

Kinetic Theory of Gases

$$P = \frac{mN\overline{C}^2}{3V}$$

R.M.S. Velocity

$$\sqrt{\overline{C}^2} = \sqrt{\frac{3RT}{M}}$$

$$C_{mp} = \sqrt{\frac{2RT}{M}}, \text{ the most probable speed.}$$

$$\overline{C} = \frac{1}{N} \int_0^\infty C dN = \sqrt{\frac{8RT}{\pi M}}, \text{ Average speed}$$

$$C_v = (3/2) R$$

$$C_p - C_v = R$$

Mean free path

$$\lambda = \frac{1}{\pi\sigma^2 \cdot \rho_N}, \text{ } \sigma \text{ is the collision diameter and } \rho_N \text{ is the number of molecules per unit volume.}$$

$$\rho_N = \frac{N_A}{V_m} = \frac{P}{kT}$$

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$$

$$\text{Collision rate (Number of collisions per unit area per unit time)} = \rho_N \frac{\overline{c}}{4}$$

$$\mu = \frac{M}{N_A \pi \sigma^2} \sqrt{\frac{8RT}{\pi M}}$$

$$k = \frac{C_v}{N_A \pi \sigma^2} \sqrt{\frac{RT}{\pi M}}$$

$$D_{AA} = \frac{RT}{PN_A \pi \sigma^2} \sqrt{\frac{RT}{\pi M}}$$

Chapter 6 - Real Gases

van der Waals Equation of State:

$$\left[P + \frac{a}{v_m^2} \right] [v_m - b] = RT$$

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

$$v_m^3 - \left(b + \frac{RT}{P} \right) v_m^2 + \frac{a}{P} v_m - \frac{ab}{P} = 0$$

$$a = \frac{27 R^2 T_c^2}{64 P_c}$$

and

$$b = \frac{RT_c}{8 P_c}$$

$$V_c = 3b ,$$

$$P_c = a/(27 b^2),$$

and

$$T_c = \frac{8a}{27 R b}$$

Compressibility Factor and Corresponding States

$$z = \frac{P v_m}{RT} \quad \text{or} \quad v_m = \frac{zRT}{P}$$

Reduced Conditions

Reduced Pressure, $P_r = P/P_c$,

Reduced Temperature, $T_r = T/T_c$,

Reduced molar volume, $V_r = V_m/V_{cm}$,

$z = f(P_r, T_r)$, The value of z can be obtained from a chart, if P_r and T_r are known.

Pitzer and Curl Method of Estimating Compressibility using Acentricity (ω) as the Third Parameter

$$\omega = -\log\left(\frac{P_v}{P_c}\right) - 1$$

$$Z = Z^{(0)}(T_r, P_r) + \omega Z^{(1)}(T_r, P_r)$$

When P_r , T_r and ω are known, value of z can be calculated by looking up the values of $Z^{(0)}$ and $Z^{(1)}$.

Real Gas Mixtures

6.8.1 The Pseudo-Critical Point Method (Kay's Method)

$$P_{pc} = \sum y_i P_{ci} = y_1 P_{c1} + y_2 P_{c2} + \dots + y_N P_{cN}$$

And

$$T_{pc} = \sum y_i T_{ci} = y_1 T_{c1} + y_2 T_{c2} + \dots + y_N T_{cN}$$

Where,

P_{pc} = the pseudo-critical pressure

T_{pc} = the pseudo-critical temperature

y_i = mole fraction of the i^{th} component

$$\omega_{pc} = \sum y_i \omega_i = y_1 \omega_1 + y_2 \omega_2 + \dots + y_N \omega_N$$

Once the pseudo-critical properties have been calculated, the mixture compressibility can be obtained from chart at known values of P and T . This involved calculating: $P_r = P/P_{pc}$, and $T_r = T/T_{pc}$.

Chapter 7. Liquids

Isothermal Compressibility, β_T

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

The isobaric coefficient of thermal expansion, α_p

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \approx \left(\frac{\Delta V/V}{\Delta T} \right)_p$$

The pressure coefficient

$$\gamma_v = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_v \approx \left(\frac{\Delta P/P}{\Delta T} \right)_v$$

The relationship between the three coefficients is:

$$\gamma_v = \frac{\alpha_p}{P\beta_T}$$

Thermal Expansion of Liquids

$$V(T) = V_o [1 + A\theta + B\theta^2 + C\theta^3]$$

Tait's Equation

$$\beta_T = \frac{c}{P+d}$$

Where, c and d are constant. Combining the Tait's equation with the definition of compressibility, you can get

$$-\frac{\Delta V}{V_o} = \frac{V_o - V}{V_o} = c \ln \frac{P+d}{d}$$

Trouton's Rule for Estimating ΔH_v at 1 atm.

$$\frac{\Delta H_v}{T_b} \approx 88 \frac{kJ}{kmol.K}$$

The Classius – Clapeyron Equation

The slope of vapour pressure curve

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)}$$

$$\ln P = \frac{\Delta H_v}{R} \left(\frac{-1}{T} \right) + C_o$$

$$\ln P = \frac{C_1}{T} + C_2$$

$$C_1 = -\Delta H_v/R$$

To calculate C1 and C2, you need two pieces of information, which can be

- Vapour pressure at two different temperatures
- Normal Boiling point and vapour pressure at another temperature,
- Normal boiling point and latent heat of vaporization

If the use of Trouton's rule is allowed, then only the normal boiling point or latent heat is needed.

Equilibrium Pressure Above Liquid Mixtures

Raoult's Law

$$\bar{P}_i = P_{vi} x_i$$

For binary mixtures,

$$y_1 = \frac{x_1 P_{v1}}{x_1 P_{v1} + x_2 P_{v2}} = \frac{x_1}{x_1 + (P_{v2} / P_{v1}) x_2}$$

$$x_1 = \frac{y_1}{y_1 + (P_{v1} / P_{v2}) y_2}$$

Henry's Law,

$$P_i = H_i x_i$$