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Reading Assignment # 7

03/30/20

Macro Physical chemistry

7.1 Real Gases and Ideal Gases

- Ideal gas equation of state can be sufficiently accurate for P-V-T relationships of real gases at low densities and high temp. This works at higher densities and low temps molecular interactions cannot be neglected
- $PV = nRT$
IDEAL GAS LAW
- K_p in terms of partial pressure using ideal gas law:
- P-V relationship for water and P+V within $\pm 10\%$ only for $T > 1300^\circ K$

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

- Several equation of state for real gases and range of variables P, V, T over which they accurately describe a real gas are discussed. Must exhibit P-V-T behavior identical for that of ideal gas at low density. Also deviations similar that real gases exhibit at moderate + higher densities

van der Waals equation of state:

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

Redlich-Kwong equation of state:

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

* Values of a and b differ for different gases

Beattie-Bridgeman equation of state

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

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

Virial equation of state

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

Maxwell constructions justified a theoretical grounds Van der Waals +
Rellich good for reproducing $P-v$ isotherms for real gases only
in single phase gas region $T > T_c$ + for densities will below
critical density

$$P_c = m/v_{mc}$$

7.3 The compression Factor

- Used for how large error in $P-v$ curves if ideal gas law is used rather than Van der Waals + Rellich compression factor,

$$Z = \frac{v_m}{v_{m,ideal}} = \frac{P v_m}{RT}$$

for ideal gas $Z=1$ for all values of P, v_m

$Z > 1$ real gas exert greater pressure ^{than} ideal.

$Z < 1$ real gas exerts smaller pressure than ideal

Boyle temperature, $T_B = \frac{a}{Rb}$

Figure 7.6 shows

$$\text{if } \lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_T < 0 \text{ for a}$$

particular gas, $T < T_B$, attractive part of potential dominates. If $\lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_T > 0$ for a gas

$T > T_B$ and repulsive part of potential dominates

7.4 The Law of Corresponding states

- different gases have ~~different~~ ^{same} equation of state if each gas is described by the dimensionless reduced variables $T_r = T/T_c$, $P_r = P/P_c$ and $V_{mr} = V_m/V_{mc}$, rather than by T, P, V, m . If 2 gases have same ~~same~~ ~~values~~ values T_r, P_r, V_m they are in corresponding states

van der Waals equation written in the form:

$$P_r P_c = \frac{R T_r T_c}{V_{mr} V_{mc} - b} - \frac{a}{V_{mr}^2 V_{mc}^2}$$

↓

$$\frac{a P_r}{27 b^2} = \frac{8 a T_r}{27 b (3b V_{mr} - b)} - \frac{a}{9 b^2 V_{mr}^2} \quad \text{or}$$

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

using compression factor

$$\text{Error} = 100\% \times \frac{Z-1}{Z}$$

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

7.5 Fugacity and The Equilibrium Constant for Real Gases

- how does the pressure exerted by a real gas can be greater/less than that 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)

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

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

Fugacity and pressure related

$$a G_m = V_m dp$$

after substitutions what you get is

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

or

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

γ is fugacity coefficient

under typical lab conditions, 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?

diff substances are at diff phases depending on factors such as temp + pressure

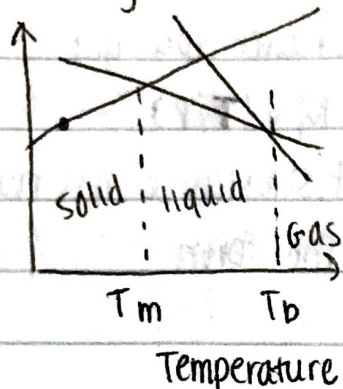
reminder Gibbs energy, $G(T, P, n)$

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

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



boiling point elevation

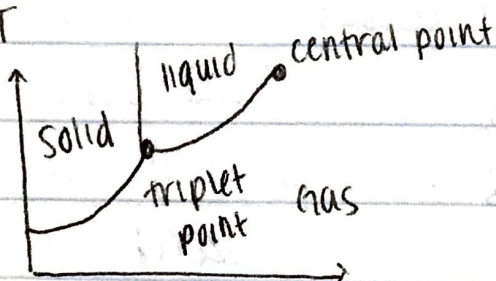
freezing point elevation

freezing point depression

8.2 The Pressure - Temperature Phase Diagram

- phase diagrams 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 as in changes of the substances it self.
- important to note things such as the ~~critical~~ critical sublimation triplet points

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 rule for a pure substance takes the form:

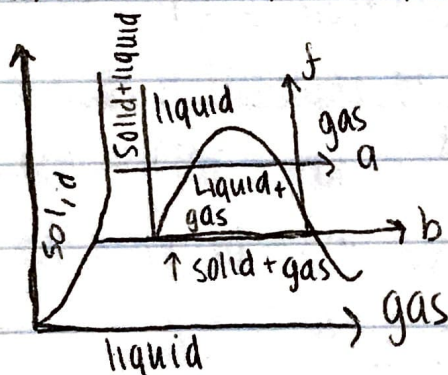
$$F = 3 - p$$

F = # of degrees of freedom

p = # phases

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

- P-V phase diagrams used for seeing 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 displaying at P-T, P-V, etc

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

- The Claapeyron equation is developed which allows us to calculate the slope of the coexistence in 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 Trouton's rule, which states that $\Delta S_{\text{vaporization}} \approx 90 \text{ J mol}^{-1} \text{ K}^{-1}$ for liquids
- Slope of liquid-gas coexistence ~~curve~~ curve given by

$$\left(\frac{dP}{dT}\right)_{\text{vaporization}} = \frac{\Delta S_{\text{vaporization}}}{\Delta V_{\text{vaporization}}} = \frac{90 \text{ mol}^{-1} \text{ K}^{-1}}{2.0 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}} \approx 4.5 \times 10^3 \text{ Pa K}^{-1}$$

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

- Clausius - Clapeyron equation - obtained assuming ideal gas law. For a liquid-gas coexistence curve, we have $\Delta V \approx \Delta V_{\text{gas}}$

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

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

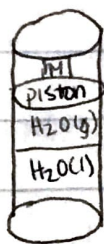
$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta H_{\text{vaporization}}}{R} \times \int_{T_i}^{T_f} \frac{dT}{T^2}$$

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

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

to calculate partial pressure of which water in organic water mixture following equilibrium condition holds

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



(state of system in which P remains constant at $3.16 \times 10^3 \text{ Pa}$ as long as temp remains constant)

$$P_{\text{external}} = 0.0316 \text{ bar}$$

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

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

surface tension has units of energy/area of Jm^{-2} equivalent to Nm^{-1}

capillary rise / capillary depression ~ consequences of pressure differential across a curved surfaces

contact angle θ

$$\text{wetting } \theta = 0^\circ$$

$$\text{nonwetting } \theta = 180^\circ$$