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Thermodynamics

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Reading Homework 7.

7.1- Real Gases and Ideal Gases

Ideal Gas Equation of State

- ↳ Describe the P-V-T relationship for a real gas
- ↳ Allowed calculations of expansion works and K_p in terms of partial pressures

Microscopic Model on which the ideal gas law is based on

- ↳ Gas molecules are point masses: Real gasses cannot be compressed to a volume that is less than the total molecular volume.
- ↳ Gas molecules do not interact: Real gasses do interact with one another through a potential. However the P-V-T relationship of a real gas is the same as that for an ideal gas @ sufficient ↓ densities and ↑ temps.

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

Van der Waals equation of state - One of the real gas equations of state.

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

Redlich-Kwong equation of state - Another real gas equations of state

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

↳ Where a is a measure of the strength of the attractive ^{Part} force of the intermolecular potential

↳ Where b is a measure of the ~~minimum~~ ^{minimum} volume that a mole of molecules can occupy.

Beattie-Bridgeman equation of state - The third real gas equation of state

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

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

Viral Equation of State - Written in the form of a power series in $\frac{1}{V_m}$

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

\hookrightarrow where $B(T)$, $C(T)$, and so on are called the second, third, and so on viral coefficients.

\hookrightarrow This equation is usually terminated after the second viral coefficient because values for the higher coefficients are not easily obtained from experiments.

\hookrightarrow If $B(T) < 0$, the attractive part dominates the value of T & vice versa.

$\hookrightarrow B(T)$ can be expressed as $B(T) = b - (a/RT)$.

Vapor Pressure - The temperature-dependent equilibrium pressure

Critical Temperature - The temperature at which the range of V_m has shrunk to a single value.

\hookrightarrow The isotherm exhibits an inflection point so that

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

\hookrightarrow When the system approaches the critical point the density of molecule in (l) \downarrow and the density of molecules in (g) \uparrow , and at $T=T_c$ the densities are equal.

Critical Constants - Corresponding values of P_c and V_c that take on particular significance in describing the phase diagram of a pure substance.

\hookrightarrow Parameters a and b for the van der Waals and Redlich-Kwong equations of state can best describe real gas data by using the values of P , V , and T @ critical points T_c , P_c , and V_c .

$V_{\text{waals equation}}$	$\hookrightarrow a = \frac{27R^2T_c^2}{64P_c}$	$\hookrightarrow a = \frac{R^2T_c^{5/2}}{9P_c(2^{11/3}-1)}$	} R.W equation
	$\hookrightarrow b = \left(\frac{8RT_c}{3P_c} \right)$	$\hookrightarrow b = \frac{(2^{11/3}-1)RT_c}{3P_c}$	

Maxwell Construction - Below T_c , all calculated isotherms have an oscillating region that is unphysical because $V \uparrow$ as $P \uparrow$. In this construction, the oscillating region is replaced by a horizontal line for which the areas above and below the line are equal:

$\left[\begin{array}{l} \text{Van der Waals} \\ \text{Reproduce P-V isotherms for real} \\ \text{gases only in the single-phase gas} \\ \text{region } T > T_c \text{ + for densities} \\ p_c = M/V_{mc} \end{array} \right.$

 $\left[\begin{array}{l} \text{Redlich-Kwong} \\ \text{Accurate above } T_c \text{ for } \uparrow \text{ temps.} \end{array} \right.$

 $\left[\begin{array}{l} \text{Beattie-Bridgeman} \end{array} \right.$

\rightarrow Where V_{mc} is the molar volume
 @ a critical point.

7.3 - The Compression Factor

Compression Factor $\rightarrow "Z"$

$$\rightarrow Z = \frac{V_m}{V_{ideal}} = \frac{PV_m}{RT}$$

$\rightarrow Z = 1$ - Ideal Gas @ all values of P and V_m

$\rightarrow Z > 1$ - Real gas exerts a greater pressure than an ideal gas

$\rightarrow Z < 1$ - Real gas exerts a smaller pressure than an ideal gas

Same values of T and V_m .

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

\rightarrow The slope of Z as a function of P as $P \rightarrow 0$.

$$\rightarrow \lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left(b - \frac{a}{RT} \right) \text{ as } V_m \rightarrow \infty$$

$$\rightarrow \frac{RT}{(V_m - b)^2} + Z \frac{a}{V_m^3} \rightarrow - \frac{RT}{V_m^2} \text{ as } V_m \rightarrow \infty$$

Boyle Temperature - The corresponding temperature at which the initial slope of Z versus P curve is 0 when $b = a/RT$.

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

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

$$\rightarrow T_r = T/T_c, P_r = P/P_c, \text{ and } V_{mr} = V_m/V_{mc}$$

Law of corresponding States

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

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

$$\rightarrow \text{Where } P_c = \frac{a}{27b^2}$$

$$\rightarrow \text{Where } V_m = 3b$$

$$\rightarrow \text{Where } T_c = 8a/27Rb$$

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

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

→ Assumption is only sufficient enough if the molecules are nearly spherical.

→ At Using the compression factor, the error in assuming that the pressure can be calculated using the ideal gas law.

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

→ At or slightly above the critical temperature, a real gas is much more compressible than an ideal gas.

$$\rightarrow Z_c = \frac{P_c V_c}{RT_c} = \frac{1}{R} \times \frac{a}{27b^2} \times 3b \times \frac{27ab}{8a} = \frac{3}{8}$$

\rightarrow Predicts that the critical compressibility is independent of the parameters a and b and should, therefore, have the same value for all gases.

7.5 - Fugacity and the Equilibrium Constant for Real Gases

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

↓
Analogous expression
for a real gas

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

\rightarrow Where f is the fugacity of the gas.

Fugacity - Effective pressure that a real gas exerts.

Attractive range of the intermolecular potential, $G_m^{\text{real}} < G_m^{\text{ideal}} \rightarrow f < P$.

Repulsive range of the intermolecular potential, $G_m^{\text{real}} > G_m^{\text{ideal}} \rightarrow f > P$.

\rightarrow The fugacity has the limiting behavior that $f \rightarrow P$ as $P \rightarrow 0$.

Standard State of Fugacity (f°) - The value that the fugacity would have if the gas behaved ideally @ 1 bar.

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

Calculation for fugacity of a given gas

$$dG_m = V_m dP \begin{cases} \rightarrow d\mu_{\text{ideal}} = V_m^{\text{ideal}} dP \\ \rightarrow d\mu_{\text{real}} = V_m^{\text{real}} dP \end{cases}$$

The chemical potential of a real gas will change differently with pressure than the chemical potential of an ideal gas: $V_m^{\text{ideal}} \neq V_m^{\text{real}}$

$$\rightarrow d\mu_{\text{real}} - d\mu_{\text{ideal}} = (V_m^{\text{real}} - V_m^{\text{ideal}}) dP$$

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

$$= \int_{P_i}^P (V_m^{\text{real}} - V_m^{\text{ideal}}) dP_i$$

$$\text{Set } P_i \rightarrow 0 \text{ so that } \mu_{\text{real}}(P_i) = \mu_{\text{ideal}}(P_i)$$

$$\mu_{\text{real}}(P) - \mu_{\text{ideal}}(P) = \int_0^P (V_m^{\text{real}} - V_m^{\text{ideal}}) dP_i$$

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

$$\text{Because } Z = V_m^{\text{real}} / V_m^{\text{ideal}}$$

$$\ln F = \ln P + \int_0^P \frac{Z-1}{P_i} dP_i \quad \text{or} \quad F = P \exp \left[\int_0^P \left(\frac{Z-1}{P_i} \right) dP_i \right] \quad \text{or} \quad F = \gamma(P, T) P$$

Fugacity Coefficient - The proportionality factor γ that relates F and P .

$$\rightarrow \text{Where } \gamma = e^{bP/RT}$$

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 temperature and pressure is Gibbs Energy $G(T, P, n)$

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

$n \rightarrow$ number of moles of substance in the system

$$\partial \mu = -S_m dT + V_m dP \rightarrow \text{differential } (d\mu = dG_m)$$

$\hookrightarrow \mu$ 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 temperature increases

μ increases as pressure decreases.

Endothermic (heat absorbed) $\Delta H > 0 \quad S \rightarrow L \rightarrow G$

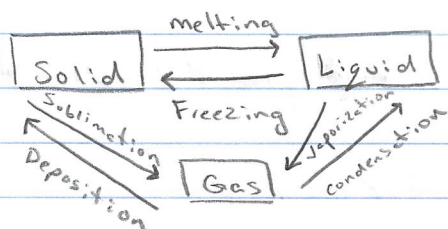
Exothermic (heat released) $\Delta H < 0 \quad G \rightarrow L \rightarrow S$

$S \rightarrow L \rightarrow G$, T increase so P explained by $(\partial \mu / \partial T)_P = -S_m$ and $S_m^{\text{gas}} > S_m^{\text{liquid}} > S_m^{\text{solid}}$

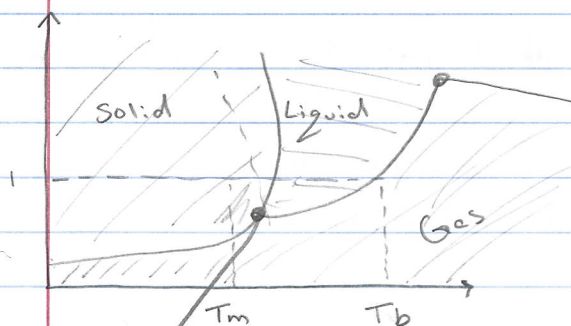
$V_m^{\text{gas}} > V_m^{\text{liquid}} > 0$, increasing $P =$ boiling point elevation.

$V_m^{\text{liquid}} > V_m^{\text{solid}}$, 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.



→ Critical Point:

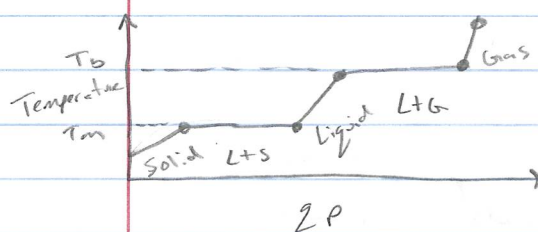
- Point on phase diagram at which both liquid and gas phases of substance have same density and are indistinguishable.

Triple Point = Temperature and Pressure at which the solid, liquid and vapor phases of a pure substance can coexist in equilibrium

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

Super critical fluids = $T > T_c$ and $P > P_c$

↳ unusual properties.



8.3 - The phase rule

$$\text{coexistence of two phases} \Rightarrow \mu_{\alpha}(T, P) = \mu_{\beta}(T, P)$$

$$\text{Three coexist in equilibrium} \Rightarrow \mu_{\alpha}(T, P) = \mu_{\beta}(T, P) = \mu_{\gamma}(T, P)$$

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

↳ pure substance $F = 3 - P \rightarrow$ number of phases

→ degrees of freedom

8.4 - The Pressure - volume - and Pressure - volume - temperature Phase Diagrams