

George Paxos Reading HW >

7.1 Real Gases and Ideal Gases

Interactions of real gasses can higher or lower pressure than an ideal gas at the same density and temperature.

We are trying to determine what factors affect this.

7.2 Equations of State for Real Gases and their range of Applicability

VanderWaals equation of state

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

Redlich-Kwong equation of state

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

P = Pressure

V = volume

V_m = molar volume

n = moles

T = temp.

C = concentration

b = repulsive forces (volume)

a = attractive forces (intermolecular forces)

R = ideal gas constant

Bartle-Bridgeman equation of state

$$P = \frac{RT}{V_m} \left(1 - \frac{C}{V_m T^3}\right) (V_m + B) - \frac{A}{V_m^2} \quad A = A_0 \left(1 - \frac{a}{V_m}\right)^{\text{one}} \quad B = B_0 \left(1 - \frac{b}{V_m}\right)$$

Virial equation of state Taylor Series in $\frac{1}{V_m}$

$$P = RT \left[\frac{1}{V_m} + \frac{BCT}{V_m^2} \dots \right]$$

Ideal gas law has limited use because it does not predict that a gas can be liquefied under appropriate conditions

+ temp. dependent eq. pressure is called vapor pressure

(T_c) Critical Temperature = temp. at which the range for V_m is a single value

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

[A supercritical fluid is a substance where the gas and liquid phases are not distinguishable
happens at P_c and V_c, T_c [critical constants]]

7.3 Compression factor

Compression factor $\bar{z} = \frac{V_m}{V_{\text{ideal}}} = \frac{PV_m}{R+T}$

V = volume
 P = pressure
 T = temp.

$\bar{z} = 1$ for ideal gasses

$\bar{z} > 1$ real gas exerts more pressure

$\bar{z} < 1$ real gas exerts less pressure

\bar{z} is a function of temperature

$\bar{z} \uparrow$ linearly to T

for P

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

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

vanderwaals eq predicts slope of z vs p to equal 0 if $b = a/RT$. Corresponding temp is

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

for $T >> T_B$ always positive because repulsive forces are favored

for $T < T_B$ always negative because attractive forces are favored

7.4 The Law of Corresponding States

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

Reduced T, P, V_m Critical T, P, V

The above expression is known as ^{the} law of corresponding states

If T_r , V_{mr} , and P_r are the same for two gasses they are in the same state.

a and b removed because we are using reduced variables

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

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

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

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

law of corresponding states only good for spherical molecules and not good for dipolar molecules because intermolecular potential is not only described by a and b

We calculate z using different values of T_r and P_r in order to account for error in van der Waals law

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

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

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

7.5 Fugacity and Eq. Constant for Real Gases

For a real gas

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

f = fugacity
 = effective pressure of a real gas

attractive force
 dominates

$$G_m^{\text{real}} < G_m^{\text{idéal}} \quad f < P$$

repulsive force
 dominates

$$f \rightarrow P \text{ as } P \rightarrow 0$$

$$\ln f = \ln P + \int_0^P \frac{z-1}{P'} dP' \text{ or } f = P \exp \left[\int_0^P \left(\frac{z-1}{P'} \right) dP' \right] \\ = f = \gamma(P, T) P$$

We can know f if we know z

fugacity coefficient = γ

\hookrightarrow relates f and P

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

Gibbs, $G(T, P, n)_{T, P}$

Chemical potential = $\mu = \left(\frac{\partial G}{\partial n} \right)_{T, P} = \left(\frac{\partial \ln G_m}{\partial n} \right)_{T, P} = \bar{G}_m$

G = Gibbs energy

$n = \text{moles}$

$$\Delta \mu = \bar{G}_m$$

$$\Delta \mu = -S_m \Delta T + V_m \Delta P$$

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

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

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S_m$$

T changes fast \Rightarrow may not be reacted
BP elevation:

$\uparrow P$ always \uparrow Boiling point

freezing point elevation

if $V_m^{\text{liq}} > V_m^{\text{solid}}$, when $P \uparrow$ FP \uparrow

Freezing point depression

if $V_m^{\text{liq}} < V_m^{\text{solid}}$, when $P \uparrow$ FP \downarrow

The P , V_m , T values for the intersection of all 3 phases on the μ graph represent the triple point



Critical point $T = T_c$, $P = P_c$

Supercritical fluid $= T > T_c$, $P > P_c$

8.2 The Pressure-Temp. Phase diagram

Phase diagram relates P , T , and V to state

Coexistence curve shows where solid-liquid, solid-gas, and liquid-gas exist

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

Normal boiling temp. is the temp. at which the vapor pressure is 1 atm.

Critical point: $T \geq T_c$, $P = P_c$

Supercritical fluid: $T > T_c$, $P > P_c$

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

Phase diagrams are useful for identifying ΔH and understanding how different conditions affect our system

8.3 The Phase Rule

$$f_a(T, P) = f_b(T, P)$$

Pure substances have two degrees of freedom (T and P)

The system has 2 and 3 phase coexistences have one and zero degrees of freedom respectively

Phase rule

$$F = 3 - P$$

↗ ↑
 degrees of freedom Phases

8.4 The pressure-Volume and pressure-Volume-Temperature phase diagram

P-V phase diagram
and P-V-T

$$V_m^{\text{solid}} < V_m^{\text{lif}} \ll V_m^{\text{gas}}$$

Smaller range larger range

going from solid \rightarrow solid + gas \rightarrow gas
is called freeze drying done at -10°C

The P-V-T graph shows how all 3 variables change and effect pressure (change)

8.5

Providing a theoretical basis for the P-T phase diagram

$$\mu_A(P, T) = \mu_B(P, T)$$

$$d\mu_A = d\mu_B$$

$$d\mu_A = S_{mA}dT + V_{mA}dP \text{ and } d\mu_B = -S_{mB}dT + V_{mB}dP$$

$$(S_{mB} - S_{mA})dT = (V_{mB} - V_{mA})dP$$

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

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

Solid-liquid
curve:

$$\left(\frac{dP}{dT}\right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx \pm 55 \text{ bar k}^{-1}$$

Liquid-gas
curve

$$\left(\frac{dP}{dT}\right)_{\text{vap.}} \approx \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} \approx 4.8 \times 10^{-2} \text{ bar k}^{-1}$$

The curves slope will ↑ with an ↑ T, ΔS↑,
 $\Delta V \downarrow$, P↑

78.8

8.8 Using the Clausius - Clapeyron Eq. to calculate vapor pressure as a function of T

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

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

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

$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta H_{\text{vap}}}{R} + \int_{T_i}^{T_f} \frac{dT}{T^2}$$

~~Clausius
Clapeyron
equation~~

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

8.7 The Vapor Pressure of a pure substance depends on the Applied Pressure

P here is partial pressure of water in gas phase

$$P = \text{water partial pressure} \quad \mu_{\text{liq}}(T, P) = \mu_{\text{gas}}(T, P)$$

$$P = \text{argon partial pressure} \quad \left(\frac{\partial \mu_{\text{liq}}(T, P)}{\partial P} \right)_T = \left(\frac{\partial \mu_{\text{gas}}(T, P)}{\partial P} \right)_T + \left(\frac{\partial P}{\partial P} \right)_T$$

or

$$\frac{V_m^{lif}}{2} = V_m^{\text{gas}} \left(\frac{\partial P}{\partial P} \right)$$

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

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

8.8 Surface Tension

$$dA = \gamma d\sigma \quad \begin{matrix} \text{unit element for area} \\ \uparrow \\ \text{Helmholtz energy} \end{matrix} \quad \begin{matrix} \uparrow \\ \text{Surface tension } \left(\frac{N}{m} \right) \text{ or } \left(\frac{J}{m^2} \right) \end{matrix}$$

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

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

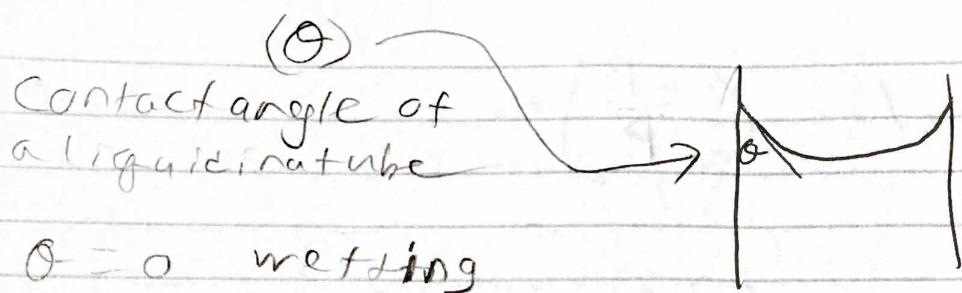
$$4\pi r^2 P_{\text{outer}} + 8\pi \gamma r = 4\pi r^2 P_{\text{inner}}$$

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

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

capillary rise
capillary depression

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



$\theta = 0$ wetting

$\theta = 180$ nonwetting

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

tensile strength of liquid \rightarrow inward can repel on a water column to create negative pressure before it breaks