Kevin Marry 4-5-20

7.1 Real Gases and Ideal Gases

Real gases can't be compressed to a volume less than the molecular volume and has molecular interaction. This isn't true for an ideal gas.

The first law of thermodynamics is applied here.

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

van der Waals equation – $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$

Redlich-Kwong equation – $P = \frac{RT}{V_m - b} - \frac{a}{T^{1/2} V_m (V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2 a}{T^{1/2} V (V + nb)}$

a = strength of intermolecular potential
b = minimum volume a mole of molecules can occupy
V_m = volume (constant mass) (L)
n = # moles
R = ideal gas constant (8.314×10^{-2} L bar/mol K)
T = temperature (K)
P = pressure (bar)
V = volume (L)

Beattie-Bridgeman equation – $P = \frac{RT}{V_m^2}\left(1 - \frac{c}{V_m T^3}\right)(V_m + B) - \frac{A}{V_m^2}$

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

c, A_0, B_0, A, B = parameters

virial equation – $P = RT\left[\frac{1}{V_m} + \frac{B(T)}{V_m^2} + \cdots\right]$ $B(T) = b - \frac{a}{RT}$

The first law of thermodynamics is applied here.

7.3 The Compression Factor

$$Z = \frac{V_m}{V_m'} = \frac{PV_m}{RT}$$ $V_m' =$ volume (constant mass) (ideal gas) (L)

$Z =$ compression factor

$$\left(\frac{\partial Z}{\partial P}\right)_T = \left(\frac{\partial Z}{\partial (RT/V_m)}\right) = \frac{1}{RT}\left(\frac{\partial Z}{\partial (1/V_m)}\right)_T = \frac{b}{RT} - \frac{a}{(RT)^2}$$

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

The First law of thermodynamics is applied here.

7.4 The Law of Corresponding States

$$P_r = \frac{8T_r}{3V_{mr} - 1} - \frac{3}{V_{mr}^2}$$ where $T_r = \frac{T}{T_c}$ $P_r = \frac{P}{P_c}$ $V_{mr} = \frac{V_m}{V_{mc}}$

2 gases are in the same corresponding state if they have the same T_r, P_r, and V_{mr}.

$$\text{error} = \frac{Z-1}{Z}(100\%)$$

The First law of thermodynamics is applied here.

7.5 Fugacity and the Equilibrium Constant for Real Gases

$$\ln f = \ln P + \int_0^P \frac{Z-1}{P'}\,dP' \rightarrow f = P + e^{\int_0^P \frac{Z-1}{P'}\,dP'} = \gamma(P, T)P$$

γ - fugacity constant $f =$ fugacity (efficient pressure)

The first law of thermodynamics is applied here.

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

$\left(\frac{\partial \mu}{\partial T}\right)_P = -S_m$ $\left(\frac{\partial \mu}{\partial P}\right)_T = V_m$ where $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P}$ G = Gibbs free energy (kJ/mol)

μ = chemical potential S_m = entropy ($J mol^{-1} K^{-1}$)

$S_m^g > S_m^l > S_m^s$

The second law of thermodynamics is applied here.

8.2 The Pressure-Temperature Phase Diagram

$\Delta H = \Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vaporization}$ H = enthalpy (kJ/mol)

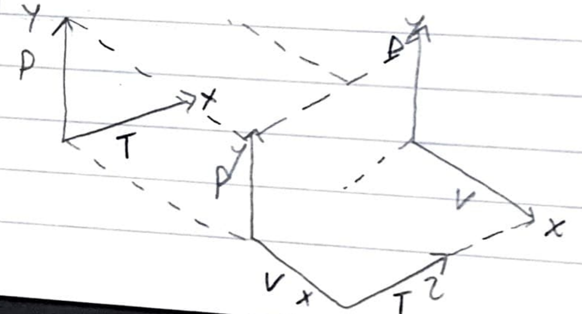
The first law of thermodynamics is applied here.

8.3 The Phase Rule

$F = 3 - p$ F = degrees of freedom p = phase

The first law of thermodynamics is applied here.

8.4 The Pressure-Volume and Pressure-Volume-Temperature Phase Diagrams



The first law of thermodynamics is applied here.

8.5 Providing a Theoretical Basis for the P-T Phase Diagram

Clapeyron equation - $\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$ $\Delta G_{fusion} = \Delta H_{fusion} - T\Delta S_{fusion} = 0$

The second law of thermodynamics is applied here.

8.6 Using the Clausius-Clapeyron Equation to Calculate Vapor Pressure as a Function to T

Clausius-Clapeyron equation - $\frac{dP}{dT} = \frac{\Delta S_{vap}}{\Delta V_{vap}} \approx \frac{\Delta H_{vap}}{T V_m^g} = \frac{P \Delta H_{vap}}{RT^2}$

$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \rightarrow \ln \frac{P_f}{P_i} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

The first law of thermodynamics is applied here.

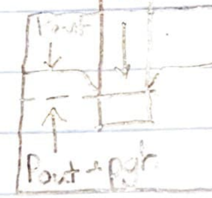
8.7 The Vapor Pressure of a Pure Substance Depends on the Applied Pressure

$RT \ln\left(\frac{P}{P^*}\right) = V_m^l (P - P^*)$ P^* - pressure of a pure substance (bar)

The first law of thermodynamics is applied here.

8.8 Surface Tension

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



γ = surface tension r = radius (m)

$\rho g h$ = gravitational field

The first law of thermodynamics is applied here.

References

Engel, T.; Reid P. Students solutions manual [to accompany] Physical Chemistry, third edition, 3rd ed.; Pearson: Boston, 2012; pp. 165-176, 181-200.