Example 2.1

For a liquid 'A' at 350K and 1 bar, κ = 50x10^{-6} bar^{-1}. To what pressure must water be compressed at 350 K to change its density by 0.5%? Assume that κ is independent of P.

At T = constant (using expression for κ)

$$\frac{dP}{P} = \kappa dP$$

$$Or : \ln\frac{P_2}{P_1} = \kappa\Delta P$$

Now P_2 =1.005P_1

$$\Delta P = \frac{\ln(1.005)}{K} = \frac{\ln(1.005)}{50\times10^{-6}}\text{bar} = 100\text{bar}$$

P_2=P_1+ ΔP = 100 bar

Example 2.2

Calculate the molar volume for butane at 2.5bar and 298 K using the truncated virial EOS using the following data: $T_C = 425.1K;\ P_C = 37.96bar;\ \omega = 0.2.$

T = 298 K, T_c = 425.1 K, $T_r = T/T_c$ = 0.701

P = 2.93 bar, P_c = 37.96 bar, $P_r = P/P_c$ = 0.069

ω = 0.200, Mol. Wt. = 58

Using truncated viral EOS

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.661$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = -0.624$$

$$V = \frac{RT}{P} + (B^0 + wB^1)\frac{RT_c}{P_c} = 9.4\times10^3\text{cm}^3/\text{mol}$$

Example 2.3

For methane at 298K and 2 MPa compute the molar volume using SRK equation.

T_c= 190.7 K, P_c= 46.41 bar, ω = 0.011, $T_r = T/T_c$ = 1.56395

$$Let\ S = 0.48 + 1.574\omega - 0.176\omega^2 = 0.48 + 1.574X0.011 - 0.176(0.011)^2 = 0.4972$$

$$\alpha(SRK) = \left[1 - S\left(1 - \sqrt{T_r}\right)\right]^2 = 0.07664$$

$$a = \frac{0.42748R^2T_C^2\alpha(SRK)}{P_C} = 0.1774\ Pa.(m^3/mol)^2$$

$b = 0.08664 \frac{RT_c}{P_c} = 2.9598\ X\ 10^{-5}\ m^3 / mol$

$\therefore A = \frac{aP}{(RT)^2} = 5.7765\ X\ 10^{-2}, B = \frac{bP}{RT} = 2.3881\ X\ 10^{-2}$

The SRK EOS can be expressed as: $Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$

Here, $\alpha = -1;\ \beta = A - B - B^2 = 3.3813\ X\ 10^{-2}, \gamma = -AB = -1.3510\ X\ 10^{-2}$

Refer to method of solution for cubic equation and solving the cubic equation yields Z = 0.9665. Thus, the molar volume is given as follows.

V = ZRT/P = (0.9665)(83.14cm^{3}bar/molK)(298K)/20bar = 1197.3 cm^3/mol

Example 2.4

A rigid 0.5-m^3 vessel at 25^{o}C and 2500kPa holds ethane; compute the number of moles of ethane in the vessel. For ethane: T_c = 305 K; P_c = 48.72 bar, ω = 0.1.

T = 298 K, T_c = 305 K; T_r = 0.977

P = 220 KPa, P_c = 48.72 bar, P_r = 0.452

V_{total} = 0.5 m^3, ω = 0.1

Using plots for Z^0 and Z^1, at given T, P we have: Z^0 = 0.8105, Z^1 = -0.0479

Thus: $Z = Z_0 + \omega Z^1 = 0.806$

$V_1 = Z_1 RT_1 / P_1 = 798.8 cm^3 mol^{-1}$

Moles of ethane in vessel $= 0.5x10^6 cm^3 / 798.7 cm^3 mol^{-1} \approx 626\ moles.$

Example 2.5

Compute the saturate liquid phase molar volume for methane at 150K. For methane T_c= 190.7 K, P_c= 46.41 bar, V_C = 98.6cm^3/mol, Z_C = 0.286, ω = 0.011.

At the given condition: $T_r = T/T_c \sim 0.8$

Using Rakectt Equation: $V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$; where $T_r = T / T_C$ = reduced temperture.

Thus:

$V^{sat} = (98.6)(0.286)^{(1-0.8)^{0.2857}} = 44.7 cm^3 / mol.$

Example 2.6

Estimate the second virial coefficient for an equimolar mixture of propane and n-pentane at 500K and 10 bar.

	T_c (K)	P_c (bar)	V_c x 10^3 (m^3/mol)	Z_c	ω	y_i
Propane (1)	369.9	42.57	0.2	0.271	0.153	0.5
Pentane (2)	469.8	33.75	0.311	0.269	0.269	0.5

$$K_{12} = 1 - \frac{8(V_{c1}V_{c2})^{0.5}}{\left(V_{c1}^{\frac{1}{3}} + V_{c2}^{\frac{1}{3}}\right)^3} = 8.902\ X\ 10^{-3}$$

$$T_{c12} = \sqrt{T_{c1}T_{c2}}(1 - K_{12}) = 413.2\ K$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} = 0.202$$

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2} = 0.27$$

$$V_{c12} = \left(\frac{V_{c1}^{\frac{1}{3}} + V_{c2}^{\frac{1}{3}}}{2}\right)^3 = 0.2516\ X\ 10^{-3}\ m^3/mol$$

$$P_{c12} = \frac{Z_{c12}KT_{c12}}{V_{c12}} = 3.6866\ MPa$$

$$T_{r12} = \frac{500}{T_{c12}} = \frac{500}{413.2} = 1.21$$

$$\therefore B_{12}{}^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.2281$$

$$B_{12}{}^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 6.1762\ X\ 10^{-2}$$

$$\therefore\ \frac{B_{12}P_{c12}}{RT_{c12}} = B_{12}^0 + \omega_{12}B_{12}^1 = -0.2156 \therefore B_{12} = -2.0091\ X\ 10^{-4}\ m^3/mol$$

Similarly, for pure components $T_{r1} = \frac{500}{369.9} = 1.3571,\ T_{r2} = 1.0643$

Following the same procedure above (K_{11} = K_{22}= 0), [K_{ij} = 0 where i = j]

B_{11} = - 1.1833×10^{-4} m^3/mol, B_{22} = - 3.4407×10^{-4} m^3/ mol

$$\therefore B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} = -2.16\ x\ 10^{-4}\ m^3/mol$$

Example 2.7

Calculate the molar volume of an ethylene and propylene mixture comprising 70 mole percent ethylene and 30 mole percent propylene at 600 K and 60 bar. Assume that the mixture follows the Redlich-Kwong equation of state.

	T_c (K)	**P_c (bar)**
Ethylene (1)	283.1	51.17
Propylene (2)	365.1	46.0

R-K parameters for pure species and mixture are obtained first

$$a_1 = \frac{0.42748 R^2 T_{c1}^2}{P_c T^{0.5}} = \frac{0.42748\ X\ (8.314)^2\ X\ (283.1)^2}{51.17\ X\ 10^5\ X\ \sqrt{600}} = 0.3179\ Pa \left(\frac{m^3}{mol}\right)^2$$

$$b_1 = \frac{0.08664 R T_c}{P_c} = \frac{0.08664\ X\ 8.314\ X\ 283.1}{51.17\ X\ 10^5} = 3.9852\ X\ 10^{-5}\ \frac{m^3}{mol}$$

Similarly, $a_2 = 0.6679\ Pa \left(\frac{m^3}{mol}\right)^2, b_2 = 5.7172\ X\ 10^{-5}\ m^3/mol$

$$\therefore a_m = y_1^2 a_1 + 2y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2^2 = 0.4094\ Pa \left(\frac{m^3}{mol}\right)^2$$

$$b_m = y_1 b_1 + y_2 b_2 = 4.5048\ X\ 10^{-5}\ m^3/mol$$

$$\therefore \frac{b_1}{b_m} = 0.8847; \frac{b_2}{b_m} = 1.2691$$

Now, solve for Z from cubic EOS,

$$A = \frac{aP}{(RT)^2} = \frac{a_m P}{(RT)^2} = \frac{0.4094\ X\ 60\ X\ 10^5}{(8.314\ X\ 600)^2} = 9.8713\ X\ 10^{-2}$$

$$B = \frac{bP}{RT} = \frac{b_m P}{RT} = \frac{4.5048\ X\ 10^{-5}}{8.314\ X\ 600} = 5.4183\ X\ 10^{-2}$$

It follows, $\alpha = -1, \beta = A - B - B^2 = 4.1594\ X\ 10^{-2}$

$$\gamma = -AB = -9.8713\ X\ 10^{-2}\ X\ 5.4183\ X\ 10^{-2} = -5.3486\ X\ 10^{-3}$$

$$\therefore p = \beta - \frac{\alpha^2}{3} = -0.2917; q = \frac{2\alpha^3}{27} - \frac{\alpha\beta}{3} + \gamma = -6.5558\ X\ 10^{-2}$$

$$D = \frac{q^2}{4} + \frac{p^3}{27} = 1.5519\ X\ 10^{-4};\ \sqrt{D} = 1.2457\ X\ 10^{-2}$$

Since $D > 0$, one real root only exists,

$$Z = \left\{-\frac{q}{2}+\sqrt{D}\right\}^{1/3} + \left\{-\frac{q}{2}-\sqrt{D}\right\}^{1/3} - \frac{\alpha}{3} = 0.9626$$

The mixture molar volume = $V = Z_m RT / P = (0.9626)(83.14)(600)/60 \approx 800 cm^3/mol$

Example 2.8

Find the molar volume and internal energy of a system containing water and steam at 50% quality at 200^{0}C.

From saturated steam tables one has the following data at 200^{0}C.

$V^V = 0.13 m^3/kg; V^L = 0.0012 m^3/kg; U^V = 2593 kJ/kg; U^L = 851 kJ/kg$

System molar volume: $V = V^L + x^V(V^V - V^L) = 0.065 m^3/kg$

System molar internal energy: $U = U^L + x^V(U^V - U^L) = 1722.0 kJ/kg$

Example 9

Using Riedel's correlation, estimate the enthalpy of vaporization of water at its normal boiling point and compare the result with that given in steam tables.

Solution: For water, P_c = 221.2 bar, T_c = 647.3 K and T_{br} = 373.15/647.3 = 0.5765.

$$\Delta H_n^{vap} = 1.093 RT_c \left[T_{br} \frac{\ln P_c - 1.013}{0.930 - T_{br}} \right] = 1.093 \text{ x } 8.314 \text{ x } 647.3 \left[0.5765 \frac{(\ln 221.2 - 1.013)}{0.930 - 0.5765} \right]$$

= 42.075 kJ/mol = 2337.5 kJ/kg

We get from steam tables = 2256.94 kJ/kg and error = $\frac{(2337.5 - 2256.94)}{2256.94}$ x 100 = 3.57%

Example 2.10

The enthalpy of vaporization of water at 100^{o}C is 2256.94 kJ/kg. Determine the value at 150^{o}C, and compare the value with that listed in the steam tables.

Solution: For water, T_c = 647.3 K.

$$T_{r1} = \frac{373.15}{647.3} = 0.5765; \quad T_{r2} = \frac{423.15}{647.3} = 0.6537$$

$$\Delta H_2^{vap} = \Delta H_1^{vap} \left(\frac{1 - T_{r2}}{1 - T_{r2}} \right)^{0.38} \quad \text{or} \quad \Delta H_2^{vap} = 2256.94 \left(\frac{1 - 0.6537}{1 - 0.5765} \right)^{0.38} = 2090.78 \; kJ/kg$$

ΔH^{vap} from steam tables = 2113.25 kJ/kg