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Reading Assignment 7

7.1 Real Gases and Ideal Gases

- The ideal gas law provides an accurate description of the P-V-T relationship for many gases, such as He, for a wide range of P, V, and T values.
- The two main deficiencies in the microscopic model on which the ideal gas law is based were discussed.

First Assumption - gas molecules are point masses.

Second Assumption - the molecules in the gas do not interact, but molecules in a real gas do interact with one another through a potential.

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

- The first two equations of state considered here include two parameters a and b , that must be experimentally determined for a given gas.
- The parameter a is a measure of the strength of the attractive part of the intermolecular potential.
- The parameter b is a measure of the minimum volume that a mole of molecules can occupy.

Van der Waals Equation of state:

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

Redlich-Kwong Equation of State:

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

Beattie - Bridgeman Equation of State:

$$P = \frac{RT}{V_m^3} \left(1 - \frac{C}{V_m T^3} \right) - (V_m + B) - \frac{A}{V_m^2} \quad \text{with}$$

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

The Viral Equation of State:

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

The temperature-dependent equilibrium pressure is called the vapor pressure of the liquid.

The temperature at which the range of V_m has shrunk to a single value is called the critical temperature, T_c .

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

T_c and the corresponding values P_c and V_c together are called the critical constants. Take on particular significance in describing the phase diagram of a pure substance.

In Maxwell's construction, the oscillating region is replaced by the horizontal line for which the areas above and below the line are equal.

7.3 The Compression Factor

Compression factor, z , defined by ...

$$z = \frac{V_m}{V_{ideal}} = \frac{P V_m}{R T}$$

The compression factor for a given gas is a function of temperature.

To understand why the low pressure value of the compression factor varies with temperature for a given gas, we use van der Waals equation of state.

$$\left(\frac{\partial z}{\partial P}\right)_T = \left(\frac{\partial z}{\partial P} \Big|_{Vm}\right)_T = \frac{1}{RT} \left(\frac{\partial z}{\partial (1/Vm)}\right)_T$$

The corresponding temperature is known as the Boyle temperature T_B .

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

The parameters a and b are substance dependent, T_B is different for each gas.

7.4 The Law of Corresponding States

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

$$Tr = \frac{T}{T_c} \quad Pr = \frac{P}{P_c} \quad \text{and} \quad Vmr = \frac{Vm}{Vm_c} \quad \text{rather than by } T, P, \text{ and } Vm$$

This is known as the law of corresponding states.

If two gases have the same values of Tr , Pr , Vmr they are in corresponding states.

The van der Waals equation in the form

$$\frac{Pr P_c}{Vm_r V_m c} = \frac{RT_r T_c}{Vm_r V_m c} - \frac{9a}{V_m^2 V_m c}$$

$$\frac{a Pr}{27b^2} = \frac{8a Tr}{27b(3b Vmr - b)} - \frac{a}{9b^2 V^3 mr} \quad \text{or}$$

$$P_r = \frac{8T_r}{3Vm_r - 1} - \frac{3}{V^2 m_r}$$

Using the compression factor

$$Vm_r = 100\% \cdot \frac{2-1}{2}$$

$$Z_c = \frac{P_c V_c}{T_c (m_r) R T_c} = \frac{1}{R} \times \frac{a}{27b^2} \times 3b \times \frac{27Rb}{8a} = \frac{3}{8}$$

7.5 Fugacity and the Equilibrium Constant for Real Gases

The pressure exerted by a real gas can be greater or less than of an ideal gas affect the value of equilibrium constant for a mixture of reactive gases.

For a real gas:

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

* f = fugacity (effective pressure that a real gas exerts)

$$G_m^{\text{real}} < G_m^{\text{ideal}}, f < P \text{ (attractive range)}$$

$$G_m^{\text{real}} > G_m^{\text{ideal}}, f > P \text{ (repulsive range)}$$

Fugacity and Pressure related

$$\alpha f_m = V_m dp$$

After substitutions what you get is

$$\ln f = \ln P + \int_0^P \frac{2-1}{P_1} dp \text{ or } f = P e^{\int_0^P \left(\frac{2-1}{P_1} \right) dp}$$

or

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

~ γ is fugacity coefficient

$$\frac{d\ln f}{dP} = \frac{2-1}{P}$$

Fugacity of a gas can be set equal to its partial pressure if P , V , and T are not close to their critical values.

8.1 What determines the relative stability of a solid, liquid and gas phases?

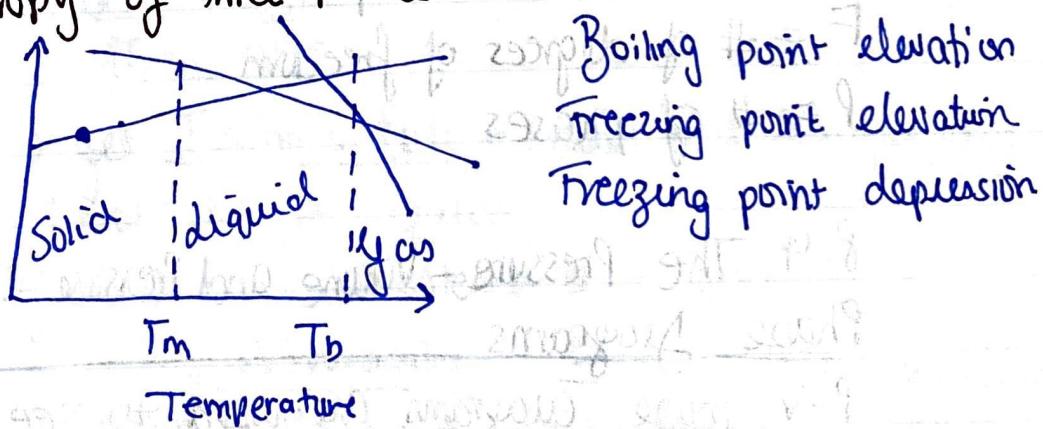
Different substances are at different phases depending on factors such as temperature + pressure Gibbs Energy, $G(T, P, n)$

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T, P} = \left(\frac{d(nGm)}{dn} \right)_{T, P} \quad T, P = \text{constant}$$

Changes in P and T

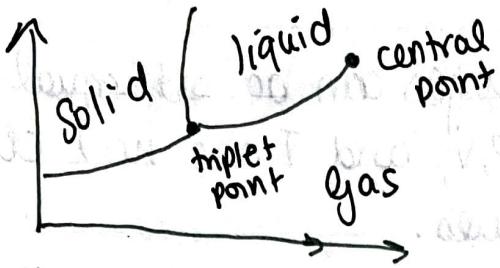
$$\left(\frac{\partial m}{\partial T} \right)_P = -S_m \quad \text{and} \quad \left[\frac{\partial m}{\partial P} \right]_T = V_m$$

Entropy of three phases



8.2 The pressure - temperature phase diagram

Phase diagrams are used to show pure substances in single / two phases in equilibrium. $P - T$



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

The various types of phase diagrams may change depending on the factors value measuring as well in changes of the substance itself.

8.3 The Phase Rule

3 phases α, β, γ exist in equilibrium you get

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

degrees of freedom - a system of substance has two phase

The rule for a pure substance takes the form:

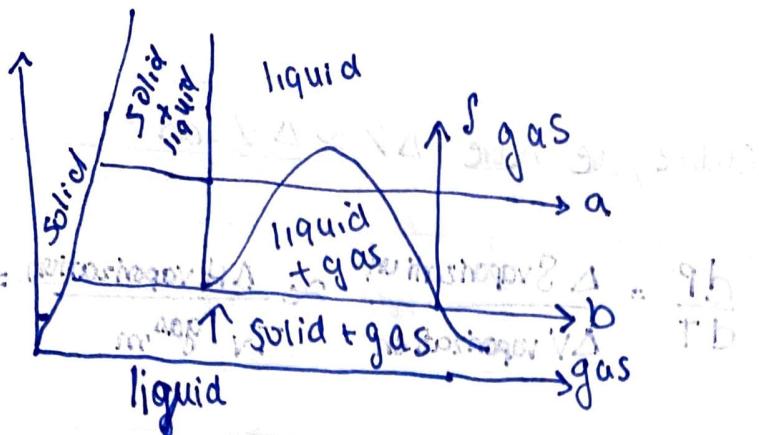
$$F = 3 - p_f$$

~~only 1 phase present~~
F = # of degrees of freedom

~~only 1 phase present~~
P = # of phases

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

P-V phase diagrams are used to see the complement of information contained in the P-T phase diagram.



$$V_m^{\text{solid}} < V_m^{\text{liquid}} < V_m^{\text{gas}}$$

In the figure process b is freeze drying.

P-V-T phase diagram - 3 dimensional diagram d is playing at P-T, P-V, etc.

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

The Clapeyron equation is developed which allows us to calculate the slope of the P-T phase diagram if ΔS_m and ΔV_m for the transition are known

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

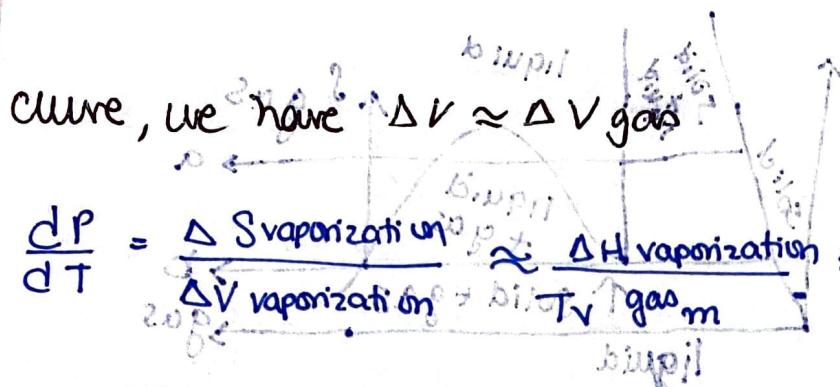
We also get Trotton's Rule - States that $\Delta S_{\text{vapORIZATION}}$ $\approx 90 \text{ J mol}^{-1} \text{ K}^{-1}$ for liquids

Slope of liquid-gas coexistence line given by

$$\left(\frac{dP}{dT}\right)_{\text{vapORIZATION}} = \frac{\Delta S_{\text{vapORIZATION}}}{\Delta V_{\text{vapORIZATION}}} = \frac{95 \text{ mol}^{-1} \text{ K}^{-1}}{4.8 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} \approx 4.8 \times 10^3 \text{ Pa K}^{-1}$$

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

Clausius-Clapeyron Equation - Obtained assuming ideal gas law has for a liquid-gas coexistence



$$\frac{dP}{dT} = \frac{\Delta V_{\text{vaporization}}}{\Delta H_{\text{vaporization}}} \approx \frac{\Delta H_{\text{vaporization}}}{RT^2} = \frac{P \Delta H_{\text{vaporization}}}{RT^2}$$

$$\frac{P_f}{P_i} = \frac{\Delta H_{\text{vaporization}}}{R} \times \frac{1}{T^2} \quad T_f > T_i$$

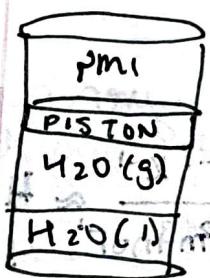
$\int \frac{dp}{p} = \frac{\Delta H_{\text{vaporization}}}{R} \times \int_{T_i}^{T_f} \frac{dT}{T^2}$

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

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

To calculate partial pressures of which water in organic Water mixture following equilibrium condition holds.

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



→ the state in which P is constant at $3.16 \times 10^3 \text{ Pa}$

as long a temperature remains constant

$P_{\text{external}} = 0.0316 \text{ bar at } 20^\circ \text{C}$

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

8.8 Surface Tension

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

$$dA = \gamma d\sigma$$

A = helmholtz energy

γ = surface tension

σ = unit element of area

The surface tension has units of energy of Jm^{-2} equivalent to Nm^{-1} capillary rise | capillary depression ~ consequence of pressure differential across a curved angle surface

Contact angle θ

wetting $\theta = 0^\circ$

nonwetting $\theta = 180^\circ$