clausius-Clapeyron Equation: } \frac{dP}{dT} = \frac{\Delta S_{\text{vaporization}}}{\Delta V_{\text{vaporization}}} \approx \frac{\Delta H_{\text{vaporization}}}{T V_{\text{gas}}} = \frac{P \Delta H_{\text{vaporization}}}{R T^2}$$

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

B. Assuming that $\Delta H_{\text{vaporization}}$ remains constant over the range of temperature of interest, the variation of vapor pressure of liquid with temperature is:

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

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

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

I. $N_{\text{liquid}}(T, P) = N_{\text{gas}}(T, P)$ at equilibrium

A. Vapor pressure P increases if total pressure P increases.

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

I. For external pressure 1 bar, the effect is negligible

8.8 Surface Tension

I. γ is the surface tension with units of energy/area or $J m^{-2}$ or $N m^{-1}$.

A. Work associated with the creation of additional surface area at constant V and T is $dA = \gamma d\sigma$

I A = Helmholtz energy and σ is unit element of area

B. 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 from the pressure in the liquid.

$$1. 4\pi r^2 P_{\text{outer}} + 8\pi \gamma r = 4\pi r^2 P_{\text{inner}}$$

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

C. The capillary rise or depression is given by $h = \frac{2\gamma}{P g r}$.