Problem 1

Obtain the relations for $\hat{u}_k - \bar{u}_{k,0}$, $\hat{s}_{10}(T,P) - \hat{s}_1(T,P)$ and $\hat{h}_k - \hat{h}_{k,0}$ for a gas mixture following RK equation and RK mixiing rule $\bar{a}_m = (\Sigma\, Y_k\, \bar{a}_k^{\ 1/2})^2$, $\bar{b}_m = \Sigma\, Y_k\, \bar{b}_k$

$U - U_0 = (3/2)(Na_m/(b_m T^{1/2}))\ln(1 + N\bar{b}_m/V)$

Rewriting

$U - U_0 = (3/2)(A_m/(B_m T^{1/2}))\ln(1 + B_m/V)$

Let where $A_m = N^2 a_m$, $B_m = N\, b_m$

$\bar{a}_m = (\Sigma\, Y_k\, \bar{a}_k^{\ 1/2})^2$ (6)

$N^2 a_m = (\Sigma\, N_k a_k^{\ 1/2})^2$

$M(N^2 a_m)/MN_1 = 2(\Sigma\, N_k a_k^{\ 1/2})\, a_1^{\ 1/2} = 2N a_m^{\ 1/2} a_1^{\ 1/2}$

$\bar{b}_m = \Sigma\, Y_k\, \bar{b}_k$ (7)

$M(Nb_m)/MN_1 = b_1$

$B_m/V = b_m/v$

$A_m/B_m = Na_m/b_m$, $A_m/B_m^{\ 2} = a_m/b_m^{\ 2}$

Diffferenіating wrt N_1,

$\hat{u}_1 - \hat{u}_{10} = (3/2)(MA_m/MN_1)/(B_m T^{1/2})\ln(1 + B_m/V) - (3/2)(MB_m/MN_1)A_m/(B_m^{\ 2} T^{1/2})\ln(1 + B_m/V) + (3/2)(A_m/(B_m T^{1/2}))(1/(1 + B_m/V))((MB_m/MN_1)/V - \hat{v}_1 B_m/V^2)$

Rewriting

$\hat{u}_1 - \hat{u}_{10} = (3/2)\, 2\, a_m^{\ 1/2} a_1^{\ 1/2}/(b_m T^{1/2})\ln(1 + \bar{b}_m/\bar{v}) - (3/2)(b_1 a_m/(b_m^{\ 2} T^{1/2}))\ln(1 + \bar{b}_m/\bar{v}) + (3/2)(a_m/(b_m T^{1/2}))(b_1/\bar{v} - \hat{v}_1 \bar{b}_m/\bar{v}^2)/(1 + \bar{b}_m/\bar{v})$

Note that $\hat{u}_{10} = \bar{u}_{10}$. Knowing ideal gas energy at T, one can determine partial molal energy at given composition.

$\hat{h}_1 = \hat{u}_1 + P\hat{v}_1$

$s_0(T,v) - s(T,v) = R\ln(v/(v-b)) - (1/2)(a/(T^{3/2} b))(\ln(v/(v+b)))$ (50)

Multiplying by N

$S_0(T,v) - S(T,v) = NR\ln(V/(V-B_m)) + (1/2)(A_m/(T^{3/2} B_m))(\ln(V+B_m)/V))$ (50)

Differentaiting wrt N_1,

$\hat{s}_{10}(T,v) - \hat{s}_1(T,v) = R\ln(v/(v-b)) - R(b_1/v + b_m/v^2)/(1-b_m/v) + (1/2)\, MA_m\, 2\, a_m^{\ 1/2} a_1^{\ 1/2}/(b_m T^{3/2})(\ln(1 + b_m/v)) - (1/2)(b_1 a_m/(b_m^{\ 2} T^{3/2}))\ln(1 + \bar{b}_m/\bar{v}) + (1/2)(a_m/(b_m T^{3/2})(b_1/\bar{v} - \hat{v}_1 \bar{b}_m/\bar{v}^2)/(1 + \bar{b}_m/\bar{v})$

Similarly

$S_0(T,P) - S(T,P) = -NR\ln(V/V_0) + (S_0(T,v) - S(T,v))$ (52)

$\hat{s}_{10}(T,P) - \hat{s}_1(T,P) = -R\ln(Z) - R(1/Z)\hat{v}_1/v_0 + R$

Obtaining fugacity coefficient of mixture

$\ln\phi_m = (v/(v-b_m) - a_m/(RT^{3/2}(v+b_m)) - 1 + \ln(v/(v-b_m)) + (a_m/(b_m RT^{3/2}))\ln(v/(v+b_m)) - \ln Z_{RK}$ (P)

$\hat{g}_1 = M/MN_1(\hat{g}_1 N)_{T,P,N2,N3,..}$

Recall that

$\ln\phi = (g(T,P,x_1, x_2,..) - g_0(T,P,x_1,x_2,..))/RT$

$\ln\underline{\triangle}_1 = (\hat{g}_1(T,P,x_1, x_2\, ..) - \hat{g}_{10}(T,P,x_1,x_2,..))/RT$

$N \ln \phi = (G(T,P) - G_0(T,P))/RT$

Differentaiting wrt N_1

$\ln \underline{\triangle}_1 = M/MN_1 (N \ln \phi) = (\hat{g}_1 (T,P,x_1, x_2 ..) - \hat{g}_{10} (T,P,x_1,x_2,..))/RT$

Multiply P by N

$N \ln \phi_m = (NV/(V-B_m) - A_m/(RT^{3/2} (V+ B_m)) -N + N \ln (V/(V-B_m))+(A_m/(B_m RT^{3/2}))\ln (V/(V+ B_m))- N \ln Z$ (P)

and differentiating wrt N_1, we obtain $\underline{\triangle}_1$ of component 1 in the mixture.

$Z = V(T,P,N_1,...)/V_0 (T,P,N_1, N_2..)$

$\ln \underline{\triangle}_1 = (v/(v-b_m)) + \hat{v}_1 /(v -b_m) - (v/(v-b_m)^2) (\hat{v}_1 -b_1)$

$- \quad 2 a_m^{1/2} a_1^{1/2} /(RT^{3/2} (v+b_m)) + (a_m /(RT^{3/2} (v+b_m)^2)) (\hat{v}_1 + b_1) -1 + \ln (v/(v-b_m)) + ((v-b_m) /v)((\hat{v}_1 /(v-b_m)) - \bar{v}(\hat{v}_1 - b_1)/(\bar{v}-b_m)^2) + 2 a_m^{1/2} a_1^{1/2} /(b_m RT^{3/2}) \ln (v/(v+b_m)) - a_m b_1 /(b_m{}^2 RT^{3/2}))\ln (v/(v+b_m)) + (a_m /(b_m RT^{3/2})) ((v+b_m)/v) ((\hat{v}_1 /(v+b_m)))- \bar{v}(\hat{v}_1 + b_1 /(\bar{v}+b_m)^2)) - R \ln (Z) - R (1/Z) \hat{v}_1/v_{10} + R$

Problem 2

Obtain an expression for vapor presure in air and vapor mixture just above the liquid surface of a lake which is at T. Assume that liquid is pure distilled water and pressure is P bars. Derive the expression for mole fraction of vapor in the gas phase if gas phase is assumed to be an ideal gas mixture, b) Determine p_v and Y_v if T = 30 C, P = 0.9 bars

SOLUTION

For phase equilibrium of vapor (v) above liquid water (w)

$\mu_w (T, P)= \mu_v (T, P, Y_v)$

$\mu_w (T, P)=h_w - T s_w$

Since Psat at T = 30 C is 0.04246 bar while given pressure is 0.9 bar (> P^{sat} at given T), then the state of lake water is compressed liquid. Looking at Tables, there is no data tabulated at 30 C, 1 bar in compressed liquid table.

$\mu_v (T, P, Y_v) =\mu_v (T, p^{sat}) +RT \ln p_v /p^{sat} = \mu_w (T, P) =\mu_w (T, p^{sat}) +I_{psat}{}^{P} v\, dP$

However

$\mu_v (T, p^{sat}) = \mu_w (T, p^{sat})$

Thus

$RT \ln p_v /p^{sat} = I_{psat}{}^{P} v\, dP$

$p_v /p^{sat} (T) = \exp ((1/RT) I_{psat}{}^{P} v\, dP)$

$p_v = Y_v P$, $Y_v = p_v /P$

Since v = 0.001, P = 0.9 bar, p^{sat} = 0.04246 bars the term ( ) is estimated as 0.0006131. Hence $p_v /p^{sat} (T)$. 1 or p_v = 0.04246 bars. Since pv = Y_v P, the Y_v = 0.04246 bars/0.9 bar = 0.04718

Problem 3

Obtain an expression for vapor spinodal curve for both P and T with respect to v assuming that b«v. Use the Berthelot equation.

Solution:

$P = RT/(v-b) - a /(T^n v^2)$ (A)

At points M and G,

$MP/Mv = - RT/(v-b)^2 + 2a/(T^n v^3) = 0$

$RT^{(n+1)} v^3 = 2a (v-b)^2$ (B)

Specify T. Then solve for v at given T. Obtain the two solutions v_M, v_G. Knowing v_M and v_G we can obtain the spinodal pressures P_M and P_G from Eq.(A).

From (B)

$T= (2a (v-b)^2/ (R v^3))^{1/(n+1)}$ (C)

Using in (A)

$P = R (2a ((v-b)^{1-n})/ (R v^3)^{1/(n+1)} - a (1/v)^{(2-n)/(n+1)} (2a (v-b)^2/ (R))^{- n/(n+1)}$

n=1; Berthelot ; then $T= (2a (v-b)^2/ (R v^3))^{1/2}$;

$P = R (2a /(R v^3))^{1/2} - a (R/(2a v (v-b)^2))^{1/2} = R (2a / (R v^3))^{1/2} - a (R/(2a v(v-b)^2))^{1/2}$

Assume b=0; you will get only vapor spinodal ; $T= (2a/ (R v))^{1/2}$;

$P == R (2a/ (R v^3))^{1/2} - a (R/(2a v^3))^{1/2} = (2a R / v^3)^{1/2} - (aR/(2v^3))^{1/2} = (aR/2v^3)^{1/2}$

Since = $(27/64) R^2 T_c^3/P_c$, $T_R = (27/32)^{1/2} /v_R'^{½}$, $PR = (27/128)^{1/2} /v_R'^{3/2}$ or eliminating v_R', $P_R = (8/27)^{1/2} T_R^{1/2}$

We can also get the spinodal curve P vs v by eliminating T between equations (B) and (A).

Thus for the case n = 0 (VW equation of state),

$P = a(v-2b)/v^3$

(Note :If $v < 2b$, then $P < 0$ from Eq. (B). The negative pressure implies tensile stress on the fluid. Recall that $b = v_c /3$ for VW; thus for $v > 2v_c/3$, $P > 0$; otherwise tensile stress may be existing).

b) In reduced form for VW

$T_R = 54/64 (v_R' - 0.125)^2 / v_R'^{3}$

and

$P_R = ((27/64)/v_R'^{2}) (1 - (1/(4 v_R')))$ (12)