

Example 6.1

Consider a solution of two species S1/S2 at 25°C such that $x_1 = 0.4$. If $\bar{V}_1 = 40 \times 10^{-6} \text{ m}^3/\text{mol}$, find \bar{V}_2 . The solution specific gravity is = 0.90 and the molecular weights of the species are 32 and 18 respectively.

$$\text{Molar mass of solution} = x_1 M_1 + x_2 M_2 \quad (M = \text{MW})$$

$$= 0.4 \times 32 + 0.6 \times 18$$

$$= 23.433 \text{ gm/mol} = 23.6 \times 10^{-3} \text{ kg/mol}$$

$$\text{Solution molar volume} = \frac{\text{Molar mass}}{\text{Density}} \Rightarrow$$

$$= \frac{23.6 \times 10^{-3} \text{ kg/mol}}{900 \text{ kg/m}^3} = 26.2 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\text{Now } V = x_1 \bar{V}_1 + x_2 \bar{V}_2$$

$$\Rightarrow \bar{V}_2 = (V - x_1 \bar{V}_1) / x_2 = \frac{(26.2 - 0.4 \times 40) \times 10^{-6}}{0.6}$$

$$= 17.0 \times 10^{-6} \text{ m}^3/\text{mol}.$$

Example 6.2

The molar enthalpy of a binary solution is given by:

$V = 500 x_1 + 1000 x_2 + x_1 x_2 (50 x_1 + 40 x_2) \text{ cm}^3/\text{mol}$. Find the expressions for \bar{V}_1 , and \bar{V}_1^∞ .

Putting $x_1 = 1 - x_2$; it follows:

$$V = 500 + 550 x_2 - 60 x_2^2 + 10 x_2^3$$

$$\frac{dV}{dx_2} = 550 - 120 x_2 + 30 x_2^2$$

$$\bar{V}_1 = V - x_2 \frac{dV}{dx_2}$$

$$= 500 x_1 + 1000 x_2 + x_1 x_2 (500 x_1 + 40 x_2) - x_2 [550 - 120 x_2 + 30 x_2^2]$$

Putting $x_2 = 1 - x_1$; and simplifying:

$$\bar{V}_1 = 540 - 60 x_1 + 20 x_1^3$$

$$\bar{V}_1^\infty = \lim_{x_1 \rightarrow 0} \bar{V}_1 = 540 \text{ J/mol}$$

Alternately one may also use the generic definitions:

$$\bar{V}_1 = \left. \frac{\partial nV}{\partial n_1} \right|_{n_2, T, P}$$

$$V = 500 + 550 x_2 - 60 x_2^2 + 10 x_2^3$$

Putting $x_2 = 1 - x_1$ and simplifying:

$$V = 1000 - 460 x_1 - 30 x_1^2 - 10 x_1^3$$

$$V = 1000 - 460 \frac{n_1}{n} - 30 \frac{n_1^2}{n^2} - 10 \frac{n_1^3}{n^3}$$

Where, $n = n_1 + n_2$ (moles of mixture)

$$\bar{V}_1 = \left. \frac{\partial nV}{\partial n_1} \right|_{n_2} ; \text{ note that: } \left. \frac{\partial nV}{\partial n_1} \right|_{n_2} = 1$$

$$\begin{aligned} \bar{V}_1 &= \frac{\partial}{\partial n_1} \left[\left(1000 - 460 \frac{n_1}{n} - 30 \frac{n_1^2}{n^2} - \frac{10 n_1^3}{n^3} \right) n \right]_{n_2} \\ &= \frac{\partial}{\partial n_1} \left[1000 n - 460 n_1 - 30 \frac{n_1^2}{n} - \frac{10 n_1^3}{n^2} \right]_{n_2} \\ &= 640 - 60 \frac{n_1^2}{n^2} + 20 \frac{n_1^3}{n^3} \\ &= 640 - 60 x_1^2 + 20 x_1^3 \dots [\text{same as the earlier expression}] \end{aligned}$$

The same exercises may be carried for obtaining \bar{V}_2 .

Example 6.3

What is the change in entropy when 0.6 m³ of CO₂ and 0.4 m³ of N₂, each at 1 bar and 25°C blend to form a gas mixture at the same conditions? Assume ideal gases.

For an ideal gas, mole fraction = volume fraction

CO₂ (1) / N₂(2); $y_1 = 0.6$, $y_2 = 0.4$

$$(\Delta S)_{mix} = -R \sum y_i \ln y_i = 5.5 J / molK$$

Example 6.4

Estimate the fugacity of ethane at 122.2 K and 5 bar using the truncated virial EOS.

For ethane $T_c = 305.4K$, $P_c = 48.84$ bar, $\omega = 0.099$

$$\therefore T_r = \frac{122.2}{305.4} = 0.4, P_r = \frac{5}{48.84} = 0.041$$

$$\text{Now, } B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -1.7452$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = -7.9311$$

$$\ln \phi = (B^0 + \omega B^1) \frac{P_r}{T_r} = -0.25936 \rightarrow \phi = 0.7715$$

$$\therefore f = \phi P = 3.9 \text{ bar}$$

Example 6.5

Estimate the fugacity of ammonia vapor at 4.0 MPa and 321K assuming that it obeys the RK equation of state.

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c T_c^{0.5}} = \frac{0.42748 * (8.314)^2 * (405.5)^{2.5}}{112.77 * 10^5 * (321.55)^{0.5}} = 4.8383 \times 10^{-1} \text{ Pa} \left(\frac{\text{m}^3}{\text{mol}} \right)^2$$

$$b = \frac{0.08664 R T_c}{P_c} = \frac{0.08664 * 8.314 * 405.5}{112.77 * 10^5} = 2.5902 * 10^{-5} \text{ m}^3/\text{mol}$$

Now,

$$\ln \phi = \frac{b}{V-b} - \frac{a}{RT(V+b)} - \frac{a}{bRT} \ln \left(\frac{V+b}{V} \right) - \ln \left(\frac{V-b}{V} \right) - \ln \left[\frac{V}{V-b} - \frac{a}{RT(V+b)} \right]$$

In the above equation $T = 321.55\text{K}$, V is not known.

So solve RK-EOS for V_{vapour} at the given temperature and pressure, i.e., at $P = 1.95 \text{ MPa}$, $T = 321.55 \text{ K}$ (see example 2.3)

V_{vapour} turns out to be $\approx 1.1987 * 10^{-3} \text{ m}^3/\text{mol}$

Thus on substitution in eq. (1) $\ln \phi = -0.1189 \rightarrow \phi = 0.888$

$$\therefore f = \phi P = 0.888 * 5.0 = 4.4 \text{ MPa}$$

Example 6.6

Estimate the fugacity of methane at 32C and 9.28 bar. Use the generalized correlation approach.

For methane $T_c = 190.7 \text{ K}$, $P_c = 46.41 \text{ bar}$, $\omega = 0.011$

$$\therefore T_r = \frac{305}{190.7} = 1.6, P_r = \frac{9.28}{46.41} = 0.9$$

For given T_r and P_r , read off ϕ^0 and ϕ^1 from figures of fugacity coefficients.

$$\text{Then } \phi = (\phi^0)(\phi^1)^\omega = 0.9865$$

$$\therefore f = \phi P = 9.155 \text{ bar}$$

Example 6.7

Estimate the fugacity of cyclopentane at 110 C and 275 bar. At 110 C the vapor pressure of cyclopentane is 5.267 bar.

For cyclopentane $T_c = 511.8 \text{ K}$, $P_c = 45.02 \text{ bar}$, $\omega = 0.196$, $Z_c = 0.273$, $V_c = 258 \text{ cm}^3/\text{mol}$,

$T_n = 322.4 \text{ K}$

$T = 383 \text{ K}$, $P = 275 \text{ bar}$, $P^{\text{sat}}(383 \text{ K}) = 5.267 \text{ bar}$

$T_r = 0.7486$, $P_r^{\text{sat}} = P^{\text{sat}}/P_c = 0.117$

Calculate f^{sat} at the given Vapour pressure by

Virial EOS $\Rightarrow \ln \phi^{\text{sat}} = BP^{\text{sat}}/RT \Rightarrow f^{\text{sat}} = \phi^{\text{sat}} P^{\text{sat}}$

Here $T = 383 \text{ K}$, B is obtained as in problem 18, by B^0 , B^1 .

Final $\varphi^S = 0.9$

Now by Rackett equation $V^{\text{sat}} = V_c Z_c^{(1-T_{nbr})^{0.2857}}$

$T_{nbr} = 322.4 / 54.8 = 0.63 \Rightarrow V^{\text{sat}} = 97.092 \frac{\text{cm}^3}{\text{mol}}$

$\therefore f^{\text{sat}} = \phi^{\text{sat}} P^{\text{sat}} \cdot \exp[V^{\text{sat}}(P - P^{\text{sat}})/RT] = 10.79 \text{ bar}$

Example 6.8

For the following system compute the species fugacity coefficients for an equimolar mixture at 20 bar and 500K.

	$T_c \text{ (K)}$	$P_c \text{ (bar)}$	$V_c \times 10^3 \text{ (m}^3/\text{mol)}$	Z_c	ω	y_i
Propane (1)	369.9	42.57	0.2	0.271	0.153	0.4
Pentane (2)	469.8	33.75	0.311	0.269	0.269	0.6

$P = 20 \text{ bar}$, $T = 500 \text{ K}$, $y_1 = y_2 = 0.5$

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

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

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

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

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

$$P_{c12} = \frac{Z_{c12} K T_{c12}}{V_{c12}} = 3.6866 \text{ MPa}$$

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

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

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

$$\therefore \frac{B_{12} P_{c12}}{R T_{c12}} = B_{12}^0 + \omega_{12} B_{12}^1 = -0.2156$$

$$\therefore B_{12} = -2.0091 \times 10^{-4} \text{ m}^3/\text{mol}$$

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

Following the same procedure above ($K_{11} = K_{22} = 0$), [$K_{ij} = 0$ if $i \neq j$] it may be shown that:

$$B_{11} = -1.1833 \times 10^{-4} \text{ m}^3/\text{mol}, B_{22} = -3.4407 \times 10^{-4} \text{ m}^3/\text{mol}$$

Thus:

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} = 1.5665 \times 10^{-4} \text{ m}^3/\text{mol}$$

$$\ln \widehat{\phi}_1 = \frac{P}{RT} [B_{11} + y_2^2 \delta_{12}] = \left\{ \frac{20 \text{ bar}}{83.14 \frac{\text{cm}^3 \text{ bar}}{\text{mol K}} \cdot 500 \text{ K}} [-1.1833 + 0.25(1.5665)] \right\} \\ \times 10^{-4} \times 10^{-6} \text{ cm}^3/\text{mol}$$

$$\ln \widehat{\phi}_1 = -0.03808 \rightarrow \widehat{\phi}_1 = 0.9626$$

Similarly,

$$\ln \widehat{\phi}_2 = \frac{20}{83.14 \times 500} [-2.3923 + 0.25 \times 1.5665] \times 10^{-4} \times 10^6 \frac{\text{cm}^3}{\text{mol}} = -0.9625$$

$$\therefore \widehat{\phi}_2 = 0.9082$$

Example 6.9

Calculate the fugacities of ethylene and propylene in a mixture of 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

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

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

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

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

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

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

Now, solve for Z from cubic EOS,

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

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

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

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

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

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

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

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

$$\ln(Z - B) = -9.6052 \times 10^{-2}; \ln\left(\frac{Z + B}{Z}\right) = 5.4761 \times 10^{-2}$$

$$2\sqrt{\frac{a_1}{a_m}} = 1.7624; 2\sqrt{\frac{a_2}{a_m}} = 2.5546$$

$$\frac{a}{bRT} = 1.8218$$

$$\ln \widehat{\phi}_1 = \frac{b_1}{b_m} (Z - 1) - \ln(Z - B) + \frac{a_m}{b_m RT} \left(\frac{b_1}{b_m} - 2 \sqrt{\frac{a_1}{a_m}} \right) \ln \left(\frac{Z+B}{Z} \right) = -0.0246$$

$$\therefore \widehat{\phi}_1 = 0.9757; \widehat{f}_1 = \widehat{\phi}_1 y_1 P = 40.98 \text{ bar}$$

$$\ln \widehat{\phi}_2 = \frac{b_2}{b_m} (Z - 1) - \ln(Z - B) + \frac{a_m}{b_m RT} \left(\frac{b_2}{b_m} - 2 \sqrt{\frac{a_2}{a_m}} \right) \ln \left(\frac{Z+B}{Z} \right) = -0.07965$$

$$\therefore \widehat{\phi}_2 = 0.9234; \widehat{f}_2 = \widehat{\phi}_2 y_2 P = 16.62 \text{ bar}$$

Example 6.10

Methanol (1)-acetone (2) system is described by the Van Laar activity coefficient model. At 60°C, the model parameters are $A_{12} = 0.47$; $A_{21} = 0.78$. Estimate the activity coefficients for a solution containing 10mole% of methanol.

$$\ln \gamma_1 = \frac{A_{12}}{\left(1 + \frac{A_{12}x_1}{A_{21}x_2}\right)^2}; \ln \gamma_2 = \frac{A_{21}}{\left(1 + \frac{A_{21}x_2}{A_{12}x_1}\right)^2}$$

$$\text{For } x_1 = 0.1, \gamma_1 = 1.5219, \gamma_2 = 1.0032$$

Example 6.11

Use of Regular Solution Model to estimate activity coefficients for an equimolar benzene (1) / cyclohexane (2) solution 350°K. The solubility parameters are: $\delta_1 = 9.2 \text{ (cal/cm}^3)^{1/2}$; $\delta_2 = 8.2 \text{ (cal/cm}^3)^{1/2}$. The molar volumes: $V_1^L = 88 \text{ cm}^3/\text{mol}$; $V_2^L = 107 \text{ cm}^3/\text{mol}$

$$\text{Volume fraction} = \Phi_1 = x_1 V_1^L / (x_1 V_1^L + x_2 V_2^L) = 88 / (88 + 107) = 0.45$$

$$\Phi_2 = 1 - \Phi_1 = 0.55$$

$$RT \ln \gamma_1 = V_1^L \Phi_2^2 (\delta_1 - \delta_2)^2 = 88 \times 0.55^2 [9.2 - 8.2]^2$$

$$R = 1.987 \text{ cal/mol, } T = 350^\circ\text{K}$$

$$\text{Hence } \ln \gamma_1 = 0.038 \Rightarrow \gamma_1 = 1.04$$

$$\text{Similarly } RT \ln \gamma_2 = V_2^L \Phi_1^2 (\delta_1 - \delta_2)^2$$

$$\text{Hence } \gamma_2 = 1.03$$

Example 6.12

Use UNIFAC model to estimate activity coefficients for an equimolar n-pentane (1) /acetone (2) solution 350°K.

$$B_{11} = -963, B_{22} = -1523, B_{12} = 52 \text{ cm}^3 / \text{mol}$$

$$\therefore \delta_{12} = 2B_{12} - B_{11} - B_{22} =$$

$$\Phi_1 = \exp \left[\frac{B_{11} (P - P_1^s) + P y_2^2 \delta_{12}}{RT} \right]$$

$$\Phi_2 = \exp \left[\frac{B_{22} (P - P_2^s) + P y_1^2 \delta_{12}}{RT} \right]$$

Follow the algorithm provided in the text for bubble pressure calculation.

Final Answer: $P_b = 85.14 \text{ KPa}$, $y_1 = 0.812$, $y_2 = 0.188$