CHE 3173 FINAL May 12, 1989

Solution

I.

$$\ln \phi_1 = \frac{P}{RT}\left(B_{11} + y_2^2 \delta_{12}\right)$$

$$\ln \phi_2 = \frac{P}{RT}\left(B_{22} + y_1^2 \delta_{12}\right)$$

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

$$B_{12} = \frac{RT_{cij}}{P_{cij}}\left(B^\circ + \omega_{ij} B'\right)$$

$$B^\circ = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B' = 0.139 - 0.172/T_r^{4.2}$$

ij	T_{cij}	P_{cij}	V_{cij}	z_{cij}	ω_{ij}	B°	T_r
11	540.2	27	432	0.263	0.351	0.699	1.43
22	33.2	12.8	65	0.305	0	0.043	23.3
12	133.9	16.1	194.1	0.284	0.1755	0.173	5.77

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} = 0.1755$$

$$T_{c12} = \left[(540.2)(33.2)\right]^{1/2} = 133.9$$

$$V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3 = 194.1$$

$$z_{cij} = \frac{z_{ci} + z_{cj}}{2} = 0.284$$

$$P_{cij} = \frac{(0.284)(82.05)(133.9)}{194.1} = 16.07$$

ij	B^0	B^1
11	−0.155	0.101
22	0.0803	.139
12	0.0574	.139

$$B_{11} = \frac{(82.05)(540.2)}{27}\left(-.155 + (.351)(.101)\right) = -196.25$$

$$B_{22} = \frac{(82.05)(33.2)}{12.8}\left(0.0803\right) = 17.1$$

$$B_{12} = \frac{(82.05)(133.9)}{16.1}\left(.0574 + (.1755)(.139)\right) = 55.8$$

$$S_{12} = 2(55.8) + 196.25 - 17.1 = 290.75$$

$$\ln \phi_1 = \frac{10}{(82.05)(773)}\left[-196.25 + (.8^2)(290.75)\right] = -0.016$$

$$\ln \phi_2 = \frac{10}{(82.05)(773)}\left[17.1 + (.2)^2(290.75)\right] = 0.005$$

$$\boxed{\begin{aligned}\phi_1 &= 0.998\\ \phi_2 &= 1.005\end{aligned}}$$

II.

$$y_1 P = \gamma_1 x_1 P_1^S$$
$$y_2 P = \gamma_2 x_2 P_2^S$$

w/ $T = 200°C$, $P_1^S = 9.514$ atm (7230 torr)
$P_2^S = 7.377$ atm (5606 torr)

$$(0.040) P = \gamma_1 x_1 (9.514)$$
$$(0.160) P = \gamma_2 x_2 (7.377)$$

$$\gamma_1 x_1 \left(\frac{9.514}{0.040}\right) = \gamma_2 x_2 \left(\frac{7.377}{0.160}\right)$$
$$237.85\, \gamma_1 x_1 = 46.11\, \gamma_2 x_2$$

$$237.85 \left[\exp\left(A\left(\frac{Bx_2}{Ax_1+Bx_2}\right)^2\right)\right] x_1 = 46.11 \left[\exp\left(B\left(\frac{Ax_1}{Ax_1+Bx_2}\right)^2\right)\right] x_2$$

$$\ln(237.85) + \ln x_1 + A\left(\frac{Bx_2}{Ax_1+Bx_2}\right)^2 = \ln 46.11 + \ln x_2 + B\left(\frac{Ax_1}{Ax_1+Bx_2}\right)^2$$

$x_1 = .13556$
$x_2 = .86444$
$\gamma_1 = 1.24389$
$\gamma_2 = 1.00617$

Check $\dfrac{\gamma_1 x_1 P_1^S}{y_1} = 40.11$ $\dfrac{\gamma_2 x_2 P_2^S}{y_2} = 40.11$

$\therefore$ **$P = 40.11$ atm**

III.

$$(1) \rightarrow (2) + 4(3)$$

$\Delta G^\circ_{R,298} = 29228 - 1920 = 27308$ cal/mole

$\Delta H^\circ_{R,298} = 11950 - (-44885) = 56835$ cal/mol

$\Delta S^\circ_{R,298} = \dfrac{\Delta H - \Delta G}{T} = 99.08$ cal/mole°K

$\Delta\alpha = 19.562 \quad \Delta\beta = -26.834\times10^{-3} \quad \Delta\gamma = 7.492\times10^{-6} \quad \Delta\delta = .48\times10^{5}$

at 500°C = 773°K

$$\Delta H^\circ_{R,500^\circ C} = 56835 + (19.562)(773-298) - 26.834\times10^{-3}(773^2-298^2)/2 + 7.492\times10^{-6}(773^3-298^3)/3 - .48\times10^5\left(\frac{1}{773}-\frac{1}{298}\right)$$

$\int \frac{dT}{T^2}$

$\int T^{-2}\,dT$

$T^{-1}(-1)\Big|_{T_1}^{T_2}$

.15819

$\int T^{-3}\,dT$

$-\frac{1}{2}T^{-2}$

$\Delta H^\circ_{R,500^\circ C} = 56835 + 9292 - 6827.6 + 1088 + 98.9$

$\Delta H^\circ_{R,500^\circ C} = 60486$ cal/mole

$$\Delta S^\circ_{R,500^\circ C} = 99.08 + 19.562\ln\left(\frac{773}{298}\right) - 26.834\times10^{-3}(773-298) + 7.492\times10^{-6}(773^2-298^2)/2 - 0.48\times10^5\left(\frac{1}{773^2}-\frac{1}{298^2}\right)/2$$

$\Delta S^\circ_{R,500^\circ C} = 99.08 + 18.64 - 12.75 + 1.91 + .23$

$\Delta S^\circ_{R,500^\circ C} = 107.11$ cal/mole°K

$\Delta G^\circ_{R,500^\circ C} = 60486 - (773.16)(107.11)$

$\Delta G^\circ_{R,500^\circ C} = -22327$

$K_a = \exp\left(\dfrac{22327}{(1.987)(773.16)}\right) = 5999$

$K_a = 2{,}049{,}644$

$$K_a = \frac{y_{TOL}\, y_{H_2}^4}{y_{HEPT}}\, P^4$$

$$\left(\frac{K_a}{P^4}\right) = \frac{y_{TOL}\, y_{H_2}^4}{y_{HEPT}}$$

	Start	Finish	y	y
HEPT	1	$1-\xi$	$(1-\xi)/(5+4\xi)$	$(.2)/8.2$
TOL	0	ξ	$(\xi)/(5+4\xi)$	$(.8)/8.2$
H_2	4	$4+4\xi$	$(4+4\xi)/(5+4\xi)$	$(7.2)/8.2$
		$5+4\xi$		

Given: $\xi = 0.8$

$$\left(\frac{K_a}{P^4}\right) = \frac{\left(\frac{.8}{8.2}\right)\left(\frac{7.2}{8.2}\right)^4}{\left(\frac{.2}{8.2}\right)} = \frac{(.8)(7.2)^4}{(.2)(8.2)^4} = 2.378$$

$$\frac{2049644}{2.378} = P^4$$

$$\boxed{P = 30.47 \text{ atm}}$$