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Reading Assignment 7

7.1 Real Gases & Ideal Gases

- ideal gas law provides a relationship for P - V - T
- for ideal gas law:
 - assume that gas molecules are point masses, however molecules occupy a finite volume.
 - A real gas cannot be compressed to a volume that is less than the total molecular volume.
 - Assume that molecules in the gas do not interact, but molecules in a real gas do not interact through a potential.
- potentials have a short range so is negligible at low densities, molecular volume is also negligible at low densities.
- The P - V - T relationship of a real gas is the same as that of an ideal gas at low densities high temperatures.

7.2 Equations of state for Real Gases & the Range of Applicability

- parameters of equation of state:
 - $a \rightarrow$ a measure of the strength of the attractive part of the intermolecular potential.

$b \rightarrow$ a measure of the minimum volume that a mole of molecules can occupy.

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

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

These equations of state will give different answers

- Beattie-Bridgeman:
$$P = \frac{RT}{V_m^2} \left(1 - \frac{C}{V_m T^3} \right) (V_m + B) - \frac{A}{V_m^2}$$

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

$$A = A_0 \left(1 - \frac{a}{V_m} \right)$$

$$B = B_0 \left(1 - \frac{b}{V_m} \right)$$

- theoretical

- if $B(T)$ is negative, the attractive part of the potential dominates

- $B(T)$ for van der Waals is $b - (a/RT)$

- Vapor Pressure - the temperature-dependent equilibrium pressure of a liquid.

- A system consists of a single phase or two phases separated by a sharp interface, depending on the values of T & V_m .

- Pressure changes rapidly with $\downarrow V$

- Critical temperature - the temperature at which the range of V_m has shrunk to a single value (T_c)

$$\left(\frac{dP}{dV_m} \right)_{T=T_c} = 0 \quad \& \quad \left(\frac{d^2P}{dV_m^2} \right)_{T=T_c} = 0$$

Maxwell construction: the oscillating region is replaced by the horizontal line for which the areas above and below the line are equal.

- Used in generating isotherms.
- Use van der Waals + Redlich Kwong for low density + single phase $T > T_c$.
- Use Beattie-Bridgeman for densities above T_c (high densities)

7.3 The Compression Factor

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

ideal gas, $z = 1$

if $z > 1$, real gas exerts a greater pressure than the ideal gas

if $z < 1$, real gas exerts a smaller pressure than the ideal gas for the same value of T & V_m .

z is functionally dependent on P for different T values.

Use Van der Waals to understand why the low P value of z varies with T . $\left(\frac{dz}{dP}\right)_T = \left(\frac{dz}{d(RT/V_m)}\right)_T = \frac{1}{RT} \left(\frac{dz}{d(1/V_m)}\right)_T$

Van der Waals equation predicts $\lim_{1/V_m \rightarrow 0} \left(\frac{dz}{dP}\right)_T = \frac{b}{RT} - \frac{a}{(RT)^2}$

that the initial slope of z vs. P curve is

zero if $b = a/RT$

Boyle Temperature - T_B

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

• molecules primarily feel the repulsive part of the potential for $T > T_b$

• for high enough values of P , $z > 1$ for all gases \rightarrow repulsion dominates at high gas densities

• if $T < T_b$, then the attractive part of the potential dominates

7.4 The Law of Corresponding States

• Real gases differ from one another primarily in the value of the molecular volume and in the depth of attractive potential

• Critical temp is a measure of the depth of the attractive potential

• Critical volume is a measure of the molecular volume

• Law of corresponding states

- if 2 gases have the same values of $T_r, P_r, V_{mr} \rightarrow$ they are in corresponding states.

$$T_r = T/T_c \quad P_r = P/P_c \quad V_{mr} = \frac{V_m}{V_{mc}}$$

$P, V,$ and T can still differ greatly

• can eliminate parameters a & b with the reduced variables $T_r, P_r,$ & V_{mr}

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

• can be used for many different gases as long as $T_r > 1$

• assumes the 2 parameters are sufficient to describe an inter molecular potential.

- Not good for dipolar molecules

- error in assuming pressure error: $100\% \frac{z-1}{z}$
- critical variables can be expressed in terms of parameters a & b , so the compression factor at the critical point can also be calculated. $z_c = \frac{P_c V_c}{RT_c}$

7.5 Fugacity & the Equilibrium Constant for Real Gases

- for a pure ideal gas, the chemical potential as a function of a pressure has a form.

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

- for a real gas:

$$\mu(T, P) = \mu^\circ(T) + RT \ln \frac{f}{P^\circ} \rightarrow \text{fugacity} \rightarrow \text{the effective pressure that a real gas exerts.}$$

for densities corresponding to:

- attractive potentials: $G_m^{\text{real}} < G_m^{\text{ideal}}$ & $f < P$
- repulsive potentials: $G_m^{\text{real}} > G_m^{\text{ideal}}$ & $f > P$

- fugacity has limiting behavior that $f \rightarrow P$ as $P \rightarrow 0$

Standard State fugacity - (f°) the value of fugacity would have if the gas behaved ideally at 1 bar pressure
 $\hookrightarrow f^\circ = P^\circ$

- fugacity + pressure relationship:

$$dG_m = V_m dP$$

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

- Phase - a form of matter that is uniform with respect to chemical composition & the state of aggregation.
- Gibbs energy needs to be minimized for stability at constant temperature + pressure.
- For a pure substance: $\mu = \left(\frac{dG}{dn} \right)_{T,P} = \left(\frac{d[\ln G_m]}{dn} \right)_{T,P} = G_m$
- how μ varies with changes in P & T : $\left(\frac{d\mu}{dT} \right)_P = -S_m$ & $\left(\frac{d\mu}{dP} \right)_T = V_m$ at moles of substance in the system.
 - S_m & V_m are always positive
 - μ decreases as temp increases
 - μ increases as pressure increases
 - S varies slowly with T
- entropy phase order: $S_m^{\text{gas}} > S_m^{\text{liquid}} > S_m^{\text{solid}}$
- On a graph:
 - the molar entropy of a phase is the negative of the slope of μ vs. T
- The stable state of the system at any T is that phase that has lowest μ .
 - if the temp is changed too quickly, the equilibrium state of the system may not be reached.
- An increase in P leads to a boiling point elevation for $V_m^{\text{gas}} \rightarrow V_m^{\text{liquid}} > 0$.
- An increase in P leads to a freezing point elevation for $V_m^{\text{liquid}} > V_m^{\text{solid}}$

- Sublimation Temperature - The solid sublimates + the transition Temp.
- Triple Point - P, V_m & T coexist in equilibrium when all 3 phases intersect.

8.2 The Pressure-Temperature Phase Diagram

- Phase Diagram - displays multiple phases in equilibrium graphically.
- P-T Phase Diagram,
 - displays stability regions for a pure substance as a function of pressure & temperature.
 - most P, T points correspond to a single phase
 - at the triple point, all 3 phases coexist.
- Co-existence Curve - the curve in which all P, T points for which the same 2 phases coexist in equilibrium.
- Boiling Point - the temp at which vapor pressure of the substance is equal to external pressure.
- Standard Boiling Temperature - the temp at which the vapor pressure of the substance is 1 bar.
 - normal boiling temperature $\rightarrow 1 \text{ atm}$
 - 1 bar is slightly less than 1 atm \rightarrow standard slightly less than normal.
 - since the magnitude of slope is large, T_m is a weak function of pressure.
 - if the solid is more dense than the liquid the slope of this curve is positive + the melting temp \uparrow with pressure \uparrow .

- The slope of the liquid-gas coexistence curve is much smaller than that of the solid-liquid curve
- the boiling point is a much stronger function of the pressure than freezing point.
- the boiling point always increases with pressure.

8.3 The Phase Rule

- a two-phase system has one degree of freedom.
- a three-phase system has zero degrees of freedom.
- Phase Rule - links the # of degrees of freedom to the # of phases in a system at equilibrium.
 - for a pure substance; $F = 3 - P \rightarrow \# \text{ of phases}$
 - no more than 3 phases of a pure substance can be in equilibrium as F cannot be a negative #.
- The # of degrees of freedom increases if a system contains several chemically independent species

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

- Any phase diagram that includes only two/three state variables is limited because it does not contain info on the 3rd variable.
- $P-V$ Diagram \rightarrow displays a single & a two phase coexistence region, a critical point + a triple line.
- for pressures well below the critical point, the range in V

8.4 Continued

over which the solid & liquid coexist is large compared to the range in V over which the solid & liquid coexist, because $V_m^{\text{solid}} < V_m^{\text{liquid}} < V_m^{\text{gas}}$.

the gas-liquid coexistence region is broader than the solid-liquid one.

- V can range between a maximum value for which the system consists almost entirely of gas with traces of the liquid + solid phases, and a minimum value for which the system consists almost entirely of solid traces of the liquid + gas phases.

- Freeze Drying -

- P-V-T Phase Diagram \rightarrow combination of P-T & P-V diagrams

- it is a 3-dimensional projection of the P-T & P-V planes

- this does not make it easier to observe the variety of phase regions & the processes they undergo.

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

- If 2 phases α & β are in equilibrium at P, T :

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

- if the variables change by a small amount & still lie on coexistence curve:

- such as $P, T \rightarrow P + dP, T + dT$

$$\mu_\alpha(P, T) + d\mu_\alpha = \mu_\beta(P, T) + d\mu_\beta$$

- For the 2 phases to remain in equilibrium $dU_a = dU_b$
- Express dU in terms of dT and dP
- $dU_a = -S_m dT + V_m dP$ & $dU_b = -S_m dT + V_m dP$
- to equate them: $-S_m dT + V_m dP = -S_m dT + V_m dP$ or $(S_m - S_m) dT + (V_m - V_m) dP = 0$
- if $P, T \rightarrow P + dP, T + dT$ an incremental amount of phase α is transformed to β .

$$\Delta S_m = S_{m\beta} - S_{m\alpha} \quad \& \quad V_m = V_{m\beta} - V_{m\alpha}$$

Clapeyron Equation: $\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$

- Use to estimate the slope of a solid-liquid coexistence curve.
- at melting tem: $\Delta G_{\text{fusion}} = \Delta H_{\text{fusion}} - T \Delta S_{\text{fusion}} = 0$
- average value of $\Delta S_{\text{fusion}} = 22 \text{ J/mol} \cdot \text{K}$
- for fusion transition, ΔV is small
- average value of $\Delta V_{\text{fusion}} = 4.0 \times 10^{-6} \text{ m}^3/\text{mol}$
- this is negative only for H_2O
- Use the averages to estimate the solid-liquid slope.
- $\left(\frac{dP}{dT}\right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx \frac{22 \text{ J/mol} \cdot \text{K}}{4.0 \times 10^{-6} \text{ m}^3/\text{mol}} = 5.5 \times 10^6 \text{ Pa/K} = 55 \text{ bar/K}$

Slope of the liquid-gas coexistence curve:

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

- much smaller than the solid-liquid slope
- the slope of both curves increases w/ T because ΔS increases with increasing T & ΔV decreases with increasing T
- $T + \Delta T$ takes only a modest increase in the pressure to increase the boiling point of a liquid by a significant amount.

- Entropy is a state function so its change is the same throughout all phase transitions.

$$\Delta S_{\text{sub}} = \Delta S_{\text{fusion}} + \Delta S_{\text{vapor}} > \Delta S_{\text{vapor}}$$

$$\Delta V_{\text{sub}} \propto \Delta S_{\text{vap}} \quad \left(\frac{dP}{dT}\right)_{\text{sub}} > \left(\frac{dP}{dT}\right)_{\text{vap}}$$

- Can conclude that the slope of the solid-gas coexistence curve will be greater than that of the liquid-gas coexistence curve.

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

- Vapor pressure of a liquid increases rapidly with increasing temp - also for a solid, below the triple point.

- To calculate vapor pressure at different temp, must use the Clapeyron Equation.

Solid-liquid coexistence curve: $\int_{P_i}^{P_f} dP = \int_{T_i}^{T_f} \frac{\Delta S_{\text{fus}}}{\Delta V_{\text{fus}}} dT = \int_{T_i}^{T_f} \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}} T} dT$

if assume ΔH_{fus} & ΔV_{fus} are independent of T.

$$\approx \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \int_{T_i}^{T_f} \frac{dT}{T}$$

$$P_f - P_i = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \frac{T_f}{T_i} = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \frac{T_i + \Delta T}{T_i} \approx \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{\Delta T}{T_i}$$

- Vapor pressure of a solid varies linearly with ΔT
- for liquid-gas coexistence curve:

$$\Delta V \approx V^{\text{gas}}$$

- assume ideal gas laws apply.

Clausius-Clapeyron Equation:

$$\frac{dP}{dT} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} \approx \frac{\Delta H_{\text{vap}}}{T V_m} = \frac{P \Delta H_{\text{vap}}}{R T^2}$$

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

• assume that ΔH_{vap} remains constant temp range, the variation of the vapor pressure of the liquid with temp:

$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta H_{\text{vap}}}{R} \times \int_{T_i}^{T_f} \frac{dT}{T^2} \quad \left| \ln \frac{P_f}{P_i} = - \frac{\Delta H_{\text{vap}}}{R} \times \left(\frac{1}{T_f} - \frac{1}{T_i} \right) \right.$$

- Vapor pressure of a liquid rises exponentially with temp
- Use this for the solid-gas coexistence curve too, but ΔH_{sub} instead of ΔH_{vap}
- ΔH_{vap} is independent of temp.

8. 7 The Vapor Pressure of a Pure Substance Depends on the Applied Pressure

- Equilibrium Vapor pressure of water is $P^* = 3.16 \times 10^5 \text{ Pa}$ or 0.0316 bar
- Mass is reduced so P is exactly equal to the vapor pressure of water.
- The piston can be pulled outward or pulled inward while maintaining this P
- P will be constant at $3.16 \times 10^5 \text{ Pa}$ as long as T of the system is constant.

- To calculate the partial pressure of water in the argon-water mix:
 $\mu_{\text{liq}}(T, P) = \mu_{\text{gas}}(T, P) \rightarrow \left(\frac{d\mu_{\text{liq}}(T, P)}{dP} \right)_T = \left(\frac{d\mu_{\text{gas}}(T, P)}{dP} \right)_T \left(\frac{dP}{dP} \right)_T$

$$d\mu = -S_m dT + V_m dP \quad \left(\frac{d\mu}{dP} \right)_T = V_m$$

6.7 continued

$$V_m^{liq} = V_m^{gas} \left(\frac{dP}{dP} \right)_T \text{ or } \left(\frac{dP}{dP} \right) = \frac{V_m^{liq}}{V_m^{gas}}$$

- Vapor pressure P increases if the total pressure P increases

- rate of increase is small because $V_m^{liq}/V_m^{gas} \ll 1$

- if need to, can replace V_m^{gas} with RT/P

$$\frac{RT}{P} dP = V_m^{liq} dP \text{ or } RT \int_{P^*}^P \frac{dP'}{P'} = V_m^{liq} \int_{P^*}^P dP'$$

$$RT \ln(P/P^*) = V_m^{liq}(P - P^*)$$

• for external pressure of 1 bar, the effect is negligible

• for $P = 100$ bar, $P^* = 0.0339$ bar, amounting to an increase in vapor pressure of 7.1.

8.8 Surface Tension

• The interaction b/w molecules in a liquid is attractive, so minimizing the surface-to-volume ratio minimizes the energy.

• The work associated w/ the creation of additional surface area at constant $V+T$: $dA = \gamma d\sigma \rightarrow$ the unit element area

Helmholtz

energy surface tension \rightarrow units of energy/area $\rightarrow J/m^2 \rightarrow N/m$

• If the radius of a water droplet is increased from r to $r+dr$, the area increases by $d\sigma \rightarrow \sigma = 4\pi r^2$ so $d\sigma = 8\pi r dr$

• The work done in the expansion of the droplet: $8\pi \gamma r dr$

force $\leftarrow F = 8\pi \gamma r$ or work/distance

the net effect of this force is to generate a pressure differential across the droplet surface.

At equilibrium, there is a balance between the inward + outward forces

• Inward acting force - the sum of the force exerted by the external pressure and the force arising from the surface tension

• Outward Acting Force - Arises from the pressure in the liquid

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

$$P_{inner} - P_{outer} \rightarrow 0$$

$$r \rightarrow \infty$$

• The pressure differential exists only for a curved surface

- coarsening / Ostwald ripening

• 2 air filled bubbles of liquid with same surface tension γ

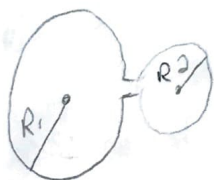


• R_1 = a large radius,
 R_2 = a small radius

• assume uniform pressure outside both bubbles

• to obtain the difference between the pressures $P_1 + P_2$:

$$P_1 - P_2 = \frac{2\gamma}{R_1} - \frac{2\gamma}{R_2} = 2\gamma \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$

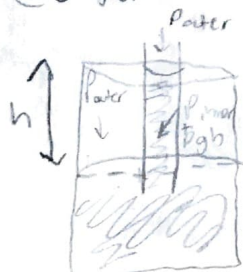


• Assume 2 bubbles come into contact

• $R_1 > R_2$, so P_2 inside bubble 2 $>$ P_1 in bubble 1

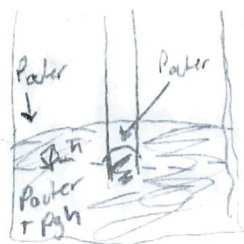
• air will flow from bubble 2 to 1 until the small bubble disappears entirely.

Curvature is equal to the capillary radius.



• if the liquid wets the interior wall of the capillary rise is observed

• ex. Pyrex water



• if the liquid does not wet the capillary surface, a capillary depression is observed

• ex. Pyrex-mercury

• Capillary rise or depression: $h = 2\gamma / \rho g r$

Cavitation - When bubbles are nucleated in a liquid + grow rapidly as the piston is pulled outward - Bubble Pressure: $h = 2\gamma / \rho g r$