CHE 3173 FINAL May 9, 1988

SOLUTION

a) $K_a = \dfrac{a_B^2}{a_A^2} = \dfrac{\gamma_B^2 x_B^2}{\gamma_A x_A}$

b) at 373°K

$$0.7 = \frac{\gamma_B^2}{\gamma_A}\left(\frac{(Y_2)^2}{(Y_2)}\right) = \frac{\gamma_B^2}{\gamma_A}(Y_2)$$

$$\frac{\gamma_B^2}{\gamma_A} = 1.4 \quad \text{for} \quad \begin{matrix} x_A = Y_2 \\ x_B = Y_2 \end{matrix}$$

at 393°K

$$.6 = \frac{\gamma_B^2}{\gamma_A}\left(\frac{.378^2}{.622}\right) = \frac{\gamma_B^2}{\gamma_A}(.22972)$$

$$\frac{\gamma_B^2}{\gamma_A} = 2.612 \quad \text{for} \quad \begin{matrix} x_A = .622 \\ x_B = .378 \end{matrix}$$

at 373°K

$$2\ln\gamma_B^* - \ln\gamma_A = \ln(1.4) = 0.3365$$

~~$.3365 = \{[\alpha + 2(\beta-\alpha)(Y_2)](Y_2)\}^2 - [\beta + 2(\alpha-\beta)(Y_2)](Y_2)^2$~~

$$.3365 = 2\left\{\left[\beta + 2(\alpha-\beta)(Y_2)\right](Y_2)^2\right\} - \left[\alpha + 2(\beta-\alpha)(Y_2)\right](Y_2)^2$$

$$.3365 = 2\left\{Y_4\beta + Y_4\alpha - Y_4\beta\right\} - \left[Y_4\alpha + Y_4\beta - Y_4\alpha\right]$$

$$\boxed{.3365 = Y_2\alpha - Y_4\beta}$$

at 393°K

$$2\ln\gamma_B - \ln\gamma_A = \ln(2.612) = .9601$$

$$(.9601) = 2\left\{\left[\beta - 2(\alpha-\beta)(.378)\right](.622)^2\right\} - \left[\alpha + 2(\beta-\alpha)(.622)\right](.378)^2$$

$$.9601 = 2\left\{(.3869)\left[\beta + 2(\alpha-\beta)(.378)\right]\right\} - (.1429)\left[\alpha + 2(\beta-\alpha)(.622)\right]$$

$$.9601 = .7738\beta + 0.585(\alpha-\beta) - (.1429\alpha) - (.1778)(\beta-\alpha)$$

$$.9601 = 0.0110\beta + .6199\alpha \quad (\div .6199)$$

$$1.549 = \alpha + 0.0178\beta$$

$$-(.673 = \alpha - 0.5\beta) \quad \text{(previous eqn x2)}$$

$$.876 = .5178\beta$$

$$\boxed{\begin{aligned}\beta &= 1.6913\\ \alpha &= 1.5186\end{aligned}}$$

check

$x_A = .5$ $\quad \gamma_A = 1.5263$ $\quad \gamma_B = 1.4618$

$x_B = .622$ $\quad \gamma_A = 1.2810$ $\quad \gamma_B = 1.8291$

$$K_{a1} = \frac{(1.4618)^2(.5)^2}{(1.5263)(.5)} = .7 \quad \checkmark$$

$$K_{a2} = \frac{(1.8291)^2(1-.622)}{(1.2810)(.622)} = .6 \quad \checkmark$$

c) for $\Delta H^\circ_R = \text{const}$

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^\circ_R}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{.6}{.7}\right) = \frac{\Delta H^\circ_R}{R}\left(\frac{1}{373} - \frac{1}{393}\right)$$

$$\boxed{\Delta H^\circ_R = -2247 \text{ cal/mole}} \qquad = -9,401 \frac{\text{KJ}}{\text{mole}}$$

at 140°C

$$\ln\left[\frac{(.6)}{K_{140}}\right] = \frac{-2247}{1.987}\left(-\frac{1}{393} + \frac{1}{413}\right)$$

$$\boxed{K_{140} = .522}$$

assume we start w/ pure A

guess x_A → calc. γ_A & γ_B, calc $\frac{\gamma_B^2 x_B^2}{\gamma_A x_A}$

$$\boxed{x_A = 0.7}$$

II.

$x_A = 0.405$ $\quad P_A^s = 103.1$ torr

$x_B = 0.595$ $\quad P_B^s = 73.6$ torr

$T = 35°C$ $\quad y_A = 0.547$

$P = 152.4$ torr $\quad y_B = 0.453$

$$x_A \gamma_A P_A^s = y_A \phi_A P \qquad \text{take } \phi_i^s = 1$$

$$(.405)\gamma_A (103.1) = (0.547)(1)(152.4)$$

$$\boxed{\gamma_A = 1.996}$$

$$(.595)(\gamma_B)(73.6) = (0.453)(1)(152.4)$$

$$\boxed{\gamma_B = 1.576}$$

For Van Laar

$$A = \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right]^2$$

$$B = \ln \gamma_2 \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right]^2$$

$$A = \ln(1.996)\left[1 + \frac{(.595)(\ln 1.576)}{(.405)(\ln 1.996)} \right]^2$$

$$B = \ln(1.576)\left[1 + \frac{.405 \ln 1.996}{.595 \ln 1.576} \right]^2$$

$$\boxed{\begin{aligned} A &= 2.674 \\ B &= 1.882 \end{aligned}}$$

for $x_A = 0.6$

$x_B = 0.4$

$$\ln \gamma_A = 2.674 \left[\frac{1.882(.4)}{(2.674)(.6) + (1.882)(.4)} \right]^2$$

$$\ln \gamma_B = 1.882 \left[\frac{2.674(.6)}{(2.674)(.6) + (1.882)(.4)} \right]^2$$

$\gamma_A = 1.314$

$\gamma_B = 2.391$

$y_A(P) = (0.6)(1.314)(103.1)$

$y_B(P) = (.4)(2.391)(73.6)$

$P = 151.7$

$$y_A = \frac{(0.6)(1.314)(103.1)}{(151.7)}$$

$$y_B = \frac{(.4)(2.391)(73.6)}{151.7}$$

$$\boxed{\begin{aligned} y_A &= 0.5358 \\ y_B &= 0.4640 \end{aligned}}$$

III.

$$\ln\phi = \frac{P_R}{T_R}\left(B^\circ + \omega B'\right)$$

$T_c = 507.4\,K$

$P_c = 29.7\,bar$

$\omega = 0.296$

$$T_R = \frac{773.16}{507.4} = 1.524$$

$$P_R = \frac{20}{29.7}\,\frac{1}{.987} = 0.6823$$

$$B^\circ = 0.083 - \frac{.422}{T_R^{1.6}} = -.1321$$

$$B' = 0.139 - \frac{.172}{T_R^{4.2}} = 0.1097$$

$$\ln\phi = \frac{0.6823}{1.5237}\left(-.1321 + (.296)(.1097)\right)$$

$$\ln\phi = -0.0446$$

$$\boxed{\phi = 0.9564}$$

$$\boxed{f = (0.9564)(20) = 19.13\ atm}$$