

Ch. 7 Properties of Real Gases

7.1 Real gases and ideal gases

- real gas cannot be compressed to a volume that is less than the total molecular volume
- molecules in a real gas do interact w/ one another, through a potential

7.2 equation of state for real gases + their range

vander waals eqn 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 eqn of state: $p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m(V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2 a}{\sqrt{T} V(V + nb)}$

- more accurate!

Beattie-Bridgeman eqn of state: $p = \frac{RT}{V_m^2} \left(1 - \frac{C}{V_m} \right) (V_m + B) - \frac{A}{V_m^2}$ with

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

Virial eqn of state: $p = RT \left[\frac{1}{V_m} + \frac{B(T)}{V_m^2} + \dots \right]$

vapor pressure: temperature dependent equilibrium pressure

critical temp T_c : temp @ which the range of V_m has shrunk to a single value

T_c, p_c, V_c are critical constants!

7.3 compression factor

compression factor Z : $Z = \frac{V_m}{V_{ideal}} = \frac{pV_m}{RT}$

initial slope of Z vs p curve is 0 if $b = a/RT$

Boyle temp: $T_b = \frac{a}{Rb}$



2

only @ $T = T_B$ does a real gas exhibit ideal behavior as $P \rightarrow 0$ with $\lim_{P \rightarrow 0} (\partial Z / \partial P)_T = 0$.

Above T_B : $(\partial Z / \partial P)_T > 0$ as $P \rightarrow 0$

Below T_B : $(\partial Z / \partial P)_T < 0$ as $P \rightarrow 0$

- helps us predict whether $Z \uparrow$ or \downarrow w/ P at low pressures for a given value of T

If $\lim_{P \rightarrow 0} (\partial Z / \partial P)_T < 0$ $T < T_B$ and attractive part of the potential dominates.

If $\lim_{P \rightarrow 0} (\partial Z / \partial P)_T > 0$ $T > T_B$ and repulsive part of the potential dominates

1.4 Law of corresponding states

- real gases differ in value of molecular volume + in depth of attractive potential.

law of corresponding states

If 2 gases have the same values of T_r , P_r , and V_{mr} , they are in corresponding states

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

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

1.5 Fugacity and the equilibrium constant for real gases

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

f = fugacity: effective pressure
 $f \rightarrow P$ as $P \rightarrow 0$

f^c = standard state $=$ value that fugacity would have if gas behaved ideally @ 1 bar pressure

For any gas at constant T: $dG_m = V_m dp$

$$d\mu_{ideal} = V_m^{ideal} dp$$

$$d\mu_{real} = V_m^{real} dp$$

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

ch 8: phase diagrams and relative stability of s, l, g

8.1 what determines relative stability?

Phase: form of matter that is uniform w/ chemical composition and state of aggregation on micro + macroscopic levels.

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -S_m \quad \text{and} \quad \left(\frac{\partial \mu}{\partial p} \right)_T = V_m \quad \text{④ } \mu \downarrow \text{ as Temp } \uparrow$$

entropy of phases: $S_m^{gas} > S_m^{liquid} > S_m^{solid}$

\uparrow in P \rightarrow freezing point elevation if $V_m^{liquid} > V_m^{solid}$

\uparrow in P \rightarrow freezing point depression if $V_m^{liquid} < V_m^{solid}$

solid \rightarrow gas sublimation! sublimation temp = T_s

Triple point: point where all 3 phases coexist in equilib

8.2 pressure-temp phase diagram

p-T diagram displays stability region for a pure substance as a function of p & T

Coexistence curve: where 2 phases coexist in equilib
 standard boiling temp: temp @ which vapor pressure of substance is 1 bar

normal boiling temp: temp @ which the vapor pressure of substance is 1 atm.

- along 2 phase curves: p = vapor pressure
- Liquid-gas curve ends @ critical point $T = T_c$ $P = P_c$
- supercritical fluids: substances for which $T > T_c$ and $p > P_c$
- ★ look @ figure ★

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

8.3 Phase Rule

$$\mu_{\alpha}(T, P) = \mu_{\beta}(T, P) = \mu_{\gamma}(T, P)$$

Because T and P can be varied independently in a single phase region, a system of pure substances has 2 degrees of freedom. two phase coexistence region: 1 d.o.f
3-phase coexistence region: 0 d.o.f

pure substance phase rule

$$F = 3 - P$$

\uparrow \uparrow
 # d.o.f number of phases

8.4 p-V and p-V-T phase diagrams

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

freeze drying = food dehydrated @ low temp @ which the food is not cooked

8.5 Thermodynamic Basis for P-T phase diagram

Claapeyron eqn: $\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$

slope of s-l coex. curve: $\left(\frac{dp}{dT}\right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx \pm 55 \text{ bar/K}^{-1}$

Trouton's rule: $\Delta S_{\text{vap}} \approx 90 \text{ J/mol K}$

slope of l-g coex. curve: $\left(\frac{dp}{dT}\right)_{\text{vap}} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} = 4.8 \times 10^{-2} \text{ bar/K}$

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

$(dp/dT)_{\text{sublimation}} > (dp/dT)_{\text{vaporization}}$

8.6 calc vapor p as function of T

$\int_{p_i}^p \frac{dp}{p} = \frac{\Delta H_{\text{vap}}}{R} \times \int_{T_i}^{T_f} \frac{dT}{T^2}$

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

- The above equation shows the variation of vapor pressure of the liquid w/ temperature and assuming that ΔH_{vap} remains constant over the range of temperature

8.7 vap pressure of a pure substance depends on Applied Pressure

• piston and cylinder assembly

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

$p = 1 \text{ bar}$

vapor pressure of a pure substance depends on applied pressure

8.8. Surface tension

work associated w/ creation of additional surface area @ constant V and T : $dA = \gamma d\sigma$

Surface tension unit: N/m

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

or

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

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

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

contact angle θ characterizes the liquid surface

complete wetting: $\theta = 0^\circ$
nonwetting: $\theta = 180^\circ$

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

8.9 Chemistry in supercritical fluids

SCTs

- have high density
- exhibit favorable properties of L & G
- solubility is high
- lower viscosity
- more gas-like than liquid

8.10 Liquid crystal displays

glass: liquids of high viscosity that cannot achieve equilib. on a human lifetime

- liquid crystals : have properties intermediate between liquids + solids

- Twisted nematic phase

- LCD lights + sensor strips

LCD display: twisted nematic liquid crystal film b/w
2 transparent conducting electrodes