

THE PROPERTIES OF REAL GASES

7.1. Real Gases and Ideal Gases

Ideal Gases

- Gas molecules are point masses
- Molecules do not interact

Real Gases

- Molecules occupy a finite V → real gas cannot be compressed to a volume less than total molecular V
- Molecules do interact with one another
 - + low density, high temp. → real ≈ ideal
 - + High density, low temp. → real ≠ ideal

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

- van der Waals

(more accurate)

- Redlich - Kwong

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

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

a, b different b/w 2 equations

- Beattie - Bridgeman

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

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

- Virial equation of state

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

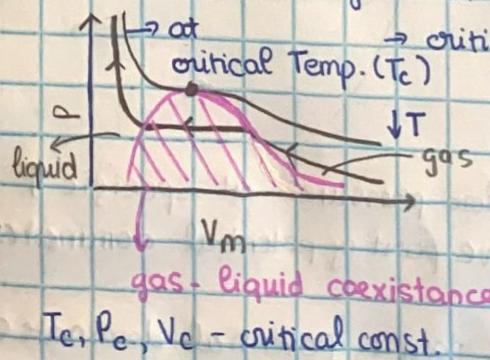
- + B(T), C(T), ... - the second, third ... virial coefficients
- + Practical use, the series is usually terminated after 2nd viral coefficient
- + If B(T) is - (+), the attractive (repulsive) part of potential dominates at that value of (T)

$$+ B(T) \text{ for van der Waals} \rightarrow B(T) = b - \frac{a}{RT}$$

- Large V ↓ → P ↑ then becomes const. then ↑ rapidly

★ Value of V at which P become const. depend on T

↳ critical isotherm. Reason vapor pressure of liquid



T_c, P_c, V_c - critical const.

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

- T_c is approached: d(l) ↓ d(g) ↑
- T = T_c: d(e) = d(g) → supercritical fluid
- T > T_c: can not distinguish gas and liquid

- van der Waals : $a = \frac{27 R^2 T_c^2}{64 P_c}$ and $b = \frac{R T_c}{8 P_c}$
- Redlich - Kwong : $a = \frac{R^2 T_c^{5/2}}{9 P_c (2^{1/3} - 1)}$ and $b = \frac{(2^{1/3} - 1) R T_c}{3 P_c}$
- Both van der Waals and Redlich - Kwong cannot reproduce the range in which P is const. or the discontinuity in $(\partial P / \partial V)_T$ at the end of this range for $T < T_c$ BUT do a good job of reproducing P - V isotherms for real gases only in single-phase gas region for $T > T_c$ and for densities well below the critical density $P_c = M / V_{mc}$.
- Beattie - Bridgeman is accurate above T_c for higher densities

7.3. The Compression Factor

$$z = \frac{V_m}{V_{\text{ideal}}} = \frac{P V_m}{RT} \rightarrow V = \frac{nRT}{P} z$$

for ideal gases : $z = 1$

$z > 1$: $P(\text{real gas}) > P(\text{ideal gas})$

$z < 1$: $P(\text{real gas}) < P(\text{ideal gas})$

$z \rightarrow 1$ as $P \rightarrow 0$

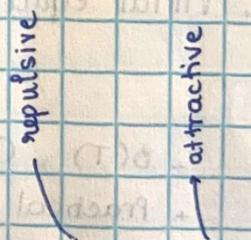
↳ If P is sufficiently small, ideal gas law is obeyed

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

For van der Waals

$$V_m \rightarrow \infty$$

$$\left(\frac{\partial z}{\partial P} \right)_T = \frac{b}{RT} - \frac{a}{(RT)^2}$$



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

$$\rightarrow \text{Boyle temperature } T_B = \frac{a}{Rb}$$

+ $T = T_B$: ideal behavior as $P \rightarrow 0$ with respect to $\lim_{P \rightarrow 0} (\partial z / \partial P)_T$

+ $T > T_B$: $P \rightarrow 0 \rightarrow (\partial z / \partial P)_T > 0$

+ $T < T_B$: $P \rightarrow 0 \rightarrow (\partial z / \partial P)_T < 0$

Predict whether $z \uparrow$ or \downarrow with P at low pressures at specific T

If $\lim_{P \rightarrow 0} (\partial z / \partial P)_T < 0$, $T < T_B \rightarrow$ attractive part of potential dominates

if $\lim_{P \rightarrow 0} (\partial z / \partial P)_T > 0$, $T > T_B \rightarrow$ 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

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

rather than by T , P , V_m which can be very different for 2 gases that are in corresponding states

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

↳ not really universal because the material-dependent quantities enter through P_c , T_c , and V_{mc}

This law implicitly assumes that 2 parameters are sufficient to describe an intermolecular potential. This assumption is best for molecules that are nearly spherical

Calculated z using \downarrow as a function of P_r for different $T_r \rightarrow$ Graph

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

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

↳ predict critical compressibility is independent of the parameters a and b and should have same value for all gases (van der Waals)

$$\text{Redlich - Kwong} \rightarrow z_c = 0.333$$

7.5. Fugacity and the Equilibrium Constant for Real Gases

- f - fugacity - effective pressure that real gas exerts.

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

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

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

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

$$\ln f = \ln P + \int_0^P \frac{z-1}{P'} dP' \quad \text{or} \quad f = P e^{\int_0^P \frac{z-1}{P'} dP'}$$

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

↓
not const. ← fugacity coefficient

$$aA + bB \rightarrow cC + dD$$

$$K_f = \frac{P_c^c P_d^d}{(P_A)^a (P_B)^b}$$

$$\ln \bar{\gamma} = \ln \frac{f}{P} = \int_0^P \frac{z-1}{P'} dP'$$

PHASE DIAGRAMS AND THE RELATIVES STABILITY OF SOLIDS, LIQUIDS, GASES

3.1. What Determines the Relative Stability of the solid, liquid, and Gas Phases?

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

$$d\mu = dG_m = -S_m dT + V_m dP$$

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

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

$$V_m^{\text{gas}} \gg V_m^{\text{liquid}} > V_m^{\text{solid}}$$

↳ μ vs. T curve for gas changes much more rapidly compared to liquid and solid with P

↳ $P \uparrow$ → curves intersect shifts

+ $P \uparrow$, $V_m^{\text{gas}} \gg V_m^{\text{liquid}} > 0$ → boiling point elevation

+ $P \uparrow$, $V_m^{\text{liquid}} > V_m^{\text{solid}}$ → freezing point elevation

+ $P \uparrow$, $V_m^{\text{liquid}} < V_m^{\text{solid}}$ → freezing point depression

• $\uparrow T$, normal order solid → liquid → gas

• Gas-solid intersect at lower T than Gas-liquid intersect
→ favor solid → gas

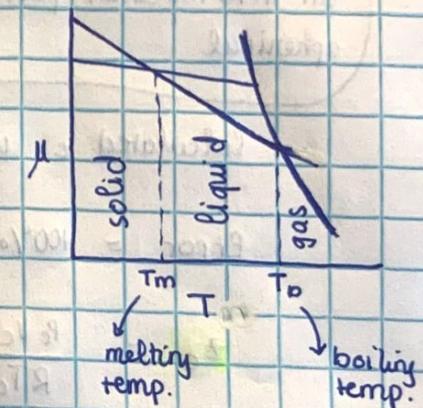
T_s - sublimation temperature

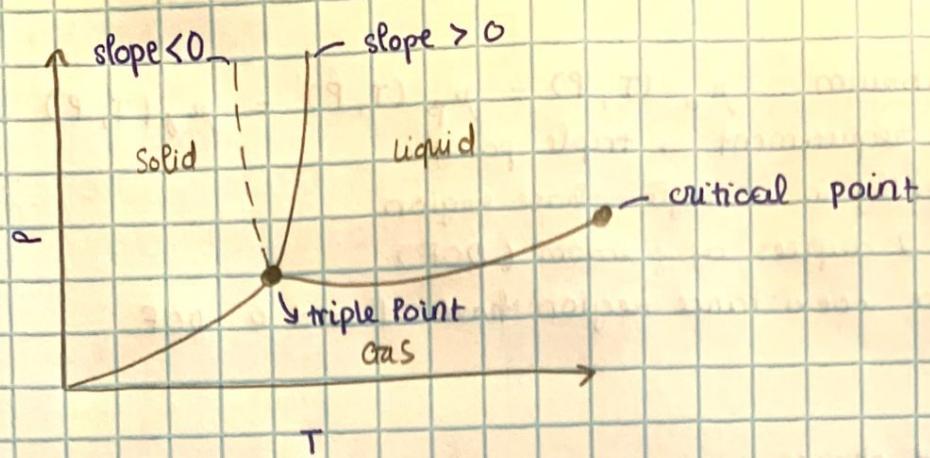
• 3 phases intersect → P, V_m, T : triple point

3.2. The Pressure - Temperature Phase Diagram

• P-T phase diagram

→ Coexistence curve - 2 phases coexist at equilibrium fall on a curve





Boiling point - temp at which $P_{\text{vapor of substance}} = P_{\text{external}}$

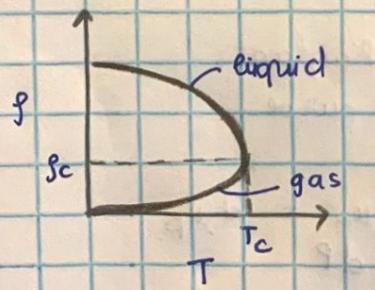
Standard $P = 1 \text{ bar}$

Normal $P = 1 \text{ atm}$

- Solid is more dense than liquid (most substances)
 - slope of solid-liquid coexistence curve is positive
 - $T_{\text{melting}} \uparrow$ with $P \uparrow$

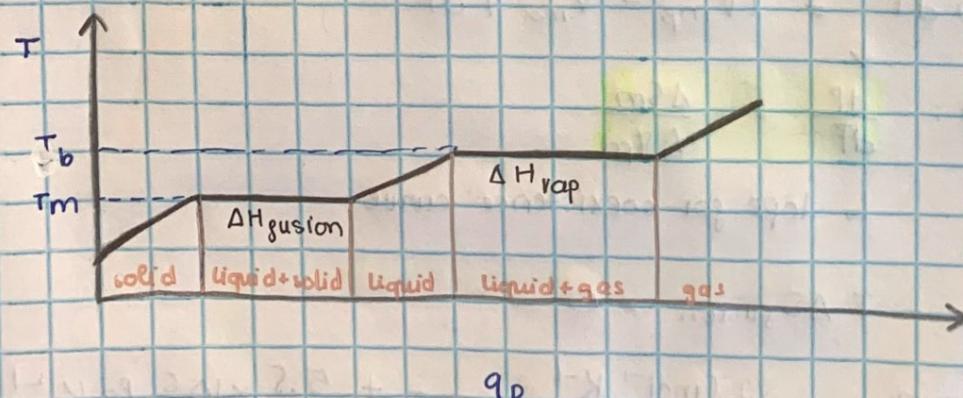
- Solid is less dense than liquid (H_2O)
 - slope of solid-liquid coexistence curve is negative
 - $T_{\text{melting}} \downarrow$ with $P \uparrow$

- Boiling point always increases with P



• liquid-gas curve ends at critical point
 $T > T_c$ | liquid and gas have same density
 $P > P_c$ | $\Delta H_{\text{vap}} \rightarrow 0$ as $T \rightarrow T_c$

↓
supercritical fluids



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

8.3. Phase Rule

- 3 phases coexist in equilibrium: $\mu_\alpha(T, P) = \mu_\beta(T, P) = \mu_\gamma(T, P)$
- ↳ 1 (T, P) satisfies this requirement → triple point
- T, P are varied independently in a single-phase region
→ pure substance has 2 degrees of freedom (DOF)
- 2-phase, 3-phase coexistence regions have 1 and 0 DOF
- For a pure substance

$$f = 3 - p$$

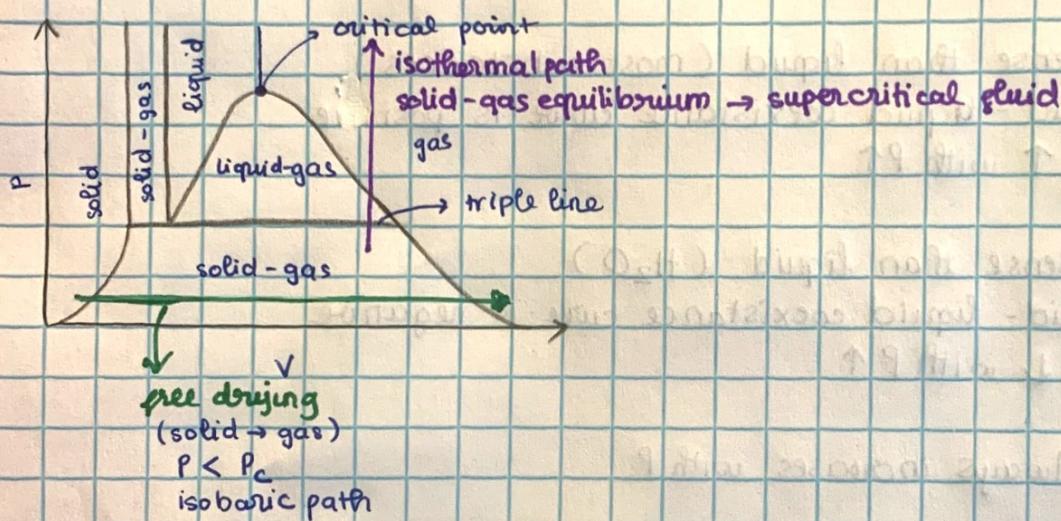
DOF # phases

+ No more than 3 phases in equilibrium $\rightarrow f > 0$

+ F↑ if system contains several chemically independent substances.

8.4. The Pressure - Volume and Pressure - Volume - Temperature Phase Diagram

- $V_m^{\text{liquid}} > V_m^{\text{solid}}$



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

- Small change, T and P still lie on the coexistence curve

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

In order for 2 phases to remain in equilibrium: $d\mu_\alpha = d\mu_\beta$

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

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

↓

(Raoult's) equation:
$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

↳ slope for coexistence curve

- Solid → liquid

$$\Delta G_{\text{fusion}} = \Delta H_{\text{fusion}} - T \Delta S_{\text{fusion}} = 0$$

$$\left(\frac{dP}{dT} \right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx \frac{22 \text{ J mol}^{-1} \text{ K}^{-1}}{\pm 4 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} = \pm 5.5 \times 10^6 \text{ Pa K}^{-1}$$

$$= \pm 5.5 \text{ bar K}^{-1}$$

- Liquid - Gas
 $\Delta V_{\text{vap}} = V_m^{\text{gas}} - V_m^{\text{liquid}} > 0$

$$\Delta S_{\text{vap}} \approx 90 \text{ J mol}^{-1} \text{ K}^{-1}$$

liquid has strong intermolecular interactions $\rightarrow \Delta S_{\text{vap}} > 90 \text{ J mol}^{-1} \text{ K}^{-1}$

$$V_m^{\text{gas}} \gg V_m^{\text{liquid}} \rightarrow \Delta V_{\text{vap}} \approx V_m^{\text{gas}} = 20 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$$

$$\left(\frac{dP}{dT} \right)_{\text{vap}} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} \approx \frac{95 \text{ J mol}^{-1} \text{ K}^{-1}}{20 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} = 4.8 \times 10^3 \text{ Pa K}^{-1} = 4.8 \times 10^{-2} \text{ bar K}^{-1}$$

- Solid \rightarrow Gas

$$\Delta V_{\text{vap}} = V_m^{\text{gas}} - V_m^{\text{solid}} \approx V_m^{\text{gas}} \quad (V_m^{\text{gas}} \gg V_m^{\text{solid}})$$

$$\Delta S_{\text{sub}} = \Delta S_{\text{gas}} + \Delta S_{\text{vap}} > \Delta S_{\text{vap}}$$

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

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

$$\int dP = \int \frac{\Delta S_{\text{gas}}}{\Delta V_{\text{gas}}} dT = \int \frac{\Delta H_{\text{gas}}}{\Delta V_{\text{gas}}} \frac{dT}{T} \approx \frac{\Delta H_{\text{gas}}}{\Delta V_{\text{gas}}} \int \frac{dT}{T}$$

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

Solid - liquid

- Liquid - Gas (assume ideal gas)

Clausius - Clapeyron equation

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

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

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

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

- Solid - Gas

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

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

partial P of water
in gas phase

Σ of vapor and water partial P

\downarrow = external pressure applied on
the system

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

vapor pressure
of water

8.8. Surface Tension

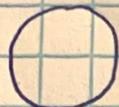
Helmholtz energy

$$dA = \gamma d\sigma \rightarrow \text{unit element of area}$$

surface tension

$$(J/m^2) \sim (N/m)$$

- Substance tends to minimize surface tension $\rightarrow dA < 0$ - spontaneous



$$\sigma = 4\pi r^2 \rightarrow d\sigma = 8\pi r dr$$

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

$\rightarrow F = 8\pi \gamma r$ - force which is normal to the surface of droplet

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

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

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

$\hookrightarrow \Delta P$ exists only for a curved surface

Higher P on concave side of the interface

- Capillary rise and capillary depression

$$h = \frac{2\gamma}{\rho g r}$$

- Liquid-surface is characterized by the contact angle θ

+ Complete wetting $\rightarrow \theta = 0$

+ Nonwetting $\rightarrow \theta = 90^\circ$

+ Intermediate

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

$$h = \frac{2\gamma \cos \theta}{\rho g r}$$

