Reading HW 7.1-7.5, 8.1-8.8

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7.1 Real Gases & Ideal Gases

→ real gases behave differently from ideal gases → only at high T & low density

Problems w/ ideal gas law

assumes gas molecules as point masses

gas molecules don't interact w/ each other

7.2 Equations of State for Real Gases & their Range of Applicability

also have different values for each

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

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

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

Virial eq. of state $P = RT\left[\frac{1}{V_m} + \frac{B(T)}{V_m^2} + \dots\right]$ virial coefficients → hard to obtain from experiments

Ideal gas law does not predict that a gas can be liquefied under appropriate conditions

Critical temperature - T at which the range of V_m is shrunk to 1 value

→ $\left(\frac{\partial P}{\partial V_m}\right)_{T=T_c} = 0$ & $\left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T=T_c} = 0$

7.3 The Compression Factor

Compression factor, z, $z = \frac{V_m}{V_m^{ideal}} = \frac{PV_m}{RT}$ way to see error of P-V curves if ideal gas law is used

→ $z = 1$ for ideal gases for all P & V_m

→ $z > 1$ → real gas exerts greater P than ideal gas

→ $z < 1$ → real gas exerts smaller P

→ function of T

$$\left(\frac{\partial z}{\partial P}\right)_T = \left(\frac{\partial z}{\partial [RT/V_m]}\right)_T = \frac{1}{RT}\left(\frac{\partial z}{\partial [1/V_m]}\right)_T$$

→ i.e. for van der Waals → as $1/V_m \to 0$ $\left(\frac{\partial z}{\partial P}\right)_T = \frac{b}{RT} - \frac{a}{(RT)^2}$

if $b = \frac{a}{RT}$ → slope of z vs. $P = 0$

→ Boyle temperature $T_b = \frac{a}{Rb}$ → at T_b $z = 1$

a $T = T_b$ a real gas exhibits ideal behaviour $\left(\frac{\partial z}{\partial P}\right)_T = 0$ as $P \to 0$

$\lim_{P\to 0}\left(\frac{\partial z}{\partial P}\right)_T < 0 \to T < T_b$ attractive part dominates

$\lim_{P\to 0}\left(\frac{\partial z}{\partial P}\right)_T > 0 \to T > T_b$ repulsive part of potential dominates

7.4 The Law of Corresponding States

Different gases have the same equation of state if each gas is described by the dimensionless reduced variables $T_r = \frac{T}{T_c}$, $P_r = \frac{P}{P_c}$, $V_{mr} = \frac{V_m}{V_{mc}}$

Law of corresponding states

→ $P_r P_c = \frac{RT_r T_c}{V_{mr} V_{mc} - b} - \frac{a}{V_{mr}^2 V_{mc}^2}$ $P_c = \frac{a}{27b^2}$ $V_{mc} = 3b$ $T_c = \frac{8a}{27Rb}$

$$\frac{P_r a}{27b^2} = \frac{8a T_r}{27(3bV_{mr} - b)} - \frac{a}{9b^2 V_{mr}^2} \iff P_r = \frac{8T_r}{3V_{mr} - 1} - \frac{3}{V_{mr}^2}$$

→ good for many gases as long as $T_r > 1$

→ best for molecules that are nearly spherical → not good for dipolar ones i.e. HF

→ error $= 100\% \times \frac{z-1}{z}$

van der Waals compression factor at critical point $z_c = \frac{P_c V_c}{RT_c} = \frac{1}{R} \times \frac{a}{27b^2} \times 3b \times \frac{27Rb}{8a} = \frac{3}{8}$ → independent of a & b

7.5 Fugacity and the Equilibrium Constant for Real Gases

$$\mu(T,P) = \mu^\circ(T) + RT\ln\frac{P}{P^\circ} \quad \text{pure ideal gas}$$

$$\mu(T,P) = \mu^\circ(T) + RT\ln\frac{f}{f^\circ} \quad \text{real gas}$$

f : fugacity, the effective pressure that a real gas exerts.

$G_m^{real} < G_m^{ideal} \rightarrow f < P$ attractive intermolecular potential

$G_m^{real} > G_m^{ideal} \rightarrow f > P$ repulsive

$f \rightarrow P$ as $P \rightarrow 0$

f° = standard state of fugacity – the value f if gas behaved ideally at 1 bar

$\rightarrow f^\circ = P^\circ$

$$dG_m = V_m dP \implies d\mu_{ideal} = V_m^{ideal} dP$$

$$d\mu_{real} = V_m^{real} dP \qquad V_m^{ideal} \neq V_m^{real}$$

$$d\mu_{real} - d\mu_{ideal} = (V_m^{real} - V_m^{ideal})dP \quad \Big/ \int$$

$$\int_{P_i}^{P} (d\mu_{real} - d\mu_{ideal}) = [\mu_{real}(P) - \mu_{real}(P_i)] - [\mu_{ideal}(P) - \mu_{ideal}(P_i)] =$$

$$= \int_{P_i}^{P} (V_m^{real} - V_m^{ideal})\, dP'$$

let $P_i \rightarrow 0$ $\mu_{real}(P_i) = \mu_{ideal}(P_i)$

$$\mu_{real}(P) - \mu_{ideal}(P) = \int_0^P (V_m^{real} - V_m^{ideal})\, dP'$$

$$Z = \frac{V_m^{real}}{V_m^{ideal}} \qquad \ln f = \ln P + \frac{1}{RT}\int_0^P (V_m^{real} - V_m^{ideal})\, dP'$$

$$\ln f = \ln P + \int_0^P \frac{Z-1}{P'} dP' \iff f = P\exp\left[\int_0^P \frac{(Z-1)}{P'} dP'\right] = \gamma P$$

fugacity coefficient

$\gamma \rightarrow 1$ as $P \rightarrow 0$

if $T > T_b \rightarrow \gamma(P,T) > 1$, $f > P$, $\gamma > 1$

if $T < T_b \rightarrow \gamma(P,T) < 1$, $f < P$

8.1 What determines the relative stability of the solid, liquid, & gas phase?

PHASE - form of matter that is uniform w/ respect to chemical composition & the state of aggregation on both micro & macro length scales

→ can have many diff. solid, (liquid) states, just 1 gaseous state

→ solid phase is most stable at sufficiently low T → liquid is intermediate

→ gas phase is most stable at sufficiently high T

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

n = # moles in system $\quad \underline{\underline{d\mu = dG_m}} \quad d\mu = -S_m dT + V_m dP$

$$\rightarrow \left(\frac{\partial\mu}{\partial T}\right)_P = -S_m \qquad \left(\frac{\partial\mu}{\partial P}\right)_T = V_m$$

S_m & $V_m > 0$ → as T↑, μ↓ (slowly → rel. flat curve)

as P↑, μ↑

$$\Delta S = \frac{\Delta H_{transition}}{T} \rightarrow S_m^{gas} > S_m^{liquid} > S_m^{solid}$$

→ stable state is at lowest μ $\qquad V_m^{gas} \gg V_m^{liquid} > V_m^{solid}$

Boiling point elevation $\quad V_m^{gas} \gg V_m^{liquid} > 0$ → increase in P → boiling pt elevation

P↑ & $V_m^{liquid} > V_m^{solid}$ → freezing point elevation

if $V_m^{liquid} < V_m^{solid}$ → freezing point depression

Sublimation T - when solid → gas transition is more favorable

Triple point - where μ vs T curves intersect in 1 point

→ all three phases coexist in equilibrium

8.2 The Pressure–Temperature Phase Diagram

↳ must generally be determined experimentally

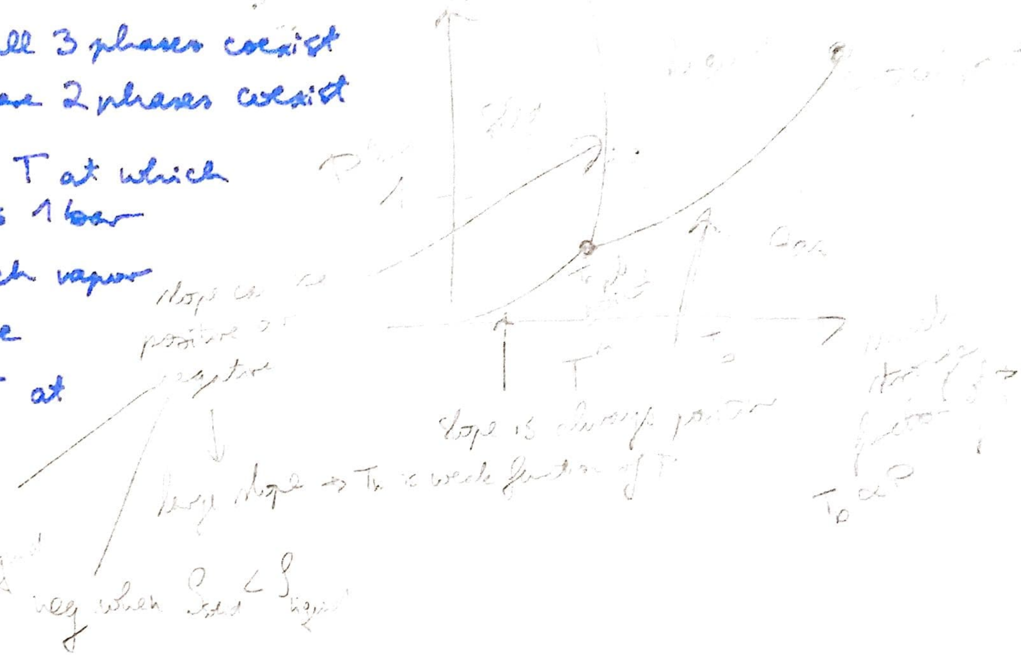
→ effect of material-specific forces between atoms

→ microscopic theoretical models are also sufficiently accurate

P–T phase diagram displays stability regions for a pure substance as a function of P & T

→ TRIPLE POINT where all 3 phases coexist

→ COEXISTENCE CURVE where 2 phases coexist



STANDARD BOILING TEMPERATURE: T at which vapor pressure of substance is 1 bar

→ BOILING POINT: T at which vapor pressure = external pressure

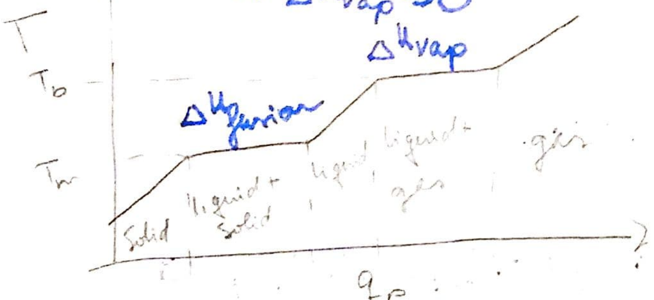
NORMAL BOILING TEMPERATURE: T at which $P_{vapor} = 1\,atm$

CRITICAL POINT: $T = T_c$
$P = P_c$

→ $\rho_{gas} = \rho_{liquid}$

→ $\Delta H_{vap} \to 0$

→ above this point are SUPERCRITICAL FLUIDS



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

↳ only at triple point

8.3 The Phase Rule

For coexistence of 2 phases, chemical potentials need to be equal.

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

$$\mu_\alpha(T,P) = \mu_\beta(T,P) = \mu_\gamma(T,P) \text{ at triple point}$$

Because T & P can be varied independently in a single phase region, a system of a pure substance has 2 degrees of freedom. In a 2-phase & 3-phase coexistence it is 1 & 0 degrees of freedom.

Phase rule - links #DOF to # phases in a system at equilibrium

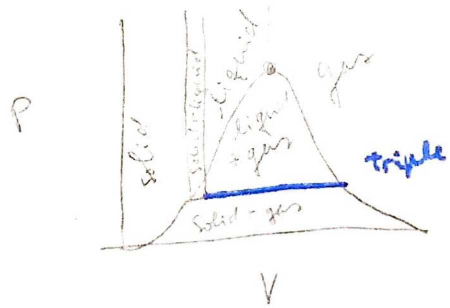
$F = 3 - P$ for pure substance

↓ #DOF ↓ #phases

→ no more than 3 phases can be in equilibrium → $F \geq 0$

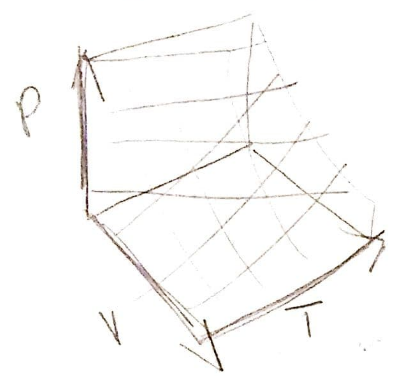
8.4 The Pressure-Volume & Pressure-Volume-Temperature Phase Diagrams

P-V phase diagram



$V_m^{solid} < V_m^{liquid} << V_m^{gas}$ → gas+liquid region larger than liquid+solid

P-V-T phase diagram → combines all 3



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

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

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

for equilibrium $d\mu_\alpha = d\mu_\beta$

$d\mu_\alpha = -S_{m\alpha}\,dT + V_{m\alpha}\,dP$ & $d\mu_\beta = -S_{m\beta}\,dT + V_{m\beta}\,dP$

$-S_{m\alpha}\,dT + V_{m\alpha}\,dP = -S_{m\beta}\,dT + V_{m\beta}\,dP$

$(S_{m\beta} - S_{m\alpha})\,dT = (V_{m\beta} - V_{m\alpha})\,dP$

→ $\dfrac{dP}{dT} = \dfrac{\Delta S_m}{\Delta V_m}$ Clapeyron equation

→ can calculate slope of coexistence curve in P-T diagram if ΔS_m & ΔV_m are known for the transition at melting T (T_m) $\Delta G_{fusion} = \Delta H_{fusion} - T\Delta S_{fusion} = 0$

$\rightarrow$ can calculate ΔS_m

TROUTON'S RULE: $\Delta S_{vaporization} \approx 90 \frac{J}{mol K}$ for liquids

$\rightarrow$ fails for liquids w/ strong interactions (w/ -OH or -NH_2 groups)

$\rightarrow$ their $\Delta S_{vap} > 90 \frac{J}{mol K}$

$\Delta S_{sublimation} = \Delta S_{fusion} + \Delta S_{vaporization} > \Delta S_{vaporization}$

$\Delta V_{sublimation} \approx \Delta V_{vaporization}$

$\rightarrow \left(\frac{dP}{dT}\right)_{sublimation} > \left(\frac{dP}{dT}\right)_{vaporization}$

$\downarrow$

greater slope for solid-gas than liquid-gas

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

Solid-liquid coexistence curve

$$\int_{P_i}^{P_f} dP = \int_{T_i}^{T_f} \frac{\Delta S_{fusion}}{\Delta V_{fusion}} dT = \int_{T_i}^{T_f} \frac{\Delta H_{fusion}}{\Delta V_{fusion}} \frac{dT}{T} \approx \frac{\Delta H_{fusion}}{\Delta V_{fusion}} \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\rightarrow P_f - P_i = \frac{\Delta H_{fusion}}{\Delta V_{fusion}} \ln \frac{T_f}{T_i} = \frac{\Delta H_{fusion}}{\Delta V_{fusion}} \ln \frac{T_i + \delta T}{T_i} \approx \frac{\Delta H_{fusion}}{\Delta V_{fusion}} \frac{\Delta T}{T_i}$$

Liquid-gas coexistence curve

ideal gas

$$\Delta V \approx V^{gas} \quad \rightarrow \frac{dP}{dT} = \frac{\Delta S_{vap}}{\Delta V_{vap}} \approx \frac{\Delta H_{vap}}{T V_m^{gas}} = \frac{P \Delta H_{vap}}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H_{vap}}{R} \frac{dT}{T^2}$$ // Clausius-Clapeyron equation

$$\rightarrow \ln\left(\frac{P_f}{P_i}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$ $\rightarrow$ assume ΔH_{vap} independent of T

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

$$\mu_{liquid}(T, P) = \mu_{gas}(T, P) \quad /: \partial P$$

$$\left(\frac{\partial \mu_{liquid}(T,P)}{\partial P}\right)_T = \left(\frac{\partial \mu_{gas}(T,P)}{\partial P}\right)_T \left(\frac{\partial P}{\partial P}\right)$$

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

$$\rightarrow V_m^{liquid} = V_m^{gas}\left(\frac{\partial p}{\partial P}\right)_T \Leftrightarrow \left(\frac{\partial p}{\partial P}\right)_T = \frac{V_m^{liq}}{V_m^{gas}}$$

vapor pressure p increases as total pressure P increases

$\rightarrow$ yet the rate of increase is small as $\frac{V_m^{liq}}{V_m^{gas}} \ll 1$

$$\frac{RT}{p}\,dp = V_m^{liq}\,dP \Leftrightarrow RT\int_{p^0} \frac{dp'}{p} = V_m^{liq}\int_{p^0} dP'$$

$$\rightarrow RT\ln\left(\frac{p}{p^*}\right) = V_m^{liq}(P - p^*)$$

8.8 Surface Tension

minimize surface-to-volume ratio

creating more SA : $dA = \gamma\, d\sigma \leftarrow$ area

Helmholtz energy, surface tension

SURFACE TENSION units : $\frac{\text{energy}}{\text{area}}$

$$\frac{J}{m^2} = \frac{N}{m}$$

$dA < 0$ for spontaneous process at const. V & T

for spherical droplet $\sigma = 4\pi r^2 \rightarrow d\sigma = 8\pi r\,dr$

$$\rightarrow dA = 8\pi\gamma r\,dr$$

$$\rightarrow F = 8\pi\gamma r$$

force normal to surface of droplet

$\rightarrow$ at equilibrium, there is a balance between inward & outward forces

$$4\pi r^2 P_{outer} + 8\pi\gamma r = 4\pi r^2 P_{inner} \Leftrightarrow P_{inner} = P_{outer} + \frac{2\gamma}{r}$$

as $r \rightarrow \infty$ $P_{inner} - P_{outer} \rightarrow 0$

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

if $\gamma_{liquid} < \gamma_{solid}$ $\rightarrow$ the liquid will wet surface $\rightarrow \Theta = 0°$

$\gamma_{liquid} > \gamma_{solid}$ $\rightarrow$ the liquid will avoid the surface $\rightarrow \Theta = 180°$

$$P_{inner} = P_{outer} + \frac{2\gamma\cos\Theta}{r} \quad \& \quad h = \frac{2\gamma\cos\Theta}{\rho g r}$$

$h = \frac{2\gamma}{\rho g r}$ $\rightarrow$ capillary rise or depression

gravitational field