

Reading HW #7
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Macroscopic Chemistry

Chapter 7: The Properties of Real Gases

7.1 Real Gases and Ideal Gases

Real Gas	Ideal Gas
• High Pressure	• Low Pressure
• Low Temperature	• High Temperature
• Interactions	• No interactions

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

a and b are parameters that must be experimentally determined for a given gas

- ↳ a = measure of strength of attractive part of intermolecular potential
- ↳ b = measure of minimum volume that a mole of molecules can occupy

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: More accurate

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

Battie-Bridgeman Equation of state:

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

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

Virial Equation of State

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

* most firmly grounded

* a series expansion always valid in its convergence range

* $B(T)$, $C(T)$, and so on are virial coefficients

IF $B(T)$ is negative, the attractive part of potential dominates at value T
positive, the repulsive

the value of V at which P becomes constant depends on T .

As the volume of the system is decrease further, the pressure suddenly increases rapidly as V decreases

$$\hookrightarrow P \uparrow \text{ so } V \downarrow$$

Temperature-dependent equilibrium pressure = vapor pressure of liquid
↳ as volume decreased further, system becomes single-phase

Temperature at range of V_m has shrunk to a single value is called critical temperature

When $T = T_c$, isotherm exhibits inflection point

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

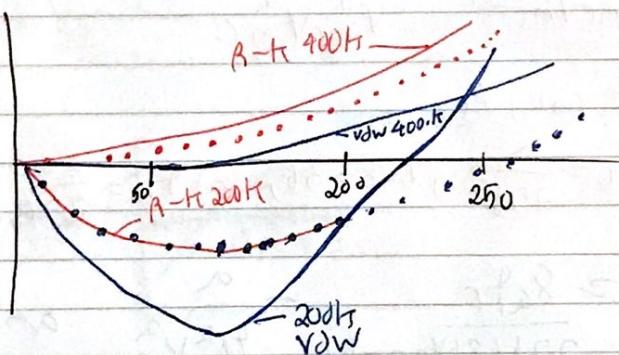
T_c, P_c , and V_c } critical constants that describe phase diagram of pure substance

parameters a and b for van der waals and Redlich-Kwong chosen to best represent real gas, can be done by using P, V , and T at critical points T_c, V_c , and P_c

7.3 The compression factor

$$z = \frac{v_m}{v_m^{\text{ideal}}} = \frac{PV_m}{RT}$$

- compression factor - z
- For ideal gas $z=1$ for all values P and V_m
- If $z > 1$ real gas exerts greater pressure than ideal gas
- If $z < 1$ real gas exerts smaller pressure than ideal gas for some values of T and V_m
- Compression factor for given gas is function of temperature
 - For $T=200\text{K}$, z decreases with pressure
 - For $T=400\text{K}$, z increases linearly with T



$$R-T = R_{\text{eff}} - T_{\text{vander}}$$

v_{dW} = vanderwaals

- accurate V_m values
for $R-T$

- accurate V_m values
for v_{dW}

Boyle Temperature, $T_B = \frac{a}{b}$
is different for each gas

At Boyle temperature both $z \rightarrow 1$ and $(\partial z / \partial P)_T \rightarrow 0$ as $P \rightarrow 0$
is exhibited by an ideal gas

It is only at $T=T_B$ that a real gas exhibits ideal behavior as $P \rightarrow 0$ with respect to $\lim_{P \rightarrow 0} (\partial z / \partial P)_T$

- Above Boyle temperature $(\partial z / \partial P)_T > 0$ as $P \rightarrow 0$
- Below Boyle temperature $(\partial z / \partial P)_T < 0$ as $P \rightarrow 0$

29

7.4 The Law of Corresponding States

$$\hookrightarrow T_r = T / T_c \quad (1)$$

$$P_r = P / P_c \quad (2)$$

$$V_{mr} = V_m / V_{mc} \quad (3)$$

If two gases have the same values of T_r , P_r , and V_{mr} they are in corresponding states, values of P , V , and T can be very different though for gases in corresponding states.

\hookrightarrow dimensionless reduced variables

Vander waals in corresponding states

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

\rightarrow replace T_c , V_{mc} , P_c

$$P_c = \frac{a}{27b^2}, V_{mc} = 3b, \text{ and } T_c = \frac{8a}{27Rb}$$

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

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

\hookrightarrow material-dependent quantities enter through values of P_c , T_c , and V_c ~~not a and b~~

$$\text{Error} = 100\% \approx \frac{2-1}{2}$$

7.5 Fugacity and the Equilibrium Constant for Real Gases

Value of the equilibrium constant for a mixture of reactive gases.

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

$$\text{Real Gas: } \mu(T, P) = \mu^\circ(T) + RT \ln \frac{f}{P^\circ}$$

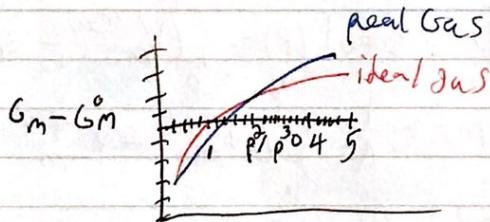
f = fugacity, viewed as the effective pressure that a real gas exerts

$$G_m^{\text{real}} < G_m^{\text{ideal}}$$

and $f < P$ \Rightarrow attractive range of intermolecular potential

$$G_m^{\text{real}} > G_m^{\text{ideal}}$$

and $f > P$ \Rightarrow repulsive range of intermolecular potential



Fugacity of gas has limiting behavior that $f \rightarrow P$ as $p \rightarrow 0$

f° - value fugacity would have if gas behaved ideally at 1 bar pressure
 $\hookrightarrow f^\circ = P^\circ$

Real Gas or Ideal Gas at constant Temp

$$\hookrightarrow dG_m = V_m dP$$

Therefore

$$d\mu_{\text{ideal}} = V_m^{\text{ideal}} dP$$

$$d\mu_{\text{real}} = V_m^{\text{real}} dP$$

Since $v_m^{\text{ideal}} \neq v_m^{\text{real}}$ chemical potential of real gas will change
strongly with pressure than the chemical potential of ideal gas

\hookrightarrow difference from Ram

$$\hookrightarrow \Delta \mu_{\text{real}} - \Delta \mu_{\text{ideal}} = (v_m^{\text{real}} - v_m^{\text{ideal}}) dP$$

integrate

$$\hookrightarrow \int_{P_i}^P (\Delta \mu_{\text{real}} - \Delta \mu_{\text{ideal}}) dP = [\mu_{\text{real}}(P) - \mu_{\text{real}}(P_i)] - [\mu_{\text{ideal}}(P) - \mu_{\text{ideal}}(P_i)]$$

$$\hookrightarrow \int_{P_i}^P (v_m^{\text{real}} - v_m^{\text{ideal}}) dP$$

Let $P_i \rightarrow 0$, $\mu_{\text{real}}(P_i) = \mu_{\text{ideal}}(P_i)$

$$\hookrightarrow \mu_{\text{real}}(P) - \mu_{\text{ideal}}(P) = \int_0^P (v_m^{\text{real}} - v_m^{\text{ideal}}) dP$$

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

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

$$\text{or } f = \gamma(P, T) P$$

Fugacity coefficient = dependent on P and T

Chapter 8 : Phase Diagrams and the Relative Stability of Solids, Liquids, and Gases

8.1 What Determines the Relative Stability of Solid, Liquid, and Gas phases

Phase - form of matter that is uniform with respect to chemical composition and the state of aggregation on both microscopic and macroscopic scales

Stability at constant temp and pressure is Gibbs Energy $G(T, P, n)$

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

n = number of moles of substance in the system

$$\delta \mu = -S_m dT + V_m dp \rightarrow \text{differential } (d\mu = \delta G_m)$$

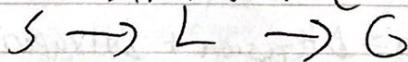
$\hookrightarrow \mu$ varies with changes in P and T

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

μ decreases as temp increases

μ increases as pressure increases

Endothermic (heat absorbed) $\Delta H > 0$



\hookleftarrow Exothermic (heat released) $\Delta H < 0$

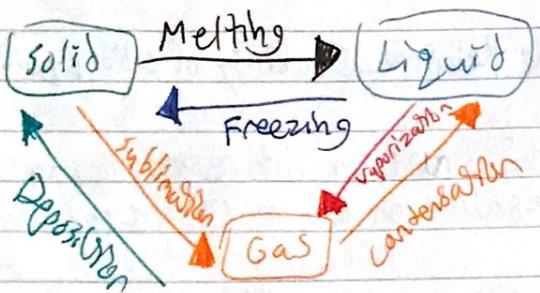
$S \rightarrow L \rightarrow G$, T increases so P explained by $\left(\frac{\partial \mu}{\partial T} \right)_P = -S_m$ and

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

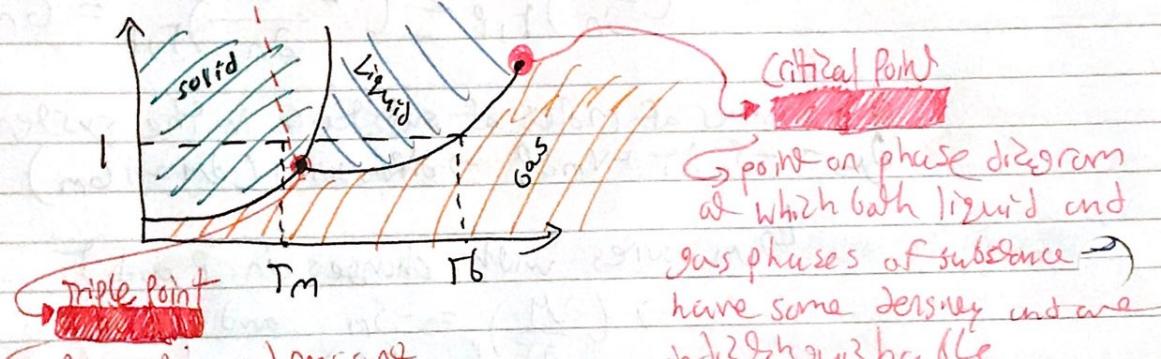
$V_m^{\text{gas}} >> V_m^{\text{liquid}} > 0$, increasing P = boiling point elevation

$V_m^{\text{liquid}} > V_m^{\text{solid}}$, increase P = freezing point elevation

$V_m^{\text{liquid}} < V_m^{\text{solid}}$, increase P = freezing point depression



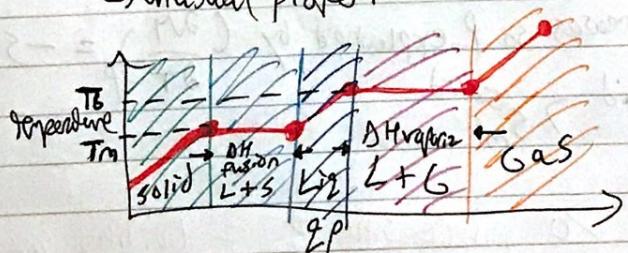
8.2 The pressure-temperature phase diagram



Temperature and pressure at which the solid, liquid, and vapor phases of a pure substance can coexist in equilibrium

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

Supercooled fluids $\Rightarrow T > T_c$ and $P > P_c$
 ↳ unusual properties



8.3 The Phase Rule

Coexistence of two phases

$$n_d(T, P) = m_p(T, P)$$

Three coexist in equilibrium

$$n_d(T, P) = m_p(T, P) = m_g(T, P)$$

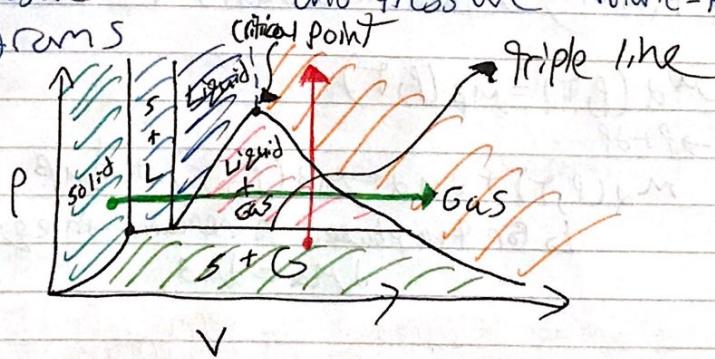
System of pure substance = two degrees of freedom

J.W. Gibbs derived phase rule = links number of degrees of freedom to the number of phases in a system at equilibrium

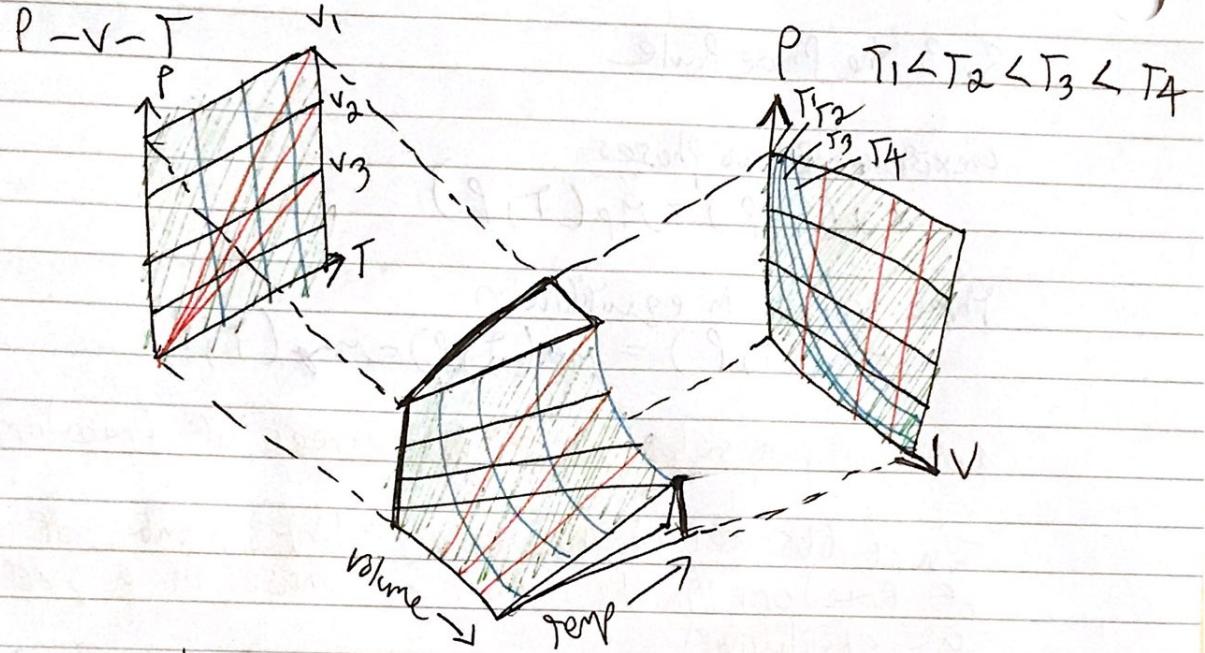
\hookrightarrow pure substance $F = 3 - P \rightsquigarrow$ number of phases

$F = \text{degrees of freedom}$

8.4 The Pressure-volume and pressure-volume-temperature phase diagrams



P-V diagram displays single and two phase coexistence regions, a critical point, and a triple line.



$P-V-T$ diagram for ideal gas. Constant pressure, constant volume, and constant temperature paths are shown as gray, red, and blue curves, respectively.

8.5 Providing a theoretical basis for the $P-T$ phase Diagram

$$d\mu(P, T) = \mu_B(P, T)$$

$P, T \rightarrow P + dP$

$$d\mu_d(P, T) + d\mu_d = \mu_B(P, T) + d\mu_B$$

For two phases to remain in equilibrium

$$d\mu_d = d\mu_B$$

Because $d\mu$ can be expressed in terms of dT and dP

$$d\mu_d = -S_{pd}dT + V_{pd}dP \quad \text{and} \quad d\mu_B = -S_{Bd}dT + V_{Bd}dP$$

$d\mu$ can be equated giving

$$(S_{pd} - S_{Bd})dT = (V_{pd} - V_{Bd})dP \quad \text{or}$$

$$-S_{pd}dT + V_{pd}dP = -S_{Bd}dT + V_{Bd}dP$$

Claudey-Ron equation

$$\frac{\partial P}{\partial T} = \frac{\Delta S_m}{\Delta V_m} = \frac{S_{ab} - S_{md}}{V_{mp} - V_{md}}$$

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

$$\left(\frac{\partial P}{\partial T}\right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx \frac{22 \text{ J/m K}}{\pm 4.0 \times 10^{-6} \text{ m}^3/\text{m}}$$

$$= \pm 5.5 \times 10^6 \text{ Pa K}^{-1} \approx \pm 55 \text{ bar K}^{-1}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\text{vaporization}} = \frac{\Delta S_{\text{vaporization}}}{\Delta V_{\text{vaporization}}} \approx \frac{95 \text{ J/m}^2 \text{ K}^{-1}}{\frac{2 \times 10^{-2} \text{ m}^3}{2 \times 10^{-2} \text{ m}^3} \text{ mol}^{-1} \text{ K}^{-1}} \approx 4.8 \times 10^3 \text{ Pa K}^{-1}$$

8.6 Using Clausius-Claudey-Ron Equation to calculate vapor pressure as a function of T

$$\left. \begin{array}{l} p_f \\ p_i \end{array} \right\} \frac{\partial P}{\partial T} = \left. \begin{array}{l} T_f \\ T_i \end{array} \right\} \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \frac{\partial T}{\partial T} = \int_{T_i}^{T_f} \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{\partial T}{T} \ln \frac{P_f}{P_i} = \int_{T_i}^{T_f} \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{1}{T} dT$$

simplified

$$P_f - P_i = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \frac{T_f}{T_i} = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \underbrace{\ln \frac{T_f}{T_i} + \Delta P}_{T'_i} \approx \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{\Delta T}{T_i}$$

Clausius-Claudey-Ron Equation:

$$\frac{\partial P}{\partial T} = \frac{\Delta S_{\text{rap}}}{\Delta V_{\text{rap}}} \approx \frac{\Delta H_{\text{rap}}}{\Delta V_{\text{das}}} = \frac{P \Delta H_{\text{rap}}}{R T^2}$$

$$\frac{\partial P}{P} = \frac{\Delta H_{\text{rap}}}{R} \frac{dT}{T^2}$$

$$\left. \begin{array}{l} p_f \\ p_i \end{array} \right\} \frac{\partial P}{P} = \frac{\Delta H_{\text{rap}}}{R} \times \int_{T_i}^{T_f} \frac{dT}{T^2}$$

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

8.7 The vapor pressure of a pure substance depends on the Applied pressure

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

↳ respect to p

$$\Rightarrow \left(\frac{\partial n_{\text{liquid}}(T, p)}{\partial p} \right)_T = \left(\frac{\partial n_{\text{gas}}(T, p)}{\partial p} \right)_T \left(\frac{\partial p}{\partial p} \right)_T$$

Since $\Delta_n = -S_m \Delta T + V_m \Delta P$, $(\Delta n / \Delta P)_T = V_m$

$$\sqrt{\frac{V_m^{\text{liquid}}}{m}} = V_m^{\text{gas}} \left(\frac{\partial P}{\partial P} \right)_T \quad \text{or} \quad \left(\frac{\partial P}{\partial P} \right)_T = \frac{\sqrt{V_m^{\text{liquid}}}}{V_m^{\text{gas}}}$$

$$R \int \frac{\partial P}{P} = \sqrt{\frac{V_m^{\text{liquid}}}{m}} \partial P \quad \text{or} \quad R \int_{P^*}^P \frac{dP'}{P'} = \sqrt{\frac{V_m^{\text{liquid}}}{m}} \int_{P^*}^P dP'$$

↳ integrate above ↑

Result

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

Note: $P^ = 3.16 \times 10^3 \text{ Pa}$

equilibrium vapor pressure
of water at 25°C

$$V_m^{\text{liquid}} = 1.81 \times 10^{-5} \text{ m}^3/\text{mol}$$

$$\ln \left(\frac{P}{P^*} \right) = \frac{\sqrt{\frac{V}{m}} (P - P^*)}{RT}$$

$$P = 1 \text{ bar}$$

$$P^* = 0.0316 \text{ bar}$$

$$= \frac{1.81 \times 10^{-5} \text{ m}^3/\text{mol} \times (1 - 0.0316 \times 10^5 \text{ Pa})}{8.314 \text{ J/mol K} \times 298 \text{ K}}$$

$$\approx 7.04 \times 10^{-4}$$

$$P = 1,000 \times P^* \approx 0.0316$$

8.8 Surface Tension

↳ (N/m) acting force over the surface of the liquid per unit length of the surface perpendicular to the force

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

$$\Delta A = \gamma \Delta \theta$$

↳ ΔA is helmholtz energy

↳ γ is surface tension

↳ $\Delta \theta$ unit element of area

$\Delta A < 0$ For spontaneous process at constant V and T

If droplet radius increases r to $r + dr$, area increases by dA

$$\theta = 4\pi r^2 \text{ so } d\theta = 8\pi r dr$$

$$\frac{d\theta}{dr} \xrightarrow{\text{take derivative}} \frac{8\pi r}{2}$$

work done in expansion of droplet $= 8\pi r \gamma r dr$

Normal force w/distance $= 8\pi r \gamma r$

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

Net effect of force: $4\pi r^2 P_{\text{outer}} + 8\pi r \gamma r = 4\pi r^2 P_{\text{inner}}$ or

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

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

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

Capillary rise — liquid above the level of zero pressure due to net upward force by attraction of H₂O molecules to solid surface

capillary depression — where liquid does not wet walls of container

Capillary rise/depression Equation:

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

Contact angle — liquid-surface, difference in surface tension at solid-liquid interface

Intermediate cases

↪ complete wetting $\theta = 0^\circ$

↪ nonwetting, complete $\theta = 180^\circ$

$$P_{inner} = P_{outer} + \frac{2\gamma \cos \theta}{r} \quad \text{and} \quad h = \frac{2\gamma \cos \theta}{\rho g r}$$

High tensile strength — water supply to top of surface