Ideal gases equation has assumed to be accurate to describe P-V-T relationship for a real gas

Real gas cannot be compressed to a volume that is less than the total molecular volume.

$\uparrow$ Density $\downarrow$ Temp $\Rightarrow$ molecular interaction can't be neglected.

2.21 Equations of State for Real Gases and Their Range of Applications

Real gas equations

$\Rightarrow$ 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

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

Beattie-Bridgeman equation state.

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

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

Viral equation of state.

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

Critical Temperature → range of V_m has shrunk to a single value → T_c.

$P_c \} V_c$ → Critical Constants → describe the phase diagram of pure substance.

Maxwell Construction - generate isotherms

7.3 | The Compression Factor

- Compression factor

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

Boyle temperature, T_b

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

7.4] The law of corresponding states

law of corresponding states — If 2 gases have the same values of T_i, P, and V_m, they are corresponding states.

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

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

7.5] Fugacity and Equilibrium Constant for real Gases

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

$f \rightarrow$ fugacity of the gas.

$\hookrightarrow$ Effective pressure that a real gas exerts.

$$\ln f = \ln P_t \int_0^P \frac{z-1}{P'}$$

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

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

fugacity coefficient $\rightarrow$. f and P are
related proportionally factor γ.

8.[ ] What determines the Relative Stability of solid, Liquid and Gas phases?

phase → A form of matter that is uniform with respect to chemical composition and the state of aggregation

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

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

$V_m^{gas} >> V_m^{liquid} > V_m^{solid} \geq 0$, $\uparrow P$ leads to boiling point elevation

$\uparrow P$ leads to freezing point elevation if $V_m^{liquid} > V_m^{solid}$ and to freezing point depression if $V_m^{liquid} < V_m^{solid}$

energetically favored with respect to the solid → gas transition at this pressure

Solid Sublimes and a transition temperature. Ts is called the sublimation temperature.

The P, V_m T for this point Spectrally.
the triple point.

[8.2]. The pressure - temperature Phase diagram.

Phase diagram — it displays the information graphically.

P, V, T construct phase diagrams

$P-T$ phase diagram → Stability regions for a pure substance as a function of pressure and temperature.

All P, T points for the same 2 phases coexist at equilibrium fall on a curve → co existence curve.

Standard boiling temp — temp. at which the vapor pressure of the substance is 1 bar.

Normal boiling temp — temp at which the vapor of the substance is 1 atm

Along 2-phase curves in which one of the coexisting phases is the gas. P_i refers to the vapor pressure.

liquid-sold. coexistance curve extends indefinitely round gas curve ends at the Critical point → $T = T_c$ & $P = P_c$

$T > T_c$ & $P > P_c$ are Superficial fluids

8.3 | Phase Rule

$$N_a (T,P) = N_b (T,P) = N_c (T,P)$$

T & P can be varied independently in a single region a system of pure substance has 2 degrees of freedom

Phase rule → links the # of degrees of freedom to the # of phases in a system

8.4 | The pressure - volume and pressure - volume - Temp. phase diagrams.

P-T phase diagram with a P-V phase diagram → combine two representations into a P-V-T. phase diagram.
└ 3 Dimension

8.5 | Providing a Theoretical Basis for the P-T. phase diagram

Clapeyron equation. $\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$

Trouton's rule - $\Delta S_{vaporization} \approx 90 \text{ J/mol K}$. for liquids.

8.6 | Using the Clausius - Clapeyron Equation to. Calculate vapor pressure as a function of T.

Clausius - Clapeyron- equation.

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

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

8.7 - The vapor pressure of a pure substance Depends on the Applied Pressure

$$\mu_{liq}(T,P) = \mu_{gas}(T,P)$$

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

$$\frac{RT}{P}dP = V_m^{liquid}dP \quad \text{or} \quad RT\int_{P'}\frac{dP'}{P'}$$

$$= V_m^{liquid}\int_P^{P'}dP$$

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

8.8 Surface Tension

$$dA = \gamma d\sigma$$

Surface Tension $\rightarrow$ energy/area   or J/m^2

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

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

$$4\pi r^2 P_{outside} \cdot 8\pi r \gamma = 4\pi r^2 P_{inner} \rightarrow P_{inner} = P_{out} + \frac{2\sigma}{r}$$

Capillary rise and capillary depression
are consequences of the pressure
differential across a curved surface.

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

liquid-surface is characterized by
the contact angle, θ.

complete wetting corresponds to
$\theta = 0°$. and complete non wetting
corresponds to $\theta = 180°$

$$P_{inner} = P_{out} + \frac{2\gamma \cdot \cos\theta}{r \cdot g \gamma r}$$

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